ANNUAL REPORTS ON NMR SPECTROSCOPY

Volume 25

ANNUAL REPORTS ON

NMR SPECTROSCOPY

This Page Intentionally Left Blank

ANNUAL REPORTS ON

NMR SPECTROSCOPY

Edited by

G. A. WEBB

Department of Chemistry, University of Surrey, Guildford, Surrey, England

VOLUME 25

ACADEMIC PRESS

Harcourt Brace Jovanovich, Publishers

London • San Diego • New York
Boston • Sydney • Tokyo • Toronto

ACADEMIC PRESS LIMITED
24–28 Oval Road,
LONDON NW1 7DX

U.S. Edition Published by

ACADEMIC PRESS INC.
San Diego, CA 92101

This book is printed on acid free paper

A catalogue record for this book is available from the British Library

ISBN 0-12-505325-8
ISSN 0066-4103

Phototypesetting by Alden Multimedia Ltd, Northampton
Printed by Hartnolls Limited, Bodmin, Cornwall

List of Contributors

L. Stefaniak, *Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland.*

G. A. Webb, *Department of Chemistry, University of Surrey, Guildford, Surrey GU2 5XH, England.*

M. Witanowski, *Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland.*

Preface

Annual Reports on NMR Spectroscopy contain several reports in earlier volumes on the very important topic of nitrogen NMR. The present volume consists of an update on these, the most recent of which appeared in Volume 18 published in 1986. The main aim of this account is to provide some coverage of the literature which has appeared since then. Once more I am very pleased to welcome Professors Stefaniak and Witanowski as my coauthors on this review. I would also like to take this opportunity to thank them most sincerely for their kind cooperation during the period of production of the present volume.

University of Surrey
Guildford, Surrey
England

G. A. WEBB
February 1992

Contents

This Page Intentionally Left Blank

Nitrogen NMR Spectroscopy

M. WITANOWSKI, L. STEFANIAK

Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland

G. A. WEBB

Department of Chemistry, University of Surrey, Guildford, Surrey, England

ANNUAL REPORTS ON NMR SPECTROSCOPY
VOLUME 25 ISBN 0-12-505325-8

1. INTRODUCTION

Our main aim in preparing this review is to attempt to extend the comprehen-

sive survey of nitrogen NMR spectroscopy we have presented in our earlier accounts.[1-5] Taken together with the previous reports this review increases the literature coverage of nitrogen NMR to a period of 40 years from 1950 to 1990. Our most recent report[5] dealt with the literature appearing between late 1980 and the end of 1983. Thus the present review addresses the progress made during the past seven years. It is an ineluctable fact that during this period the applications of nitrogen NMR have continued to advance on many fronts. Progress has been recorded in such a wide variety of areas that we feel it inappropriate to consider coverage to the same degree of thoroughness in all of them. Thus *exceptis excipiendis* we have taken our remit to include more detailed accounts of specific interests. Among these are an indication of the specific assets of nitrogen NMR in dealing with problems of structural elucidation; a consideration of the importance of solvent effects on nitrogen NMR shieldings as a means of gaining insight into molecular interactions, and recent developments in the study of tautomeric equilibria using nitrogen NMR data in combination with those of other nuclei. Particular attention is to be paid to nitrogenous heterocycles and heteroaromatic compounds, including mesoionic structures and those commonly found in systems of biological interest. Applications of nitrogen NMR data to problems of molecular recognition are also to be mentioned.

As in our earlier accounts consideration is given to studies dependent upon either, or both, of the ^{14}N and ^{15}N isotopes. Emphasis is given to the importance of the lone-pair electrons, which are responsible for rendering the NMR parameters of nitrogen much more sensitive to changes in molecular environment than are the corresponding parameters of the commonly studied ^{1}H and ^{13}C nuclei.

Without wishing to claim access to an unusual degree of prescience we feel that it is highly likely that nitrogen NMR spectroscopy will continue to play a leading, and expanding, role in molecular science for a number of years hence.

2. THEORY OF NITROGEN NMR PARAMETERS

The basic theory of NMR parameters has been presented in our earlier reports[1-4] and covered in some detail in a monograph.[6] Thus, with a view to being fairly efficacious, only passing reference to the theoretical backgrounds of nuclear shielding spin–spin coupling and relaxation interactions is made here.

2.1. Calculations of nitrogen shielding

Nuclear shielding calculations usually consist of the evaluation, and summation, of some positive diamagnetic terms and some negative paramagnetic contributions to the total shielding. A comparison of the various shielding expressions for nitrogen atoms in different chemical environments shows that, in general, the diamagnetic contributions remain relatively constant whereas variations in the paramagnetic contributions account for the observed shielding differences.

The individual gauge for localized orbitals (IGLO) procedure has been used to calculate the nitrogen shielding for a number of molecules. Although reasonably successful for calculations of carbon shieldings this approach is less satisfactory when applied to nitrogen shieldings. Perhaps the neglect of correlation effects, involving the nitrogen lone-pair electrons, goes some way to accounting for the observed discrepancies between calculation and experiment.

In the case of NSF, NSCl and NSF_3, the calculated nitrogen shielding for NSF is too small by about 700 ppm when compared with the experimental value.[7] Unfortunately no experimental nitrogen data appear to be available for NSCl or NSF_3. IGLO results have been presented[8] for NFH_2, NF_2H, NF_3 and CF_3CN. The replacement of H by F in NH_3 reduces the nitrogen shielding by about 200 ppm in NH_2F and by additional amounts of 123 ppm and 39 ppm, respectively, in NHF_2 and NF_3. The calculated results for these molecules are found to be rather basis set dependent and in fairly satisfactory agreement with experiment.

Another report covers the application of the IGLO procedure to calculate nitrogen shieldings for some amines, aziridine, some nitriles, an isonitrile, diazomethane, hydrazine and some diazenes.[9] The agreement between calculation and experiment is more satisfactory for the singly bonded nitrogen atoms than for the multiply bonded ones, the least satisfactory agreement being observed for the nitrogen atoms in nitrogen–nitrogen multiple bonds. The results are found to be fairly basis set dependent. However, even if large sets, close to Hartree–Fock quality, are used, the calculated shieldings of multiply bonded nitrogen atoms are too small owing to an overestimation of the paramagnetic contributions.

Similar conclusions are reached from IGLO calculations on some azines and azoles.[10] In this case it is reported that the disparity between the observed and calculated nitrogen shieldings is less pronounced for the partial N–N double bonds in conjugated rings than for genuine N–N multiple bonds. The dominating role of the nitrogen lone-pair electrons is noted for the pyridine-type nitrogen atoms. However, the calculated pyridine-type nitrogen shieldings differ from experiment by more than 120 ppm.

It is found that the lone-pair contribution to the shielding is highly anisotropic and this governs the direction of the principal components of the nitrogen shielding tensors.

Cytosine, uracil, thymine, adenine and guanine have formed the basis of further IGLO calculations.[11] To obtain a reasonable agreement with the experimental nitrogen shieldings a basis set of triple zeta quality, and polarization functions, become necessary. Even for calculations using larger basis sets deviations of up to 45 ppm exist between the calculated and observed nitrogen shieldings. This is especially noticeable for the pyrrole-type nitrogen nuclei.

Nitrogen protonation shifts are calculated for adenine protonated at N-1, N-3 and N-7. By comparison with the experimental results it is predicted that the second adenine protonation site is N-3 whilst N-7 has only a marginal involvement.

In general it seems that IGLO calculations of nuclear shielding are to be preferred to coupled Hartree–Fock methods using a common gauge origin. However, for nitrogen the results are not entirely satisfactory even when extended basis sets are employed.

Some time-dependent Hartree–Fock calculations on N_2 have appeared;[67] the calculated paramagnetic contribution to the nuclear shielding is significantly overestimated. A similar conclusion[10] is reached from the IGLO calculations on N_2. A closer approximation to the experimental result is obtained when a complete active space multiconfiguration time-dependent Hartree–Fock calculation is performed.[67] Polarization propagator theory has been used to calculate the paramagnetic contribution to the nitrogen nuclear shielding in N_2[71] and HCN.[72] Results are reported both in the first-order approximation, which is equivalent to the coupled Hartree Fock (CHF) method, and in the second-order polarization propagator approximation (SOPPA). The difference between the two sets of results for each molecule represents the shielding from correlation effects. This difference is found to be large for both molecules. The SOPPA nitrogen shieldings are -72.2 ppm and -17 ppm for N_2 and HCN, respectively, both of which are in good agreement with experiment.

The localized orbital/local origin (LORG) procedure has been applied to the calculation of nitrogen shieldings in ethylene imine and diazirine.[68] In general the shielding results produced by LORG and IGLO calculations are in close agreement. An advantage of these approaches is that the results may be discussed in terms of particular electronic excitations. In the case of diazirine, large nitrogen shielding contributions arise from the lone-pair orbitals as well as from the ring bonds.[68] It is noted from the LORG calculations that the shielding anisotropy and the antisymmetric component of the shielding tensor both arise from paramagnetic contributions. However, the

two are not related, as demonstrated by the diazirine results where the in-plane anisotropy is small and the in-plane antisymmetric component is large.[68]

A comparison of the results of LORG and IGLO calculations of ^{15}N isotropic shieldings for pyridine and some azines shows that the two sets of calculated data are normally in good agreement with each other. However, with respect to the observed shieldings, variations of up to about 80 ppm are observed when comparison is made with the calculated results.[70] Larger variations are found between the results of LORG calculations and those measured for the nitrogens of 1,2,4-triazine.[70]

Ditchfield's method[12] for calculating nuclear shieldings using gauge included atomic orbitals (GIAO) has been applied to the Watson–Crick base pairs.[13] Shielding variations due to intermolecular hydrogen bond formation between the two complementary bases are analysed as arising from geometric effects, polarization effects and those due to charge transfer and exchange. It appears that the polarization term plays the major role in accounting for the nitrogen shielding differences upon hydrogen bond formation.[13] These results are based upon the use of a minimal set of Gaussian functions which produces variable agreement between the calculated and observed relative nitrogen shielding data both within the base molecules and between the purine and pyrimidine base pairs. Similar calculations have been applied to the hydration of formamide and imidazole.[14] For both the formamide-$(H_2O)_4$ and imidazole-$(H_2O)_2$ systems the largest contribution to the nitrogen shielding hydration shift is found to be due to the polarization interaction. Calculations of the various shielding tensors of nucleic acids have been reviewed.[15] The results obtained show, at best, a rather mixed agreement with the observed nitrogen shieldings of nucleosides and nucleotides.

The shielding model introduced by Ditchfield[12] has been employed[16] in conjunction with basis sets of intermediate size to determine the shieldings, and shielding dependence upon bond modification, for NH_3, N_2, HCN and CH_3NH_2. The calculated nitrogen shieldings and their anisotropies compare favourably with the available experimental data. The calculated first and second shielding derivatives, with respect to bond lengthening are negative. This suggests that the nitrogen shieldings for these molecules are expected to display a negative temperature coefficient.

Similar calculations have been reported for the same four nitrogen compounds as well as for N_2O and CH_3CN.[69] A major difference is that locally dense basis sets are employed for the atom containing the nucleus of interest. In general the agreement of the calculated nitrogen shieldings with experiment is not good, owing to the calculated paramagnetic contribution being too large. *Ab initio* SOS-CI calculations of the nitrogen shielding of N_2H_4 have been reported as a function of the dihedral angle between the

lone-pair electrons on the nitrogen atoms.[73] A nitrogen shielding variation of about 7 ppm is predicted between the *cis* and *trans* forms, whereas the corresponding change in the shielding anisotropy is about 11 ppm.

Theoretical discussions of nitrogen nuclear shielding are most frequently based upon the results of semiempirical molecular orbital calculations. As noted previously[5] the INDO/S parameter set appears to be fairly successful in describing the excited molecular states which make significant contributions to the important paramagnetic shielding terms. Calculations based on the INDO/S procedure, together with Pople's shielding model,[17] have been employed in making the nitrogen NMR signal assignments in some monocyclic azoles,[18] some 1-hydroxybenzotriazoles,[19] some 3-hydroxyindazole derivatives,[20] some fused polyazaheterocyclic ring systems,[21] some benzimidazolones,[22] some mercaptotetrazoles,[23] some 1-hydroxybenzimidazoles,[24] some 1,2,4-triazoles and related compounds,[25] some 3-methylthio-1,2,4-triazoles and related compounds,[26] some heteroaromatic compounds[27] and dibenzo[1,3a,4,6a]tetrazapentalene.[28] In a similar manner, some CNDO/S parametrized shielding calculations have been used for assignment purposes for some 5-substituted tetrazoles.[29]

The solvaton model has been used in conjunction with INDO/S calculations in studies on the influence of solvent polarity on nitrogen shielding for 2-methyl-2-nitrosopropane,[30] t-butyl nitrite,[31] methyl nitrate,[31] 1,1-dimethylazoethane,[31] methyl nitrite,[32] methyl isothiocyanate,[32] some alkyl cyanides[33] and pyridine *N*-oxide.[34] The significance of the results of these calculations is discussed later.

Finite perturbation theory, together with INDO parameters, has been employed for calculations of the nitrogen shieldings of acetyl-Ala-Gly-NHMe, acetyl-Ser-Gly-NHMe, acetyl-Gly-Ala-NHMe and acetyl-Gly-Ser-NHMe in order to assist in the assignment of signals for *Bombyx mori* silk fibroin protein.[35] A similar approach has been used for calculations on a dipeptide fragment in a study of the conformational dependence of ^{15}N chemical shifts of the α-helix and β-sheet forms of some homopolypeptides.[74] A MNDO-GIAO procedure, based on Ditchfield's approach,[12] has been applied to the calculation of the nitrogen shieldings of NH_3, CH_3NH_2, N_2H_4, C_2H_5CN, pyrrole and some azines.[36] The overall agreement between calculation and experiment appears to be satisfactory. CNDO/BW calculations have provided a realistic account of the effect on the nitrogen shielding of pyridine due to adsorption at the surface of silica.[37] Similar calculations, using CNDO/Z parameters, have been reported for some *para*-substituted benzenediazonium salts.[75]

As discussed elsewhere[5,6] the use of Pople's shielding model[17] can lead to a possible interpretation of variations in nuclear shielding due to changes in local charge densities, bond orders and the energies of electronically excited

states. *A priori* there is no reason to expect a good correlation between charge density and nitrogen shielding for a given series of molecules. However, such a correlation may occur when the bond order and excitation enregy contributions to the shielding are either constant or vary in a cancelling manner. This appears to be the case for selected alkylamines, nitroalkanes, isonitriles and azines.[38] It is claimed that an increase in the nitrogen π charge density corresponds to an increase in shielding, whereas deshielding is observed if an increase in σ charge density occurs.

By means of an independent particle model an approximately linear relationship between the first ionization potential and nuclear shielding has been predicted.[39] Application to some 4-substituted pyridines reveals the existence of the predicted correlation. A solvent cavity model is incorporated to account for the solvent-induced changes in nitrogen shielding. These changes are discussed in terms of the solvent-dependent HOMO energy for pyridine in solvents with different dielectrics.[39]

MM2 force field calculations have been applied in a study of the nitrogen shieldings of some saturated amines.[40] A correlation is found between the local steric Van der Waals energy and the nitrogen shielding. For a series of 35 nitrogen nuclei the root mean square error is 5.9 ppm. Repulsive Van der Waals interactions appear to give rise to nitrogen deshielding and attractive interactions to shielding. The attractive potential leads to an expansion of the nitrogen atomic orbitals and thus to a decrease in the paramagnetic shielding term. Hence the γ shielding effect is associated with an attractive interaction. Similarly, β-effects are attributed to repulsive interactions, which are larger than the attractive ones, and lead to orbital contraction and nitrogen deshielding due to an enhanced paramagnetic contribution.

2.2. Calculation of nitrogen spin–spin couplings

The spin–spin coupling interaction between a pair of nuclei is usually expressed as the sum of contact, orbital and dipolar terms. The expressions for these terms are discussed elsewhere and are not reproduced here.[6,41,42]

Various perturbation techniques may be encountered in the evaluation of the spin–spin interaction expressions. Additionally, the relevant eigenvalues and eigenvectors may be calculated at various levels of approximation. Large-basis-set *ab initio* calculations of spin–spin couplings have become more reliable in recent years.

By means of second-order polarization propagator calculations, using an extended basis set, the ^{15}N–^{14}N spin–spin coupling of N_2 has been evaluated.[43] The calculation shows that the contact contribution is 0.82 Hz, the orbital contribution is 3.35 Hz and the dipolar term yields -1.57 Hz, giving a total

of 2.60 Hz which compares with the experimental value of 1.8 ± 0.6 Hz. It is of interest to note that the contact term makes the smallest contribution to this spin–spin coupling interaction. Often the contact term is taken to dominate one-bond spin–spin couplings. This is an assumption which needs to be treated with caution for couplings between two non-hydrogen nuclei.

The positive sign calculated for $^{1}J(^{15}N–^{14}N)$ is reproduced in some *ab initio*, equations-of-motion, calculations on hydrazine, diazene, isodiazene, the azide ion and nitrogen.[44] The sign of $^{1}J(^{15}N–^{14}N)$ is expected to be positive irrespective of the bond multiplicity and the geometrical arrangements around the nitrogen atoms. The only exception is for the *trans*oid arrangements of hydrazine. This is in agreement with the experimental data reported for a *trans*-diazene.[45] *Ab initio* SCF-CI calculations of the contact and orbital contributions to the various spin–spin couplings in $H_2C{=}NH$ and HCN show that all of the terms calculated can make significant coupling contributions.[76]

For larger molecules semiempirical molecular orbital techniques are normally used. INDO parametrized calculations of $^{15}N–^{15}N$ and $^{15}N–^{13}C$ spin–spin couplings have been reported for 3-methyl- and 3,6-dimethylpyridazines.[46] Reasonable agreement is found between the calculated and observed couplings. INDO calculations of $^{15}N–^{13}C$ couplings have appeared for a number of molecular conformations in order to study the dihedral angle dependence[47] and for some cyanides and merocyanines.[48] Similar calculations have involved the use of partially restricted molecular orbitals.[49] The procedure permits a study of the σ and π transmitted components of $^{15}N–^{13}C$ and $^{15}N–^{1}H$ spin–spin couplings. Qualitatively satisfactory agreement with experiment for a collection of molecules is reported.[49]

$^{1}J(^{31}P–^{15}N)$ data have been qualitatively interpreted by means of CNDO/2 calculations on some *N*-methylimide diphosphoric acid derivatives.[50] Calculations on some silylamines have assumed that the contact term dominates the $^{1}J(^{29}Si–^{15}N)$ interaction.[51] It is claimed that the coupling is very sensitive to the extent of $d\pi$-$p\pi$ bonding.

The lone-pair overlap theory has been envoked to account for a through-space $^{19}F–^{15}N$ coupling.[52] This appears to account for the value of 22.4 Hz found for the $^{19}F–^{15}N$ coupling in 3,4-dihydro-8-fluoro-5-methyl-1(2H)-naphthalene oxime, compared with 3.2 Hz for the corresponding coupling in *o*-fluorobenzaldehyde oxime.

A simple sum-over-states model appears to account for the effect on the contact contribution to spin–spin couplings of various lone-pair influences.[53] The point is illustrated by reference to a number of one-, two- and three-bond couplings involving nitrogen nuclei.[53] INDO-SOS calculations show that the contact interaction makes the major contribution to ^{1}J(N–C) of some *para*-substituted benzenediazonium salts.[77]

2.3. Calculations of nitrogen electric field gradients

In contrast to the quantum-mechanical description of nuclear shielding and spin–spin coupling, nuclear relaxation processes are usually considered on the basis of quasiclassical mechanics. However, quadrupolar relaxation is usually the dominant process for ^{14}N nuclei. This depends critically upon the electric field gradient present at the relaxing nucleus. Such field gradients are amenable to molecular orbital calculations.

A calculation[54] on N^+, using a full valence shell and full configuration interaction atomic wavefunctions, leads to an electric field gradient of -0.94 ± 0.01 au, the resulting ^{14}N nuclear quadrupole moment being predicted to be $(2.07 \pm 0.04) \times 10^{-30} m^2$. This compares with a value of $2.05 \times 10^{-30} m^2$ from a fully numerical and large-basis-set calculation on NO^+ and N_2.[55] Comparable large-basis-set calculations,[56,57] with f functions on nitrogen and d functions on hydrogen and with configuration interaction, have been reported for NH_3. The best value for the ^{14}N quadrupole moment from these calculations is $2.08 \times 10^{-30} m^2$. A similar value of $(2.05 \pm 0.02) \times 10^{-30} m^2$, is obtained from calculations using extensive Gaussian basis sets on N_2, NO^+, NO, CN, CN^-, HCN, HNC and NH_3.[58] The same procedure has been used in a study of the changes in the electric field gradients at the ^{14}N nuclei, induced by hydrogen bonding, in the complexes N_2—HF, N_2—HCl, $(HCN)_2$ and NH_3—HCN. A favourable comparison with the corresponding microwave results is obtained.[59]

Other *ab initio* molecular orbital calculations have been concerned with the electronic distribution around ^{14}N nuclei as estimated from microwave and NQR data. Triple zeta functions have been employed in such calculations[60] on N_3^-, HN_3, NCN_3 and H_3CN_3 and for a series of nitriles.[61]

Large-basis-set calculations of electric field gradients reveal the importance of intermolecular interactions in determining the differences between microwave and NQR data for the gas phase and solid state, respectively, in the case of pyrazole,[62] maleic hydrazide,[63] formamide[64] and acetamide.[64] Similar calculations have been reported for some imidazolium cations[78] and some cyclic amides and thioamides.[79] The ^{14}N electric field gradient in nitriles has been calculated from an *ab initio* procedure using localized orbitals.[80] The effect of substituents on the electric field gradient is found to result mainly from the polarization and conjugation of the C–N bonds with a small contribution from the nitrogen lone-pair electrons. An examination of the basis set dependence of *ab initio* calculations of electric field gradients has revealed the importance of using large basis sets when possible. However, for bigger molecules mixed basis sets, rather than minimal ones, are recommended.[65] Semiempirical molecular orbital methods have also been considered for ^{14}N electric field gradient calculations.[66] In general the semiempirical results

compare qualitatively with those from *ab initio* double zeta basis set calculations and are better than the results found when smaller basis sets are used.

3. CALIBRATION TECHNIQUES AND SIGN CONVENTIONS

The problem of referencing nitrogen NMR shieldings has been adequately dealt with in refs. 5 and 4, and we will consider here only some aspects thereof that are relevant to recent research in nitrogen NMR. We employ consistently the sign convention that ascribes the *plus* sign to the direction of *increasing* magnetic shielding, and we simply use the term "nitrogen shielding" rather than "nitrogen chemical shift", in order to avoid confusion, since the latter term is often associated with a reverse sign convention. Arguments in favour of our choice, which retains the sign of the nuclear magnetic screening constant σ with respect to any reference value thereof, have been presented elsewhere (ref. 5, p. 18).

The use of *internal* referencing procedures, where the standard is dissolved in the sample examined, has practically been abandoned in nitrogen NMR, save for few exceptions, since variations induced in the nitrogen shielding of a standard by molecular interactions in liquids and solutions are quite remarkable, usually 10–40 ppm. Sometimes it is tempting to use the resonance of NH_4^+, that may be present in biochemical samples, as internal reference, but this practice can hardly be recommended in view of the variations in the nitrogen shielding concerned (Table 2). Another demerit of internal standards comes from the fact that they simply contaminate the sample, and can affect the nitrogen shieldings in the latter. However, this technique also has an appeal which lies in getting rid of any bulk magnetic susceptibility effects which are inherent in external referencing procedures. The latter effects are a particular nuisance in the case of paramagnetic samples. Since the range of nitrogen shieldings in such samples is usually much larger than that for diamagnetic substances, and the precision requirements can be something like ± 2 ppm, it may be safer to employ an internal reference, provided that the reference concentration and the solvent are the same throughout the series of samples examined, and the reference employed is calibrated against a primary standard such as neat liquid nitromethane. The idea of internal referencing of nitrogen shieldings has recently gained some momentum, since molecular nitrogen (dinitrogen, N_2) is present in practically all solutions and its concentration is high enough to give a clear, sharp signal in ^{14}N NMR spectra, and it would be quite easy to expose samples to ^{15}N-labelled N_2 for ^{15}N NMR measurements. Such an inert internal standard would afford a good method of referencing nitrogen shieldings provided that the shielding in nitrogen N_2 is immune to solvent effects.

The recent data presented in Table 31 (notes (b) and (c)) show that it is not quite the case, particularly if bulk susceptibility corrections are taken into account, and the variations span a range of about 2 ppm. Nevertheless, this is probably the best internal reference for nitrogen NMR, and it can compete with external references used without bulk susceptibility corrections.

The *external* referencing technique, where typically a set of coaxial tubes is employed, with the reference in the inner tube, and the sample in the annulus, is used almost invariably in present-day nitrogen NMR spectroscopy. An ideal solution would be to use *concentric spherical* sample/reference containers, in order to nullify the effects of any magnetic bulk susceptibility difference between the sample and the standard. Such measurements have actually been carried out, using high-precision ^{14}N NMR, for a number of substances which are potential standards in nitrogen NMR spectroscopy (see Table 1, and references therein). In practice, however, cylindrical coaxial tubes are used, and this results in the appearance of bulk susceptibility effects in the observed, apparent shielding differences. The effects depend on the difference in the relevant susceptibilities, but they are also critically affected by the orientation of the external magnetic field with respect to the axis of the concentric tubes. If the orientation is parallel, such as that in superconducting solenoids, the error is twice as large and of opposite sign with respect to the perpendicular orientation which is characteristic of electromagnet systems. This seemingly obvious point is raised here since nowadays a considerable majority of nitrogen NMR measurements are performed using cryomagnet systems, but many authors do not seem to be aware of the necessity of allowing for this and are quite adamant in employing various "conversion factors", those brought from old measurements where electromagnet systems were used. While it is not improper as such, it simply leads one into errors whose expressions include three susceptibilities, those of the sample, of the actual reference, and of the primary reference, according to schemes IVc and IVd in Table 1. This table shows expressions for the errors involved in various calibrating schemes using the external referencing technique in coaxial tubes. Schemes I and II apply also to the situations where a given nitrogen shielding is measured directly against the primary standard, e.g. neat liquid nitromethane, so that ref. II = ref. I. A way around the problem of bulk susceptibilities is to use a secondary standard whose susceptibility is equal to, or close to, that of the sample, and then to employ a true (intrinsic) conversion constant from Table 2 in order to refer the measured value to the primary standard (scheme II, Table 1). The expressions in Table 1 are based on susceptibility values in the SI system of units, such as those reported in ref. 5, p. 221.

If we exclude brominated solvents, and if we do not need to use schemes IVc or IVd, the largest error due to bulk susceptibility effects is about 2 ppm

for superconducting magnet systems, and about 1 ppm for electromagnets. All this applies to samples and references which do not contain *paramagnetic* impurities or additives. The latter are used frequently, as relaxation reagents, in natural-abundance ^{15}N NMR.

We recommend *neat liquid nitromethane*, $MeNO_2$, as a primary external reference for nitrogen shieldings, according to considerations of various standards presented elsewhere (ref. 5, pp. 27–29). In addition to the latter, there is another point concerned with recent measurements of isotope effects on the nitrogen shielding in $MeNO_2$ (Table 26, footnote (B)). Since it is convenient when the standard used also provides a deuterium lock signal, deuterated nitromethane can be used for this purpose, since its shielding does not differ significantly (-0.038 ppm) from that of CH_3NO_2. If one employs nitromethane in some solvent, e.g. deuterated acetone, it is better to prepare a rather dilute solution and use a true conversion constant (Tables 2 and 26), since solvent-induced shifts in the nitrogen shielding of $MeNO_2$ cover a range of about 10 ppm (ref. 81). It is not recommended to add, for example, 10–20% C_6D_6 to nitromethane, since one then has to interpolate between the shielding in neat nitromethane (arbitrarily set to zero) and that of its dilute solution in benzene ($+4.4$ ppm).

Nitromethane as a direct external reference accounts for about 50% of recent measurements of nitrogen shieldings, but some of these are reported after recalculation vs liquid NH_3 standard, taken at $+380.2$ ppm from neat nitromethane. The latter value, uncorrected for bulk susceptibility effects (Table 6), comes from an electromagnet spectrometer system, while the values recalculated were mostly measured in cryomagnet systems, and therefore we use the term *fictitious ammonia standard* in comments to the tables in such instances. Needless to say, such recalculations are simply confusing and can hardly be recommended. Liquid ammonia as such has rarely been used as a reference, in about 8% of cases, but even then one cannot be quite sure whether it was actually employed.

If dilute solutions of samples are measured, it is quite justified to assume that the bulk susceptibility involved is practically that of the solvent employed. For dilute aqueous solutions, which are common in biochemical investigations, it is advantageous to use analogous solutions of reference substances, in order to get rid of bulk susceptibility effects on the shieldings, but it is recommended that the standards be chosen from those in Table 2, for which true shieldings relative to neat liquid nitromethane are available. If one is careless about concentrations, pH, and gegenions in reference solutions, the uncertainty involved in any attempt to bring the shieldings to a common scale, such as that based on the nitromethane reference, can easily exceed 10 ppm; this is particularly the case for NH_4^+, NO_3^- and HNO_3 (Table 2). Attention is drawn to a considerable difference in the NH_4^+ nitrogen

shielding between solid ammonium nitrate and solid ammonium chloride, which are frequently employed as external references for solid-state spectra.

For *solid* samples, which are usually packed or machined into a cylindrical shape whose axis of rotation is tilted at a magic angle with respect to the vector of the external magnetic field (MAS spectra), bulk susceptibility corrections seem to be negligible.[82] Bulk susceptibility effects should actually vanish for an infinitely long cylinder which is spun at the magic angle, and experimental results obtained for neat liquid nitromethane (ref. 82, see also Table 2) indicate that this seems to hold even for rather short cylinders. Thus, various solid reference substances (Table 2) seem to have a sound footing in recalculations of nitrogen shieldings to the nitromethane scale. Solid NH_4Cl (+341.2 ppm shielding with respect to neat liquid nitromethane) can be recommended for solid-state nitrogen NMR, because of the small width of its ^{15}N resonance.[82]

There are reasons to believe that the *absolute* nuclear screening (shielding) constant σ for the nitrogen nuclei in neat liquid nitromethane, i.e. that referred to bare nitrogen nuclei, is about -130 ppm (ref. 5, pp. 17–30, and references therein), and this can give rough estimates of absolute shieldings in other molecules.

The influence of temperature variations on nitrogen NMR shieldings, and also those of reference substances, can lead to quite measurable shifts of the resonance signals involved. This sounds rather obvious, but sometimes one does not realize that proton decoupling dissipates power into the sample, and that it is large enough to shift the signals via the temperature dependence of nitrogen shieldings. This point has been raised recently[82] and it was shown that the effect is rather negligible for neat liquid nitromethane (*ca.* +0.03 ppm) but is about +0.3 ppm for neat liquid formamide in proton-decoupled MAS spectra with respect to those without proton-decoupling. The relevant temperature coefficients are $+0.0045$ ppm K^{-1} for neat nitromethane, and $+0.0089$ ppm K^{-1} for neat formamide, but the latter has a specific inductive heat capacity which is three times that of nitromethane. This factor should also be taken into consideration in selecting reference substances for nitrogen NMR shieldings, and neat nitromethane seems to be a good choice also from this point of view.

4. EXPERIMENTAL TECHNIQUES

The properties of the naturally occurring nitrogen nuclei, ^{14}N (99.64%, $I = 1$, non-zero quadrupole moment) and ^{15}N (0.36%, $I = \frac{1}{2}$, negative gyromagnetic ratio) have already been presented in ref. 5, pp. 31–64, together with a detailed discussion of various experimental methods involved in

nitrogen NMR spectroscopy; we consider here only some new trends and developments.

4.1. Spectra of liquids and solutions

As far as ^{14}N NMR is concerned, the pulsed Fourier-transform (PFT) technique is commonly employed, but in order to obtain precise values of nitrogen shieldings from ^{14}N NMR spectra one should apply lineshape fitting procedures, with the possible exception of some scanty cases where the resonance signals are sharp enough, i.e. the concomitant rates of ^{14}N quadrupole relaxation are slow. ^{14}N NMR offers a good sensitivity for small and medium-sized molecules, where the signal half-height widths are often below 1 kHz, particularly at high magnetic fields (> 7 T). In such cases, it is easy to obtain good spectra within a couple of minutes for solutions whose concentrations are of the order of 0.1 M. If the signal width is a few tens of hertz, as can happen for some types of molecules and ions, particularly in non-viscous solvents, that limit can easily be pushed down to about 0.001 M. A major drawback of ^{14}N NMR lies in the fact that it is difficult or impossible to resolve, even by lineshape fitting, signals of comparable widths which are close to each other; on the other hand, if the widths are vastly different, it is feasible in ^{14}N NMR spectra to resolve signals which have even exactly the same position on the shielding scale. Spin–spin coupling patterns appear rather exceptionally in ^{14}N spectra, owing to the usually efficient quadrupolar relaxation mechanism for ^{14}N nuclei. Among such exceptions to the rule, one should notice the observation of $^{1}J(^{14}\text{N}-^{31}\text{P})$ in pyrrole moieties bound to phosphorus.[83] A new technique, which is still in its infancy, seems to bring some hope for experimental measurements of indirect (*J*-type) spin–spin couplings where one or two of the nulei involved are quadrupolar.[84–87] This relies on the use of *supercritical* (or *close-to-critical*) *fluids* as solvents, such as CO_2, ethane or ethylene, at around their critical temperatures. Examples include the ^{14}N spectra of some nitrogenous compounds like N_2O, acetonitrile, and nitro compounds, and these yielded the relevant $^{14}\text{N}-^{14}\text{N}$, $^{14}\text{N}-^{1}\text{H}$ and $^{14}\text{N}-^{17}\text{O}$ couplings, owing to drastically reduced quadrupolar relaxation rates and the subsequent appearance in the spectra of the corresponding spin–spin coupling patterns. The apparently old-fashioned continuous-wave (CW) technique seems to show some of its merits in the field of ^{14}N NMR, particularly in the differential saturation variant (ref. 5, p. 56; ref. 4, p. 23) coupled with the use of concentric spherical sample/reference containers. Such applications include precise quantitative measurements of the dimerization of nitroso compounds[30] as well as bulk-susceptibility-free measurements of nitrogen shieldings in a variety of nitrogenous compounds.[88–90]

In ^{15}N NMR, the PFT technique is employed exclusively, since it gives a considerable advantage over continuous-wave from the point of view of sensitivity (narrow resonance signals within a large spectral width) and because of the ease of various manipulations which take advantage of nuclear spin–spin interactions. However, ^{15}N NMR spectroscopy is generally hampered by low sensitivity which results from the low magnetic moment of ^{15}N, its negative gyromagnetic ratio, its natural abundance of only *ca.* 0.4%, and $T_1 >> T_2$. The problem of optimizing the measurements from the point of view of sensitivity has already been considered in detail in ref. 5, and we will survey here only the recent trends in experimental techniques.

A simple remedy for the inherently low sensitivity of ^{15}N NMR measurements is to enrich the substances examined with the ^{15}N isotope. Practical consequences of this are shown[91] in the case of pyrimidine, where a *single* exciting pulse yields a decent, proton-coupled ^{15}N spectrum of a 100% labelled sample. Quite often, the enrichment does not have to come close to 100%, and 5–10% labelling is satisfactory. Selective ^{15}N-labelling is of utmost importance in some spectral assignments, examining reaction pathways, etc. If the former is combined with selective ^{13}C-labelling at adjacent sites, various polarization transfer techniques allow one to trace, by means of ^{15}N spectroscopy, the fate of carbon–nitrogen bonds in chemical and biochemical systems. Another measure acting against the adverse effects of relatively long spin–lattice relaxation times of ^{15}N (as compared with the corresponding T_2 times) relies on the use of *flow-cells*,[92] where the sample flows through a probe system which includes a premagnetization chamber and an "observation volume". Such a cell has been described[92] and actually employed for obtaining a ^{15}N spectrum of *N*-methylimidazole. The ratio of the premagnetization to the observation volume, and the flow rate, play a role which is analogous to that of the relaxation delays in conventional PFT spectroscopy. Flow cells not only reduce the effects of long T_1 times but can also quench nuclear Overhauser effects, which are frequently a nuisance rather than an asset in ^{15}N NMR because of the negative gyromagnetic ratio of the ^{15}N nucleus.

Still another method for sensitivity enhancement in ^{15}N NMR, often by an order of magnitude, makes use of magnetic polarization transfer (PT), where either the polarization of strong nuclear magnets (usually protons) is transferred to other nuclei, e.g. ^{15}N, which is called a *straightforward transfer*, or vice versa, which is a *reverse transfer*, where one detects indirectly the ^{15}N spectrum concerned via proton NMR spectral transitions. The latter solution is gaining popularity in modern NMR spectrometers since it provides an additional gain in sensitivity over the straightforward transfers.

For *one-dimensional* (1-D) ^{15}N spectra, the INEPT (insensitive nuclei enhancement by polarization transfer) pulse sequence is commonly employed

(see ref. 5, pp. 43–50). Its typical version is *non-selective* (polarization transfer from all protons which fulfil certain requirements on the magnitude of ^{1}H–^{15}N coupling in a given experiment), and either *non-refocused* (proton-coupled ^{15}N spectra with phase shifts and inversions of multiplet components) or *refocused* (proton-decoupled and proton-coupled ^{15}N spectra, the latter with the same phase of multiplet components, e.g., upright absorption). The method has to be adjusted, as most PT methods have, a certain range of magnitudes of proton–nitrogen spin–spin couplings which are involved in the transfer. At the outset of INEPT applications in ^{15}N NMR, *one-bond* proton–nitrogen couplings, $^{1}J(^{15}N$–$^{1}H)$, of about 90 Hz were used for that purpose, and this is still a routine way of enhancing the ^{15}N resonances of NH-type nitrogenous moieties in molecules. The effectiveness of the method can be illustrated with the ^{15}N INEPT spectrum (via ^{1}J(NH), refocused) of ^{15}N-labelled trimethoprim,[93, 94] where the sample concentration was only 0.0005 M. Further examples of analogous spectra of ^{15}N-labelled compounds include gramicidin A;[95] phage P22 c2 repressor, 0.006 M;[96] oxytocin and 8-arginine vasopressor, 0.0016 M.[97] As far as natural-abundance ^{15}N INEPT spectra via ^{1}J(NH) are concerned, there are also some outstanding results from the point of view of sensitivity: turkey ovomucoid protein, 0.0015 M,[98] and bilirubin systems, 0.034 M.[99–101] In the latter case,[99] a modified version of INEPT was employed, that including the SINEPT option, where one makes use of the sinewave-like response of INEPT enhancement to obtain the variation of the preset magnitude of proton–nitrogen coupling, thus providing a one-dimensional substitute for 2-D proton–nitrogen spectra. The ^{1}J(NH) INEPT can be employed to differentiate between NH, NH_2, and NH_3 moieties as such, and with respect to non-protonated nitrogen atoms; it can also yield information about whether a given NH moiety undergoes proton exchange, since the latter quenches the polarization transfer via ^{1}J(NH). Numerous examples of such applications include purine systems,[102] flavins,[103] fulvic acid,[104] nucleosides,[105,106] pyridone,[107] protonated Schiff bases,[108] vancomycin,[109] silk fibroin peptides,[110] copolypeptides,[111–113] filamentous bacteriophage M13 coat protein,[114, 115] glyoxal–guanine adducts,[116] nitrotyrosine,[117] aminoazirines,[118] aziridines,[119] aminoboranes,[120] and aminonitrones.[121]

The INEPT method is not limited to the polarization transfer via ^{1}J(NH), and *long-range* couplings between ^{1}H and ^{15}N have recently been employed on a large scale for that purpose, in spite of some pessimistic opinions expressed earlier. It is now fairly common in ^{15}N NMR to employ INEPT pulse sequences adjusted to the relatively large, 5–18 Hz, ^{2}J(NH) and ^{3}J(NH) couplings that exist in aza-aromatic ring systems (pyridine and other azines, azoles, and related structures, including nucleosides, pterins, etc.).[105, 122–128] Much smaller ^{2}J(NH) and other long-range couplings, within a range of

1–3 Hz, have also turned out to be quite useful in ^{15}N INEPT for non-protonated nitrogen atoms.[83,109,129–143]

So far, we have considered non-selective INEPT, while its *selective* variant, that based on "soft" (i.e. relatively long) ^{1}H pulses, yields resonance enhancement only for those ^{15}N nuclei which are coupled to protons covered by a narrow range of excitation by the soft pulse, and which fulfil the conditions on the magnitude of the coupling with respect to the relevant, preset interpulse delays. Examples can be found in the field of azine systems,[144] azoloazines[145] and peptides.[146] The latter case is especially important, since long-range INEPT provides spectral access to non-protonated nitrogen atoms in peptide links; the resonances of the latter cannot be enhanced by $^{1}J(NH)$ polarization transfer. It has been demonstrated[146] that non-selective long-range INEPT yields unwanted effects of ^{1}H magnetization dephasing during the interpulse delays involved in the INEPT sequence. A method has been reported, based on a combination of INEPT and Spin Echo Fourier Transform (SEFT) sequences, that allows one to distinguish various ranges of magnitude of long-range proton–nitrogen couplings.[147,148] Analogous to selective INEPT are *selective population transfer* (SPT) techniques via $^{1}J(NH)$.[149]

Specific applications of INEPT involve the observation of weak satellites that result from ^{15}N coupling to ^{29}Si or ^{209}Pb.[99,150–154] There are also examples of INEPT where the polarization transfer to ^{15}N takes place from nuclei other than protons, e.g. via $^{2}J(^{31}P–^{15}N)$ in P–Au–N moieties of phthalimido complexes,[155] and via $^{2}J(^{19}F–^{15}N)$ of about 52 Hz in fluoroderivatives of azine ring systems.[156]

A competitive method for executing polarization transfer to ^{15}N is the well-known *DEPT sequence* (distortionless enhancement by polarization transfer). This was employed, via $^{1}J(NH)$, for 0.006 M solutions of ^{15}N-labelled nucleosides,[157] for ^{15}N-labelled flavins,[158] vitamin B_{12},[159] and protein backbone;[160,161] in the last case, the DEPT method was also used to distinguish the mobility of individual parts of the backbone, and adjusted such that the ^{15}N resonances from rigid parts appeared in the upright adsorption mode while those from mobile parts were inverted. DEPT via long-range proton–nitrogen couplings has also been employed successfully in heteroaromatic systems,[122,162,163] and for the nitro group in biosynthetically labelled 2-$^{15}NO_2$-propanoic acid.[164] A generalized version of DEPT, DEPT-GL, was employed in order to simultaneously optimize the measurement for both $^{2}J(NH)$ of about 7.5 Hz and $^{1}J(NH)$ of about 90 Hz;[165] this is important for identification of glycine units, which include —CH_2—NH— moieties, in peptide chains. Theoretical simulations of long-range DEPT and INEPT, using the density matrix formalism, combined with model experiments, suggest that ^{15}N long-range INEPT is more promising.[166]

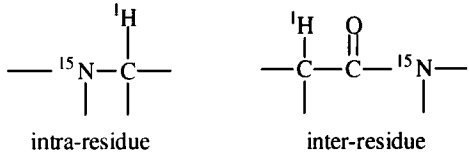
Heteronuclear magnetization transfer by fulfilment of the Hartmann–Hahn condition is usually limited to solid-state experiments, but recently it has been adapted to ^{15}N-labelled His units in peptides in solution[167] and turned out to be slightly more effective than INEPT in ^{15}N signal intensity enhancement.

Two-dimensional (2-D) experiments have recently been engaged on a large scale in ^{15}N NMR spectroscopy, particularly for peptide systems and other biologically important structures. Such methods are usually involved in tracking down proton–nitrogen connectivities. *Straightforward* experiments are those where the 2-D spectra are detected by collecting free-induction decays within the ^{15}N frequency domain, while *reverse* measurements use detection within the ^{1}H domain. The latter have been introduced into common practice quite recently, with the advent of specially constructed probe heads, where the decoupler coils are fed with ^{15}N resonance frequencies. The reverse methods give, in principle, a considerable gain in sensitivity over the straightforward techniques. Usually, 2-D ^{15}N/^{1}H pulse sequences involve polarization transfer and multiple quantum filtering (zero and double quantum, in most cases); the latter enables one to filter out "singlets", i.e. the resonances of nuclei which are not coupled within the frequency framework concerned, for example the proton resonances of ^{14}N—H moieties in reverse 2-D ^{1}H–^{15}N NMR measurements. Special sequences whose aim is quenching of the unwanted signals of solvents (usually those of water) are also important in reverse 2-D methods; recently, the use of *gradient pulses* for that purpose[168] seems to enable one to carry out the ^{1}H detection in reverse 2-D and 3-D experiments, including ^{15}N, even right at the place occupied by the proton signal of water. Typical 2-D experiments have to be adjusted to a certain range of $J(^{15}\text{N}-^{1}\text{H})$ couplings, and these we will call *heteronuclear 2-D COSY* (correlation spectroscopy); sometimes, they are known as 2-D FE (forbidden echo) methods. One can employ proton–nitrogen decoupling at appropriate stages of measurements and then the method yields a map of singlet cross-peaks (*decoupled COSY*); otherwise, two-dimensional multiplet clusters appear which bear information about the couplings involved (*coupled COSY*). Theoretical simulations of 2-D spectra, using the density matrix approach, have been presented[169] by means of the SPHINX algorithm, which covers also cases of tightly coupled nuclei.

Examples of *straightforward* (i.e. ^{15}N-detected) 2-D COSY via ^{1}J(NH), at natural abundance of ^{15}N, include: 0.05 M gramicidin A, 42 h of accumulation,[170] and 24 h;[171] 0.07 M antamanide;[172] bilirubin systems;[173] 0.15 M vancomycin;[109] cyclosporin A;[174] cyclic heptapeptides;[175] and phosphazoles.[176] Analogous methods have been applied for ^{15}N-labelled samples of proteins of molecular weight 6000–155 000;[177] yeast tRNA;[178] *Escherichia coli* 5S RNA, 120 nitrogen bases;[179] filamentous bacteriophage coat protein in

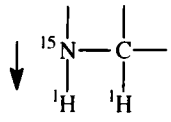
micelles;[160, 180] and 0.02 M actinomycin D.[181] One can also employ *long-range* proton–nitrogen couplings in straightforward COSY, as has been done for peptides,[182] using the well-known COLOC sequence; analogous measurements were done for nitrocellulose and other saccharide nitrates.[183,184] While straightforward COSY is, in theory, less sensitive than its reverse variant, it has been argued that the difference can be offset by larger sample volumes in the former method, and the difficulties inherent in the latter as far as effective suppressing of solvent peaks is concerned for aqueous solutions which are typical in peptide chemistry and biochemistry.[177]

However, most recent 2-D COSY measurements involving ^{15}N have been performed by means of the *reverse* (i.e. ^{1}H-detected) version, using multiple quantum filtering and therefore called HMQC (heteronuclear multiple quantum correlation).[185-187] Most often, ^{1}H–^{15}N HMQC employs *one-bond* couplings, $^{1}J(NH)$, of about 90 Hz, and there have been examples of such measurements at natural abundance of ^{15}N, e.g. 0.011 M human Ahx little gastrin hormone in micelles,[188] where HMQC was aided with double INEPT (NEMESIS); Met-enkephalin;[189] 0.04 M Leu-enkephalin;[190] hen egg white lysozyme;[191] bovine pancreatic trypsin inhibitor;[191] 0.15 M turkey ovomucoid third domain;[98] bleomycin A_2;[192] 3-aminoacrylic esters;[193] pentacarbonylchromium aminophosphane complexes;[152] model peptides;[187] oligonucleotides;[194] and trypanothione disulphide.[195] However, labelling with ^{15}N is often unavoidable for complete or nearly-complete spectral assignments in the case of large molecules, and a good example is provided by the HMQC spectra of 0.023 M bovine pancreatic trypsin inhibitor whose molecular weight is about 6500. Further examples of ^{15}N labelled samples and ^{1}H–^{15}N HMQC spectra thereof include: 0.002–0.003 M T4 lysozyme, mol. wt 18 700;[198-200] 0.006–0.009 M flavodoxin from *Anabaena 7120*, mol. wt 21 000;[103,201,202] 0.002–0.003 M ferrocytochrome c_2;[177,203] *Escherichia coli* thioredoxin,[204] tRNA,[205-207] and 5S RNA;[208] 0.015 M DNA-binding protein *ner* from phage Mu;[209] human *N-ras* p21 protein, mol. wt 21 000;[210] Pf1 coat protein;[211] 0.0026 M M13 coat protein;[212] repressor protein;[96] Lys and Leu units in *λ-cro* repressor;[213] staphylococcal nuclease,[214-216] where 127 residues out of 136 have been assigned in the backbone; *Taq*I endonuclease;[217] 0.02 M actinomycin D;[181] aridicin aglycon complexed with model peptides;[218] purine pancreatic phospholipase A_2;[219] amanitin and its analogues;[220] human carbonic anhydrase II;[221] oxytocin and 8-argininevasopressin;[97] adenosine and deoxycytidine;[222] adenosine in A–G and A–C mispairs in some duplexes;[223] DNA oligomers;[224] uridine units in *Escherichia coli* $tRNA^{Phe}$ obtained from *his*T mutants;[225] nitrogenous metabolites of yeast;[226] and cyclic structures containing N and S.[227] A scheme has been proposed[228] for assignments of proton and nitrogen resonances in peptide systems by varying ^{15}N label contents and recording the intensities of $^{1}H/^{15}N$ correlation peaks in the relevant HMQC spectra.



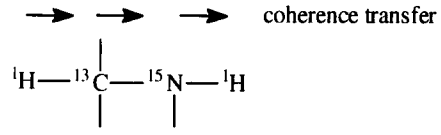
[1]

In reverse heteronuclear COSY (HMQC), *long-range* spin–spin couplings, such as ^{2}J(NH) and ^{3}J(NH), can also be exploited and this has been done for DNA-binding protein *ner* from phage Mu,[229] staphylococcal nuclease,[230] cytochrome *c*-553,[231] flavodoxin,[231] and ^{15}N-labelled leucine units in P22c2 repressor protein.[96] The use of such couplings is important for peptide system investigations, from the point of view of tracking *intra-residue* and *inter-residue connectivities* such as [1], rather than those within NH moieties. This can be done directly, by HMQC oriented for the two-bond and three-bond couplings concerned, or by *relayed HMQC*[229] where the information is passed through ^{1}J(NH) from nitrogen to proton in NH, and then from the latter to the target proton, by the corresponding proton–proton coupling, for example [2]. Quite recently, reverse COSY (from the point of view of ^{15}N NMR) has been used in measurements of ^{13}C/^{15}N connectivities, via ^{13}C detection and ^{1}J(CN) couplings, in uniformly and selectively ^{13}C/^{15}N-labelled proteins, *Anabaena 7120* ferrodoxin,[233] and acetamide.[234]



[2]

More complicated schemes of relayed COSY include coherence transfer between protons through carbon–proton, carbon–nitrogen, and nitrogen–proton couplings, e.g. [3], and these can also yield nitrogen connectivities to carbon and hydrogen, as has been done for model tripeptides[235] and polypeptides.[236]



[3]

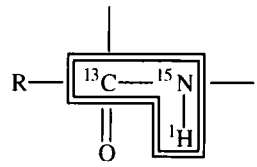
While 2-D HMQC techniques involve sensitivity enhancements which are related to the one-dimensional DEPT, there seems to be a revival of reverse

2-D experiments, $^{1}H/^{15}N$, based on single quantum connectivities and INEPT-type polarization transfer, combined with water proton peak quenching sequences. These are called *HSQC* (heteronuclear single quantum correlation), methods, and their applications include: bovine pancreatic trypsin inhibitor;[237] H-*ras* p21 protein, including labile NH protons;[238] phosphotransferase protein III^{Glc};[239] *λ-cro* repressor protein;[240] and binding of metal ions to *Escherichia coli* ribonuclease HI.[241]

Now we turn to *three-dimensional* (3-D) COSY in its reverse, HMQC variant, and divide this into *hetero–hetero* 3-D COSY, where three kinds of nuclei are involved (e.g. ^{15}N, ^{13}C and ^{1}H), and *homo–hetero* 3-D COSY, where proton–proton correlations are unfolded into the third dimension, that of ^{15}N resonance frequencies. The additional dimension, with respect to 2-D experiments, offers a considerable aid in unravelling complicated spectra of large peptide systems, up to a molecular weight of about 25 000;[242] usually, ^{15}N- and ^{13}C-labelling is a prerequisite.

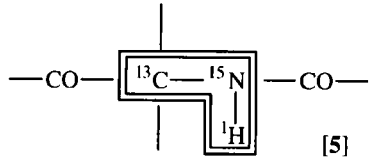
Hetero–hetero 3-D COSY, $^{1}H/^{13}C/^{15}N$, proton-detected, via one-bond couplings, has been employed in nearly complete spectral assignments of backbone peptide units in 0.0007 M inflammatory protein C5a, mol. wt 8500, 177 h including 47 h of input–output operations;[243] and in calmodulin, mol. wt. 16 700, in 2 days.[244, 245] The latter experiments included the following variants.

(i) *HNCO* – this correlates ^{1}H and ^{15}N within a given NH moiety, and these with ^{13}CO in the preceding amino acid residue [**4**].



[4]

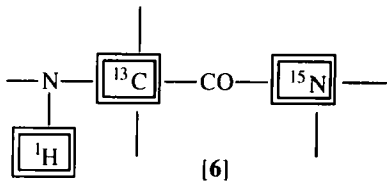
(ii) *HNCA* – this yields intra-residue correlations [**5**], together with some weak correlations with C_α in the preceding unit.



[5]

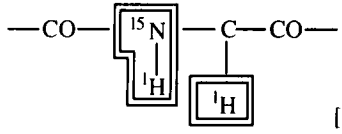
(iii) *HCACO*, which correlates NH protons with intra-residue carbons, but only those coupled to ^{15}N.

(iv) *3-D RELAY HCA(CO)N*, which correlates $^{1}H/^{13}C$ with ^{15}N of the succeeding unit, i.e. [**6**] where the intervening nuclei act as relays.



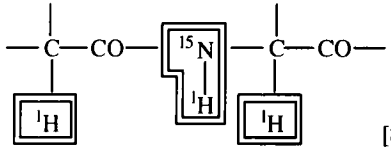
[6]

(v) ^{15}N *HOHAHA HMQC*, a homo–hetero 3-D experiment, which correlates ^{1}H and ^{15}N in the system **[7]**.



[7]

Homo–hetero 3-D COSY can be thought of as proton–proton 2-D COSY unfolded into the dimension of ^{15}N frequencies. This technique has been employed in the case of 0.002 M ribonuclease H[246] (mol. wt. 17 600), labelled with ^{13}C and ^{15}N, where the proton–proton connectivities in **[8]** were resolved with respect to ^{15}N. Further examples include ^{15}N-labelled samples of model tripeptides,[247] CMP-KDO synthetase,[248] and interleukin-1β from *Escherichia coli* (153 amino acid residues).[249] This scheme can also include relays, e.g. $^{13}C_{\alpha}$, as in the H(CA)NNH scheme[250] that was employed for calmodulin 3-D spectra as an example of optimization of the method with respect to ^{13}C–^{15}N-labelled peptide linkages. Three-dimensional $^{1}H/^{13}C/^{15}N$ experiments can also be adapted to measurements of long-range proton–proton couplings in peptides,[251-253] and for samples labelled with ^{15}N only.[254]



[8]

Recently, *four-dimensional* (4-D) techniques have been introduced in protein research,[255] those based on the HCA(CO)N method described above. The fourth dimension is provided by the ^{13}CO frequency domain, while the parent 3-D experiment uses the latter nuclei simply as magnetization relays. Such 4-D $^{1}H/^{13}C/^{13}CO/^{15}N$ spectra were employed in unravelling the corresponding resonances and inter-nuclear connectivities in calmodulin.[255,256]

Measurements which bear some formal relation to homo–hetero 3-D COSY are those based on proton–proton 2-D NOESY (nuclear Overhauser effect correlation spectroscopy) resolved with respect to ^{15}N frequencies.[257]

These can be called *IDNOESY* (isotope directed NOESY), where the isotope concerned is ^{15}N. NOESY spectra are based on correlations where cross-relaxation processes and/or proton chemical exchange phenomena are involved. Under certain conditions, such spectra are commonly employed in estimating proton–proton distances in globular macromolecules, usually proteins. The unfolding into the relevant ^{15}N resonance frequency dimension greatly facilitates such applications to peptide systems, and examples of these include: T4 lysozyme;[198-200] staphylococcal nuclease;[215,258] inflammation protein C5a;[243] ribonuclease H;[246] interleukin-1β;[249] porcine pancreatic phospholipase A_2;[219] DNA-binding protein *ner* from phage Mu;[209] and *Salmonella* phage P22 c2 repressor.[259]

Various combinations of the 2-D, 3-D, and 4-D techniques described above have been employed recently in full or nearly full assignments of nitrogen shieldings (and those of the other nuclei concerned) in protein and peptide systems: *Escherichi coli* ribonuclase H,[260] oxidized and reduced forms of thioredoxin,[261] and apocytochrome b_{562};[262] ribonuclease T1;[263] *Lactobacillus casei* dihydrofolate reductase;[264] calmodulin;[245,256] oxidized flavodoxin from *Anacystis nidulans*;[265] interleukin-1β;[266] phosphotransferase protein III^{Glc};[239] *Bacillus subtilis* enzyme III^{Glc};[267] and λ-*cro* repressor protein.[240]

Finally, we turn back to 2-D ^{15}N NMR in its less common variants and applications. 2-D $^1H/^{15}N$ NOESY experiments have been performed for staphylococcal nuclease,[268] together with measurements of the relaxation times concerned. The use of pseudo-single-quantum COSY (PS-COSY) for ^{15}N-labelled peptides shows that the method effectively removes dipolar broadening from the ^1H spectra of the ^{15}NH peptide moieties, owing to the zero-quantum coherences employed.[269] A special case is presented by the 2-D $^{15}N/^{15}N$ exchange spectra of model peptides,[270] where the relations are based on *cis–trans* amide bond interconversions. One should also mention the two-dimensional version of SINEPT applied to pyridone;[271] 1-D SINEPT has already been mentioned in considerations of INEPT pulse sequence applications in ^{15}N NMR.

We shall also consider some substitutes for 2-D and 3-D methods in nitrogen NMR, those performed within the general scheme of *double* and *triple resonance*. The $^1H\{^{15}N\}$ INDOR (internuclear double resonance) technique detects ^{15}N resonance frequencies via ^{15}N decoupling effects in ^1H spectra, by sweeping or incrementing the decoupling frequency,[271-275] a special case is $^6Li\{^{15}N\}$ INDOR.[276] A modification of $^1H\{^{15}N\}$ INDOR consists in recording *difference spectra*, where one subtracts undecoupled spectra from decoupled ones. The latter technique has been applied to large molecules: staphylococcal nuclease;[277] *Escherichia coli* RNA;[278,279] thioredoxin;[204] 7-^{15}N-labelled guanosine oligonucleotides;[280] and yeast tRNA.[178] Analogous triple-resonance experiments include: a pyridone derivative (^{15}N-labelled) where

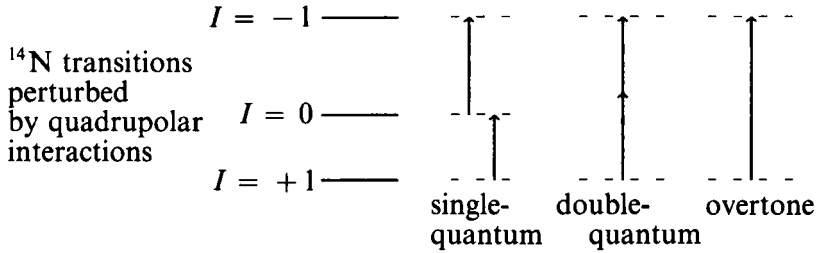


Fig. 1.

the ^{13}C nuclei were noise-decoupled from protons and selectively decoupled from ^{15}N, ^{13}C{^{1}H, noise/^{15}N, selective};[281] pyrimidine ring, ^{1}H{^{1}H, selective/^{15}N, selective}, and ^{13}C{^{1}H, noise/^{15}N, selective}.[282] Such methods are also suitable for determining magnitudes and relative signs of the spin–spin coupling constants involved. Related to ^{1}H{^{15}N} INDOR techniques is a report on the method of calibrating the ^{15}N decoupler radiofrequency field strength.[283]

4.2. Solid-state nitrogen NMR

A great deal of nitrogen NMR investigation of solids has recently been carried out. As far as ^{14}N NMR is concerned, some new techniques have been introduced. We start our considerations with something which is not actually solid-state ^{14}N NMR but ^{14}N NMR *imaging* of liquid N_2 in contact with a high-temperature superconductor.[284] If a plastic rod is immersed in liquid dinitrogen, the image obtained shows a sharp boundary, but when a superconductor of the $Y_1Ba_2Cu_3O_{7-\delta}$ type is used, there is a dark region extending 5–8 mm into the liquid, owing to the high gradient of magnetic field in the vicinity of the superconducting solid which exerts strong bulk-susceptibility effects. This enables one to distinguish, by ^{14}N NMR imaging, between the superconducting and non-conducting states at liquid nitrogen temperatures.

An interesting example of *zero-field* NMR is provided[285] by proton–^{14}N double resonance in solid methylammonium perchlorate, which shows a high-temperature transition for the anion.

A novel approach to ^{14}N NMR in solids is that based on *overtone* ^{14}N NMR transitions[286–290] at nearly twice the resonance frequency of ^{14}N, which are detected indirectly via ^{1}H transitions and ^{1}H–^{14}N dipolar couplings.

The overtone signals are broadened only by second orders in the quadrupolar perturbations (Fig. 1). This technique, when applied to single crystals, removes the large quadrupolar splittings involved, and reduces the spectral

width from about 1.5 MHz for single-quantum ^{14}N NMR to about 100 kHz for overtones. The method has been employed for investigations of peptide backbone conformations by two-dimensional ^{1}H/^{14}N spectra[291] and for 2-D ^{13}C/^{14}N spectra of crystalline amino acids, via ^{1}H/^{13}C/^{14}N triple resonance.[286,290]

More conventional ^{14}N *single-crystal* spectra are typically employed in determinations of ^{14}N quadrupole coupling, electric field gradient, and magnetic shielding tensors as well as in detecting molecular reorientations in crystals. Such studies include: L-asparagine monohydrate under high-power proton decoupling;[292] L-histidine hydrochloride monohydrate;[293] KNO_3;[145,294] silver, barium, and lead nitrates;[295] ammonium perchlorate;[296] and polychlorinated dinitrobenzenes.[297] Effects of spin diffusion in single-crystal ammonium sulphate were examined by ^{14}N NMR and the results were compared with theory, from the point of view of single- and double-quantum spin diffusion mechanisms.[298] Expressions for ^{14}N NMR lineshapes were derived[299] for crystalline $Me_4N^+ZnCl_4^-$ in the commensurate phase. A double-resonance ^{14}N/^{1}H probe for crystal samples has been described.[300]

In some experiments, the NMR characteristics of ^{14}N nuclei in solids can be obtained indirectly, e.g. the electric field gradient tensor at ^{14}N via ^{13}C CPMAS spectra (see below) and ^{13}C–^{14}N residual dipolar splittings.[301,302] Effects of ^{14}N relaxation in the solid state have been observed for single-crystal alanine, via 2-D ^{13}C/^{1}H spectra; and ^{14}N–deuterium dipolar couplings were determined in urea-d_4 from deuterium quadrupole echo spectra.[304]

^{14}N NMR of *powdery solids* is also useful in gaining an insight into their structure. Merits and demerits of ^{1}H $\leftarrow$ ^{14}N magnetic polarization transfer (cross-polarization, CP) in such NMR measurements have been discussed in detail[305] for amino acid residues in peptides, for glycine, and for ammonium sulphate. There is a problem in using rather high radiofrequency fields for executing such a transfer via single-quantum ^{14}N transitions because of the large spectral width of the ^{14}N frequencies involved, and the use of the corresponding double-quantum transitions seems to be a suitable solution. The latter problem is of the same nature as that considered in the case of overtone ^{14}N NMR

Conventional ^{14}N *static* (i.e. *non-spun*) *powder NMR* spectra are typically used for estimating electric field gradient tensor characteristics at ^{14}N, as was the case for trifluoroaminoboranes[306] and ammonium thiocyanate;[307] and for the identification of reorientation transitions within solids: the β-phase of $^{14}N_2$ in liquid helium bath;[308] ammonium thiocyanate;[307] methylammonium nitrate;[309] perovskites;[310] polycrystalline choline salts,[311-313] also in the presence of paramagnetic ions;[314] and phosphatidylcholine bilayers.[315]

With ^{15}N NMR *in solids*, there are obviously no quadrupolar effects save for those exerted by other nuclei. *Single-crystal* studies in ^{15}N NMR are usually oriented towards magnetic shielding tensors of ^{15}N, dipolar

couplings, and molecular motions within the crystal lattice. Usually, ^{15}N-labelling is employed. Investigations of this type include: ammonium perchlorate;[316] tris-sarcosine calcium chloride;[317,318] peptides;[319] and ^{13}C- and ^{15}N-labelled glycylglycine–H_2O–HCl.[320] A special case is the ^{15}N spectrum of the β-phase of solid $^{15}N_2$ in a liquid helium bath,[321] where the signal width reached 4 kHz, and a comparison with the analogous spectrum of the ^{14}N isotopomer indicated that there is a significant difference in molecular rotations between solid $^{15}N_2$ and $^{14}N_2$.

Similar applications involve *static powder* ^{15}N spectra and ^{15}N MASS (magic angle spinning sidebands) spectra; in the latter the solid ample is spun at a magic angle with respect to the external magnetic field, but the rate of rotation is slow enough to generate families of sidebands which flank the central signals concerned. Examples of such studies by means of static powder spectra include: ferroelectric phase transitions at 130 K in tris-sarcosine calcium chloride;[322] polypeptides;[319,323] dipeptides;[324] Ala–Pro peptide linkages;[325] terminal glycine moiety in Boc-Gly-Gly-[^{15}N]-Gly;[326] nylon-6;[327] asparagine,[328] ^1H-decoupled and dipole-modulated spectra; bacteriorhodopsin;[329] acetophenone oxime;[330] *p*-substituted benzonitriles;[331] azobenzene;[332] and KCN–KBr systems.[333] Extensive studies of this kind have been carried out for micelles and bilayers containing membrane-bound fd coat protein;[161,334–337] gramicidin A;[95,338,344] and a hydrophobic peptide, Boc-Leu-Phe-OMe.[309] Static ^{15}N spectra of solid $^{15}N^{14}NO$ at low temperatures, under O_2 atmosphere, were employed in motion analysis in the solid.[345]

While single-crystal ^{15}N NMR measurements are usually better suited to the determination of the magnetic shielding anisotropy tensor orientation with respect to the relevant molecular frame, this can also be done with polycrystalline samples, as was shown in the case of L-[1-^{13}C]alanyl-L-[^{15}N]alanine,[346,347] where a ^1H-dipole-modulated, ^{13}C-dipole-coupled ^{15}N spectrum was measured.

^{15}N MASS spectra have been employed for analogous purposes for ^{15}N-labelled samples of bacteriorhodopsin;[348] amminoplatinum complexes;[349] 1-aminoethylphosphonic acid, Ala-P;[350] *p*-substituted benzonitriles;[331] ammonium thiocyanate;[351] and ammonium nitrate.[352,353]

The largest area of applications of solid-state ^{15}N NMR is concerned with the *magic angle spinning* (MAS) technique, which is usually combined with magnetic polarization transfer, usually from ^1H, by fulfilling the Hahn–Hartmann condition. This *cross-polarization* (CP) and MAS combination is conventionally abbreviated as CPMAS, with a tacit assumption that the spinning rate involved is high enough to preclude the appearance of significant spinning sidebands. The method gives high-resolution or nearly high-resolution ^{15}N spectra of solids, and provides a powerful tool for insight into the solid-state structure of nitrogenous substances. There are some special

problems concerned with the cross-polarization transfer from ^{1}H to low-magnetogyric-ratio nuclei, such as ^{15}N, and these have recently been considered.[354]

So far, there have been rather few applications of ^{15}N CPMAS NMR at the natural abundance of the isotope; these included: two types of environment for tetrapropylammonium cations occluded in MFI-type zeolites;[355] aminonaphthalene derivatives and the tetrazole anion;[356] indolinones;[357] trimethoprim–sulphamethoxazole complex;[358] α-helix and β-sheet structures in homopolypeptide polymers[74] and nylons;[359–362] synthetic and natural melanins;[363] elastin;[364] copper(I) complexes of 1,10-phenanthroline;[365] conducting polymers containing —CR=N—N=CR— units oxidized with iodine,[366] and their polyimine precursors.[367]

In most cases, ^{15}N-labelling is employed in ^{15}N CPMAS NMR. This technique was used for observations of crystalline and amorphous domains in nylon-type polymers.[368–375] Other polymer studies include polyaniline;[376] acetonitrile polymers obtained in a plasma chamber;[377] HCN polymers;[378] nitrocellulose and nitramines;[379,380] polypyrrole,[381] and polypyrrolenemethine polymers;[382] allantoin;[383] and tetracycline antibiotics.[384] Investigations on a large scale have been carried out for peptide and protein systems: terminal ^{15}N-glycine units in di- and tripeptides, including hydrogen bond effects on the shieldings;[385] carboxypeptidase A,[386] and $^{13}C/^{15}N$-labelled glycyltyrosine as a substrate in a complex with the former,[387] ^{15}N-labelled valine units in staphylococcal nuclease;[388] [^{15}N]His-57 in the catalytic triad of α-lytic protease[389–391] and analogous studies on serine protease;[392] cell-wall peptidoglycan in intact lyophilized cells of *Aerococcus viridans*,[393] and effects of penicillin on the peptidoglycan;[394] tissue cultures of alfalfa, *Medicago sativa*;[395] nitrogen fixation by *Methanobacterium halobium* and *Methanospirillum hungatei*,[396] and also by *Methanobacterium thermoautotropicum*;[397] lyophilized cells of *Klebsiella pneumoniae* grown on labelled ammonium and dinitrogen;[398] glyphosate metabolism in *Pseudomonas*;[399] metabolism of [^{15}N]His and [^{15}N]Lys in insect cuticles, those of tobacco hornworm;[400,401] [^{15}N]Lys in collagen fibres; peat incubated with [^{15}N]glycine;[402] ammoniated straw;[403] melanoidins obtained from xylose and [^{15}N]glycine.[404,405] Other ^{15}N-labelled systems of biological importance, studied by ^{15}N CPMAS NMR, included DNA (uniformly labelled) in *Escherichia coli* infected with filamentous bacteriophage fd, 1-D and 2-D spectra, including effects of proton exchange among nitrogen atoms;[406] and bacteriorhodopsin systems,[329,407–409] also including effects of proton exchange.[410]

Studies on simpler chemical structures include aminophosphonic acids;[411] azo hydrazone tautomerism in the solid state;[412] azobenzene;[330,332] phthalimide–Au–PEt_2 systems;[413] nitroguanidine;[414] silicon nitrides,[415] oxynitrides,[416] and YSiAlON nitride-type glasses.[417] In ammonium nitrate,[353,418]

there was also the observation of nuclear Overhauser effects,[419] contrary to the belief that motions in crystals are too slow to provide cross-relaxations. In ammonium sulphate[420] two inequivalent sites in the crystal have been detected, 0.3 ppm apart in the spectrum at 290 K, but 1.2 ppm apart at temperatures below the phase transition at 223 K – this is quite important from the point of view of calibration techniques for nitrogen shieldings in solid-state NMR, since ammonium sulphate is sometimes employed as a reference. Attention is drawn to the first report on the nitrogen shielding in an iminophosphonium cation, $R-N{\equiv}P^+$, based on the ^{15}N CPMAS NMR of a labelled sample.[421]

Applications of ^{15}N CPMAS of labelled samples also include substances adsorbed on solids, such as ammonia and trimethylamine on zeolites;[422] pyridine on γ-alumina;[423] and pyridine on coals.[424] However, in some cases, conventional ^{15}N NMR methods give resonance signals which are sharp enough to differentiate various environments of the adsorbate, like those for acetonitrile adsorbed on zeolites.[425] The same may be true for objects like live rats[426] where ^{15}N-labelled glycine was detected in a specially constructed probe with a radiofrequency coil which was implanted between the liver lobes of the animal and fixed to the abdominal wall.

Especially important from the point of view of methodology are extensive studies on *dynamic effects* in variable-temperature ^{15}N CPMAS NMR spectra of ^{15}N-labelled molecular systems with intramolecular proton exchange pathways.[427–439] These will be considered in Section 4.6 on dynamic nitrogen NMR.

An interesting variant of ^{15}N CPMAS NMR includes a delay introduced between the CP phase and acquisition, during which the ^{15}N magnetization evolves under the influence of dipolar couplings with protons (proton–nitrogen decoupling is turned off); this is called *interrupted decoupling*, *dipolar dephasing*, or *dipolar rotational spin echo* ^{15}N CPMAS. This can be employed for attenuating the signals of NH-type moieties with respect to those of non-protonated nitrogens, as was done for cured urea–formaldehyde resins;[440] 4,4′-methylene-bis(phenyl isocyanate)-based resins;[441] phenolic resins cured with hexamethylene tetramine;[442] and polyimide polymers.[443] Analogous experiments, with proton–proton couplings removed by means of multiple pulse irradiation, were used in studies of peptidoglycan mobility,[393] and effects on the latter of penicillin.[394] Carbon–nitrogen dipolar couplings can also be used in such methods, for $^{13}C/^{15}N$ doubly labelled bonds, by performing CP from ^1H to either ^{13}C or ^{15}N, and then by leaving the relevant magnetization to evolve for a certain period under the influence of the dipolar coupling, as was done for solid peptide structures.[346,347] The latter technique is a substitute for double-cross-polarization methods which will be considered below. Related to the above are ^{13}C-detected *rotational-echo-double-*

resonance $^{13}C/^{15}N$ measurements (REDOR), for $^{13}C/^{15}N$-labelled bonds in alanine crystals[444,445] and HCN polymers,[446] where the ^{13}C magnetization was dephased by ^{15}N 180° pulses to yield the relevant dipolar carbon–nitrogen couplings; the latter were then used in estimations of carbon–nitrogen distances.

Double-cross-polarization ^{15}N MAS NMR (^{15}N DCPMAS) is employed typically for detecting and tracing the fate of individual, $^{13}C/^{15}N$ doubly labelled bonds, usually those involved in peptide linkages in solid samples, or those in such labelled amino acids which are fed to biological systems. The magnetization transfer, via cross-polarization, takes place in two steps,[446–448] usually along the pathway

$$^{1}H \xrightarrow{CP} {}^{13}C \xrightarrow{CP} {}^{15}N$$

Such applications of ^{15}N DCPMAS NMR include: methionine metabolism in soybean cotyledons;[449] allantoin[450] and alanine[451] metabolism in *Aerococcus viridans*; heteropeptide polymers;[452] and HCN polymers.[453]

Finally, we should mention the application of CPMAS in ^{14}N NMR,[454] where spin–rotational relaxation was examined in the rotor solid KCN; and a discussion[455] of the effects exerted on ^{13}C CPMAS NMR spectra by spin $I = 1$ nuclei, such as ^{14}N.

4.3. Nitrogen NMR in partially oriented phases including liquid crystals

Partial orientation of molecules in solution can give spectral effects which resemble those characteristic of fully oriented solid phases. We start our considerations with molecular alignment that is effected by strong *electric fields*. Non-spun samples of neat liquid pyridine and pyrimidine,[456] placed in a field $E = 5.68 \times 10^5\,V\,m^{-1}$ provided by gold-plated electrodes 3 mm apart, show signal doubling of *ca.* 250 Hz in ^{14}N NMR as a manifestation of ^{14}N quadrupole coupling and partial orientation of the molecules. Similar results were obtained for neat liquid nitromethane,[457] and for 2-D-propene-2-nitrile ($E = 8.1 \times 10^6\,V\,m,^{-1}$ spacing *ca.* 830 Hz).[458]

More often, molecular alignment is effected in NMR experiments by the *external magnetic field*, via diamagnetic anisotropy of the solute concerned or by that of the solvent, usually a liquid crystal phase. In solutions of bacteriophage fd coat protein the ^{15}N spectra show that the virus particles become oriented,[319] particularly their Trp-26 sidechains; this orientation was employed for obtaining two-dimensional spectra of the nitrogen shieldings against the corresponding dipolar ^{1}H–^{15}N splittings ("^{15}N–^{1}H separated local-field spectra", as they were called). Similar spectra were obtained for ^{15}N-labelled gramicidin A in oriented phosphatidylcholine bilayers,[342, 459, 460]

yielding information about torsion angles in the peptide backbone; and also for calcium and spermine interactions in such bilayers.[461] Quadrupole splittings were observed in the ^{14}N NMR spectra of the choline moieties of the bilayers.[462, 463]

^{14}N NMR of partially oriented molecules and ions is typically employed for observations of ^{14}N quadrupole splittings. Disodium cromoglycate (DSCG) liquid-crystal phase can dissolve inorganic salts; DSCG–H_2O solutions of ammonium and tetramethylammonium nitrates[464] showed such splittings in the ^{14}N spectra, thus indicating that the symmetry of the ammonium ions is distorted in such phases. Quadrupole splittings were also observed in the ^{14}N spectra of acetonitrile in nematic phases,[465] but an evidently anomalous value of the ^{14}N quadrupole coupling constant in the molecule concerned was found in the thermotropic liquid crystals 2LI 1167 and Phase IV (Merck);[466] the constant was linearly dependent on temperature – 170.8 kHz at 5°C to 205.2 kHz at 65°C – while gas-phase microwave measurements give a value of 489.4 kHz. Quadrupole splittings were observed in the ^{14}N spectra of surfactants in lamellar lyotropic mesophases, including dimethyldodecylammonium bromide[467] as well as dodecyl- and hexadecyl-bound $NMe_3^+ Cl^-$ moieties.[468]

^{15}N NMR measurements for liquid-crystal solutions included ^{15}N- and ^{13}C-labelled HCN,[469] where ^1J(NH) was found to be negative; and phosphatidylcholine multilayers and bilayers in sonicated vesicles,[470] where the temperature-dependent ^{15}N resonance linewidths were used to monitor the "melting" of the liquid crystal phases concerned. Doubly ^{15}N-labelled N_2 in nematic phases, EBBA and Merck 2L 1132, shows a doublet in the ^{15}N spectrum whose spacing indicates that the anisotropy of the nitrogen shielding is 590 ± 50 ppm.[471]

4.4. Quantitative nitrogen NMR

The problem of relationships between nitrogen NMR signal intensities and the relevant numbers of nuclei in a sample is quite complicated, since there are various other factors which can significantly affect the intensities. In ^{14}N NMR, there are problems resulting from quite diversified quadrupolar relaxation times, and in ^{15}N NMR serious difficulties arise from variable nuclear Overhauser effects upon proton decoupling, from relatively long T_1 relaxation times, from the low sensitivity of measurements at the natural abundance of the isotope, and from effects of various polarization-transfer techniques that are frequently employed. There are also some general problems concerned with the use of the pulsed Fourier transform technique with its inherent, non-linear phase drift across a spectrum, effects of pulse

breakthrough, and saturation effects which simply quench signals without inducing any signal broadening, thus quenching the corresponding integral intensities.

In quantitative ^{14}N NMR, the best results seem to come from the old-fashioned, field-swept continuous-wave technique, in its differential saturation variant combined with lineshape fitting. This was applied to the dimerization equilibria of a nitrosoalkane, Bu^tNO, in various solvents;[30] an analysis of errors indicated that the percentage compositions assayed in that way were accurate within ± 0.9 to $\pm 0.1\%$. The effects of diversified relaxation rates of ^{14}N have to be accounted for in any serious attempts at quantitative measurements, and a good example is also found in the studies of ammonia uptake by perfused rat salivary glands.[472] There have been numerous attempts at using ^{15}N NMR spectra for at least semiquantitative monitoring of various reactions, most often in biological systems. However, examples where ^{15}N NMR results are confronted with those from other methods often show significant discrepancies. In following the assimilation of $^{15}NH_4^+$ in *Streptomyces venezuelae* by ^{15}N refocused INEPT spectra, with intensity calibration against a reference, ^{15}N-labelled *cyclo*-(Gly-Pro-Gly)$_2$, a comparison with amino acid analysis showed overall discrepancies of 15–20%.[473] Similar inconsistencies were found in investigations on rat organs[474, 475] by ^{15}N NMR and by emission spectroscopy. It seems that without a suppression of nuclear Overhauser effects, ^{15}N NMR should be rather hopeless from the point of view of quantitative analysis, but we should note a report[476] on the assimilation of $^{15}NH_4^+$ by Beech, where a comparison of results obtained from conventional, proton-decoupled ^{15}N spectra with those from gas chromatography combined with mass spectrometry shows deviations within only 10%.

In general, however, one should be cautious in assigning too much significance to quantitative analyses by ^{15}N NMR alone, such as those reported for ammoniated straw;[403] silk fibroins;[110, 477] nitrogen fixation by methanogenic bacteria;[396] marine algae;[478] and nitration of hexachloro complexes of iridium.[479] More reliable are those where some intensity references have been employed,[398, 480, 481] but one should remember the limitations in accuracy that have been considered above.

4.5. Chemically induced dynamic nuclear polarization (CIDNP) in nitrogen NMR

Nitrogen resonance intensity enhancements which result from the involvement of radical pairs in the course of chemical reactions can be described by Kaptein's rules (see ref. 5, p. 63, and references therein). Applications to ^{15}N CIDNP effects observed in photochemical dediazonation processes of

arenediazonium salt solutions[75,482] show that the excitation goes first to singlet states. Analogous ^{15}N CIDNP effects, both negative (enhanced emission) and positive (enhanced absorption), have been employed in following the mechanisms of nitration and subsequent nitro group migrations for *p*-nitrophenol,[483] arylamines,[484] mesitylene,[485] durene[486] and naphthalene,[487] and also in investigations of 2,6-dichloro-*N*-nitroaniline rearrangements into the corresponding *C*-nitro isomers.[488] However, recent results[489] on the nitration of nitrobenzene, naphthalene and mesitylene with HNO_3 + $MeSO_3H$ + $NaNO_3$ suggest that the contributions of radical-pair-mediated mechanisms in such reactions are fairly small. This seems to be a general problem with CIDNP effects in NMR, since they are large enough to monitor even quite marginal mechanisms of reactions.

4.6. Dynamic nitrogen NMR

A major advance in ^{15}N dynamic NMR in the solid state has recently been made in the field of ^{15}N-detected proton transfers in ^{15}N-labelled molecules containing the tautomeric system shown in Fig. 2, where two protons can jump among four nitrogenous sites; the molecules concerned included porphins, phthalocyanins and related enamino–imino systems.[427–439] Theoretical derivations of the ^{15}N lineshapes concerned for various proton-transfer mechanisms, confronted with variable-temperature ^{15}N CPMAS spectra, were employed in detecting non-concerted double proton transfers in such systems. The dynamic behaviour of such spectra also led to the proposal of a novel, convenient NMR thermometer for variable-temperature CPMAS measurements in the range 86 K to 495 K.[428, 429]

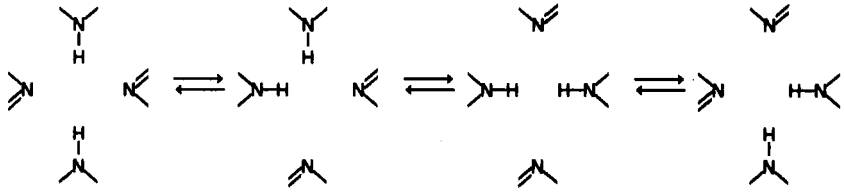


Fig. 2.

One should also notice the SELEX pulse sequence[490] for selective observation of spin exchange among NH moieties in 2-D ^{15}N spectra of solid samples, and the magnetization transfer from ^{1}H in hydration water to ^{15}NH in solid hydrated proteins for estimating proton exchange rates.[410]

For solutions, analogous exchange rates were monitored by time-dependent INEPT enhancement decay of the ^{15}N resonances of detergent-solubilized M13 coat protein, after dissolving it in water.[114] A special example

of nitrogen dynamic NMR in solutions is that of NO_3^- exchange among diamagnetic and paramagnetic centres, which was monitored by dynamic ^{14}N spectra, owing to the relatively small linewidths for the ion, and the large nitrogen shielding differences concerned.[491]

5. GENERAL CONSIDERATIONS OF NITROGEN SHIELDING

5.1. Isotope effects on nitrogen NMR shielding

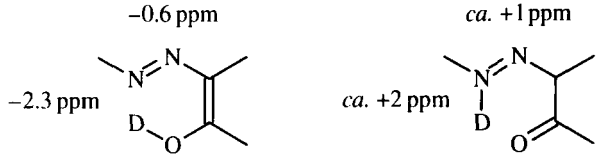
While *primary isotope effects* on nitrogen shieldings, i.e. those between ^{14}N and ^{15}N, are within the experimental errors involved in two independent measurements (see ref. 5, p. 66), *secondary* isotope effects – those induced by isotopic exchange in the vicinity of a nitrogen atom – can be measured with a high accuracy provided that the isotopomers concerned appear as separate resonances in a given nitrogen NMR spectrum. Methods based on comparing two or more spectra are rather unreliable, because of the errors concerned with their calibration (see Section 3) and even minor variations in experimental conditions (temperature, concentration, paramagnetic impurities, etc.).

Deuterium effects on nitrogen shieldings have already been observed in the NH_4^+ ion, *ca.* +0.3 ppm per each D atom introduced; and for ammonia, where the effects are twice as large, +0.65 ppm per D atom[492,293] (see also ref. 5, p. 67). More recent measurements for the ammonium ion[494] are essentially in accord with the older data, but they show minor variations of the effects between solutions in H_2O/D_2O and in 1 M HCl or HNO_3. The latter measurements[494] also provide data for a variety of nitrogenous structures:

Structure (solvent)	*Deuterium isotope effect* (ppm) *on nitrogen shielding*
Pyridine-d_6 (neat)	+0.58
ND^+ in pyridinium ion (CF_3COOD)	+0.60
ND in pyrrole ($CDCl_3$)	+0.24
PhNDMe (neat)	+0.70
$PhND_2$ (neat, $CDCl_3$)	+1.45, +1.09
$PhND_3^+$ (CF_3COOD)	+1.21
PhNDCOMe ($CDCl_3$)	+0.62
$PhNHCOCD_3$ ($CDCl_3$)	−0.05
HCONDH (H_2O, DMSO)	+0.51, +0.56
$HCOND_2$ (H_2O, DMSO)	+1.04, +1.09
CD_3CN (neat)	−0.16

The data also included CD_3NO_2, +0.07 ppm, but more recent measure-

ments[495] of proton- and deuterium-coupled ^{15}N spectra in a single batch show that the effect is only +0.038 ppm; this is important from the point of view of neat liquid nitromethane as a primary reference and a source of deuterium lock for nitrogen NMR spectra (Section 3). For N^{π} in histidine in ferricytochrome,[496] an effect of +2.5 ppm was observed for D_2O vs H_2O solutions, but this involved two independent spectra. A method was proposed[497] for estimating equilibria between NH and ND moieties in ammonium salts, on the basis of average shieldings observed, with respect to reference solutions in D_2O and in H_2O; plots of the nitrogen shielding against the percentage of D_2O in water were non-linear, but this is again the case of measurements not on a single batch, where the relatively small isotope effects can be seriously affected by experimental errors. Deuterium effects on nitrogen shieldings in systems exhibiting azo–hydrazone tautomerism[498] shows a change in their signs between the tautomers involved [**9**].



[**9**]

Nitrogen-14 isotope effects on ^{15}N NMR shieldings are exemplified[499] by $^{15}N{\equiv}^{15}N$ in $CDCl_3$, +0.061 ± 0.002 ppm with respect to $^{14}N{\equiv}^{15}N$; this led to an estimate of −912 ± 42 ppm per angstrom of the bond length, in accord with theoretical calculations which gave values within −640 to −1425 ppm.

The *^{13}C isotope effect* on the nitrogen shielding of nitromethane[495] was found to be small, +0.019 ppm.

Isotope effects of ^{18}O on nitrogen shieldings have been found in the nitrite ion, NO_2^-, +0.15 ppm per ^{18}O, and in the nitrate ion, NO_3^-, +0.06 ppm per ^{18}O, and they were employed in following the fate of $H_2{}^{18}O$ and $^{15}N^{16}O_2^-$ in the oxidation of ammonia by *Nitrosomonas europaea*;[500,501] and the course of nitrite-to-nitrate oxidation by *Nitrobacter vinogradskyi*,[502,503] where the oxygen source turned out to be mainly $H_2{}^{18}O$. In 3-nitropropanoic acid,[164] the effect on the nitrogen shielding is *ca.* +0.08 ppm per ^{18}O. Such effects of ^{18}O have been examined in a variety of molecules:[501,504,505]

Molecule	*^{18}O effect on nitrogen shielding* (ppm)
MeCH=NOH	+0.069 to +0.030
Nitrobenzene	+0.075
1-Nitrobutane	+0.08
Isoxazoles	+0.153 to +0.159
Isoxazolines	+0.074
HCNO	+0.027

and the relatively large effect in oxazoles has been attributed to the short N–O bond in the aromatic ring. Effects on nitrogen shieldings induced by ^{18}O are important, since they allow one to monitor ^{18}O labels by NMR.

5.2. Shift reagents in nitrogen NMR

Lanthanide chelates usually bind to nitrogen atoms which bear lone electron pairs, and induce considerable shifts in the nitrogen NMR shieldings concerned, mostly via the contact mechanism (see ref. 5, p. 68, and references therein). Recently, the Co^{2+} ion has been proposed as a shift reagent for nitrogen NMR in aqueous solutions;[506] in ^{14}N NMR measurements, the cobalt-to-substrate ratio can reach 4:1, inducing shifts of −25 ppm for glycerophosphorylcholine, +10 ppm for betaine, and +5 ppm for the ammonium ion, thus increasing the spectral resolution of the latter.

Another interesting approach relies on the use of silver salts, such as Ag(tfa), which bind to the π-electron systems of multiple and aromatic C–C and C–N bonds.[507] Such shift reagents act via the pseudo contact mechanism, and examples of the shifts induced are shown below.

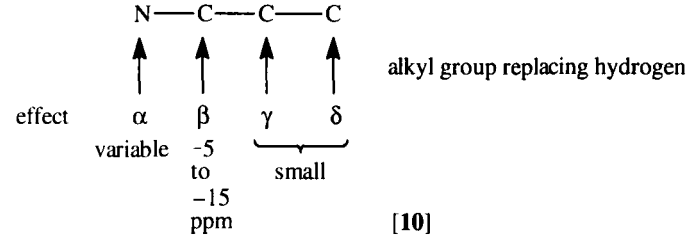
Substrate (in $CDCl_3$)	*Ag(tfa)/substrate ratio*	*Nitrogen shielding induced* (ppm)
Azobenzene	0.15	+3.0
PhCN	0.15	+4.6
Thiazole	0.03	+1.8
Imidazole N-3	0.03	+3.0

5.3. Some general considerations of nitrogen shielding in diamagnetic species

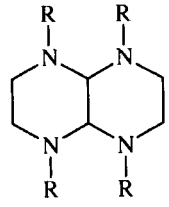
The range of nitrogen NMR shieldings in diamagnetic compounds and ions,

referenced to that in neat nitromethane, is from about -600 ppm (aromatic nitroso compounds) to about $+450$ ppm (NH_3 as a ligand in ammino-type complexes), as was shown in ref. 5, where a large table of characteristic ranges for individual nitrogenous structures was also published. Quantum-mechanical calculations of nitrogen shieldings were considered in Section 1, but there have been also some attempts at correlating the shieldings with calculated electron charge densities at the relevant nitrogen atoms. All these show only *local* correlations, within closely related molecular structures, and their signs vary from one group to another; this evidently excludes the simple diamagnetic mechanism of nitrogen magnetic shielding as a source of the range observed. Such local correlations were found using *ab initio* quantum-mechanical calculations with a STO-3G minimal basis set of electron charge densities: for ring nitrogen shieldings in aminoazine heterocycles,[508] a *parallel* correlation, i.e. increasing electron charge at N $\rightarrow$ increasing nitrogen shielding, including also *N*-oxidation effects, but only for non-oxidized nitrogens; separate, parallel correlations[38] for alkylamines, R_3N, R_2NH, and RNH_2, where R = CH_3, $R'CH_2$, R'_2CH, and R'_3C, and also for azine heterocycles, and for 4-substituted pyridines; *antiparallel* correlations[38] of this kind for nitroalkanes, RNO_2, and for alkyl isocyanides, RNC. Parallel correlations for *meta*-substituted benzamides,[509] using a Gaussian-80 set; and rather rough correlations for substituted pyridines.[39] There have been also some attempts at using π-electron densities from the rather old-fashioned Pariser–Parr–Pople SCF calculations, but the results seem to be contradictory, since for pyrrole moieties in pigments a parallel correlation was reported,[510] while in azines and azoles[511] the pyridine-type nitrogen atoms showed a parallel correlation, but that for pyrrole-type nitrogens was antiparallel.

Alkyl group effects on nitrogen NMR shieldings play an important role (see ref. 5, p. 72), since they span a range of about 50 ppm in a given group of nitrogenous compounds. For molecules where internal rotations are not appreciably hindered, such shielding variations can usually be expressed in terms of the additive effects [**10**]. A good example of such additive effects is provided by a study of acrylamides[512] (Table 12, note (k); the α- and β-effects found there amounted to $+4.9$ and -11.9 ppm, respectively). The long-



[**10**]



[11]

range effects, γ and δ, are usually small, and can easily be hidden under solvent and concentration effects. However, a systematic study of nitriles, R—CN, where R = Me, Et, Pr^i or Bu^t, revealed a small but solvent-independent γ-effect of about +2 ppm.[33] More elaborate schemes are required in order to account for alkyl group effects in saturated azacyclic systems, such as those of tetraazadecalins **[11]**[513] in $CDCl_3$, H_2O and cyclohexane solutions, where the α, β and γ-effects were subdivided further, according to spatial relationships (in ppm, the first number refers to polar solvents, the other to cyclohexane as a solvent):

$$\alpha(\text{equatorial}) = +1.3;\ +6.2 \quad \alpha(\text{axial}) = ?;\ +23.5$$
$$\beta(\text{equatorial}) = -15.3;\ -17.6 \quad \beta(\text{axial}) = -7.0;\ -8.7$$
$$\beta(N_{eq}\text{–}C\text{–}N_{ax}) = +1.6;\ ?$$
$$\gamma(\text{anti, equatorial}) = +1.2;\ 0.0$$
$$\gamma(\text{gauche, axial}) = +9.1;\ \textit{ca.}\ 9$$
$$\gamma(N_{ax}\text{–}C\text{–}C\text{–}N_{ax}) = +2 \text{ to } +8;\ ?$$

Recently, a new approach has been presented[514] for alkyl group effects on nitrogen shieldings, expressed by the equation:

$$\sigma_N = m\Sigma\sigma_a(i) + b$$

where σ_N is the nitrogen shielding concerned, m and b are parameters to be fitted, and $\sigma_a(i)$ are alkyl group parameters estimated by projecting the relevant C–C and C–H bond refractions (1.296 and 1.676, respectively) onto the C–N bond axis concerned. The latter parameters assume values:

$$\text{Me} + 1.678; \quad \text{Et} + 0.126; \quad \text{Pr}^n + 0.644; \quad \text{Pr}^i - 1.426;$$
$$\text{Bu}^n + 0.471; \quad \text{Bu}^i + 1.162; \quad \text{Bu}^s - 0.908; \quad \text{Bu}^t - 2.978.$$

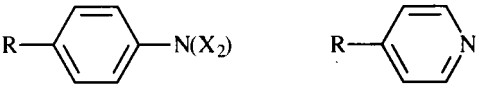
This scheme gave good correlations with the nitrogen shieldings in a variety of alkylamines, alkylammonium ions, amides, isonitriles, imines, *N*-nitrosoamines, nitrile *N*-oxides, nitroalkanes and $R_2N{=}PX_2$ structures.[514]

Various additive schemes have also been employed for explanations of nitrogen shielding changes within individual groups of related molecules and ions (ref. 5, p. 73); if they use only few parameters they usually reflect rather rough trends, and if there are numerous parameters the problem comes close to that of solving n equations in n unknowns, with no predictive value

whatsoever. A recent example is concerned with $N(R^1)(R^2)(R^3)$ structures, where the substituents include chlorine atoms, nitro groups, etc.,[515] and the shieldings are expressed as sums of substituent effects; the overall correlation coefficient appears to be good, 0.992, but this seems to result from the large range of the shieldings concerned, since individual deviations reach 20 or even 50 ppm in some cases.

Quite a different approach has been proposed for nitrogen shielding assignments using such additive schemes, based on a set of *self-adjusting increments*,[516] and tested for a large group of azine heteroaromatic rings. In the first step, we construct a set of additivity rules for nitrogen shieldings in molecules where the assignments to individual nitrogens are either obvious or are based on reliable assignment procedures. Then we check the system adopted, by least-squares fitting over all possible permutations of assignments, and obtain a set of structural increments to the nitrogen shieldings. Now, if we want to assign the shieldings in a new compound or compounds, we add the new data to the original database, and carry out the least-squares fitting over all permutations of assignments, including the new structures, in order to obtain the assignment required and also a new, improved set of the increments.

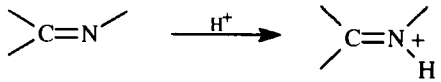
A special case of looking for linear correlations of nitrogen shieldings with some simple parameters which characterize chemical structures is that of substituent effects across aromatic rings **[12]** in terms of the Hammet equation or modifications of it. Generally, electron-donating substituents (—OR, $-NR_2$, etc.) increase the nitrogen shielding in such structures, while electron-attracting moieties R (such as NO_2, CN) exert a deshielding effect. However, solvent effects on nitrogen shieldings are usually at least of the same order of magnitude, and various correlations reported in terms of Hammett substituent constants are usually just rough trends. In aniline itself, the range of *para*-substituent effects is appreciable, *ca.* 30 ppm, but for other arylamines this amounts to about 10 ppm (Table 7). In *para*-substituted benzonitriles (Table 16) and 4-substituted pyridines (Table 19), the range is about 15 ppm; in a variety of amido and thioamido moieties attached to phenyl rings (Table 12), the range is quite small, 5–7 ppm; it amounts to about 10 ppm in nitrobenzene derivatives (Table 26). In $X_2P{=}N{-}Ph$ structures the effects are within 30 ppm, but they are negligible in $X_2P{=}N{-}SO_2Ph$ (Table 23).



[12]

Protonation effects on the nitrogen shieldings of the atoms involved are

variable, but they can attain values up to about 150 ppm. For alkylamines (Table 3), a typical effect is *ca.* − 10 ppm, but for ammonia it is about − 50 ppm, and for hydroxylamine (Table 8) it is + 20 ppm. The amino group in glyphosate[517] shows a typical protonation effect of about − 10 ppm. The situation is more complicated for arylamines (Table 7); if the lone electron pair at the amino group is involved in a delocalized π-electron system, the protonation results in an increased (*ca.* + 10 ppm) shielding of the nitrogen nucleus, but when steric effects attenuate the conjugation, e.g. in *N,N*-dimethylaniline, the protonation effect is comparable to those observed in alkylamines, about − 10 ppm. Such shielding changes belong to the low limit of protonation effects in nitrogen NMR, but they are quite useful in titration experiments. The upper limit is represented by protonation effects in systems such as [**13**] which include both open-chain structures and heteroaromatic



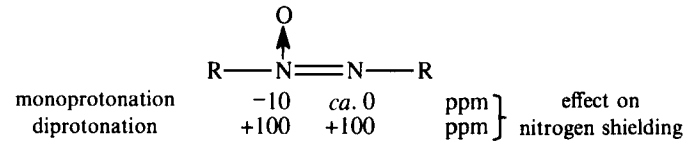
[13]

rings. In hydrazones, $R_2C{=}N{-}NR_2$ (Table 9) the effect on C=N is about + 30 ppm, and about − 10 ppm for NR_2, but for imines (Table 24, including also complexation effects), it reaches + 80 to + 150 ppm; the same is true for azine heteroaromatic ring systems (Table 19, and Table 3, note (h)) and for pyridine-type nitrogen atoms in azole ring systems (Table 17). Attention is drawn to the protonation effects on the nitrogen shieldings in histidine imidazole moieties (Table 13, notes (b) and (c); also refs 518, 519), where pH effects on the His resonance in cytochrome c_2 was observed. One should notice that for pyrrole-type moieties in strongly acidic media, protonation takes place at carbon atoms, and the resulting shift of the nitrogen resonance concerned is in the deshielding direction, about − 100 ppm (Table 17, notes (d) and (e)). The protonation of nitriles

$$R{-}C{\equiv}N \xrightarrow{H^+} R{-}C{\equiv}\overset{+}{N}{-}H$$

results in a large increase in the nitrogen shielding, by about + 100 ppm (Table 16); this is also true for complexation at nitrogen (Table 16, note (w)).

Such large shielding effects on nitrogen upon its protonation are a typical tool for tracking nitrogenous protonation sites in a variety of chemical and biochemical structures. This has been done for deazapurine systems (Table 18, note (i)) where 3-deaza and 1-deaza derivatives show preferential protonation at N-1 and N-3, respectively. Similar studies included nucleosides and related structures (Table 22): purine pseudonucleosides (notes (c), (d), (h), (r), (w), (x)), protonation at either N-7 or N-9, depending on whether one of these is substituted with a pseudosugar moiety; adenosine (notes (c), (d)),



[14]

preferential protonation at N-1, sometimes at N-7; guanosine (notes (i), (l), (t), see also ref. 520), protonation at N-7, but at N-1 for the betaine structure of *N*-7-Me-guanosine (notes (h), (i)); xanthosine (note (n)), only weak effects at N-7; cytidine (notes (c), (r), (t)), protonation at N-3; pyrimidone derivatives (note (c)), weak effects at N-3; and wyosine (ref. 521, see also Table 22, notes (g), (v)). Recent *ab initio* quantum-mechanical calculations by the IGLO method[11] are in accord with the experimental data, predicting large shielding increments in pyridine-type nitrogen atoms of adenine (predicting also the preferential protonation site at N-1), guanosine, cytosine, thymine and uracil. Trimethoprim (Table 19, notes (v) and (w), see also refs. 94, 522, 523), was shown to undergo protonation at N-1 (or complexation with dihydrofolate reductase), with an effect of about +80 ppm for the nitrogen shielding concerned. A large number of flavin systems (Table 21, notes (a), (g), see also refs. 524–528) have been investigated by nitrogen NMR; the reduced forms show preferential protonation at N-1 (an effect of about +40 ppm), while the oxidized forms are protonated mostly at N-3 (*ca.* +55 ppm shielding effect). Imidazo [1, 2-a]pyrazine was shown to undergo protonation at N-1, by means of ^{15}N NMR titration;[529] analogous studies on 2-methoxypyrazine[530] indicate N-4 as the protonation site.

Indirect protonation effects, those exerted on nitrogen atoms by protonation at some other atom, are revealed in the nitrogen shieldings of a variety of structures: the nitro group, about +30 ppm upon the protonation of its two oxygen atoms (Table 26, note (g)); the *O*-protonation of diazoates (Table 27, note (j)); the protonation equilibria in solutions containing HNO_3 or HNO_2 (Tables 26 and 29, respectively); and azoxy compounds (Table 28) in FSO_3H [**14**], where the monoprotonation takes place at the oxygen atom.

5.4. Solvent effects on nitrogen shielding

Solvent effects can be quite remarkable (ref. 531 and ref. 5, pp. 81–85), and are often underestimated in various interpretations of nitrogen shieldings in terms of molecular structure. The largest influence of this kind, as far as neutral molecular species are concerned, has recently been found in a study of azine heteroaromatics;[532] pyridazine (1,2-diazine) shows a range of about 50 ppm for its solvent-dependent nitrogen shielding (see Table 19, note (b)).

In ionic species, the largest variation was observed for the nitroso moiety of $[C(NO)(CN)_2]^- K^+$ in water and a number of alcohols (Table 29, note (m)), amounting to about 200 ppm and related to the corresponding pK_α values for the solvents. In contrast, dinitrogen, indolizine, and azo compounds show very narrow ranges (1–2 ppm) of solvents effects on their respective nitrogen shieldings.

Some examples of typical solvent effects on nitrogen shieldings are quoted below from systematic studies on dilute solutions, where bulk susceptibility effects have been accounted for, and the solvents concerned encompassed a broad range of solvent properties.

Molecule	*Range of solvent effects on nitrogen shielding* (ppm)	*Reference to table (note)*
Pyridine	38	19(b)
Pyridazine (1,2-diazine)	49	19(b)
Pyrimidine (1,3-diazine)	18	19(b)
Pyrazine (1,4-diazine)	16	19(b)
1,3,5-Triazine	11	19(b)
Pyridine *N*-oxide	30	19(d)
Indolizine		
and azaindolizine systems		
bridgehead nitrogen	1–3	18(a)
pyridine-type nitrogen	26–32	18(a)
Alkyl cyanides (nitriles)	22–26	16(a)
Nitromethane	11	26(a,b)
Methyl nitrate	5	26(d)
t-Butyl nitrite	26	29(d)
Methyl isothiocyanate	10	15(a)
Azo bridge	2	28(b)
Dinitrogen	1.3	31(b,c,d)

These values exclude effects of protonation equilibria which may be found in more acidic solvents. The latter effects are usually much larger, and they were considered in the preceding section. Most of the data quoted above have been analysed in terms of the Kamlet–Taft system of solvent properties (discussed in ref. 5, pp. 83–84, and references therein), which can be presented here in the form:

$$\sigma_N(i, j) = \sigma_N(i, \text{cyclohexane}) + a_i\alpha_j + b_i\beta_j + s_i(\pi_j^* + d_i\delta_j)$$

where i denotes a given nitrogen atom in molecule examined, j denotes solvent, σ_N is the relevant nitrogen shielding, α_j is the hydrogen-bond donor

strength of solvent j (as a bulk property with respect to a solute, expressed in arbitrary units of the scale, 0 to about 1.5 for most solvents), β_j is the corresponding H-bond acceptor strength (0 to about 1 on the scale), π_j^* is the corresponding solvent polarity/polarizability term (0 to about 1), and δ_j is a correction for "superpolarizability" of aromatic and highly chlorinated solvents. The a, b, s, and d terms are the relevant nitrogen shielding responses to the individual bulk solvent properties on that scale.

Usually, the highest responses to hydrogen bonding from solvent to nitrogen show molecules which reveal high upfield shifts upon the direct protonation of the nitrogen concerned (see the preceding section); the direction of such H-bonding effects is the same as those of protonation, and the relevant terms exhibit values from about +21 (ppm per unit scale of α) for pyridine and pyridazine,[532] also for a covalent nitrito group,[31] to about +17 for pyridine-type nitrogen atoms in the five-membered ring moieties of azaindolizines,[533] and to about +10 for covalent cyanides.[33] However, there is evidently no correlation with the magnitudes of the relevant protonation shifts, and in the case of azine ring systems the term a drops from +21 for pyridine and pyridazine to about +8 in pyrimidine and pyrazine, and to +3 in 1,3,5-triazine. There are reasons to believe[532] that the magnitudes of the a terms reflect relative strengths of the hydrogen bonds concerned, since there are reasonable correlations with the corresponding H-bond association constants, measured by other methods at very low concentrations with respect to a standard H-bond donor, and with *ab initio* calculated gas-phase protonation energies.

Nitrogen shielding responses to changes in solvent polarity are usually represented by the s term, since the d term is often rather negligible. The values of s (in ppm per unit scale of π^*) can be of either sign (the plus sign indicates an increased shielding with the increasing polarity of the medium). For pyridine-type nitrogen atoms in azines[532] and azaindolizines,[533] its value is about +5, with the exception of pyridazine for which it is unusually high, +13 ppm. This is in accord with solvaton-type MO calculations of nitrogen shieldings (the method itself has been described in ref. 534), which also correctly predict the sign of the effect in other groups of molecules:[31-34,81,88] positive in covalent cyanides, negative (−4 to −10 ppm) in *C*-nitro and *O*-nitro groups, covalent nitrites and isothiocyanates. The data and the calculations seem to suggest that the sign of the effect should be related to the sense of bond dipoles in the vicinity of the nitrogen atoms concerned. In azaindolizines[533] (see Table 18, note (a)), the s term is rather large and positive for pyridine-type nitrogens (N-1, N-2 or N-3), while it is small and negative for bridgehead nitrogens (N-4), so that the difference between the latter and the former nitrogen shieldings tends to decrease with increasing solvent polarity. This is in accord with correlations for different molecules in the

same solvent[90] which show that this is an effect of enhancing the delocalization of the lone electron pair from N-4 over the ring system with increasing medium polarity.

Solvent, concentration and gegenion effects on the nitrogen shieldings of various reference substances are presented in Table 2. The shielding in tetrabutylammonium bromide was found to be almost independent of concentration.[535] Some solvent effects on arylamine nitrogen shieldings are shown in Table 7, notes (a, b, c, d, e); they seem to reveal deshielding with increasing solvent polarity. In amido moieties (Table 12, notes (a, g, m); Table 13, note (E); also ref. 536) there seems to be a deshielding effect on the nitrogen upon hydrogen bonding of the C=O groups by the solvent (-5 to -8 ppm). Dimethylformamide–water mixtures show a non-linear plot of the nitrogen shielding against the mole percentage of the amide,[537] but there does not seem to be any discontinuity claimed by the authors, who postulated the formation of a complex between DMF and H_2O. There are some additional data for the covalent isothiocyanate (and also thiocyanate) groups, but they do not include hydrocarbon solvents. Only polar and protic solvents are included in the data for azole ring systems presented in Table 17, notes (x, z, H, J, M, R). Attention is drawn to the study of hydrogen bonding effects in the imidazole moiety of His-57 in the catalytic triad of α-lytic protease (Table 13, note (b)). For azine aromatic systems, there are some additional, fragmentary data on pyridazine and 1,10-phenanthroline,[538] and a study of 3,5-dimethylpyridine in 30 solvents, but for fairly high concentrations of the solute (Table 19, note (h)). A rough correlation of solvent effects on azine nitrogen shieldings (in substituted pyridines) with the calculated first ionization potentials has been reported.[39] The preferential sites of hydrogen bonding of 9-methylpurine by 3,5-dichlorophenol seem to be N-1 and N-7, while it is N-3 for 6,6,9-trimethyladenine,[539] according to the corresponding effects on the nitrogen shieldings concerned (see also Table 22, note (y)). Hydrogen bonding effects have been also monitored by means of nitrogen shieldings in some nucleosides, AMP-5′ (ref. 540) and UMP-5′ (ref. 541), and in amidine systems (Table 10, note (v)).

There seems to be only a small influence of solvents on the nitrogen shieldings in *trans*-azo bridges (Table 28, notes (a, b)), with the exception of CF_3CH_2OH as a solvent, which is likely to interact with the π-electron system of the N=N bond.[31] Solvent-induced effects on the nitroso group seem to be quite diversified. For Bu^t—NO, the range is about 10 ppm, and the major source of this variation seems to be solvent polarity, with little or no effects of solvent-to-solute hydrogen bonding, possibly owing to the steric hindrance from part of the bulky alkyl group (Table 29, note (a)). The *O*-nitroso group in a covalent nitrite (Table 29, note (d)) shows a larger range of such effects, about 26 ppm, with a large contribu-

tion of solvent-to-solute hydrogen bonding effects.[31] Finally, the nitroso moiety of $K^+[(ON)C(CN)_2]^-$ in water and in a number of alcohols reveals a huge range of solvent-induced effects, of about 200 ppm, on the nitrogen shielding (Table 29, notes (m, n)), where hydrogen-bonding effects must play a dominant role.

5.5. Tautomeric equilibria and nitrogen shielding

Typical applications of nitrogen NMR shieldings to estimating tautomeric contents of various substances rely on large differences between the shieldings for the tautomers concerned; a good example is provided by the system **[15]** and its vinylogues, including also aromatic rings. Generally, for a system

$$A \rightleftarrows B$$

if one observes only a dynamically averaged shielding

$$\sigma_{av} = X_A\sigma_A + X_B\sigma_B$$

where X are the corresponding mole fractions, then

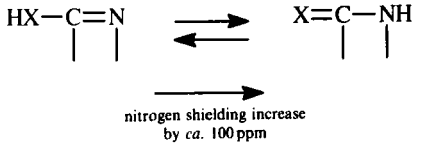
$$X_A = \frac{\sigma_{av} - \sigma_B}{\sigma_A - \sigma_B}$$

provided that we know the shieldings for the tautomers concerned. Usually, we have to resort to approximating the latter, e.g. by using the corresponding methyl derivatives, X—Me and N—Me, and this leads to errors, $\Delta\sigma_A$ and $\Delta\sigma_B$, respectively. The error in the estimated value of X_A is then, approximately,

$$\Delta X_A = \frac{\Delta\sigma_m[X_A^2 + (1 - X_A)^2]^{1/2}}{|\sigma_A - \sigma_B|}$$

where $\Delta\sigma_m$ is the average error involved in using reference shieldings taken from model compounds rather than those from the actual tautomers. As far as nitrogen shieldings are concerned, the denominator is usually large enough to keep errors at about 10 mol% in the equilibrium composition.

Recently, a method has been described[542] which improves the precision significantly. It represents a *combined approach*, which does not take account solely of the nitrogen atom that exhibits the largest value of $|\sigma_A - \sigma_B|$ but also includes other nitrogen atoms in a molecule, and other atoms as well, e.g.



[15]

carbon and hydrogen. The latter, taken alone, are usually characterized by $|\sigma_A - \sigma_B|$ values which are too small to provide a sound basis for estimating tautomeric contents. The method is iterative, and it relies on statistical weights. First, we assume some values for the errors $\Delta\sigma_m$ for each kind of the nuclei involved (nitrogen, carbon, hydrogen, etc.), and calculate, from the NMR data for each of the nuclei involved, individual values of X_A and associated errors, ΔX_A. The latter are then used as statistical weights in calculating the weighted average of X_A, and this allows us to compute new, improved values of the errors $\Delta\sigma_m$. The procedure is continued until convergence is attained. The method was applied to a large set of tautomeric aza-aromatic systems, yielding tautomeric contents with an average precision of 3 mol%; it also yielded estimates of $\Delta\sigma_m$ for nitrogen, carbon and hydrogen nulei of 4.0, 1.3 and 0.08 ppm, respectively.

There are numerous examples in the tables where nitrogen shieldings have been employed either in the identification of prevailing tautomeric forms or in estimating tautomeric equilibrium compositions. Many of these come from the field of heteroaromatic ring systems: pyrrole moieties (Table 17, notes (i, j, q, r), and for bilirubin systems, notes (l, m, n, o)). Attention is drawn to solid-state investigations of tautomerism via internal proton transfers by dynamic nitrogen NMR[151, 430-433, 435-437, 543-546] in porphins and related systems (see also Section 4.6); in pyrazoles (Table 17, notes (a, k, v, w, y, z, A); and in imidazole systems (Table 17, notes (a, B, C, F, H, I, J, K), including also imidazole moieties in histidine units[518] where slow, intermediate, and fast tautomeric exchange rates were found, depending on whether the His unit was deeply inside or close to the surface of a large protein, such as that of cytochrome c_2; see also Table 13, note (b), for studies of the His-57 imidazole units in a α-lytic protease. Further examples from Table 17 include triazole systems (notes (M, N, P, R, Q, T, S), tetrazole rings (notes (*a*, X)), oxazoles (note (F)), furoxans (note (ee)), thiazoles (note (F)), thiadiazoles (notes (R), (cc)), and phosphazoles (note (hh)). Studies on tautomeric azolo-azine systems are presented in Table 18, notes (g, h, i, m, n); those on azine heteroaromatics, in Table 19, notes (m, n, l, N), in Table 20, notes (a, b), and for flavin systems in Table 21, note (g). Nitrogen NMR applications in the field of tautomerism of nucleosides have been presented in ref. 547, and in Table 22, note (h).

Azo-hydrazone tautomerism significantly affects the relevant nitrogen shieldings, which constitute a valuable tool in its investigations (Table 9, notes (d, e, g, h, j-n), Table 28, note (f); see also ref. 548). The same applies to guanidine and amidine systems (Table 10, notes (w, u); see also ref. 549); azirine rings (ref. 118; see also Table 4) on p. 105; enaminone systems (Table 4, notes (d, i, j); see also refs. 193, 550-553); nitro-nitrito rearrangements

(Table 29, note (f), and Table 26, note (p)); P–N bond migration (Table 3, note (o)); and oxime–nitroso tautomerism (Table 24, note (w)).

6. SOME NOTES ON NITROGEN NMR IN INDIVIDUAL GROUPS OF MOLECULES AND IONS

6.1. Ammonia, ammonium ions, amino groups and related structures

The relevant data are presented in Table 3 (ammonia, alkylamines and corresponding ions); Table 4 (enamines and enaminones); Table 5 (amino groups coordinated to boron and silicon); Table 6 (amino moieties bound to elements other than carbon); Table 7 (arylamines and arylammonium ions); Table 32 (amino-type complexes); Table 13 (amino acids and related structures); and Table 8 (hydroxylamines, hydrazines, hydrazides).

There have also been some additional studies within this group of molecules. Solutions of sodium and potassium in liquid ammonia,[554] where a quartet is observed in ^{14}N NMR, reveal two types of unpaired electrons, as indicated by ^{14}N relaxation and Knight shifts. The uptake of the ammonium ion has been examined by ^{14}N NMR in the alga *Ulva lactuca*,[478] in root tissues of barley maize,[93] and in perfused rat salivary glands;[472] and uptake of ammonia in acute hyperammonaemia induced in rats.[555,556] Metabolites of hydrazine were identified in rat urine, by ^{15}N NMR.[557]

Complexation equilibria have been followed by means of ^{15}N NMR for the ammonium ion with 18-crown-6;[558] for amino groups with calcium,[461] cerium(IV)[559] and zinc(II)[560] cations; and for the tetramethylammonium ion, using ^{14}N–^{1}H couplings.[561] A phase diagram for $NH_4Cl/NaCl/H_2O$ was deduced from ^{14}N measurements.[562] Some correlation was found between amino nitrogen shieldings and the corresponding NH stretching frequencies in IR spectra.[563]

There have been some additional data for aminoglycoside antibiotics;[564] for choline groups;[462,463,565,566] for alkylammonium salts as mobile phases in liquid chromatography;[567] for alkylammonium moieties (^{15}N relaxation) in ampholytic ionomers;[568] and for piperidine derivatives,[569] trimethylsilyl derivatives of enamines,[570] teriary amino groups bound to silicon and sulphur,[143] the enamino group in 4-amino-4-deoxychorismate,[571] NMe_2 groups in 1,8-di(dimethylamino)-naphthalenes (proton sponges, in solution and the solid state),[572] and enamino groups of polyethyleneimine polymers.[573] Solid-state studies also included phase transitions in ammonium nitrate (^{15}N CPMAS)[574] and ^{14}N NQR couplings in ammonium perchlorate[296] as well as additional studies on the adsorption of tetraalkylammonium ions on zeolites.[575] Relaxation measurements for ^{15}N in

$MeCH(NH_2)CH_2CH(NH_2)Me$ show[576] that the internal rotation in the amino moieties is hindered while it is free in the corresponding ammonium ions. There are also additional data for amino-type complexes of platinum which show ^{15}N–^{195}Pt couplings[577] or are employed in following the reactions of such complexes with reduced glutathione in human red blood cells.[578,579]

Some older data on the nitrogen shieldings in substituted anilines show rough correlations with Hammett's substituent constants,[580] but the data refer to rather concentrated solutions. The shieldings of amino groups in aminopyridine derivatives seem to show correlations with *ab initio* calculated (STO-3G) charge densities at the nitrogen atoms concerned.[508] The NH_2 resonance in perfluoroaniline shows an increased shielding, by about 30 ppm, with respect to aniline.[581] Two ^{15}N resonances observed for the 2-NH_2 group in actinomycin D indicate the presence of two conformations in solution.[181]

There are additional data on lithium salts of aniline derivatives (see Table 6, notes (A, B) which show, via ^{15}N–^{6}Li coupling of about 3.5 Hz, that dimeric and trimeric structures are present in solution and each of the nitrogen atoms is bound to two lithium atoms.[276]

Solid-state studies on tautomerism involving enamino moieties have been carried out by means of ^{15}N CPMAS dynamic spectra of labelled compounds.[428,429,432,433,436,437] The NH enamino moiety in the indium salt of a dithiocarboxylic acid[582] shows a doublet in ^{14}N NMR which excludes any complexation to the cation. In addition to the data presented in Table 4, there is a further example of identification of enaminone-type tautomers.[583] It is interesting to note the low value of $^{1}J(^{15}NH)$ coupling, 64.7 Hz, in the R—O—NH—O—R system.[584]

Hydrazido complexes (Table 8), $MNNR_2$, show large differences in the nitrogen shieldings between the MN and NR_2 moieties. This is even more pronounced in the low-valent tungsten complex $(CO)_5W{=}NNMe_2$, where values of -420 ppm (W=N) and $+79$ ppm (NMe_2) were reported;[585] the latter are also significantly different from those in the table.

6.2. Hydrazones

There is a large difference in the nitrogen shieldings between the imino- and enamino-type moieties in hydrazones and related structures (Table 9). Hydrazone–azo tautomerism in a variety of structures, including those of azo dyes, has been examined on a large scale (see Tables 9 and 28, see also refs 412, 548, 586, 587), using nitrogen shieldings or deuterium isotope effects on the latter.[498] Hydrazone moieties in some semicarbazone derivatives are presented in Table 10, note (h). There have also been some additional data

on the shieldings in dithiocarbamate derivatives, $MeSC(=S)NH—N=CR_2$, which show differentiation between *E* and *Z* isomers.[588]

6.3. Amido moieties

Amido moieties are found in a number of important nitrogenous structures and these include ureas, thioureas, guanidines, amidines, amidoximes, and their derivatives (Table 10); cyanamides (Table 11); and amides, thioamides, sulphonamides (Table 12). Amide (peptide) linkages in peptides and proteins are included in Table 13 and are considered in the next section. Amide-type moieties are also found in a number of tautomeric derivatives of azole (Table 17), azoloazine (Table 18) and azine (Tables 19 and 20) ring systems, also including flavin derivatives (Table 21) and nitrogenous bases in nucleosides and nucleotides (Table 22).

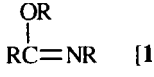
There have also been additional studies using nitrogen NMR on the identification of urea-type moieties in resins[589] and alkyl derivatives of thiourea;[590] of urea (by ^{14}N NMR) in urine of patients with chronic renal failure;[591] of *N,N*-diethylcarbamates[592] in complexes with Zn^{2+}, Cd^{2+}, and Hg^{2+}; of amidine moieties,[118, 549] also in solid HCN-polymers;[446] of *N*-aryl-guanidines;[593] and of guanidine moieties in arginine units of *TaqI* endo-nuclease.[217] Creatinine derivatives contain guanidine-type fragments, and the relevant data are shown in Table 17, note (G). Rather feeble effects (within 6 ppm) of *para*- and *meta*-substitution have been found in the nitrogen shieldings of Ph—CO—NH—CS—NHR derivatives.[594] A comparison of amide nitrogen shieldings, referenced to those in the corresponding amines, with the N–H stretching frequencies in infrared spectra did not reveal any correlation.[595] The racemization of allantoin was studied by ^{15}N NMR in DMSO solutions and in the solid state.[383]

The nitrogen shieldings in acrylamide derivatives[512] seem to be sensitive to π-electron conjugation within the amido moiety, but not to that including the vinyl group. Amido groups have been detected, by ^{15}N CPMAS NMR, in plasma-polymerized acetonitrile,[596] in HCN polymers,[446,452,453] in nylon-type polymers;[359–362,368–371,373–375,597] in alkene-*N*-maleic imide and 2,3-diethylsuccinimide polymers;[598] and also by ^{14}N NMR in poly(vinylpyrrolidone).[599] There have also been some additional data on cyclic amido moieties[600] and those bound directly to selenium.[601] Cyclic thioamides bound to furanoid carbohydrate rings seem to exhibit a downfield shift, by *ca.* 5 ppm, in nitrogen NMR with respect to those bound to pyranoid rings.[602]

A plot of the nitrogen shieldings in aqueous $HCONMe_2$ vs the mol% of the amide is non-linear and suggests the formation of hydrates.[537] Strong

association with hydroxylic solvents has been indicated by ^{14}N shielding and relaxation measurements of pyridone and its *N*-methyl derivative.[536]

The hydroxy-imino structures of iso-amides [**16**] which are isomeric (or tautomeric) with respect to amides, show typical imino nitrogen shieldings (Table 12, see also Table 24), about 150 ppm downfield of those of amides. This structure was detected by ^{15}N NMR in a silylated hydroxamic acid derivative, $MeC(OSiMe_3)=N-OSiMe_3$ (+73 and +88 ppm, *E* and *Z* isomers, respectively).[603]



[**16**]

While the nitrogen shieldings of sulphonamides and sulphinamides do not depart significantly from the range characteristic of amido groups, sulphenamide structures seem to fall within the range of amino group nitrogen shieldings (Table 12). There have been also some additional data[604] for the rather weak effects of substituents in benzenesulphonamide derivatives (see Table 12). The complexing of *p*-fluorobenzenesulphonamide with human carbonic anhydrase has been indicated by an increase in the nitrogen shielding of the former by about 10 ppm.[605]

6.4. Amino acids, peptides, proteins and related structures

The importance of these nitrogenous structures in nature makes nitrogen NMR a powerful tool in biochemical, biological, and medical studies. Actually, recent developments in nitrogen NMR techniques (see Section 4) have been oriented towards investigations of fairly large protein units. As far as chemical structures are concerned, and the relevant nitrogen shielding ranges, this group includes amino/ammonium moieties (amino acids, terminal and sidechain groups in peptides and proteins), amido groups (peptide linkages and sidechain amides), and also sidechain groups like guanidino/guanidinium or imidazole moieties which are present in some amino acid units.

The nitrogen shieldings of amino acids as such have been presented in detail in ref. 5, pp. 365–369; some additional results are shown in Table 13, and those for amino acids as ligands in amino-type complexes in Table 32. There have also been other studies by ^{15}N NMR of labelled samples, which include: taurine;[606] β-aminoglutaric acid as a major soluble component of *Methanococcus thermolithotropicus*;[607] *N*-(3,5-dinitrobenzoyl)valine methyl ester (D-, L-, and racemate) in diastereomeric complexes with *N*-butylamide of S-2-(phenylcarbamoyl)oxypropionic acid;[608] zinc–cysteine complex forma-

tion,[560,609] with the observation of ^{67}Zn–^{15}N coupling; and calcium–amino acid complexes,[610] where no significant effects on the shieldings were found. Numerous studies, by ^{15}N NMR of labelled amino acids, have been carried out in order to follow their incorporation and metabolism in a variety of biological systems: alanine,[611,612] including a discussion of competitive methods, based on radioactive ^{13}N; lysine in cell walls of *Aerococcus viridans*,[451] including effects of penicillin on cell-wall metabolism;[394] lysine in bovine rhodopsin and the purple membrane of *Halobacterium halobium*;[409] lysine and methionine,[613] and glycine[614] in collagen fibres; allantoin[450] and methionine[449] in soya bean cotyledons; glycine in melanoidins[404,405] in various rat organs,[474,475] in rat liver,[615] also by *in vivo*(!) experiments,[426] in *Nicotiana tabacum* mesophyll protoplasts,[616] and in peat incubated for 6 months under various conditions;[402] glutamate in fermentation processes effected by *Brevibacterium lactofermentum*,[617] and in the formation of a novel tetrahydropyrimidine derivative by the *in vivo* and *in vitro* syntheses effected by *Streptomyces parvulus*;[618,619] histidine in the insect cuticles of tobacco hornworm;[400,401] and microbial syntheses of tyrosine and tyramine.[620] The ^{14}N resonance signal of glycine betaine, $Me_3N^+—CH_2COO^-$, is sharp enough to be detected at low concentrations of the compound, and the relevant relaxation measurements can be used as a probe for local viscosities in cytoplasma, as was shown with the example of *Escherichia coli* K12, where the bacteria were grown in the presence of the betaine.[621]

However, most concern from the point of view of nitrogen NMR has been involved in the field of peptides and proteins. The nitrogen shieldings of *N*-acetyl derivatives of amino acids may serve here as a sort of reference (Table 13, note (h)), but the shieldings in peptide and protein systems can significantly deviate from such reference values, owing to a variety of intra- and intermolecular effects. Usually, as far as peptide linkages are concerned, the highest shieldings are observed for glycine (Gly, G) units, and the lowest for those of proline (Pro, P); the shieldings span a range of about 40 ppm, from +280 to +240 ppm with respect to neat nitromethane. They can easily be distinguished from those of terminal or sidechain amino/ammonium moieties, whose nitrogen resonances are found at higher fields, and from the imino-type moieties in arginine guanidino groups and histidine imidazole rings, which show nitrogen resonance signals at lower fields.

Recent developments in nitrogen NMR (see Section 4), particularly those which combine it with ^{1}H and ^{13}C NMR in a variety of two- and three-dimensional techniques, have brought complete or nearly complete assignments of nitrogen shieldings (and of those of the other nuclei), including internuclear connectivities, for a number of fairly large peptide and protein systems. Uniform or selective labelling with ^{15}N is usually a prerequisite for such detailed studies, and ^{13}C–^{15}N labels, in combination with various polariza-

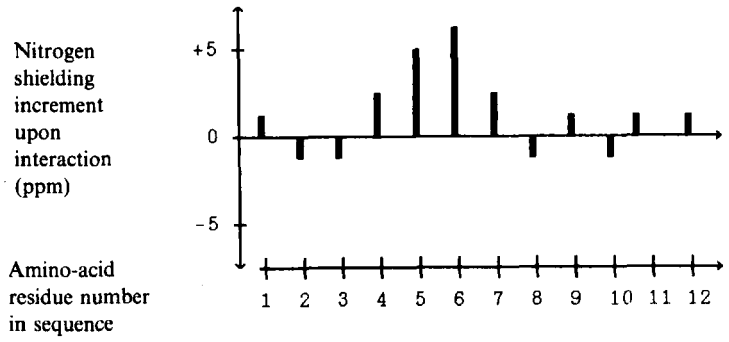


Fig. 3.

tion transfer and relay experiments, allow one to follow the fate of individual carbon–nitrogen bonds in biological systems by using ^{15}N NMR. Numerous examples can be found in Table 13. Recently, there have also been additional examples of full or nearly full assignments of nitrogen shieldings, based on combinations of various 2-D, 3-D and even 4-D techniques (see Section 4.1), in protein and peptide systems: *Escherichia coli* ribonuclease H,[260] oxidized and reduced forms of thioredoxin,[622] and apocytochrome b_{562};[623] ribonuclease T1;[624] *Lactobacillus casei* dihydrofolate reductase;[625] calmodulin;[245,256] oxidized flavodoxin from *Anacystis nidulans*;[265] interleukin-1β;[266] phosphotransferase protein III^{Glc};[239] *Bacillus subtilis* enzyme III^{Glc};[626] and λ-*cro* repressor protein.[240] Since such methods allow one to trace individual amino acid units, they constitute a potentially powerful tool for the observation of various interactions that involve in specific parts or sites of a protein molecule. However, the range of nitrogen shieldings (as well as proton and carbon shieldings) for peptide linkages is rather small; such full assignments have to be done separately for a given protein under conditions where the interaction does or does not occur. Results are conveniently presented in the form of difference shieldings (Fig. 3) which should show the protein fragments involved in the interaction. This method failed to reveal any specific sites for calmodulin (ligated to Ca^{2+}) upon its interaction with the binding domain of rabbit skeletal muscle myosin light-chain kinase.[256] However, *Escherichia coli* thioredoxin[622] shows characteristic sites,[26–37,60,75 and 92] which are affected by the transformation between its reduced and oxidized forms. The binding of Mg^{2+}, Ca^{2+} and Ba^{2+} to *Escherichia coli* ribonuclease HI, monitored by this method,[241] revealed involvement of the vicinity of residues.[10,48,70,122–126 and 134]

There have been less complete or specifically oriented studies by nitrogen NMR of a variety of peptides and proteins: bovine pancreatic trypsin inhibitor (BPTI);[191,196,237] staphylococcal nuclease from *Escherichia coli*;[214,216,230,258,277,388]

λ-*cro* repressor, labelled Leu and Lys units in interaction with operator DNA fragment;[213] porcine pancreatic phospholipase A_2;[219] arginine guanidino moieties in *TaqI* endonuclease;[217] human carbonic anhydrase II;[221] CMP-KDO synthetase;[248] calmodulin;[244] cytochromes c_2 and c';[496,518,519,627-629] ferrodoxin from *Anabaena*;[233] bacteriophage T4 lysozyme;[198,200,630] filamentous bacteriophage M 13 coat protein;[114,115,212] filamentous bacteriophage Pf1 coat protein in micelles;[211,631] fd coat protein in oriented bilayers;[180,319,334-336] DNA-binding protein *ner* from phage Mu;[209,229] H-*ras* p 21 protein;[238] Pro^3-cyclosporin;[187] bacteriorhodopsin;[329,410] gramicidin A in oriented bilayers,[95,338,340-342,459,460] Met-enkephalin;[189] terminal amino residues in Leu-enkephalin;[632] antamanide from *Amanita phalloides*;[182] interleukin-1β [2840]; AlaP in complex with alanine racemase;[350] glyphosate metabolism in *Pseudomonas*;[399] and the synthesis of trypanothione disulphide.[195]

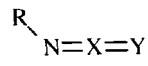
Extensive ^{15}N NMR studies have been carried out on nitrogen assimilation from $^{15}NH_4^+$ (or labelled ammonia) into peptide units of various biological systems: the fungus *Cenococcum graniforme*;[633] beech root cells symbiotically associated with soil fungi;[634] marine alga *Prochloron* species, light-dependent assimilation;[635] *Streptomyces venezuelae*;[473] *Streptomyces parvulus* and *Saccharomyces cerevisiae*;[636] *Bacillus polymyxa*;[480] *Bacillus azotofixans*;[637] *Methanobacterium thermoautotropicum*,[334] also the uptake of labelled urea;[638] ammoniated straw;[403] metabolism in rat organs,[639] also in acute hyperammonaemia;[555,556] and metabolism in plants.[640] The assimilation of both NH_4^+ and NO_3^- has been studied in alfalfa (*Medicago sativa*)[395] and in barley, maize, and pea roots (by ^{14}N NMR);[93] and uptake of methylamine into N-methylglutamate in *Pseudomonas* species A.[641] Nitrogen fixation from $^{15}N_2$ was followed for *Klebisiella pneumoniae* (also from labelled ammonia);[398] and for *Methanococcus thermolithotropicus*, *Methanobacterium bryantii* and *Methanospirillum hungatei*,[396] also from the ammonium ions.[481]

^{15}N NMR has also been employed in the differentiation of peptide and choline units in pig kidney tissue;[566] in *in vivo* studies on cell-wall organization in *Streptomyces faecalis* and *Bacillus subtilis*;[642] in studies on peptidoglycan mobility in *Aerococcus viridans*;[393] in biosynthetical labelling of echinomycin and triostin;[643] in conformer population estimates for collagen model peptides labelled with (^{15}NGly;[644] in a study of *cis–trans* isomerism at ^{15}N–Gly–Pro bonds,[270] using two-dimensional $^{15}N/^{15}N$ exchange spectra; and in the detection of the sulphenamide-type linkage which is formed upon the inactivation of cysteine proteinase cathepsin B with its inhibitor, ^{13}C–^{15}N labelled *N*-benzyloxycarbonyl-L-phenylalanylglycine *O*-mesitoylhydroxamate.[645] The nitrogen shieldings of the terminal Gly unit in a number of solid peptides[385] seem to increase with decreasing length of the hydrogen bond between NH and CO in the crystal lattice, but there is no correlation with nitrogen–oxygen distances.

There have also been presentations of various experimental techniques which included nitrogen NMR as such or in combination with proton and carbon NMR, using peptides and proteins as model molecules[165,167,168,186,188,228,243,246,247,250–254,290,444,646,647] (see also Section 4 on Experimental Techniques).

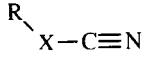
6.5. Azido, isocyanato, cyanato, isothiocyanato, thiocyanato groups and corresponding ions

These structures can be represented by the formulae [**17**] and [**18**].



[17]

X	Y	
N^+	N^-	covalent azide
C	O	covalent isocyanate
C	S	covalent isothiocyanate



[18]

X	Y	
O		covalent cyanate
S		covalent thiocyanate

The highest shielding of nitrogen nuclei within this group takes place in the R—N= moieties (Tables 14 and 15). The data for azides and the azide ion are presented in Table 14. The use of selectively ^{15}N-labelled azido groups in combination with ^{15}N NMR enables one to follow the fate of individual nitrogen atoms of the group in reactions and rearrangements; this method revealed the scrambling of the labels over the tetrazole ring in the anion of azido-substituted tetrazole (Table 14, note (c)), and also the location of the labels in the pentazole ring obtained from the azide ion as a substrate.[648] The nitrogen shieldings and the lack of ^{15}N–proton couplings were employed in localizing the position of the azido substituent, at C-1, in an iodo-azide adduct of 1-phenylcyclohexene.[649] The ^{14}N relaxation in sodium azide shows a rather poor correlation with the acceptor number of the solvent employed,[650] and the same is true for sodium thiocyanate.

There is a clear distinction, as far as nitrogen NMR shieldings are concerned, within the isomeric pairs of structures of isocyanates and cyanates, and within the pairs of thiocyanates and isothiocyanates (Table 15). Such differences are also important in using nitrogen NMR as a source of information on the mode of binding of (iso)cyanate ions or (iso)thiocyanate ions as ligands in complexes (see Table 15). There have also been systematic studies of solvent effects on the nitrogen shieldings of the isothiocyanato group (Table 15, notes (a, b); see also Section 5.4). The monitoring of the (iso)thiocyanate ion, NCS^-, by means of nitrogen NMR has also been employed in

the case of alkylammonium salts used as mobile phases in liquid chromatography;[567] in biuret-rich 4,4′-methylene-bis(phenylisothiocyanate)-based resins,[441] in following its binding to lactoperoxidase,[651] also by ^{15}N T_1 relaxation measurements, and its lactoperoxidase-catalysed oxidation with H_2O_2;[652] in a study of its interactions with horseradish peroxidase,[653] also using ^{15}N relaxation; and in following its binding to germanium in reactions of $GeCl_4$ with KNCS.[654, 655] Abnormally large ^{31}P–^{15}N couplings were observed in phosphorus-bound isothiocyanato groups.[656]

There is a large difference between the nitrogen shielding anisotropies of the ammonium ion (less than 10 ppm) and the (iso)thiocyanate ion (*ca.* 415 ppm) observed in solid NH_4NCS.[351]

6.6. Cyanides, isocyanides, fulminates and related structures

The cyanide ion, also as a ligand, covalent cyanides (nitriles) and isocyanides (isonitriles), nitrile *N*-oxides (fulminates) and other cyano moieties are considered in Table 16, but there are also additional data in Tables 9, 11, 28, 29. The cyano ligands in vitamin B_{12} and related cyanocobalamin structures are included in Table 34.

There is a clear distinction in the nitrogen shieldings between the isomeric structures of nitriles and isonitriles (Table 16). The protonation of nitriles, which yields the corresponding nitrilium ions, results in a considerable increase in the nitrogen shielding, by about 100 ppm. Generally, any involvement of the lone-pair electrons of the nitrile nitrogen in the formation of a covalent or hydrogen bond yields analogous effects on the nitrogen shielding, and examples can be found in Table 16. Attention is drawn to systematic studies of solvent effects on the nitrogen shieldings in nitriles (Table 16, note (a)), which are considered in Section 5.4.

Fulminates (nitrile *N*-oxides) show a significant increase in the nitrogen shieldings with respect to the parent nitriles (Table 16, notes (p, q)), but the effect is smaller than in the case of the nitrilium ions (notes (l, m, n, o)). The latter also include interesting structures where the nitrile nitrogen is coordinated to xenon or krypton (Table 16, notes (m, n)), and their ^{15}N spectra reveal spin–spin couplings to Xe or K. The mesoionic structures of nitrileimides, which are isomeric to diazo compounds, are considered in Section 6.12.

The nitrogen shielding in the cyanide ion, CN^-, is smaller, by about 30 ppm, than that observed in simple nitriles (Table 16, note (u)); it does not change significantly in diamagnetic complexes where the ion is coordinated via its carbon atom, but the shielding increases remarkably when the coordination takes place via its nitrogen atom (see, for example, Table 16, note

(w)). The latter effect on the shielding is analogous to that observed for nitrilium ions. Needless to say, in the case of paramagnetic complexes of CN^-, huge paramagnetic effects on the shielding are found (Table 16, notes (y, z, A, B)).

There have also been other studies where ^{15}N NMR was employed for detecting cyano moieties: acetonitrile adsorbed on zeolites;[425] cyano substituents in stable nitroxides,[657] and geminal cyano substituents at cyclobutene ring structures;[658] cyano groups in HCN polymers;[446] cyano ligands in low-spin iron(III) porphyrins in aqueous detergent micelles;[659] the fate of the cyano group in a papaine inhibitor, *N*-(*N*-acetyl-L-phenylalanyl)glycine nitrile,[660] which is transformed into an amido moiety upon interaction with papaine.

^{14}N relaxation in acetonitrile was employed[661] as a probe for surface viscosity of various phases used in gas–liquid chromatography. A specially interesting case is that of ^{14}N linewidth measurements for various nitriles which entered the solvation sphere of nickel(II) trifluoromethanesulphonate at various temperatures and under high pressures (up to 220 MPa) in a specially designed probe.[662]

Recent *ab initio* calculations for HCN, using the second-order polarization propagation approximation within the coupled Hartree–Fock method, yielded a value of -17.0 ppm for the absolute magnetic shielding of nitrogen,[72] and this seems to indicate that nitrile nitrogen shieldings are located near to the zero point (that corresponding to a bare nitrogen nucleus) on the absolute scale.

6.7. Nitrogen-containing heteroaromatic systems

These systems include six-membered rings (azines, Table 19), five-membered rings (azoles, Table 17), and combinations thereof (azolo-azines, Table 18). Azine analogues with SO_2 moieties within the rings are presented in Table 20, phosphazoles in Table 23, and the heteroaromatic systems of significant biochemical and biological interest are included in Table 21 (flavins and related pterins), Table 22 (nucleosides, nucleotides, and related structures), and Table 34 (drugs, medicines, vitamins, etc.).

There are essentially two types of bond patterns involving the nitrogen atoms in such systems. One is represented by what we call *pyridine-type nitrogen atoms*; each of these bears a lone electron pair which may be considered as a part of the relevant σ-bond system and supplies one π-electron to the delocalized aromatic π-bonds. This type is found in azine ring systems, and also in diazole, triazole, tetrazole, pentazole, oxazole, thiazole, and analogous ring systems. Their nitrogen shieldings cover a fairly wide

range, about −40 to +180 ppm with respect to that in neat nitromethane; they do not depart significantly from those for open-chain imines (Table 24). The protonation (or *N*-alkylation) of a pyridine-type nitrogen atom invariably leads to a remarkable increase in the magnetic shielding of its nucleus, often by 100 ppm or more, and this makes nitrogen NMR an important tool in following protonation–deprotonation sites and equilibria (see Section 5.3). Nitrogen shieldings similar to those observed in protonated azines are also found (about +180 ppm from nitromethane) in azine-type cationic species where the nitrogen atom lies at the junction of two six-membered rings (Table 19, note (H); some additional data on such structures can be found in ref. 663. Analogous, but somewhat smaller effects are observed upon the *N*-oxidation or hydrogen bonding of such nitrogen atoms (Table 19), and systematic studies of solvent effects on the nitrogen shieldings of azine systems[31,34,532] (see also Table 19, notes (b, d, q), and Section 5.4) show that nitrogen NMR can be employed in the estimation of relative strengths of hydrogen bonds from solvent to pyridine-type nitrogens. The huge upfield shifts of pyridine-type nitrogen resonances that occur upon the protonation of the corresponding nitrogen atoms are also observed in cases where the proton comes formally from an –OH or –SH substituent in the molecule concerned, and the resulting structure is that of the corresponding lactam (or thiolactam) tautomer, or eventuallly of a mesoionic, betaine-like tautomer. This is especially important in investigations of tautomerism and tautomeric equilibria in nitrogenous heteroaromatics (see Section 5.5), using nitrogen NMR as such or in combination with the NMR of other nuclei.[664]

The other type of bonding of nitrogen atoms in heteroaromatic systems is represented by what we call *pyrrole-type* nitrogen atoms; each of these is bound covalently to three neighbouring atoms, and supplies two electrons to the delocalized π-bond system concerned. This type is found in azole systems, with the exception of oxazole, thiazole and analogous systems, where formally the pyrrole-type nitrogen atom is replaced with that of oxygen or sulphur. It is present, however, in phosphazole rings (Table 23), where phosphorus formally replaces nitrogen atoms of the pyridine type. Pyrrole-type nitrogen atoms are also found in azolo-azine systems (Table 18), as those at the junctions of their fused five- and six-membered ring moieties (indolizine and their aza-derivatives). Rarely can one find such nitrogen atoms in azines; an example[665] is presented in Table 19 note (H), where a nitrogen atom is at the junction of three six-membered ring moieties. Generally, pyrrole-type nitrogen nuclei are magnetically more shielded that those in pyridine-type nitrogens, particularly if both kinds are present in a given molecule. This difference is usually quite remarkable, but it is not always the case. Recent studies on azaindolizine systems[90] (see also Table 18, notes (a, b, c, d, e) and Table 17, note (jj)) show that the difference diminishes with increasing degree

of delocalization of the lone-pair electrons from the pyrrole-type nitrogen atom involved in the aromatic ring system, and it can even change its sign. The same trend of the effects of the nitrogen shieldings in aza-indolizines is observed for solvent-induced enhancements of such a delocalization in systematic studies of solvent effects on the shieldings[533] (see Table 18, note (a) and Section 5.4). The nitrogen shieldings of pyrrole-type nitrogen atoms are found in the range from +80 to +230 ppm with respect to neat nitromethane, while those of lactam-type tautomers of OH- and SH-substituted azoles and azines are usually higher, in excess of +200 ppm from nitromethane.

Nitrogen NMR shieldings can be used effectively in differentiation between various isomeric or tautomeric forms of heteroaromatic systems, and there are examples galore in the tables concerned. More or less pronounced additivity of various structural effects on the shieldings, such as that observed for azine systems,[516] can be employed for this purpose, e.g. by means of constructing the so-called self-consistent sets of increments to the shieldings, described in detail in Section 5.3. There have also been some attempts at explaining the nitrogen shieldings in this class of molecules using various quantum-mechanical calculations. Those at the *ab initio* level included the outright calculations of the shieldings for azole and azine systems, by the IGLO variant of the coupled Hartree–Fock method, which gave a reasonable agreement with the experimental values, but large deviations (up to 100 ppm) were found for systems with two neighbouring nitrogen atoms, possibly owing to the neglect of electron correlation.[10] In other computations at this level of sophistication, reasonable, but local correlations were found between the STO-3G calculated charge densities and the nitrogen shieldings in amino derivatives of azines and their *N*-oxides[508] and in some mesoionic azole systems.[666] The relative stability of the tautomeric forms presented in Table 20, indicated by nitrogen NMR, was also predicted by such calculations.[667] Only rough correlations were found between the nitrogen shieldings of 4-substituted pyridines and the calculated ionization potentials.[39] Less sophisticated methods involved the CNDO calculations of the increased shielding upon the hydrogen bonding of the nitrogen atom in pyridine,[37] and rather rough correlations between PPP-calculated π-charge densities and the nitrogen shieldings in azines and azoles.[511]

There have also been other studies which are not presented in the tables. The scrambling of ^{15}N labels was observed by nitrogen NMR in 5-azidotetrazole,[668] as a result of ring opening and closure processes. Four distinct ^{15}N signals were observed[669] in the haeme part of ferrocytochrome c[553] at pH 5.5: at +195.1 (pyrrole I), +192.1 (pyrrole II), +200.3 (pyrrole III) and +193.5 ppm (pyrrole IV). The adduct of the pyrazole anion with BH_3 shows nitrogen shieldings of +140 and +80 ppm[582] which are typical of *N*-substituted pyrazoles (see Table 17). The synthesis of ^{15}N-labelled 1,2,4-triazole

was followed by means of ^{15}N NMR.[670] There have been also some additional data on the nitrogen shieldings in pyrrole-containing polymers,[381,382] substituted indoles,[580] benzodiazoles and benzotriazoles,[671] nitro-substituted benzimidazolones,[672] 1-chloro-1,2,4-triazole derivatives,[673] 1,2,3-thiadiazoles,[163,674] mesoionic azole derivatives,[675,676] imidazo [1,2-a]pyrazine[529] (which was shown to undergo protonation at N-1), and phosphazoles.[176]

The ^{14}N linewidths of pyridine were employed in studies on the solvation sphere of Ni(II) and Co(II) complexes in pyridine solutions;[677] analogous measurements were employed in a study of rotation dynamics of 2-pyridone in hydroxylic solvents;[536] and of changes in liquid organization of quinoline.[678] The nitrogen shieldings of some complexes which include pyridine rings are also presented in Table 24, notes (f, g, h). The N-1 and N-4 atoms of the quinoxaline moiety of the antibiotic triostin A were shown[643] to come from the indole and amino moieties, respectively, of tryptophan, using ^{15}N NMR of labelled samples. Two conformations of [5-^{15}N]folate were detected in a complex with dehydrofolate reductase.[679] Copper was found to bind N-7 and N-9 in Cu(II) complexes of purine.[102] Hyperfine couplings in the radical states of flavin systems were monitored by ^{14}N ENDOR.[680] There are also some additional data on the nitrogen shieldings in substituted pyridines and quinolines,[681] in trimethylsilyl-substituted quinolines and their *N*-methyl iodides,[682] in Sn(IV) derivatives of 8-*O*- and 8-S-substituted quinolines,[683] and on the relevant protonation shifts in pyridazine and phenanthroline,[538] and in 2-methoxypyrazine (protonation at N-4).[530] Solid-state copper(I) complexes of 1,10-phenanthroline show a shielding increase by about +45 ppm with respect to the parent structure.[365] Significant upfield shifts of the nitrogen resonance signals, by 12–82 ppm, were reported for $-CH_2Ph$-substituted pyridazines, pyrimidines, and pyrazines, upon the formation of the corresponding $-CH^--Ph$ anions;[684] the latter effect is in accord with the general trend in substituent effects on nitrogen shieldings in aromatic systems (see Section 5.3).

6.8. Nucleosides, nucleotides, flavins and related systems

This biologically important class of organic compounds represents, from the point of view of nitrogen NMR, azine and azolo-azine systems or tautomeric derivatives thereof, and the considerations of the nitrogen shieldings of the latter apply also to the present group. An important point here is that the nitrogen shieldings in such aromatic systems are generally lower than those of the peptide linkages in protein moieties, and they can be readily distinguished from each other in nitrogen NMR spectra of biological samples.

Flavins and related pterin systems are presented in Table 21. Attention is

drawn to the fact that there is a simple distinction between the oxidized and the reduced forms of flavins as far as the nitrogen shielding of N-5 is concerned (about + 50 ppm for oxidized, and about + 320 ppm for reduced forms); see also the data[685] for oxidized and reduced forms of glucose oxidase from *Aspergillus niger*. Conformations of a complex of *Escherichia coli* dehydrofolate reductase with 5-^{15}N-labelled folate or methotrexate were studied by ^{15}N NMR.[686]

Nucleosides, nucleotides and related systems are included in Table 22. Nitrogen NMR is an important tool in tracing tautomeric forms of the latter, protonation sites and hydrogen bonding interactions, since the nitrogen atoms are directly involved in such processes and transformations. Labelling with ^{15}N offers an additional advantage of observations of selected parts of such complicated molecular systems, and such studies by ^{15}N NMR include in addition to those presented in the table: the synthesis of labelled nucleosides[687] and deoxynucleosides[688] of [1,3-$^{15}N_2$]cytidine;[689] the incorporation of $^{15}NH_4^+$ into the nucleoside structures of *Methanobacterium thermoautotropicum*;[638] labelled oligodeoxynucleotides,[222,275,690,691] including a study of secondary isotope effects, $^1H/^2D$, on the nitrogen shieldings;[692] the detection of pseudocyclic structures in aqueous AMP-5′ and UMP-5′;[540,541] a nuleotide adduct of the carcinogen 2-acetylaminofluorene;[693] glyoxal–guanine adducts;[116] ATP and AMP complexation with *Escherichia coli* adenylate kinase;[694] the protonation of deoxydinucleotide monophosphates;[695] some additional data on guanine and uracil,[696] on uridine and guanosine,[520] and on wyosine;[521] 7-^{15}N-labelled guanosine oligonucleotides, and their interactions with nuleic acids;[280] [3-^{15}N]cytosine interaction with a threonine-containing tripeptide;[697] $^{15}N/^1H$ correlations in *Escherichia coli* 5S RNA,[179,278,279] and in cytosine;[490] labelled DNA structures,[698] also in the solid state;[406] modified adenine in (+)-CC-1065–DNA adduct;[699] the protonation at N-1 of adenine in A–C and A–G mispairs in the duplexes $\{d[CG(^{15}N)AGAATTCCCG]\}_2$ and $\{d[CGGGAATTC(^{15}N)ACG]\}_2$;[223] the protonation at N-1 and ionization at N-7 of adenosine and the keto-tautomer of 8-hydroxyadenosine;[700] the protonation of cytidine in oligonucleotides;[194] DNA oligomers;[224] uridine units in $tRNA^{Phe}$ from *Escherichia coli his*T mutants;[225] amino group protection in DNA and RNA structures by arenesulphonylethoxycarbonyl groups.[701] Nitrogen NMR studies of purines include the purine dication Cu(II) chloro complex[102] and the deamination of 1-aminopurinium salts.[702] The nitrogen shielding data[703] for nucleoside analogues which are inhibitors of replication of human immunodeficiency virus (HIV) and Moloney murine leukaemia virus (MuLV) are presented in Table 14, note (e); those for vitamin B_{12} are shown in Table 34.

Theoretical calculations at the *ab initio* level have been carried out for the

nitrogen shieldings in Watson–Crick base pairs;[704] and for DNA bases and the protonation effects on the shieldings.[11]

6.9. Phosphazenes and related structures

These structures contain P=N moieties and are presented in Table 23. There is a vast difference in the nitrogen shieldings between the derivatives of penta- and trivalent phosphorus, $R_3P{=}N{-}R$ and $R{-}P{=}N{-}R$. The latter fall in the range characteristic of imines, $R_2C{=}N{-}R$ (Table 24), and of pyridine-type nitrogen atoms in aromatic heterocycles (see Section 6.7); this is also true for the P=N moieties within the aromatic rings of phosphazoles (Table 23, note (f)). The $R_3P{=}N{-}R$ structures, however, are characterized by nitrogen shieldings of +240 to +310 ppm with respect to neat nitromethane, that is higher by about 150 ppm as compared wth $R{-}P{=}N{-}R$; this holds for the ring structures of cyclophosphazenes also. Some additional data have been reported on the latter,[705] and on the correlations of the nitrogen shieldings presented in Table 23, note (a), with Hammett's constants for *para*-substituents at the phenyl ring.[706]

Attention is drawn to the first report of the nitrogen shielding in the iminophosphenium cation structure, $R{-}N^+{\equiv}P$, presented in Table 23, note (h).

6.10. Imines, nitrones, oximes and related structures

This group of structures is presented in Table 24, and includes imines, $R_2C{=}N{-}R$, their *N*-oxides (nitrones), $R_2C{=}N(O){-}R$, and oximes, $R_2C{=}N{-}OR$, which are structural isomers of nitrones. Related to these are also the C=N moieties in guanidine, amidine, and amidoxime structures (see Table 10).

The nitrogen shieldings in imines are similar to those observed in pyridine-type nitrogen atoms in aromatic heterocycles (see Section 6.7 and Tables 17, 18, 19), and all the considerations of the latter apply also to imines, particularly with respect to the huge upfield shifts upon the protonation of the imino nitrogen atom (see Table 24, notes (j, m)), smaller but significant shifts in the same direction upon *N*-oxidation (to nitrones, in the present case), hydrogen bonding or complexation. Oxime nitrogen nuclei are generally less shielded than those in imines, and the latter are less shielded than those in nitrones, but the relevant ranges show some overlap. Ketenimines, $R_2C{=}C{=}N{-}R$, are an exception, since they show the highest shielding of the nitrogen nuclei, about +170 ppm with respect to nitromethane (Table 24, note (r)).

Enamine–imino tautomerism in the solid state, involving double proton transfers, has been studied extensively by variable-temperature dynamic ^{15}N CPMAS spectra[427–430,432,433,436,437,545,546] (see also Section 6.6, and Table 24, note (b)). There is a large difference in the nitrogen shieldings of such tautomeric species, R—NH—CR=X and R—N=CR—XH, usually of about 150 ppm, which makes nitrogen NMR a suitable tool for studies of tautomerism involving imino units, also in solution.[583]

In addition to the nitrogen NMR studies of the imino moieties in bacteriorhodopsin, presented in Table 24, notes (j, m), there have also been other investigations[407,409] in solution and the solid state. Imino groups have also been identified by means of nitrogen shieldings in a complex of [^{15}N]alaninephosphonate (AlaP) with alanine racemase,[350] and in solid melanoidins.[404]

The $[-CR^1=N-N=CR^2-]_n$ polymers,[367] which are precursors of organic conductors, give a signal at +28.1 ppm (natural-abundance ^{15}N CPMAS), within the typical imino range, but the conductors obtained by oxidation ("doping") with iodine show a broad signal at +250 ppm;[366] the latter was considered as evidence in favour of the formation of "bipolarons" (dications), $-N^+-CR=CR-N^+-$, involving nitrenium cation structures in the conducting polymer.

6.11. Sulphur–nitrogen bonds

There is a large variety of structures which contain sulphur–nitrogen multiple bonds, and these are presented in Table 25. In many instances the only feasible way to access such structures by means of NMR is via the nitrogen nuclei in view of the experimental difficulties concerned with sulphur NMR. The use of ^{15}N labels enables one to follow the fate of individual nitrogen atoms in reactions and rearrangements involving such structures, as was the case with the scrambling of the labels in the ring structure presented in Table 25, note (f), or the ring interconversion, note (i). The fate of the label in S_4N_4 was monitored in this way in a reaction with a platinum complex, *cis*-$[PtCl_2(PMe_2Ph)_2]$, using ^{15}N–^{31}P couplings also.[707] Unsymmetrical structures of $S_3N_3Cl_3$ adducts with norbornene[708] have been characterized by means of ^{14}N NMR.

Sulphur–nitrogen single bonds are found in various structural units, and these are presented in Table 6 (—S—NR_2), Table 12 (sulphonamides, sulphenamides), Table 17 (isothiazoles), Table 20 (azine analogues containing SO_2 moieties), and Table 29 (R—S—N=O, thionitrite).

6.12. Nitro groups and nitrates

There is a clear difference in the nitrogen shieldings of nitro groups bound to carbon (nitroalkanes and nitroarenes), nitrogen (nitramines) and oxygen (covalent nitrates, HO—NO_2, N_2O_5), and the latter sequence corresponds to increasing shielding (Table 26). A deviation from this is found in the case of nitroalkanes, where the aggregation of two or more nitro groups at the same carbon atom brings the resonance into the range characteristic of nitramines; the same applies to polynitro-substituted benzene rings. Nitroalkanes which have only one nitro group at a given carbon atom can readily be distinguished from aromatic nitro compounds on the basis of the nitrogen shieldings; the same applies to a distinction among primary, secondary and tertiary nitroalkanes ($MeNO_2$, R—CH_2NO_2, R_2CHNO_2, R_3CNO_2), where the differences originate from the general β-effects of the alkyl groups concerned (see Section 5.3), provided that the same solvent is used. The latter distinction in nitroalkane mixtures is quite feasible even in ^{14}N NMR, in spite of the fact that the shielding differences are usually not larger than 10 ppm, since the corresponding signals are quite sharp, particularly in low-viscosity hydrocarbon solvents; this is especially true if the measurements are carried out in supercritical fluids[269] (see Section 4.1).

However, one should be aware of the fact that the nitrogen shieldings in nitro groups are fairly sensitive to solvent effects (see Table 26, notes (a–d), and Section 5.4), mostly those of solvent polarity.

The nitrogen shielding in the nitrate ion, NO_3^-, falls into the range characteristic of *C*-nitro groups, but that in covalent nitrates (including HO—NO_2) is higher by about 40 ppm; this difference is responsible for the variation of the shielding observed in aqueous nitric acid, depending on the concentration of the latter. The shielding in the nitronium ion, NO_2^+, is still higher, about + 130 ppm with respect to nitromethane (Table 30).

The amino nitrogens in nitramines are found at about + 200 ppm from nitromethane in nitrogen NMR spectra, and this amounts to a deshielding by about 100 ppm with respect to *C*-amino groups.

There have also been other studies of nitro and nitrato moieties, in addition to those presented in Table 26. Nitro groups were monitored by ^{15}N NMR in nitration processes and nitro group migrations[487–489] (including CINDP effects, see section 4.5); in nitro group elimination via a rearrangement into the covalent nitrite;[709] in nitrimyoglobin obtained from the reaction of horse heart met-myoglobin with $NaNO_2$, where nitrogen NMR showed that a single nitrogen was introduced, as a nitro group;[710] in some 2-nitroanilines[711] and fluorinated nitrobenzenes;[581] as substituents in some stable nitroxyl radicals;[657] in the covalent nitrato and nitramino groups of nitrocellulose and nitramine explosives,[379,380,712] including also denitration processes

in nitrocellulose and monosaccharide nitrates,[183] and in cyclodextrin nitrates[184] where it was shown that the process is highly regioselective, and takes place at C-2. Studies on ionic nitrates included nitrogen shielding anisotropy and phase transitions in solid ammonium nitrate, by ^{15}N CPMAS spectra;[92] ^{14}N relaxation measurements in zirconium nitrate in aqueous and HNO_3/H_2O solutions, indicating nitrate complexation to zirconium;[713] ^{14}N quadrupole coupling[145] and shielding[294] tensors in single-crystal KNO_3; ^{14}N measurements of the nitrogen shielding tensor for single crystals of silver, barium and lead nitrates;[295] the detection of the nitrate ion in liquid organic salts used as mobile phases in liquid chromatography;[567] and some additional data on HNO_3/H_2SO_4 systems.[714] The nitrate anion, complexed to erbium (III) in aqueous solvent mixtures shows separate signals at -200 to -300 ppm with respect to nitromethane.[715]

6.13. Diazo structures, diazonium ions and diazoates

These structures are presented in Table 27. The nitrogen shieldings of the central nitrogen atoms, $=N^+=$, in diazo compounds and diazonium ions do not depart significantly from those observed in the analogous nitrogen atoms in azides (see Table 14). However, the terminal nitrogen nuclei, those in $=N^-$, are considerably less shielded than their azide counterparts. In diazo compounds, $R_2C=N^+=N^-$, there seems to be a trend of increasing the nitrogen shielding at the central atom and decreasing that at the terminal atom with increasing electron-attracting properties of substituents R (Table 27). Diazo compounds **[19]** are isomeric with the corresponding mesoionic structures of nitrile-imides **[20]**, and there is a simple distinction between them in nitrogen NMR.[716]

$R_2C=\overset{+}{N}=\bar{N}$	$R-C\equiv\overset{+}{N}-\bar{N}-R$
[19]	**[20]**
diazo compound	nitrile-imide
ca. $+120$ ppm	*ca.* $+190$ ppm (N^+)
ca. $+30$ ppm	*ca.* $+300$ ppm (N^-)

In diazonium ions, $R-N^+\equiv N$, the shielding seems to increase in both cases, but the most significant changes seem to occur at the terminal nitrogens; attention is drawn to the substituent effects on the shieldings in *para*-substituted benzenediazonium salts in dilute solutions (Table 27, notes (f, g)). So far, attempts at obtaining the nitrogen NMR spectrum of the parent diazonium ion, $N\equiv NH^+$ (which may be also considered as protonated dinitrogen), have failed.[717]

Diazoates, R—N=N—OR, whose nitrogen nuclei are deshielded with respect to the other two groups, differ also in the shieldings from azo compounds, R—N=N—R (Table 28, particularly in the R—N= moieties. There is a clear distinction, as far as the nitrogen shieldings are concerned, between *syn*- and *anti*-isomers of diazoates.

6.14. Azo, azoxy, azodioxy compounds, diazenes, triazenes and tetrazenes

This group of structures contains azo bridges, —N=N—, or their *N*-oxide forms (Table 28). The nitrogen shieldings of —N=N— seem to be quite immune to solvent effects, with the possible exception of strong hydrogen-bond donors which seem to bind to the π-electron system of the azo bridge[31] (Table 28, note (b)). There are significant differences in the nitrogen shieldings between the corresponding *syn*- and *anti*-isomers in such structures. Some OH-substituted azoarenes are in tautomeric equilibria with the corresponding hydrazone forms (see Sections 5.5 and 6.2, and also Table 9); in view of the vast difference in the relevant nitrogen shieldings, nitrogen NMR is especially suited to investigation of such tautomerism which frequently is concerned with the molecular structure of various azo dyes[360,498,548,586,718-729] and their Co(III) complexes.[606]

Azoxy structures are mono-*N*-oxides of azo compounds, and the *N*-oxidation results in a considerable shielding increase in both of the nitrogen atoms of the azo bridge. Protonation of azoxy compounds (Table 28, note (n)) does not significantly affect the nitrogen shieldings, but diprotonation results in a shielding increase by about 100 ppm, and this is analogous to the changes observed upon the protonation of azo compounds in strong acids (Table 28, note (a)).

Azodioxy compounds are *N*,*N*′-dioxides of azo structures; they are also dimers of the corresponding nitroso compounds, and exist in equilibria with them. The difference in the nitrogen shieldings involved in such equilibria reaches 500 ppm (see also Table 29), and these have been studied quantitatively by ^{14}N NMR using the differential saturation technique[30] (see also Section 4.4, Table 28, note (r), and Table 29, note (a)).

The diazene structure (Table 28, note (s)), $R_2N^+{=}N^-$, may be considered as the betaine-type isomer of the corresponding azo compound R—N=N—R, and there are vast differences in the nitrogen shieldings concerned. Triazenes may be divided into the amino-azo structures, R—N=N—NR_2, and the imino-azo structures R_2C=N—N=N—R, and they are characterized by nitrogen shieldings which are essentially those of the corresponding azo, enamino and imino moieties, respectively; the same is true for tetrazene structures, R_2N—N=N—NR_2 (see Table 28, notes

(s, t)). There have also been reported some additional data on aminoazo-type triazenes.[730,731] However, there seems to be a general, significant effect on the shieldings in systems X—N=N—R, where X is an atom which bears a lone electron pair, e.g. that in OR or NR_2 moieties; the nitrogen shielding increases, with respect to the azo structure R—N=N—R, at the =N—R moiety of X—N=N—R.

6.15. Nitroso compounds, nitrosoamines, nitrites and related structures

These structures contain the nitroso group, —N=O, bound to either carbon or nitrogen or oxygen, respectively (Table 29). The nitrogen nuclei in *C*-nitroso compounds are among the most deshielded ones in diamagnetic molecules and ions; their resonances are found at about −600 to −400 ppm with respect to the nitromethane reference. Those of covalent nitrites, nitrous acid, and the nitrite ion appear at about −200 ppm, those of the nitroso groups in *N*-nitrosoamines at about −150 ppm, and the amino nitrogen in the latter at about +130 ppm (Table 29).

Nitrosoalkanes and nitroso-arenes exist in solutions in equilibria with their dimers, which have azodioxy structures (see Section 6.13, and Table 28) that give separate nitrogen signals at about +60 ppm. Quantitative ^{14}N NMR measurements[30] show, for example, that Bu^{t}NO exists as such in 60–88%, depending on the solvent used, and the accuracy of such assays is about 0.5%. The nitrogen shielding in the latter compound (Table 29, note (a)) is moderately affected by solvent effects, but they seem to originate mostly from solvent polarity, with little effect of hydrogen bonding, possibly owing to the steric hindrance effected by the t-butyl group. This is in constrast with the huge effects exerted by protic solvents on the nitrogen shielding in the nitroso moiety of $[ON\text{–}C(CN_2)]^-$ (see Table 29, notes (m, n) and also Section 5.4).

The covalent nitrito group (Table 29, note (d)) shows a wide range of solvent effects on its nitrogen shielding, and the most pronounced one seems to be the shielding increase upon hydrogen bonding from solvent to the lone electron pair at the nitrogen atom concerned (see also Section 6.4). The nitrito group, R—O—NO, is easily identified in nitrogen NMR, because of its characteristic shielding, about −200 ppm, which differs significantly from that of the corresponding nitro isomer, $R—NO_2$ (about −30 to +30 ppm, Table 26); this has been employed in the identification of nitrito structures that appear in rearrangements of nitro groups.[709] Thionitrite nitrogen shielding (R—S—NO, see Table 29, note (g)) seems to fall close to shielding in *C*-nitroso compounds.

The nitrite ion, NO_2^- (about −228 ppm in aqueous solutions), usually shows a significant increase in its nitrogen shielding when the ion is com-

plexed to metal, in the so-called "nitro" complexes (Table 29); there have also been additional data on such complexes of cobalt,[732] but attempts at obtaining the ^{15}N resonance signal in $[Ru(^{13}CN)_5(^{15}NO_2)]^{4-}$ failed, for reasons unknown;[733] and data on complexes with ruthenium,[734] rhodium,[735] iridium,[736] and platinum[737] have been reported.

A large variety of *N*-nitrosoamine structures have been studied by nitrogen NMR (Table 29). The nitrogen shieldings can be employed in the identification of *Z*,*E*-isomerism in the latter, and numerous examples are found in the table, particularly for cyclic *N*-nitrosoamines. Substituent effects on the shieldings in *N*-methyl-*N*-nitrosoaniline derivatives seem to be significant only for the nitroso moiety (Table 29, note (t)). The nitrosoamine structures have been identified, by means of ^{15}N NMR, in some food products where sodium nitrate reacted with amino acid units.[738] Anions derived from *N*-nitrosoamine structures (Table 29, note (s)) are closely related to diazoates (see also Table 27), and various equilibria in such systems can be monitored by nitrogen NMR.

6.16. Dinitrogen and its complexes, diazenido complexes and related structures

The nitrogen shielding of dinitrogen (molecular nitrogen, N_2, see Table 31) is interesting for various theoretical and practical reasons. These include attempts at approaching the absolute scale of nitrogen NMR shieldings using quantum-mechanical calculations (see Section 3). However, the case of the two adjacent nitrogen atoms seems to be difficult at the *ab initio* level, since electron correlation effects have to be included. This point is illustrated by recent calculations,[739] where the second-order polarization propagator approximation (SOPPA) gave a value of -72.2 ppm for the absolute magnetic shielding constant for N_2, while the coupled Hartree–Fock method (electron correlation neglected) yielded -106.5 ppm. The secondary isotope effect on the ^{15}N shielding in $^{15}N{\equiv}^{14}N$, -0.0601 ppm with respect to that in $^{15}N_2$, was employed[499] in the calculation of the derivative of the shielding vs bond length, -910 ± 42 ppm/Å. The spectra of $^{15}N{\equiv}^{15}N$ in nematic-phase liquid crystals (EBBA and Merck ZLI 1132) gave a value of $+590 \pm 50$ ppm for the anisotropy of the shielding, $\sigma_{\parallel} - \sigma_{\perp}$.[471] An interesting example[284] of ^{14}N NMR imaging in liquid N_2 in contact with a superconductor was considered in Section 4.1. Upfield shifts of $+2.5$ and $+9.5$ ppm were observed for the resonance of $^{15}N_2$ upon the binding of the latter to Na^+- and Mg^{2+}-containing zeolites (types A and X), respectively, while no significant effects were found in the case of cation-free zeolites.[740] There has recently been a thorough study[741] of ^{14}N relaxation in gaseous N_2 mixtures with Ar,

Kr, Xe, CO, CO_2, HCl, CH_4 and CF_4 whose results were explained in terms of collision cross-sections for molecular reorientations.

Atmospheric N_2 dissolves in liquids to an extent which is high enough to show its resonance signal in nitrogen NMR spectra, and the latter is a potential internal reference for the calibration of nitrogen shieldings (see Section 3). However, solvent effects on the shielding in N_2 (Table 31, notes (b–d)), are small but significant enough to make this reference no better than external references without bulk susceptibility corrections.[81]

The nitrogen shieldings in dinitrogen as a ligand in metal complexes reveals the non-equivalence of the two nitrogen atoms (Table 31). In diazenido complexes, M—NN—R, the shieldings seem to depend significantly not only on the nature of the central metal atom, M, but also on the geometry of the ligand. Doubly bent diazenido ligands are characterized by nitrogen shieldings which are similar to those found in azo bridges (see Tables 31 and 28). In singly bent diazenido structures there seems to be a clear distinction, as far as nitrogen shieldings are concerned, between hexa-, penta- and tetracoordinate complexes (Table 31).

6.17. Nitrogen oxides and nitrogen–oxygen ions

Such nitrogenous species can be easily identified by means of nitrogen NMR (Table 30), in view of the large diversity of the nitrogen shieldings concerned. Nitric and nitrous acid systems have also been considered in Tables 26 and 29, respectively. As far as the relevant coupling constants are concerned, a new experimental approach has been offered by the use of supercritical fluids as solvents (see Section 4.1) for ^{14}N NMR measurements at moderate temperatures; under such conditions, the spin–spin couplings between quadrupolar nuclei appear in the ^{14}N spectra,[178] e.g. those of N_2O, and they include ^{14}N–^{14}N and ^{14}N–^{17}O couplings. The latter are especially important, since it is practically the only way of accessing nitrogen–oxygen couplings (using ^{17}O labels), while those between nitrogen nuclei can be measured in ^{15}N-labelled samples.

Attention is drawn to the unusually high shielding of the nitrogen nucleus in the NO^+ ion in a complex with the π-electron system of an arene (Table 30, note (c)). There are also some additional data on HNO_3 in tributylphosphate solutions[742] and on HNO_3–N_2O_5 systems.[743,744] Stable nitroxide radicals which are formally the products of a homolytic cleavage of the O–H bonds in the corresponding hydroxylamino moieties are presented in Table 24, notes (p, x).

The ^{15}N spectra of static solid $^{15}N^{14}NO$ under O_2 atmosphere were employed in analysing molecular motions in the solid.[345]

6.18. Nitrosyl, thionitrosyl and nitride complexes

Nitrogen NMR is a convenient tool for structural investigations of these complexes (Table 33). In analogous structures, the nitrogen nuclei in nitrosyl (NO) ligands are more shielded than those in thionitrosyl (NS) ligands. There is a large difference in the nitrogen shieldings between strongly bent and linear (or slightly bent) nitrosyl structures. Attention is drawn to the distinction between spatially non-equivalent nitrosyl ligand sites presented in Table 33, note (c). There are also additional data on nitrosyl–ruthenium complexes.[734] A case was reported[733] for nitrosylcyanoruthenates where, in spite of ^{15}N-labelling, no signal of the nitrosyl ligand could be observed.

It is difficult to outline any general range of nitrogen shieldings in nitrides, since the latter depend on the nature of atoms coordinated to nitrogen (Table 33). An interesting example of differentiation of isomeric structures is presented in Table 33 (note (d)). As far as silicon nitrides are concerned, those presented in note (i) seem to represent the coordination of three silicon atoms to a nitrogen atom, since most recent results on silicon nitrides and YSiAlON glassy solids, obtained by ^{15}N MAS NMR spectra,[417] allow one to set some characteristic ranges for individual types of nitrogen coordination in such structures:

Coordination	*Nitrogen shielding* (ppm, *vs neat nitromethane*)
NSi_3 and NSi_2Al	*ca.* +300
NSi_2	+200 to +260
NSi	*ca.* +60

Such studies also included some silicon oxynitrides,[416] SiN_2O_2 and $SiNO_3$. There have also been some additional data on Mo and W nitrido complexes.[745]

6.19. Vitamins, drugs and medicines

These do not constitute any chemical class of compounds, but their nitrogen shieldings are grouped in Table 34 for identification and analytical reasons. In addition, there has recently been a report on the nitrogen shieldings of the NMe_2 and CONHR groups in a group of tetracycline antibiotics in the solid state,[384] and on the amino groups in aminoglycoside antibiotics.[564]

7. SOME NOTES ON ^{15}N COUPLING CONSTANTS

Since indirect spin–spin couplings of ^{14}N are rarely observed, we consider only ^{15}N coupling constants. The former can easily be recalculated into the latter using the relationship

$$J(^{15}N\text{–}X) = 1.4027\, J(^{14}N\text{–}X)$$

The couplings have been considered in detail in refs 2 (pp. 261–317), 4 (pp. 110–127, 402–473) and 5 (pp. 191–200, 605–737). We present here only a shorthand-style account of the couplings and recent references in this field. For the sake of simplicity, absolute values (magnitude) of the constants are implied everywhere, except when the sign is given explicitly.

7.1. $^{1}J(^{15}N\text{–}^{1}H)$

These coupling constants are negative, and their magnitudes seem to grow with increasing s-character of the bond concerned,[1–5] with certain exceptions, particularly for ketimines, $R_2C{=}NH$. Generally one can outline the following ranges for the constants:

Ketimines, $R_2C{=}NH$	*ca.* −50 Hz
NH in three-membered rings	−50 to −65 Hz
Alkylamines and ammonium ions hydroxylamines, hydrazines	−60 to −80 Hz
Arylamines and enamines	−80 to −95 Hz
NH^+ in cations derived from aromatic azine systems and from imines	*ca.* −90 Hz
Amides and related structures	−90 to −100 Hz
NH moieties in aromatic azole systems	−95 to −110 Hz
Protonated nitriles, $R{-}C{\equiv}\overset{+}{N}NH$	*ca.* −135 Hz

These trends are also illustrated by numerous recent data in refs. 19, 21, 22, 53, 76, 84, 94, 99, 118, 120, 121, 126, 127, 148, 150, 152, 155, 162, 181, 193, 199, 203, 204, 220, 227, 235, 285, 412, 414, 495, 526, 528, 542–544, 546, 554, 563, 583, 604, 609, 618, 627, 665, 675, 693, 699, 720, 721, 723, 726–728, 745–810.

In amides and related structures, there is usually a difference of a few hertz between the relevant *Z* and *E* geometrical structures. The presence of lone-pair elecrons at the nitrogen atom concerned seems to exert a quenching effect on the *magnitude* of the coupling; the effect is strong in structures where one can ascribe a significant s-character to the lone-pair orbital, and this

seems to explain[53] the low magnitudes of ^1J(NH) in imines with respect to the corresponding cationic structures (a difference of about 50 Hz) and in alkylamines with respect to the corresponding ammonium ions (a difference of about 10 Hz). The recent observation[775] of $^1J(^{15}N\text{-}^1H) = -54.7$ Hz in the lithium salt of aniline, $PhNH^-Li^+$, when compared with the corresponding values for arylamines (about -85 Hz), seems to corroborate this line of reasoning.

One-bond proton–nitrogen couplings are commonly employed in various polarization transfer techniques, in the identification of protonation sites and of various hydrogen-bearing nitrogenous moieties, and in studies on proton migration and tautomerism.

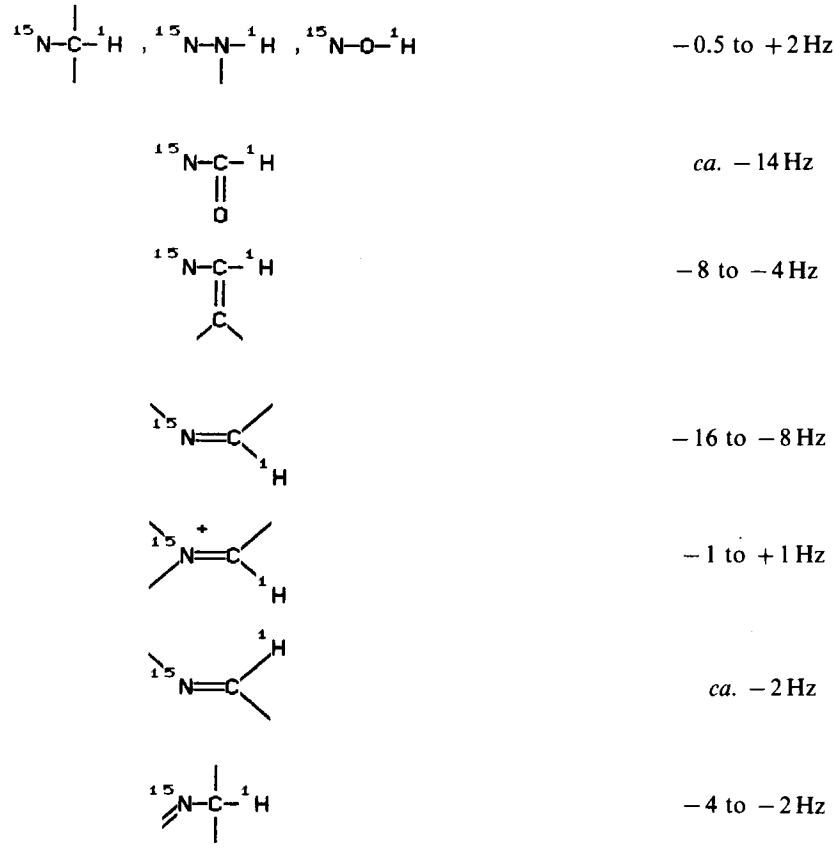


Fig. 4.

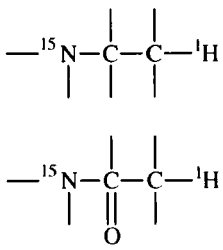
7.2. $^2J(^{15}N\text{-}X\text{-}^1H)$

Typical values[4,5] of these coupling constants are presented in Fig. 4 (p. 71); in unsaturated or aromatic systems they seem to depend critically upon the presence or absence of lone-pair electrons at the nitrogen atom, and the geometrical orientation of the lone pair with respect to the hydrogen atom involved.

Additional data can be found in refs 21, 53, 76, 91, 106, 119, 122–125, 139, 140, 144, 148, 162, 203, 469, 521, 602, 620, 665, 675, 720, 721, 746, 750, 752–754, 762, 770, 772, 777, 779–782, 785, 789, 793, 794, 799, 801, 811–835. The couplings are employed in following nitrogen–proton connectivities in multidimensional NMR of peptides and proteins, in polarization transfer techniques for nitrogenous aromatic systems, and in identifications of geometrical isomers concerned with the presence of C=N bonds.

7.3. $^3J(^{15}N\text{-}X\text{-}Y\text{-}^1H)$

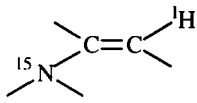
These are usually negative, and do not exceed -7 Hz, with an exception of 1-N-3-H coupling in pyrazoles, where values of about -11 Hz are observed.[1–5] An important feature of such couplings in systems like [**21**] is the relationship between the dihedral angle Φ, N–C vs C–H, and the coupling constant, where the latter attains maximum magnitudes for $\Phi = 0°$ and 180°, with a minimum at about 90°. Such relationships are commonly employed in conformational studies, particularly in the field of peptide systems. Such three-bond couplings in the systems considered are usually larger in magnitude than analogous $^2J(^{15}N\text{-}C\text{-}^1H)$ couplings.



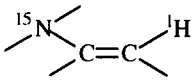
ca. 0 to −7 Hz

[**21**]

Lone electron pair effects and spatial relationships seem also to be important for $^3J(^{15}N\text{-}^1H)$ in other structures [**22**].



0 to −3 Hz



0 to −5 Hz (usually larger in magnitude than those above)

[22]

In azine aromatic rings, the magnitude of the coupling seems to grow upon the protonation of the nitrogen atom, e.g. from about −2 Hz to −4 Hz in the case of pyridine.

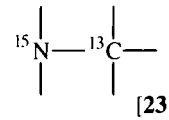
Further, recent examples of such couplings are included in refs 53, 73, 75, 91, 99, 122, 124, 127, 133, 141, 148, 182, 203, 584, 608, 620, 646, 665, 675, 720, 746, 747, 752–754, 759, 762, 763, 766, 772, 781, 782, 785, 789, 793, 794, 797, 799, 801, 805, 811–813, 816, 818, 821, 825, 830, 833–845.

7.4. Long-range ^{15}N–^{1}H couplings

Couplings across four bonds are usually positive and do not exceed 1.5 Hz, while those across five bonds are usually not larger in magnitude than 0.4 Hz.[1-5] A number of such couplings have also been reported in refs 91, 608, 746, 762, 772, 789, 791, 794, 799, 811, 813, 815, 825, 835, 846–848.

7.5. $^{1}J(^{15}N–^{13}C)$

These are usually negative, but their range is +9 to −78 Hz.[1-5] They exhibit some relationship with the s-character of the bond concerned, but lone-pair electron effects tend to overwhelm this, as can be seen from the following characteristics.



[23]

	−2 to −5 Hz (protonation enhances the magnitude)
Arylamines	*ca.* −12 Hz (about −9 Hz upon protonation)
Enamines	*ca.* −15 Hz
Amides, peptides	−5 to −11 Hz (N–C_α)
	ca. −15 Hz (N–CO)
Nitromethane	−7 Hz (see ref. 495)
Nitroaromatics	−14 to −27 Hz
Pyrrole-type nitrogens in azoles	*ca.* −13 Hz

Pyridine-type nitrogens	+3 to −3 Hz (about −13 Hz in protonated or *N*-oxide forms)
Diazo compounds	*ca.* −22 Hz (see ref. 837)
Nitriles	*ca.* −18 Hz
Nitrile *N*-oxide	−50 to −78 Hz
Isonitriles	*ca.* −9 Hz (N≡C)
Arenediazonium ions	*ca.* −15 Hz
Azo compounds	+2 to −2 Hz (*trans*-forms)
	ca. +8 Hz (*cis*-forms)
=N(O)–C in azoxy	*ca.* −18 Hz (*trans*-forms)
compounds	*ca.* −12 Hz (*cis*-forms)
Oximes	+2 to −2 Hz
Hydrazones	+4 to −4 Hz (C=N)
R—N=C=S	*ca.* −50 Hz (N=C, see ref. 730)

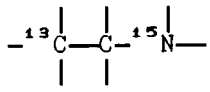
Recently there have been numerous reports on one-bond carbon–nitrogen couplings in refs. 45, 46, 48, 53, 75–77, 101, 132, 133, 141, 203, 331, 414, 438, 469, 495, 587, 600, 602, 607, 618, 720, 721, 723, 724, 731, 747, 750, 754, 762, 775, 785, 794, 801, 812, 813, 815–817, 827, 829, 849–886. The values of the couplings are important for setting up various multidimensional experiments which involve carbon and nitrogen nuclei.

7.6. Carbon–nitrogen couplings across more than one bond

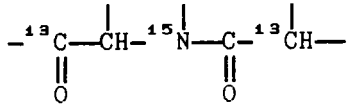
Two-bond couplings, $^{2}J(^{15}N–^{13}C)$, span a range of +10 to −11 Hz and exhibit significant sensitivity to lone-pair electron effects Fig. 5.[4,5,53] There has been an example[888] of $^{2}J(^{15}N–Fe–^{13}C)$ couplings of 2–13 Hz in $N\equiv{}^{13}C—Fe—{}^{15}NO$ moieties in iron complexes.

Three-bond couplings, $^{3}J(^{15}N–^{13}C)$, are usually negative, 0 to −5 Hz, and in saturated systems they exhibit a relationship with the dihedral angle that is similar to that considered in the case of $^{3}J(^{15}N–^{1}H)$ couplings. In some instances where one-bond and two-bond carbon–nitrogen couplings are quenched by lone-pair electron effects, three-bond couplings can be the largest in magnitude; this happens in *trans*-azoarenes and pyridine-type heteroaromatics;[53] in pyridine, the three-bond coupling is −4 Hz, and it is enhanced to about −5 Hz by protonation at the nitrogen atom concerned. Some carbon–nitrogen couplings in *N*-phenylbenzamides (about 14 Hz) which were reported[890] as $^{2}J(NC)$ or $^{3}J(NC)$ are evidently one-bond couplings, $^{1}J(NC)$.

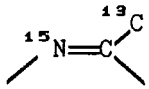
Carbon–nitrogen couplings across more than three bonds rarely exceed 1 Hz.



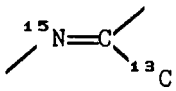
+2 to −2 Hz



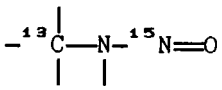
ca. −5 Hz (N—CH—CO)
−7 to −11 Hz (N—CO—CH)



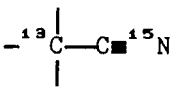
including heteroromatics +3 to −2 Hz



about −8 Hz



ca. 8 Hz (*anti*)
ca. 1 Hz (*syn*)



ca. 3 Hz

azoarenes ($^{15}N{=}N{-}^{13}C$) *ca.* +10 Hz (*cis*)
ca. 2 Hz (*trans*)

Fig. 5.

Recent reports on carbon–nitrogen couplings across more than one bond are included in refs 45–48, 53, 75, 133, 141, 203, 414, 438, 587, 600, 602, 721, 723, 724, 730, 733, 747, 750, 754, 759, 775, 785, 812, 813, 815, 817, 824, 837, 838, 852–855, 861, 863, 864, 869, 871, 881, 887–890.

7.7. ^{15}N–^{15}N couplings

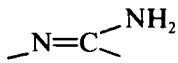
One-bond couplings, $^1J(^{15}N{-}^{15}N)$, are usually negative,[4,5] with possible exceptions for hydrazines[4] and pyrazoles;[5] the absolute values can be summarized as follows.

Dinitrogen in complexes	*ca.* 5 Hz
Benzenediazonium ions, Ph—$N^+{\equiv}N$,	*ca.* 2 Hz (ref. 75)
R—O—$N^+{\equiv}N$	*ca.* 12 Hz (ref. 75)
Diazenido ligands	10–15 Hz
Pyridazine	(−)22 Hz (ref. 46)
Pyridazine *N*-(mono)oxide	14 Hz
Azo compounds	*ca.* 15 Hz

Azide ion	*ca.* 10 Hz
Covalent azides, R—N=N^+=N^-	*ca.* 15 Hz (R—N=N^+) *ca.* 8 Hz (N^+=M^-)
Cl—N=N^+=N^-	24 Hz (Cl—N=N^+) 8 Hz (N^+=M^-)
Diazo compounds, R_2C=N^+=N^-	*ca.* 9 Hz (ref. 837)
=N—NR_2	*ca.* 10 Hz
>N—N=O	*ca.* 22 Hz
>N—NO_2	5–9 Hz
=N—NO_2	*ca.* 15 Hz (ref. 414)
Pyrazoles	*ca.* (+)13 Hz
Hydrazines R_2N—NR_2	*ca.* 3 Hz

Recent data on such one-bond couplings are included in refs 45, 46, 75, 84, 91, 205, 414, 585, 668, 720–722, 730, 745, 747, 750, 754, 812, 837, 852–855, 870, 888, 891–900.

Two-bond couplings, $^2J(^{15}N–^{15}N)$, rarely exceed 5 Hz in magnitude.[4,5]

Azides	*ca.* 2 Hz
Pyrimidine rings	0 to (+)2 Hz
R_2N—CN	*ca.* 3.5 Hz (ref. 870)
R—N=N—CN	*ca.* 5 Hz (N—CN, ref. 893)
	1–5 Hz

In some cases, such couplings have been observed for nitrogenous ligands across the central metal atom in a complex, about 4 Hz for NO ligands across Fe,[888,895] and about 2.5 Hz for ethylenediamine ligands across Co.[852] Recent reports on $^2J(^{15}N–^{15}N)$ can be found in refs 730, 852, 854, 881, 888, 893, 895.

Three-bond couplings, $^3J(^{15}N–^{15}N)$, are usually small,[4,5] but they have been observed (about 1 Hz) in R—N=N—CN systems.[893]

7.8. $^{15}N–^{31}P$ couplings

One-bond couplings, $^1J(^{15}N–^{31}P)$ not only exhibit large variations in magnitude, but can also be of either sign:[4,5]

Pentavalent phosphorus	+100 to +35 Hz
Trivalent phosphorus	+13 to −58 Hz

and without the knowledge of the sign one can devise a rule of thumb that

if the magnitude exceeds 60 Hz, pentavalent phosphorus is involved, and the constant is positive; if the magnitude is less than 35 Hz, trivalent phosphorus is concerned, but the sign of the coupling is uncertain. Recent examples are included in refs 83, 129, 152, 156, 176, 227, 656, 774, 818, 839, 885, 886, 891, 901–914.

Two-bond couplings, $^2J(^{15}N-^{31}P)$ are usually within a range of 0–8 Hz,[1-5] but they can reach 55 Hz if the coupling takes place across the central metal atom in a complex (see also recent refs 139, 140, 155, 413, 597, 745, 818, 900, 910, 915, 916):

Imine—Pd—PR_3	40 Hz (*trans*) 2 Hz (*cis*)	(ref. 139)
Imide—Au—PR_3	45 Hz	(refs 155, 413)
Cyanide—(Rh or Ir)—PR_3	55 Hz (*trans*) 3 Hz (*cis*)	(ref. 597)

In the latter example, the cyanide ion is coordinated via N; if it is C-coordinated, the corresponding $^3J(^{15}N-^{31}P)$ couplings amount to 4–9 Hz.[597]

7.9. $^{15}N-^{19}F$ couplings

One-bond couplings, $^1J(^{15}N-^{19}F)$ are large and positive,[4,5] e.g.:

NH_3F^+	+48 Hz
FN=NF	+191 Hz (*trans*) +203 Hz (*cis*)
$FN{\equiv}N^+$	+475 Hz

and there have been no recent data.

Two-bond couplings, $^2J(^{15}N-^{19}F)$ are fairly large and negative[4,5] (see also recent refs 156, 745, 824, 829, 868, 917):

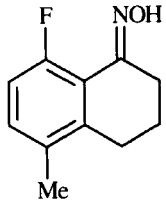
FN=NF	−102 Hz (*trans*) −52 Hz (*cis*)
fluoro-azines	*ca.* −50 Hz
CF_3NC	−15.5 Hz (ref. 829)

They can also reach significant values in complexes:

R—CN—Xe—F	−18 Hz	(ref. 868)
R—CN—Kr—F	−26 Hz	(ref. 824)
(N_2H_2)—Mo—F	−77 Hz	(ref. 745)

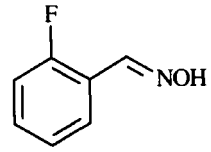
Three-bond couplings, $^3J(^{15}N-^{19}F)$, in the last example[745] are also significant, about 13 Hz; in fluoro-derivatives of azine ring systems,[156] the couplings fall into the range -3 to -9 Hz; CF_3 substituents at the carbon atoms of the three-membered ring of azirine show nitrogen–fluorine couplings within 0–2 Hz, depending on the spatial relationship between the substituent and the lone-pair electrons at the nitrogen atom.[801]

Four bond couplings, $^4J(^{15}N-^{19}F)$ in perfluoropyridine[156] are also measurable, being 1–2 Hz in magnitude. There has been an interesting example[52] of four-bond nitrogen–fluorine coupling where non-bonding ("through-space") interactions between the atoms involved seem to play a crucial role [**24**].



$^4J(^{15}N-^{19}F) = 22.4$ Hz

[24]



$^4J(^{15}N-^{19}F) = 3.2$ Hz

Nitrogen–fluorine couplings across five or six bonds are small, but they can sometimes be observed, e.g. in fluoro-substituted benzenediazonium tetrafluoroborates[75] (0–1.1 Hz).

7.10. ^{15}N couplings to other nuclei

One-bond couplings to platinum, $^1J(^{15}N-^{195}Pt)$, are useful in structural investigations of complexes[5] (see also recent refs 349, 413, 577–579, 647, 839, 908, 918–929). For NO_2^- ligands, the coupling is within 360–680 Hz in square-planar complexes and exhibits significant variations depending on the arrangement of the ligands (e.g. >470 Hz if the ligand is *trans* to halogen, and <470 Hz if it is *trans* to another NO_2^-). In ammino-complexes (NH_3 ligands), the coupling is within 220–560 Hz. For imino-ligands, the coupling amounts to about 150 Hz. Analogous couplings across two or three bonds are smaller, but significant (25–60 Hz). A value of $^2J(^{15}N-N-^{195}Pt)$ of about 70 Hz was observed in a diazenido ligand.[900]

One-bond couplings to silicon, $^1J(^{15}N-^{29}Si)$, in silylated amine systems[4,5] (see also recent refs 51, 130, 132, 134, 143, 150, 154, 502, 570, 899, 930–936) seem to reflect steric strains in such structures:

$Me_3Si—NR_2$	*ca.* 17 Hz (typical value for no or little steric strain)
$(Me_3Si)_2NH$	13 Hz
$(Me_3Si)_3N$	8 Hz
$Me_3Si—N(CH_2)_n$	< 5 Hz (n = 2)
	14 Hz (n = 3)
	16 Hz (n = 4)
	17 Hz (n = 5)

In $(RO)_3Si–NR_2$ systems, the coupling is much stronger, 20–45 Hz. In silatranes, the coupling across the dative bond, N → Si, is within 0.5–3.4 Hz.[132,932]

One-bond couplings to tin, $^1J(^{15}N–^{119}Sn)$, depend critically on the valence state of the latter[4,5] (see also recent refs. 130, 134, 140, 144, 151, 153, 931, 940–942):

Sn(II)	250 to 480 Hz (absolute values)
Sn(IV)	−80 to +175 Hz

and they are strongly influenced by geometry and lone-pair electron effects. In tin 8-quinolinothiolates,[144] the observed coupling of about 80 Hz shows the formation of tin–nitrogen bonds.

One-bond couplings to lead, $^1J(^{15}N–^{207}Pb)$, when the latter is bound to an amino moiety, range from 200 to 670 Hz[5,130,151,153] for Pb(II); in $(Me_3Pb)_3N$, the coupling to Pb(IV) is +335.7 Hz.[931]

$^1J(^{15}N–^{11}B)$ couplings are generally negative:[1–5,132,757,845,937]

$R_3N^+—BR_3^-$	*ca.* −15 Hz
$R_2N—BR_2$	0 to −45 Hz

When BR_3 is complexed to an anion (that of pyrazole[845] or isothiocyanate[937]), couplings of about 30 Hz are observed.

$^1J(^{15}N–^{27}Al)$ couplings in $AlCl_3$ complexed with isothiocyanate or isocyanate anions are about 60 Hz;[5] in acetonitrile complexed to Al, the coupling is about 30 Hz.[934] Analogous couplings to ^{71}Ga are within 100–160 Hz.[5,934]

Lithium salts of amines, $Li—NR_2$, show $^1J(^{15}N–^6Li)$ coupling constants of 3–5 Hz.[276,949]

As far as ^{15}N couplings to transition-metal nuclei are concerned, ^{195}Pt has

already been considered in the present subsection. In the case of vanadium, $^1J(^{14}N-^{51}V)$ couplings of about 105 Hz (i.e. about 145 Hz for ^{15}N) were found in $RN{=}V(OR)_3$ structures.[945] In nitrosyl complexes of Mo, $^1J(^{15}N-^{95}Mo)$ couplings amount to about 65 Hz.[5,948] In diazenido ligands attached to tungsten, $^1J(^{15}N-^{183}W)$ is about 108 Hz.[900] Iron(II) complexes of porphyrin systems reveal $^1J(^{15}N-^{57}Fe)$ coupling constants of about 8 Hz.[5] Cobalt complexes with nitrosyl and amino ligands show $^1J(^{15}N-^{59}Co)$ of about 9 and 60 Hz, respectively.[5,947] Rhodium complexes with a variety of nitrogenous ligands (nitrosyl, R—NSO, dinitrogen),[5] including cyanide,[597] diazenido,[900] and azine[140] complexes, show $^1J(^{15}N-^{103}Rh)$ constants within 5–30 Hz. In imino complexes of silver, $^1J(^{15}N-^{107,109}Ag)$ couplings of 12–57 Hz were found.[136,138,946] In mercurcy complexes of amino moieties,[5] $^1J(^{15}N-^{199}Hg)$ is in the range 300–400 Hz; in mercury fulminates,[951] $^2J(^{15}N-C-^{199}Hg)$ is about 100 Hz for R—Hg—CNO structures, while it is enhanced to about 250 Hz in $Hg(CNO)_2$.

$^1J(^{15}N-^{17}O)$ of 41.4 Hz was observed in nitromethane.[495] The use of supercritical fluids as solvents[84] (see Section 4.1) revealed the $^{14}N-^{17}O$ coupling constants in N_2O, 37 Hz across one bond, and 5 Hz across two bonds; the corresponding ^{15}N couplings should then amount to about 52 and 7 Hz, respectively.

In F_5TeNCO, $^1J(^{14}N-^{125}Te)$ of 153 Hz was observed,[938] and this yields about 225 Hz for the ^{15}N coupling. In F_5SeNCO, the $^1J(^{14}N-^{77}Se)$ coupling constant is 50 Hz;[938] this means about 70 Hz upon recalculation to ^{15}N.

$^1J(^{15}N-^{129}Xe)$ couplings in nitrile–XeF^+ complexes are typically about 300 Hz;[5,868] in analogous complexes with perfluoroazines,[952] the coupling is about 240 Hz.

8. RELAXATION PHENOMENA

8.1. ^{14}N relaxation

Relaxation is governed mostly by the quadrupolar mechanism (see ref. 5, pp. 200–209, and references therein). Recently, the ^{14}N nuclei in the NH moieties in protein peptide backbones have been employed as *relaxation sinks* in nuclear magnetic relaxation dispersion (NMRD) profiles for protons,[953–961] which are also important in proton NMR tomography. The phenomena concerned involve interactions of protons from water with the NH moieties in peptides. Another interesting observation in recent studies on ^{14}N relaxation comes from the use of supercritical fluids as solvents for nitrogenous compounds[85–87] (see also Section 4.1) where the relaxation is slowed down so that spin–spin couplings of ^{14}N with other, also quadrupolar, nuclei appear

in the spectra. On the other hand, it is possible to make some estimates of such couplings from the ^{14}N relaxation effects in the spectra of the other nuclei concerned (e.g. ^{13}C), measured in common solvents,[762,790] but this approach is certainly more prone to various errors.

The relaxation of ^{14}N nuclei has traditionally been employed in studies of molecular and ionic motions and interactions in liquids and solids.[1-5] Numerous recent examples include glycine, betaine and trehalose as probes for microviscosity in cytoplasma;[621] cyclopeptides in interactions with Co^{2+};[962,963] ^{17}O-enriched amino acids and peptides in interactions with Co^{2+}, Cu^{2+} and Mn^{2+};[964] hexamethonium^{2+} cation in interactions with NaDNA;[965] acetonitrile, in interactions with Na^+ and Pb^+,[966,967] with Ga and Al ions,[934] with D_2O–NaI,[968] with chloroform,[969] and also CD_3CN with $CDCl_3$;[970] acetonitrile in nematic phases vs isotropic solutions;[465] some nitriles, in the solvation sphere at Ni^{2+} at various temperatures and under pressures up to 220 MPa;[662] methyl isocyanide in nematic liquid crystals;[971] dimethylformamide;[972] urotropine in CCl_4 and in chloroform;[973] aniline, amides and phenylhydrazine;[974] 4-methoxyaniline;[975] pyrrole in cyclohexane, CCl_4 and perfluoropyridine;[976] thiazole and isothiazole;[977] pyridine, in complexes with Co^{2+};[978] 2-pyridone in hydroxylic solvents;[536] 2,5-dimethylpyrazine;[979] alkyltrimethylammonium salts as surfactants;[980-986] metal–ammonia solutions;[554] aqueous methyl-substituted ammonium ions;[987] aqueous ammonium cryptate;[988] phosphatidylcholine in micelles[989] and bilayers;[990,991] dinitrogen (N_2) in a variety of solvents[992] and gases, also in mixtures with Ar, Kr, Xe, CO, CO_2, HCl, CH_4, CF_4 and SF_4;[741,993] N_2O in hexane;[994] aqueous $SeCN^-$, SCN^-, OCN^- and N_3^-;[995] aqueous NO_3^-,[996] and also the retardation of the relaxation in NO_3^- by counterions,[997] in the sequence $Sc^{3+} > La^{3+} > Pb^{2+} > Ca^{2+} > Sr^{2+} > Al^{3+}$, K^+, Na^+, $Me_4N^+ > Zn^{2+}$, Mg^{2+}, Li^+, NH_4^+, H_3O^+; aqueous zirconium nitrate;[713] solid $MeND_3^+ NO_3^-$;[998] NO_3^- in barley, maize and pea roots;[93] incommensurate and commensurate phases of solid $(Me_4N)_2ZnCl_2$;[999] and spin-rotation relaxation in solid rotor KCN.[454] We should also mention the effects of ^{14}N relaxation, via NH proton transfer in solids, on the relevant ^{13}C CPMAS spectra;[1000,1001] and the scalar relaxation of homonuclear multiple-quantum coherences which yield the signs of spin–spin couplings in phenylformamide.[792]

8.2. ^{15}N relaxation

The relaxation of non-quadrupolar ^{15}N, and nuclear Overhauser effects (NOE) which appear in ^{15}N NMR proton-decoupled spectra are also employed on a large scale in studies of molecular motions and interactions (see ref. 5, pp. 36–41, 210–211). While this method offers access to individual

nitrogen atoms in complicated molecular and ionic systems, owing to the spectral resolution available in ^{15}N NMR, it suffers from the inherent low sensitivity of natural-abundance ^{15}N measurements. With few exceptions, ^{15}N-enriched samples have been used in such investigations.

Recent studies in this field include *para*-substituted anilines in $CDCl_3$, and the corresponding cations in DMSO;[1002] paramagnetic complexes of aniline with Ni(II);[1003] $MeCH(NH_2)CH_2CH(NH_2)Me$ and the corresponding cations;[576] aqueous L-aspartic acid,[1004] in interactions with Cu^{2+} and Mn^{2+}; amino acid residues in silk fibroin;[110] polyamide[368,370,372,1005,1006] and polyethyleneimine[573] polymers; aqueous coacetate of polypentapeptide elastin;[1007] staphylococcal nuclease;[277] oxidized form of ferrodoxin;[1008] cytochromes c_2 and c′;[627] adenosine;[520] 4-methylbenzenesulphonamide complexed to bovine carbonic anhydrase;[1009] ion-pair formation in aqueous potassium hexacyanocobaltate;[1010] orientational freezing in KCN–KBr solid solutions;[333] solid-rotor KCN;[454] dinitrogen, gaseous,[499] in mixtures with buffer gases (Ar, Kr, Xe, CO, CH_4, CF_4, O_2, HCl),[1011] and in Mo, W, Re and Os complexes;[1012] NH_4^+, aqueous[1013] and in a variety of solvents;[1014] phase transitions in solid NH_4ClO_4;[316,1015] solid NH_4NO_3, phase transitions,[418] and the high mobility of the ammonium ions in the plastic phase,[1016] close to the melting point; aqueous ammonium cryptate;[988] alkyltrimethylammonium surfactants,[985] in aqueous micelles and in formamide; azide ion interaction with chloroperoxidase;[1017] thiocyanate binding to lactoperoxidase[651,1018] and to horseradish peroxidase,[653,1018,1019] and also cyanide binding to the latter.[1019]

List of Tables

Table 1. Conversion schemes for nitrogen NMR shieldings (σ)

Scheme no.	Observed shielding vs secondary reference II, $(\sigma_{sample} - \sigma_{ref.II})$	Shielding of ref. II vs that of primary reference I $(\sigma_{ref.II} - \sigma_{ref.I})$	Correction which should be added to the algebraic sum of the values in columns 2 and 3 in order to obtain true ("intrinsic") value of $(\sigma_{sample} - \sigma_{ref.I})$
I	true	true	none
IIa	apparent, field *perpendicular* to sample tube	true	$\frac{1}{6}(\chi_{ref.II} - \chi_{sample})$
IIb	apparent, field *parallel* to sample tube	true	$-\frac{1}{3}(\chi_{ref.II} - \chi_{sample})$
IIIa	true	apparent, field *perpendicular* to sample tube	$\frac{1}{6}(\chi_{ref.I} - \chi_{ref.II})$
IIIb	true	apparent, field *parallel* to sample tube	$-\frac{1}{3}(\chi_{ref.I} - \chi_{ref.II})$
IVa	apparent, field *perpendicular* to sample tube	apparent, field *perpendicular* to sample tube	$\frac{1}{6}(\chi_{ref.I} - \chi_{sample})$
IVb	apparent, field *parallel* to sample tube	apparent, field *parallel* to sample tube	$-\frac{1}{3}(\chi_{ref.I} - \chi_{sample})$
IVc	apparent, field *perpendicular* to sample tube	apparent, field *parallel* to sample tube	$\frac{1}{6}(3\chi_{ref.II} - 2\chi_{sample} - 2\chi_{ref.I})$
IVd	apparent, field *parallel* to sample tube	apparent, field *perpendicular* to sample tube	$-\frac{1}{6}(3\chi_{ref.II} - 2\chi_{sample} - 2\chi_{ref.I})$

ref. I = primary reference (external neat nitromethane).
ref. II = any secondary reference actually employed.
true = true difference between NMR shieldings.
apparent = apparent (experimental) difference between the shieldings concerned in a system of coaxial cylindrical sample-reference tubes.
χ (ppm) = magnetic volume bulk susceptibility expressed in SI system (see ref. 5, p. 221).

Table 2. Nitrogen shieldings in various external reference substances with respect to neat liquid nitromethane as a primary reference

		Nitrogen shielding (ppm)[a]			
			Apparent, in coaxial cylindrical tubes whose rotation axis makes the angle specified with external magnetic field		
Substance	Solution or state	True	0°	90°	54°44′
$MeNO_2$	neat liquid	0.0000			
	0.3 M in DMSO	−2.0			
	0.3 M in MeOH	+2.0			
	0.3 M in $CHCl_3$	+3.8			
	0.3 M in benzene	+4.4			
$NaNO_3$	sat. in H_2O	+3.7	(+5.1)	(+3.0)	
	0.3 M in H_2O	+3.5	(+4.9)	(+2.8)	
KNO_3	0.3 M in H_2O	+3.5	(+4.9)	(+2.8)	
HNO_3	1.0 M in H_2O	+4.4	+6.2		
	7.0 M in H_2O	+12.6			
	10.0 M in H_2O	+18.2			
	15.7 M in H_2O (70% w/w)	+31.3			
NH_4NO_3	solid state[c]				+358.4 (NH_4^+) +5.0 (NO_3^-)
	sat. in H_2O	+359.6	(+361.0)	(+358.9)	(NH_4^+)
		+4.0	(+5.4)	(+3.3)	(NO_3^-)
	4 M in 2 M HNO_3	+359.1	(+360.5)	(+358.4)	(NH_4^+)
		+5.6	(+7.0)	(+4.9)	(NO_3^-)
	5 M in 2 M HNO_3	+359.0	(+360.4)	(+358.3)	(NH_4^+)
		+4.6	(+6.0)	(+3.9)	(NO_3^-)
	5 M in 2 M HCl	+358.0			(NH_4^+)
		+5.2			(NH_3^-)
	4.5 M in 3 M HCl	+357.1			(NH_4^+)
		+6.3			(NO_3^-)
	sat. in DMSO	+358.1			(NH_4^+)
		+3.3			(NO_3^-)
NH_4Cl	solid state				+341.2[c]
	sat. in H_2O	+352.9	(+354.7)	(+352.1)	
	sat. in 2 M HCl	+352.5			
	1 M in 10 M HCl	+349.9			
$NH_4H_2PO_3$	solid state				+356.9[c]
$(NH_4)_2SO_4$	solid state	(two non-equivalent sites)			+355.7[c] +356.0[c]

Table 2. —*cont.*

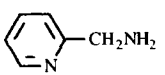
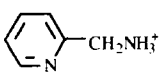
		Nitrogen shielding (ppm)[a]			
			Apparent, in coaxial cylindrical tubes whose rotation axis makes the angle specified with external magnetic field		
Substance	Solution or state	True	0°	90°	54°44′
$Me_4N^+Cl^-$	sat. in H_2O	+336.7			
	0.3 M	+337.7	+339.0	(+337.0)	
$Me_4N^+I^-$	0.3 M in H_2O	+337.3			
	sat. in DMSO	+337.0	+339.0	(+337.0)	
$NaNO_2$	sat. in H_2O	−228.9			
	0.3 M in H_2O	−227.6			
K^+NCO^-	sat. in H_2O	+302.6			
$PhNO_2$	neat liquid	+9.6		+9.9	
MeCN	neat liquid	+135.8			
	0.3 M in $MeNO_2$	+137.8			
KCN	sat. in H_2O	+102.5			
	0.3 M in H_2O	+106.1			
N_2[b]	in cyclohexane	+70.2			
	in benzene	+70.4			
	in CCl_4	+69.8			
	in $CHCl_3$	+69.6	+71.3		
	in CH_2Cl_2	+69.9	+71.7		
	in Et_2O	+70.6			
	in acetone	+70.5	+71.5		
	in DMSO	+69.8	+70.6		
	in MeOH	+70.8			
	in EtOH	+70.4	+71.6		
	in CF_3CH_2OH	+71.5			
	in H_2O	+69.6	+71.5		
Me_2NCHO	neat liquid	+277.0			
H_2NCHO	neat liquid		+268.8	+267.8	+266.7[c]
Glycine[c]	solid state				+347.6[c]
NH_3	neat liquid	+381.9		+380.2	

(a) If not stated otherwise, the values come from ref. 5, pp. 222–226, and references therein; the values in parentheses were calculated using the relevant susceptibilities.

(b) See Table 31, and references therein.

(c) Data from ref. 82, 40.561 MHz ^{15}N spectra, ^{15}N-labelled and unlabelled samples, solids and liquids, static and MAS spectra; originally referrd to neat liquid nitromethane, whose resonance frequency was shown to be constant (within 0.04 ppm), in the case of proton-coupled spectra, for cylindrical sample (spun at a magic angle as well as static) and for a spherical sample; temperature +21°C.

Table 3. Nitrogen shieldings in ammonia, ammonium ion, alkylamines, alkylammonium ions, and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
NH_3	neat liquid, +35°C	+381.9 (corr.)	(a)
		+380.2 (uncorr.)	(a)
	inf. dil. in Me_2O	+390.1 (uncorr.)	(a)
	inf. dil. in H_2O	+378.4 (uncorr.)	(a)
	gas, zero pressure	+400.9 (uncorr.)	(a)
NH_4^+	various (see also Table 2)	+324.5 to +369.6	(a)
NH_4NCS	solid	+345.8	(b)
NH_4ClO_4	solid	+359.4	(c)
$MeNH_2$	40% in H_2O	+370.6	(d)
$MeNH_3^+$	various	+357 to +361	(a)
$R—CH_2NH_2$ structures and corresponding ions			
$EtNH_2$	70% in H_2O	+349.2	(d)
$PrNH_2$	neat liquid	+356.0	(d)
$BuNH_2$	neat liquid	+353.4	(d)
Bu^tNH_2	neat liquid	+359.4	(d)
	in DMSO	+361.6	(e)
$Bu^tCH_2NH_2$	in DMSO	+366.2	(e)
$PhCH_2NH_2$	neat liquid	+357.3	(g)
$H_2N—CH_2—NH_2$	in $EtOH/H_2O$	+361.3	(g)
	in H_2O	+360.8	(h)
		+75.1 (ring N)	(h)
	in H_2O, pH = 0	+351.7	(h)
		+86.2 (ring N)	(h)

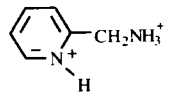
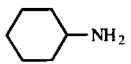
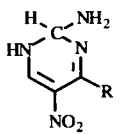
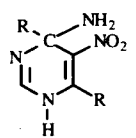
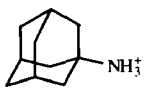
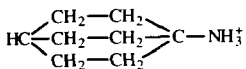
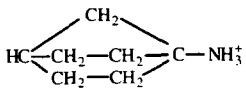
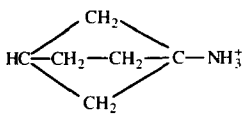
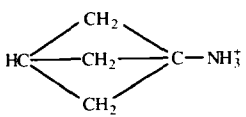
	in H_2O, pH = −0.4	+351.0 +181.1 (ring N)	(h) (h)
$R_2CH—NH_2$ structures and corresponding ions			
Pr^iNH_2	neat liquid	+332.5	(d)
Bu^sNH_2	neat liquid	+337.5	(d)
	neat liquid	+335.7	(d)
$[—CH_2—CHNH_2—]_n$	in 10% D_2O, pH > 10		(i)
(poly(vinylamine))	mm triads	+333.7	
m = meso r = rac	mr triads	+335.5 +336.0	
	rr triads	+336.8 +337.3 +337.8	
	in 10% D_2O, pH < 4 all triads	*ca.* + 328	
	in liquid NH_3 R = H R = OMe	 +326 (NH_2) +326 (NH_2)	(j)
	in liquid NH_3 R = H R = SMe R = SO_2Me	 +335 (NH_2) +327 (NH_2) +324 (NH_2)	(j)

Table 3. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$R_3C—NH_2$ structures and corresponding ions			
Bu^tNH_2	neat liquid	+317.3	(d)
$N_2N—CMe_2—CH_2—NH_2$	30% in C_6D_6	+333.3 (NCMe) +368.4 (NCH)	(k) (k)
$H_2N—CMe_2—CH_2—NHPr^i$	30% in C_6D_6	+328.6 (NCMe) +329.2 (NCH)	(k) (k)
	in H_2O	+315.2	(l)
	in H_2O	+319.6	(l)
	in H_2O	+331.3	(l)
	in H_2O	+329.7	(l)
	in H_2O	+327.2	(l)

R_2NH structures and corresponding ions

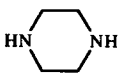
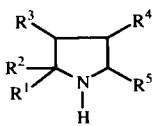
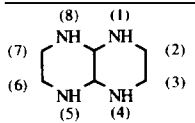
Me_2NH	various	+374 to +371	(a)
Et_2NH	in $CDCl_3$	+333.7	(m)
$(PhCH_2)_2NH$	neat liquid	+340.3	(g)
	in $CDCl_3$	+342.0 +343.2	(n) (m)
its adduct with benzylidene-*N*,*N*′-dimethylbarbituric acid and *p*-chloro derivative thereof	in $CDCl_3$	+324.2	(n)
	in $CDCl_3$	+347.8	(n)
its adduct with benzylidene-*N*,*N*′-dimethylbarbituric acid and with *p*-chloro derivative thereof	in $CDCl_3$	+331.8 to +327.6	(n)
	in $CDCl_3$	+346.4	(m)
$Bu^tNH—CH_2CH_2—NHBu^t$	30% in C_6D_6	+327.7	(k)
	in D_2O	+332.7	(o)
	neat liquids		(p)

Table 3. —*cont.*

Compound					Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
R^1	R^2	R^3	R^4	R^5						
H	H	H	H	H		+339.8				
Me	H	H	H	H		+321.7				
H	H	Me	H	H		+340.8				
Me	Me	H	H	H		+311.3				
Me	H	H	H	Me	(*cis*)	+302.0				
Me	H	H	H	Me	(*trans*)	+307.7				
Me	H	H	Me	H	(*cis*)	+324.4				
H	Me	H	Me	H	(*trans*)	+321.6				
Me	H	Me	H	H	(*cis*)	+327.4				
H	Me	Me	H	H	(*trans*)	+322.4				
Me	Me	H	H	Me		+311.4				
 (1,4,5,8-tetraazadecaline, "TAD")					in D_2O	*trans* +331.5 *cis* +339.8				(q)
TAD derivatives						N-1	N-4	N-5	N-8	(q)
2,6-Me_2-TAD					in D_2O					
					trans-e,e	+316.1	+331.1	+316.1	+331.3	
					trans-e,a	+317.7	+334.6	+317.7	+334.6	
2,2,6,6-Me_4-TAD					in D_2O	+308.9	+337.6	+308.9	+337.6	
2,2,7,7-Me_4-TAD					in D_2O	+308.3	+337.9	+337.6	+308.9	
1,5-Me_2-TAD					in $CDCl_3$					
					trans (ring)	+332.8	+341.4	+332.8	+341.4	
					cis (ring)	+340.4	+342.0	+340.4	+342.0	
					cis (ring), +50°C	+334.7	+356.9	+334.7	+356.9	

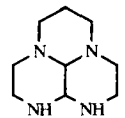
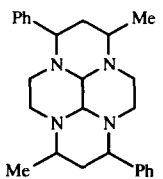
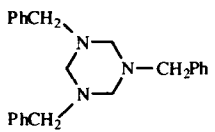
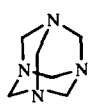
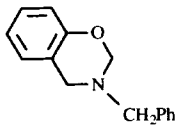
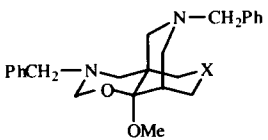
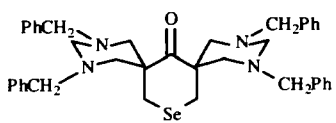
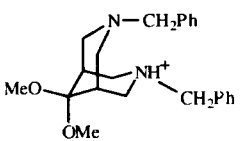
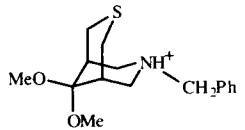
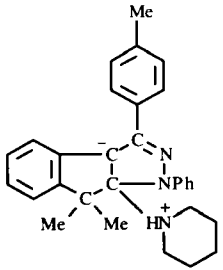
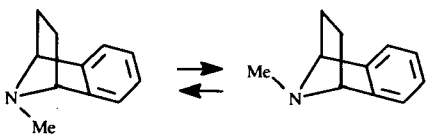
		N-1	N-4	N-5	N-8	
("BTAD")						(q)
	in D_2O					
	trans	+324.7	+332.5	+332.5	+324.7	
	in $CDCl_3$					
	trans	+324.4	+331.7	+331.7	+324.4	
	cis, +50°C	+337.6	+333.1	+341.8	+335.4	
("DBTAD")						
	in $CDCl_3$, *cis* ring junction	+334.6	+323.0	+338.6	+321.4	
R_3N structures and corresponding ions						
Me_3N	various	+373 to +362				(a)
Et_3N	various	+334 to +332				(a)
$(PhCH_2)_3N$	in Et_2O	+330.1				(g)
$Me_2N{-}CH_2CH_2{-}NMe_2$	in toluene	+355.0				(f)
	in MeOH	+332.1				(g)
	in $CDCl_3$	+330.1				(r)
	solid state	+338				(g)

Table 3. *—cont.*

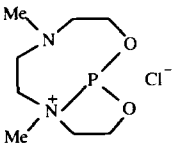
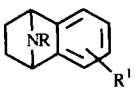
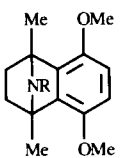
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in acetone	+339.6	(g)
	in $CDCl_3$		(r)
X = S		+342.2 (N–C–C) +332.0 (N–C–O)	
X = Se		+343.1 (N–C–C) +332.3 (N–C–O)	
	in $CDCl_3$	+335.7	(r)
	in DMSO	+326.4	(r)

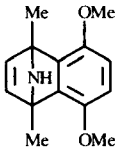
	in DMSO	+325.8	(r)
	in $CDCl_3$	+238.4 (NH^+)	(s)
 (*syn*) (*anti*)	in $CDCl_3$, −30°C	+288.3 (*syn*, 94%) +298.8 (*anti*, 6%)	(t) (t)

Tetraalkylammonium ions, NR_4^+

NMe_4^+ Cl^-	0.3 M in H_2O	+337.7	(a)
NMe_4^+ I^-	0.3 M in H_2O	+337.3	(a)
NEt_4^+ Cl^-	0.3 M in H_2O	+316.3	(a)
NPr_4^+	occluded in ZSM-5 zeolite and silicalite	+315.1	(u)

Table 3. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Some miscellaneous amino and ammonium structures			
	in D_2O, 300 K	+321.5 (doublet, 29 Hz)	(o)
	298.5 K	+344.3 (doublet, 4 Hz) +298.5 (doublet, 62 Hz)	
$N(CH_2CH_2NH_2)_3$	in $CDCl_3$	+360.9 (N) +364.4 (NH_2)	(m) (m)
	in CH_2Cl_2		(v)
R R^1			
Me 2,3,4,5-F_4		+251.5	
CH_2Ph 2,3,4,5-F_4		+243.2	
H none		+239.6	
	in CH_2Cl_2		(v)
R = H		+251.7	
R = Cl		+200.1 (*syn*) +218.3 (*anti*)	



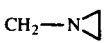
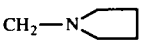
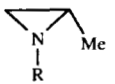
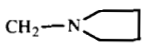
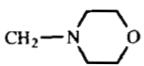
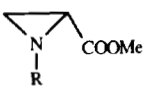
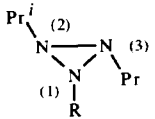
	in CH_2Cl_2	+214.4	(v)
 (aziridines)	50% in $CDCl_3$		(w)
R			
H		+390.4	
Me		+380.0	
CH_2OH		+356.0	
CH_2OMe		+363.5	
CH_2COOMe		+374.9	
$CH_2C{\equiv}CH$		+373.0	
$CH_2CH{=}CH_2$		+368.8	
CH_2CH_2CN		+367.4	
		+365.3	
		+365.7 (3-membered ring) +328.7 (5-membered ring)	
CH_2Ph		+365.6	
Cl		+330.9	
NH_2		+338.1 (N) +282.6 (NH_2)	
$SiMe_3$		+384.3	

Table 3. *—cont.*

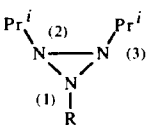
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	50% in $CDCl_3$		(w)
R			
Me		+364.8	
		+350.7 (3-membered ring) +321.6 (5-membered ring)	
		+352.3 (3-membered ring) +328.3 (6-membered ring)	
NH_2		+323.7 (N) +282.6 (NH_2)	
	50% $CDCl_3$		(w)
R = CH_2OH		+335.8	
R = Cl		+318.8	
$HSCH_2CH_2NH_2$	in $CDCl_3$	+361.5	(x)
	in CD_3OD	+359.8	(x)
$HSCH_2CH_2NH_3^+Cl^-$	in CD_3OD	+349.1	(x)

$MeSCH_2CH_2NH_2$	in $CDCl_3$	+360.6	(x)
$HSCH_2CH_2NMe_2$	in $CDCl_3$	+355.9	(x)
$HSCH_2CH_2NEt_2$	in $CDCl_3$	+335.3	(x)
	in CD_3OD	+331.6	(x)
$HSCH_2CH_2NH^+Et_2$	in CD_3OD	+325.4	(x)
$MeSCH_2CH_2NEt_2$	in $CDCl_3$	+334.2	(x)
$R^1_3SnSCH_2CH_2NR^2_2$	in $CDCl_3$		(x)
R^1 R^2			
Bu Et		+332.6	
Me Me		+353.8	
Ph Me		+354.6	
$R^1_2Sn(Cl)SCH_2CH_2NR^2_2$	in $CDCl_3$		(x)
R^1 R^2			
Et H		+351.3	
Me Me		+349.9	
Bu H		+348.9	
Me H		+348.9	
Oct H		+348.7	
Me Et		+336.0	
Bu Et		+334.5	
$R^1_2Sn(SCH_2CH_2NR^2_2)_2$	in $CDCl_3$		(x)
R^1 R^2			
Et H		+356.6	
Oct H		+356.1	
Bu H		+355.9	
Me H		+353.5	
Bu Et		+332.6	

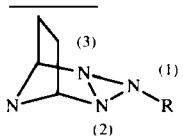
Table 3. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$Me_3SnCH_2N(Me)CH_2CH_2NMe_2$	in toluene	+348.8 (NMe) +354.6 (NMe_2)	(f) (f)
	in $CDCl_3$		(y)

R	N-1	N-2	N-3
H	+249.1	+239.0	+241.2
COOMe	+224.8	+213.4	+227.2
Me	+244.9	+225.9	+222.7
CH_2OH	+241.5	+233.2	+225.9

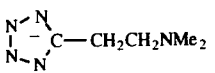
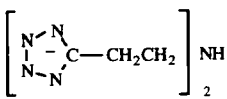
	in $CDCl_3$		(y)

R	N-1	N-2,3
H	+260.3	+236.2
COOMe	+235.2	+215.3
CH_2OH	+239.6	+223.5

	in $CDCl_3$		(y)

R		N-1	N-2, 3	
H		+285.4	+260.8	
	(in DMSO)	+285.8	+261.2	
COOMe	(−30°C)	+260.9	+241.2	
Me		+275.7	+241.8	
CH_2OH		+263.4	+248.0	
NH_3 and NMe_3 adsorbed on zeolite Y	solid state			(z)
NH_4^+ coordinated to zeolite, not removed by outgassing		+353, +357		
NH_4^+, hydrogen-bonded, removed by outgassing		+358, +361, +364		
NH_3, hydrogen-bonded		+360		
Me_3NH^+		+346		
Ammonium moieties in biochemical structures				
Dipalmitoyl-phosphatidyl-choline (DPPC)				
$-CH_2-NMe_3^+$ moieties	(aqueous dispersion)	+333.7		(A)
	(in MeOH)	+333.4		(A)
	(in chloroform)	+332.9		(A)
Dipalmitoyl-phosphatidyl-ethanolamine (DPPE)				
$-CH_2-NH_2/-NH_3^+$	(in H_2O, pH = 5 to 7)	+352.7		(A)
	(aq. disp., pH 5 to 9)	+352.7		(A)
	(aqueous, pH = 12)	+364		(A)

Table 3. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Pig heart and kidney tissues	(aq. disp.)		
NH_4^+		+359.1	(B)
choline $—CH_2NMe_3^+$		+332	(B)
betaine (trimethylglcine)—$CH_2NMe_3^+$		+333	(B)
synthetic dopa melamin ammonium/amino moieties	(solid state)	+353	(C)
$H_3N^+—CH_2CH_2PO_3H^-$	solid state	+339.7	(D)
$H_3N^+—CH_2CH_2C(OH)(PO_3H^-)(PO_3H_2)$	solid state	+339.7	(D)
	in aqueous NaOH	+349.6 (NMe_2)	(E)
	in aqueous NaOH	+247.2 (NH)	(E)

(a) See ref. 5, pp. 244–263, 290–296, and references therein.

(b) Data from ref. 351, 20.3 MHz ^{15}N CPMAS and static powder spectra, referenced originally to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(c) Data from ref. 296, 28.913 MHz ^{14}N single-crystal spectra, referenced originally to solid NH_4Cl, +341.0 ppm from neat nitromethane (uncorrected, see Table 2).

(d) Data from ref. 563, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to formamide in DMSO, +264.7 ppm from neat nitromethane (Table 2), conversion scheme IVb (Table 1); reported originally vs fictitious ammonia standard taken at +112.2 ppm from the reference employed.

(e) Data from ref. 1020, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(f) Data from ref. 1021, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(g) Data from ref. 442, 36.5 MHz ^{15}N spectra, field parallel to sample tube, and 20.3 MHz CPMAS ^{15}N spectra, referenced originally to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(h) Data from ref. 1022, 25.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, but reported vs fictitious ammonia standard taken at +380.2 ppm from the actual reference employed; the latter value does not pertain to the field-to-sample setup involved (Table 2).

(i) Data from refs 1023 and 995, 30.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4Cl in 10 M HCl, +349.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); originally reported vs fictitious ammonia standard taken at +30.3 ppm from the reference employed, see comments in footnote (h).

(j) Data from ref. 162, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to nitromethane in MeOH, calibrated (+1.97 ppm, uncorrected) against neat nitromethane, conversion scheme IVb (Table 1).

(k) Data from ref. 1024, 20.3 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced originally to 0.1 M nitromethane in $CDCl_3$, +3.8 ppm from neat nitromethane (Table 26), conversion scheme IIb (Table 1).

(l) Data from ref. 1025, 9.04 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to aqueous NH_4Cl, +352.9 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(m) Data from ref. 930, 36.5 MHz ^{15}N spectra, other details as in footnote (e).

(n) Data from ref. 1026, 25.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(o) Data from ref. 1027 and ref. 1028, 8.1 MHz ^{15}N spectra, ^{31}P-coupled, field perpendicular to sample tube, referenced to 1 M HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(p) Data from ref. 1029, 8.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane (uncorrected for bulk susceptibility effects) via a calibrated sample of aqueous HNO_3.

(q) Data from ref. 513, 40.6 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(r) Data from ref. 159, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4 in aqueous NH_4NO_3, +359.6 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1), but reported vs fictitious ammonia standard taken at +19.7 ppm from the reference employed; we retrieved the original values and recalculated them as noted above.

Table 3. —*cont.*

(s) Data from ref. 803, 40.5 MHz spectrum, details as in footnote (v).

(t) Data from ref. 1030, ^{15}N label, 9.04 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; originally reported vs liquid NH_3 reference taken at +380.2 ppm from neat nitromethane; only a broad singlet was observed at room temperature.

(u) Data from ref. 355, 30 MHz ^{15}N CPMAS spectra, referenced originally to solid NH_4Cl, +341.0 ppm from neat nitromethane, uncorrected for bulk susceptibility effects (see Table 2).

(v) Data from ref. 1031, 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; proton-coupled and decoupled spectra, $Cr(acac)_3$ added as a relaxation reagent.

(w) Data from ref. 1032, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(x) Data from ref. 768, 18.2 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects except for those resulting from the presence of some $Cr(acac)_3$ in the reference sample employed.

(y) Data from refs 119 and 1033, 20.3 and 40.6 MHz ^{15}N INEPT and DEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(z) Data from ref. 422, 20.3 MHz ^{15}N CPMAS spectra, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; 3–4 MHz spinning rate.

(A) Data from refs 461, 470 and 565, 25.34 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

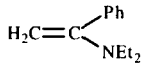
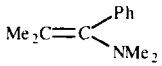
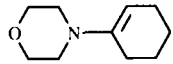
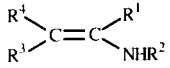
(B) Data from ref. 566, 28.91 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to 1 M $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(C) Data from ref. 363, 30.41 MHz ^{15}N CPMAS spectra, referenced originally to aqueous NH_4Cl, +352.9 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

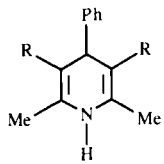
(D) Data from ref. 411, 30.4 MHz ^{15}N CPMAS spectra, referenced to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(E) Data from ref. 1034, 30.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

Table 4. Nitrogen shieldings in some enamines, enaminones and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	neat liquid	+306.4	(a)
	neat liquid	+352.1	(a)
	in $CDCl_3$	+311.9	(b)
	in DMSO or $CDCl_3$		

R^1	R^2	R^3	R^4		(in DMSO)	(in $CDCl_3$)	
H	Ph	CN	COOEt	(*Z*-isomer)	+249.6	+246.9	(c)
				(*E*-isomer)	+253.1	+250.5	(c)
H	Ph	COOEt	COOEt		+251.8	+251.8	(c)
H	Ph	COMe	COOEt	(*Z*-isomer)		+248.0	(c)
				(*E*-isomer)	+246.2	+246.3	(c)
H	Ph	COMe	COMe		+247.6	+247.5	(c)
Me	Ph	CN	H	(*E*-isomer)		+264.7	(c)
Me	Ph	CN	COOEt	(*Z*-isomer)		+245.3	(c)
Me	Ph	CN	CSSEt	(*Z*-isomer)		+231.8	(c)
H	H	CN	COOMe		+279.1	+265.0 +270.6	(c)
H	H	COOEt	COOEt		+275.4	+269.6	(c)
H	H	COOMe	COOEt	(*Z*-isomer)	+271.7	+264.8	(c)
				(*E*-isomer)	+269.7	+262.9	(c)
H	H	COMe	COMe		+274.8	+264.2	(c)
Me	H	COOMe	H		+277.0		(d)
OMe	H	CN	COOMe	(NH_2)	+288.5		(e)
				(CN)	+121.8		(e)



in DMSO
(R = COMe) +241.3 (d)
(R = COOMe) +246.3 (d)

Table 4. *—contd.*

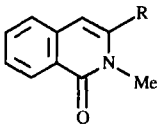
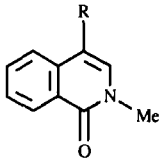
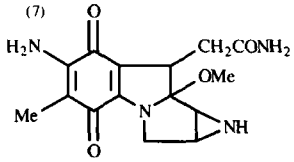
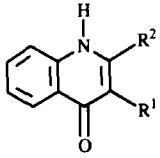
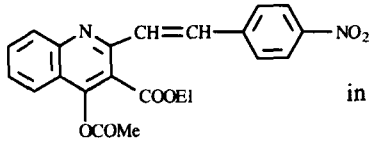
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$		(f)
	(R = H)	+234.2	
	(R = Me)	+229.7	
	(R = SEt)	+229.9	
	(R = Cl)	+231.0	
	(R = Br)	+230.0	
	(R = SOEt)	+241.7	
	(R = SO_2Et)	+244.1	
	in $CDCl_3$		(f)
	(R = Me)	+236.4	
	(R = COMe)	+233.0	
	(R = COOMe)	+231.6	
	(R = Cl)	+235.3	
	(R = Br)	+232.5	
	(R = I)	+228.0	
 (mitomycin C)	in DMSO	+286.8 (7-N)	(g)
	in DMSO + $ZnCl_2$ + CuCl	+295.3 (7-N)	(g)
	in DMSO		(h)
R^2 R^3			
H Me		+246.2	
COOEt Me		+245.1	
COOEt *p*-$NO_2C_6H_4CH{=}CH$		+255.9	
	in $CDCl_3$	+85.0 (C=N)	(h)

Table 4. *—contd.*

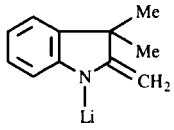
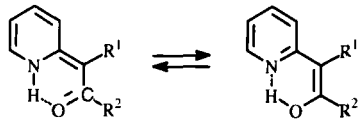
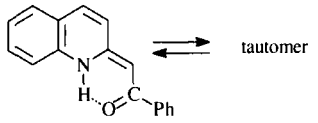
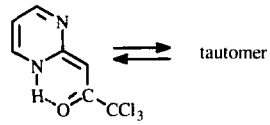
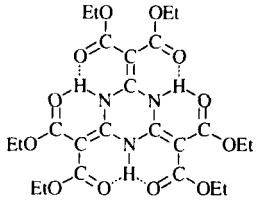
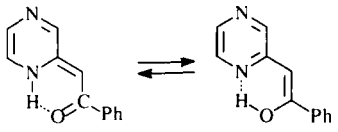
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in Et_2O, −80°C	+230.0	(i)
(complexed with ether)			
	in $CHCl_3$		(j)
R^1 R^2			
H CCl_3	(75% NH-tautomer)	+198	
CN OEt	(98% NH-tautomer)	+225	
	in $CHCl_3$ (80% NH)	+229	(j)
	in $CHCl_3$ (15% NH)	+88	(j)
	in $CHCl_3$ (100% NH)	+273	(j)
	in $CHCl_3$ (0% NH ?)	+40	(m)

Table 4. *—contd.*

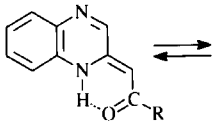
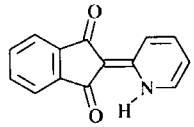
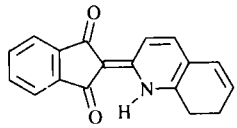
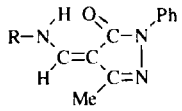
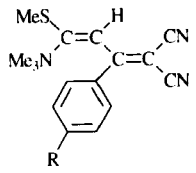
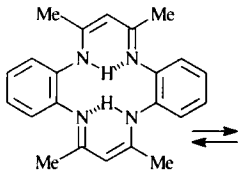
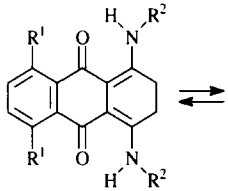
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 tautomer	in $CHCl_3$		(m)
R			
CF_3	(91% NH ?)	+216	
Ph	(70% NH ?)	+196	
4-OMe-phenyl	(85% NH ?)	+210	
4-pyridyl	(50% NH ?)	+177	
	in DMSO	+215.6	(k)
	in $CDCl_3$	+220.2	(k)
	in DMSO	+239.5	(k)
	in $CDCl_3$	+240.0	(k)
	in $CDCl_3$		(l)
R = Ph		+255.8 (NH) +189.8 (NPh) +87.5 (=N)	
R = 2-Br-phenyl		+253.4 (NH) +189.8 (NPh) +91.3 (=N)	
	in $CDCl_3$		(n)

Table 4. *—contd.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
R		(NMe_3)	
OMe		+271.6	
Me		+271.2	
H		+269.8	
Br		+268.8	
NO_2		+266.4	
 tautomers	solid state	+238.5 (NH) +92.5 (=N)	(o) (o)
 imino tautomers			(p)
R^1 R^2			
H H	in DMSO	+264.1	
H $CH_2CH_2NHCH_2CH_2OH$	in DMSO	+246.0 (enamine)	
OH CH_2CH_2OH	in DMSO	+244.5	
OH $CH_2CH_2NEt_2$	in $CDCl_3$	+249.7 (enamine)	
OH $CH_2CH_2NHCH_2CH_2OH$	in DMSO	+249.7 (enamine)	
H Ph	in DMSO, +27°C	+200.2	
	+97°C	+189.1	
	in $CDCl_3$, −33°C	+227.8	
	+57°C	+202.8	
OH Ph	in $CDCl_3$	+242.8	

(a) Data from ref. 1035, 8.1 MHz ^{15}N spectra, field perpendicular to sample tube, referred originally to 1 M HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(b) Data from ref. 1036, 40.55 Mz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported originally vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane, see comments in footnote (e).

(c) Data from ref. 771, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 1037, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referred to neat nitromethane, uncorrected for bulk susceptibility effects.

(e) Data from ref. 193, 50.7 MHz proton-coupled ^{15}N spectra, field parallel to sample tube, referenced originally to ammonium nitrate and recalculated to fictitious ammonia standard taken at +380.2 ppm from neat nitromethane (the latter value refers actually to measurements where the field is perpendicular to sample tube), conversion scheme IVd (Table 1).

(f) Data from ref. 1038, 25.32 MHz ^{15}N DEPT spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects, but reported vs fictitious ammonia standard taken at +380.2 ppm from nitromethane (see comments in footnote (e)).

(g) Data form ref. 1039, 7-^{15}N label, 25.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to the nitrate ion in NH_4NO_3 in DMSO, +3.3 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(h) Data from ref. 802, 36.5 MHz ^{15}N spectra, other details as in footnote (d).

(i) Data from ref. 1040, 33% ^{15}N label, 10.13 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to *N*-methylaniline, but reported vs liquid NH_3 (taken at +52.8 ppm from the actual standard, and at +380.2 ppm from neat nitromethane), conversion scheme IVa (Table 1).

(j) Data from refs 551, 553, 784, 791 and 1041, 30.4 MHz ^{15}N INEPT spectra, other details as in footnote (d).

(k) Data from ref. 786, 36.4 MHz ^{15}N spectra (inverse-gated decoupled or DEPT), field parallel to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); originally reported vs liquid ammonia, taken at +376.2 ppm from the standard employed.

(l) Data from 548, 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(m) Data from refs 550, 552, and 1042, 21.68 MHz ^{14}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; it is not clear which of the nitrogen atoms was actually observed in the ^{14}N spectra where signal broadening and overlap effects can take place; the estimates of the tautomeric compositions seem to be uncertain.

(n) Data from ref. 816, ^{15}N-labelled NMe_3 moiety, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected bulk susceptibility effects.

(o) Data from ref. 432, 9.12 MHz ^{15}N CPMAS spectra at −137 to +87°C, dynamic NMR effects observed in the solid; referenced originally to solid NH_4Cl, +341.0 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects.

(p) Data from ref. 783, 10.09 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

Table 5. Nitrogen shieldings in amino groups coordinated to boron and silicon

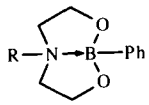
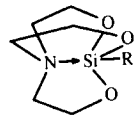
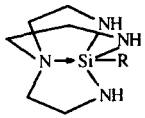
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Amine–borane adducts			
$H_3N \rightarrow BH_3$	in C_6D_6/THF	+373.0	(a)
$Et_3N \rightarrow BH_3$	in C_6D_6, +60°C	+338.8	(a)
$Me_3N \rightarrow BF_3$	in CH_2Cl_2	+345.8	(a)
$Me_3N \rightarrow BCl_3$	in CH_2Cl_2	+337.8	(a)
$Me_3N \rightarrow BBr_3$	in CH_2Cl_2	+340.8	(a)
$Me_3N \rightarrow BI_3$	in CH_2Cl_2	+351.6	(a)
other structures	various		(b)
Boratranes			
	solvent ?		(c)
R			
H		+319.1	
Me		+313.8	
Et		+305.7	
i-Pr		+298.1	
n-Bu		+306.5	
i-Bu		+305.3	
t-Bu		+291.1	
Silatranes			
			
R			
H	in DMSO	+352.1	(d)
	in DMSO	+353.9	(e)
	in acetone-d_6	+355.1	(e)
	in $CDCl_3$	+355.9	(e)
F	in CH_2Cl_2	+349.3	(f)
Cl	in DMSO	+347.8	(e)
	in $CDCl_3$	+348.8	(e)
	in CH_2Cl_2	+348.8	(f)
Br	in CH_2Cl_2	+348.0	(f)
I	in CH_2Cl_2	+346.9	(f)

Table 5. *—contd.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
CH_2Cl	in DMSO	+351.5	(d)
	in DMSO	+353.2	(e)
	in $CDCl_3$	+355.2	(e)
OMe	in DMSO	+352.3	(e)
	in $CDCl_3$	+353.1	(e)
CH_2NHPh	in DMSO	+353.7	(d)
Ph	in DMSO	+354.1	(d)
	in DMSO	+355.0	(e)
	in $CDCl_3$	+357.2	(e)
$CH{=}CH_2$	in DMSO	+354.5	(d)
	in DMSO	+355.3	(e)
	in $CDCl_3$	+357.9	(e)
Me	in DMSO	+355.9	(d)
	in DMSO	+357.0	(e)
	in $CDCl_3$	+360.0	(e)
$CH_2CH_2CH_2SH$	in DMSO	+356.3	(d)
$CH_2CH_2CH_2CN$	in DMSO	+359.3	(d)
	in $CDCl_3$		(g)
R		NSi NH	
H		+346.8 +350.1	
Me		+354.7 +352.8	
$CH{=}CH_2$		+352.8 +354.0	
Ph		+352.2 +354.1	
other silatranes and related structures	various		(h)

(a) Data from ref. 757, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 0.1 M nitromethane in $CDCl_3$, +3.8 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(b) See ref. 5, p. 299, and references therein.

(c) Data from ref. 1043, 20.3 MHz and 36.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane via a calibrated sample of aqueous $NaNO_3$, uncorrected for bulk susceptibility effects, solvent not reported.

(d) Data from ref. 1044, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(e) Data from ref. 936, 36.5 MHz ^{15}N spectra, other details as in footnote (d).

(f) Data from ref. 274, $^1H\{^{15}N\}$ INDOR spectra, spectrometer not reported, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(g) Data from ref. 930, details as in footnote (e).

(h) See ref. 5, pp. 271–276, and references therein.

Table 6. Nitrogen shieldings in amino groups bound to elements other than carbon

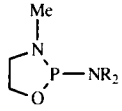
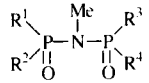
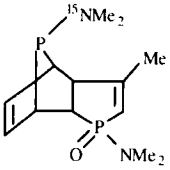
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$(Me_2N)_3P{=}X$	in C_6D_6		(a)
X			
lone pair		+349.7	
Se		+346.8	
Te		+345.5	
NEt_2		+364.7	
BH_3		+346.1	
	in C_6D_6		(b)
R		NMe NR_2	
Me		+344.0 +324.1	
Et		+345.0 +292.8	
i-Pr		+352.1 +274.1	
	in benzene		(c)
R^1 R^2 R^3 R^4			
Cl Cl Cl Cl		+274.7	
OEt Cl Cl Cl		+285.1	
OEt Cl OEt Cl	diastereoisomers	+296.9, +297.1	
OEt OEt Cl Cl		+296.6	
OEt OEt OEt Cl		+310.2	
OEt OEt OEt OEt		+324.7	
	in MeCN	+360.8 (^{15}N)	(d)

Table 6. *—contd.*

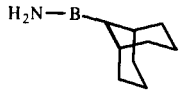
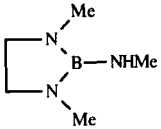
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
other P-bound amino groups		see Table 23 and ref. 5, pp. 277–283	
$Me_2B—NH_2$	in C_6D_6	+283.1	(e)
$[Me_2B—NH_2]_2$	in C_6D_6	+335.4	(e)
	in C_6D_6/ THF, +60°C	+354.5	(e)
$B(NHMe)_3$	in C_6D_6	+355.5	(e)
	in C_6D_6	+358.5 (NHMe)	(e)
$Ph_2B—NHMe$	in $CDCl_3$	+289.5	(f)
$R_2B—X$	in C_6D_6		(g)
X R			
NH_2 t-Bu		+302	
i-Pr		+307	
Et		+299	
Me		+297	
NHMe t-Bu		+297	
i-Pr		+301	
Et		+294	
Me		+293	
$NHPr^i$ t-Bu		+255	
i-Pr		+262	
Me		+263	
$NHBu^t$ t-Bu		+249	
i-Pr		+257	
Me		+248	

Table 6. *—contd.*

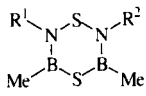
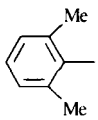
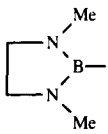
Compound		Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$NHSiMe_3$	t-Bu		+286	
	i-Pr		+291	
	Et		+292	
	Me		+286	
NHPh	t-Bu		+260	
	i-Pr		+267	
	Me		+259	
NMe_2	t-Bu		+300	
	i-Pr		+296	
	Et		+306	
	Me		+300	
NEt_2	i-Pr		+269	
	Et		+266	
	Me		+299	
		in $CDCl_3$		(h)
R^1	R^2			
$SiMe_3$	$SiMe_3$		+269.2	
t-Bu	$SiMe_3$		+260 (unresolved)	
t-Bu	t-Bu		+216.3	
$SiMe_2Cl$	$SiMe_2Cl$		+257.0	
Ph	$SiMe_2Cl$		+258 (unresolved)	
	$SiMe_3$		+270 (unresolved)	
	t-Bu		+280, +321	

Table 6. —*contd.*

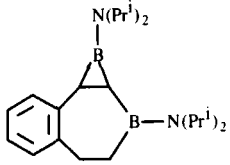
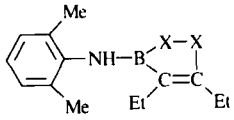
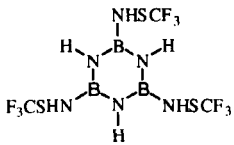
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+255.2, +245.4	(i)
	in $CDCl_3$		(j)
	X = S	+278	
	X = Se	+275	
$(CF_3S)_2N—BX_2$	neat liquids + 10% C_6D_6		(k)
X			
F		+349 ± 2	
Cl		+309	
Br		+299	
N_3		+335.2	
$NHSCF_3$		+346.6 (NH)	
$[(CF_3S)_2N]_2BX$	neat liquids + 10% C_6D_6		(k)
X			
Cl		+329.4	
Br		+325.0	
N_3		+340.0	
$NHSCF_3$		+332.4 (NH)	
$[(CF_3S)_2N]_3B$	neat liquid + 10% C_6D_6	+336.8	(k)
$(CF_3SNH)BCl_2$	50% in C_6D_6	+311 ± 5	(k)
$(CF_3SNH)_2BCl$	50% in C_6D_6	+338 ± 5	(k)
$(CF_3SNH)_3B$	50% in C_6D_6	+356.2	(k)
$(CF_3S)_2NBCl_2 \cdot NMe_3$	in CCl_4/C_6D_6	+330	(k)
	in $CDCl_3$	+309.0 (ring NH)	(k)
		+351.4 ($NHSCF_3$)	(k)

Table 6. *—contd.*

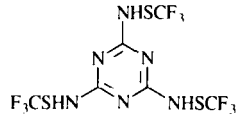
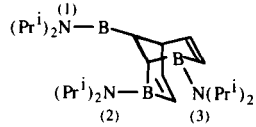
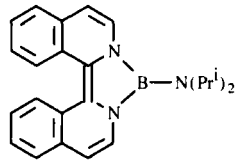
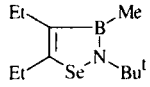
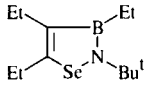
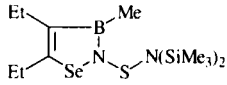
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	neat + 10% C_6D_6	+310.4 ($NHSCF_3$) +183.4 (ring N)	(k) (k)
	50% in $CDCl_3$	+243.2 (N-2, 3) +252.3 (N-1)	(l) (l)
	sat. in $CDCl_3$	+222.3 ($N\text{-}Pr^i$) +68.1 (ring N)	(m) (m)
	in $CDCl_3$	+238.2	(n)
	in $CDCl_3$	+237.2	(n)
	in $CDCl_3$	+244.7 (B–N–Se) +316.3 (N–Si)	(n) (n)
other amino groups bound to boron		see Table 5 and ref. 5, pp. 272, 285	
$H_2NSiMePh_2$	in C_6D_6	+373.8	(o)
$H_2NSi(Bu^t)Me_2$	in C_6D_6	+375.7	(q)
$H_2NSi(Me_2)CMe_2CHMe_2$	in C_6D_6	+371.8	(q)
$HN(SiMe_3)_2$	in acetone-d_6	+354.2	(p)
$HN(SiMe_2Ph)_2$	50% in $CDCl_3$	+357.8	(o)
$HN(SiMePh_2)_2$	50% in $CDCl_3$	+361.5	(o)
$Me_3SiNHSi(Bu^t)Me_2$	in C_6D_6	+360.0	(q)
$Me_3SiNHSi(Me_2)CMe_2CHMe_2$	in C_6D_6	+356.5	(q)

Table 6. *—contd.*

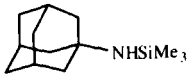
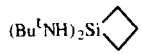
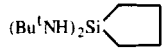
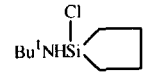
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$HN(SiMe_2Cl)_2$	50% in $CDCl_3$	+334.3	(o)
$Me_3Si—[O—SiMe_2—]_6—NH—[—SiMe_2—O—]_6—SiMe_3$	in $CDCl_3$	+335.7	(o)
	in C_6D_6	+318.4	(q)
$Me_2C(Et)NHSiMe_3$	in C_6D_6	+327.7	(q)
$Bu^tNHSiHMe_2$	in C_6D_6	+326.3	(q)
$Bu^tNHSiMe_3$	50% in $CDCl_3$	+323.9	(p)
	in C_6D_6	+325.0	(r)
$Bu^tNHSiEt_3$	in C_6D_6	+331.2	(q)
$Bu^tNHSiMe_2Ph$	50% in $CDCl_3$	+325.7	(p)
$Bu^tNHSiMePh_2$	50% in $CDCl_3$	+327.3	(p)
$(Bu^tNH)_2SiMe_2$	50% in $CDCl_3$	+317.4	(p)
$(Bu^tNH)_2SiHMe$	in C_6D_6	+317.3	(q)
$(Bu^tNH)_2Si(Me)Ph$	in C_6D_6	+317.5	(q)
$(Bu^tNH)_2Si(Me)CH=CH_2$	in C_6D_6	+315.8	(q)
	in C_6D_6	+312.4	(q)
	in C_6D_6	+317.1	(q)
$Bu^tNHSi(OEt)Me_2$	50% in $CDCl_3$	+317.6	(p)
$Bu^tNHSi(OEt)_2Me$	50% in $CDCl_3$	+321.5	(p)
$(Bu^tNH)_2Si(OEt)_2$	50% in $CDCl_3$	+324.9	(p)
$Bu^tNHSi(OEt)_3$	50% in $CDCl_3$	+330.4	(p)
$Bu^tCH_2CMe_2NHSiMe_3$	in C_6D_6	+321.7	(r)
$Bu^tNHSiMe_2Pr^i$	in C_6D_6	+326.9	(q)
	in C_6D_6	+313.7	(q)
$Pr^iNHSiMe_2Pr^i$	in C_6D_6	+337.1	(q)
$Pr^iNHSi(Bu^t)Me_2$	in C_6D_6	+338.3	(q)
$Pr^iNHSi(Me_2)CMe_2CHMe_2$	in C_6D_6	+336.2	(q)
$Pr^iNHSi(Ph)Me_2$	in C_6D_6	+334.5	(q)
$Pr^iNHCH_2CMe_2NHSiMe_3$	in C_6D_6	+330.1 ($NHPr^i$)	(q)
		+326.5 ($NHCMe_2$)	(q)
$(Pr^iNH)_2SiMe_2$	in C_6D_6	+325.1	(q)
$(Pr^iNH)_2Si(Me)Ph$	in C_6D_6	+329.1	(q)
$(Pr^iNH)_2Si(Me)CH=CH_2$	in C_6D_6	+329.1	(q)

Table 6. *—contd.*

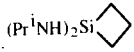
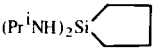
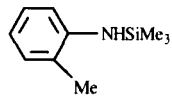
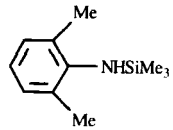
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in C_6D_6	+325.1	(q)
	in C_6D_6	+330.5	(q)
$Bu^sNHSiMe_3$	in C_6D_6	+337.2	(r)
$Bu^iNHSiMe_3$	in C_6D_6	+356.9	(r)
$(PrNH)_2SiMe_2$	50% in $CDCl_3$	+351.0	(s)
$PrNHSi(OEt)Me_2$	50% in $CDCl_3$	+348.9	(s)
$(PrNH)_3SiMe$	50% in $CDCl_3$	+351.6	(s)
$(PrNH)_3SiCH{=}CH_2$	50% in $CDCl_3$	+353.6	(s)
$(PrNH)_2SiPh$	50% in $CDCl_3$	+353.5	(s)
$(PrNH)_4Si$	50% in $CDCl_3$	+354.4	(s)
$Et_2NSi(OEt)_3$	in C_6D_6	+349.9	(s)
$EtNHSiMe_3$	in C_6D_6	+349.3	(r)
$EtNHSi(Bu^t)Me_2$	in C_6D_6	+354.8	(q)
$EtNHSi(Me_2)CMe_2CHMe_2$	in C_6D_6	+352.3	(q)
$EtNHSi(Ph)Me_2$	in C_6D_6	+351.5	(q)
$Me_3SiNHCH_2CH_2NHSiMe_3$	in C_6D_6	+358.9	(q)
$Me_3SiNHCH(Me)CH_2NHSiMe_3$	in C_6D_6	+341.4 (NHCHMe)	(q)
		+359.4 ($NHCH_2$)	(q)
$Me_3SiNHCMe_2CH_2NHSiMe_3$	in C_6D_6	+363.2 ($NHCH_2$)	(q)
		+334.5 ($NHCMe_2$)	(q)
$Bu^t(Me_2)SiNHCH_2CH_2NHSi(Me_2)Bu^t$	in C_6D_6	+364.3	(q)
$PhCH(Me)NHSiMe_3$	in C_6D_6	+335.9	(q)
$PhNHSiMe_3$	in acetone-d_6	+314.9	(p)
$PhNHSiHMe_2$	50% in $CDCl_3$	+320.4	(p)
$PhNHSiMe_2Ph$	50% in $CDCl_3$	+317.7	(p)
$PhNHSiMePh_2$	50% in $CDCl_3$	+319.5	(p)
$(PhNH)_2SiMe_2$	in acetone-d_6	+312.7	(p)
$PhNHSi(OEt)Me_2$	50% in $CDCl_3$	+310.8	(p)
$(PhNH)_3SiMe$	50% in $CDCl_3$	+313.1	(p)
$(PhNH)_2Si(OEt)Me$	50% in $CDCl_3$	+313.5	(p)
$PhNHSi(OEt)_2Me$	50% in $CDCl_3$	+314.6	(p)
$(PhNH)_2Si(OEt)_2$	50% in $CDCl_3$	+319.2	(p)
$PhNHSi(OEt)_3$	50% in $CDCl_3$	+322.3	(p)
	in cyclohexane	+321.5	(p)
	in DMSO	+320.7	(p)
	in C_6D_6	+316.9	(q)
	in C_6D_6	+328.4	(q)

Table 6. *—contd.*

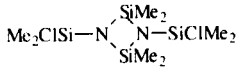
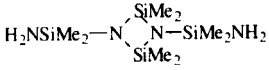
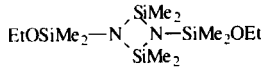
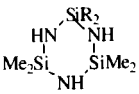
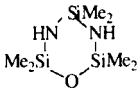
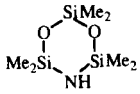
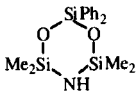
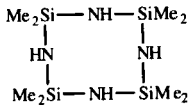
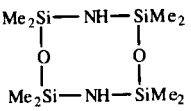
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+322.1	(o)
	in $CDCl_3$	+323.8 (N) +363.1 (NH_2)	(o) (o)
	in $CDCl_3$	+325.4	(o)
	in $CDCl_3$ R = Me R = Ph	 +347.3 +347.6, +351.0	 (o) (o)
	in $CDCl_3$	+345.4	(t)
	in $CDCl_3$	+342.9	(t)
	in $CDCl_3$	+341.9	(t)
	in $CDCl_3$	+341.7	(o)
	in $CDCl_3$	+334.9	(t)

Table 6. *—contd.*

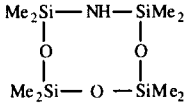
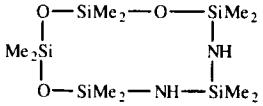
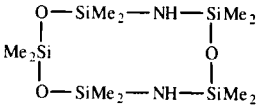
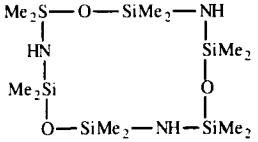
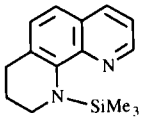
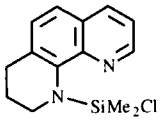
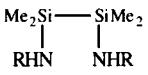
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+334.9	(t)
	in $CDCl_3$	+336.7	(t)
	in $CDCl_3$	+335.1	(t)
	in $CDCl_3$	+334.8	(t)
$Me_3SiNHCH_2CH_2NHSiMe_3$	in C_6D_6	+358.8	(r)
	in $CDCl_3$	+317.1 (N—Si) +74.8 (—N=)	(u) (u)
	in $CDCl_3$	+308.6 (N—Si) +38.9 (—N=)	(u) (u)
$N(SiMe_3)_3$	C_6D_6	+345.8	(r)
	in C_6D_6		(r)

Table 6. *—contd.*

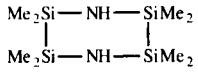
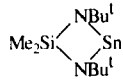
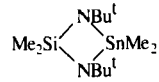
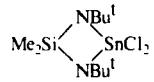
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
R			
Me		+378.4	
Et		+354.3	
Bu^i		+362.0	
Pr^i		+337.4	
Bu^s		+342.0	
Bu^t		+326.9	
$Bu^tCH_2CMe_2$		+326.5	
$SiMe_3$		+359.4	
$Si(Me_2)Bu^t$		+367.3	(q)
$[(RNH)_2SiMe—SiMe(NHR)_2]_2$	in C_6D_6		(q)
R			
Bu^t		+314.4	
Pr^i		+325.1	
Bu^s		+328.3, +328.4, +328.5, +328.8, +328.9, +329.0	
	in C_6D_6	+360.2	(r)
$Bu^t_2PNHSiMe_3$	in C_6D_6	+360.9	(q)
other Si-bound amino groups		see Table 5 and ref. 5, pp. 271, 273–276, 284	
	in C_6D_6	+200.1	(v)
	in C_6D_6	+314.4 (*)	(v)
	in C_6D_6	+272.0 (*)	(v)

Table 6. —*cont.*

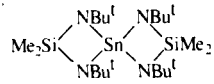
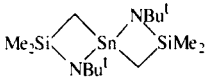
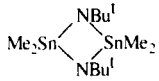
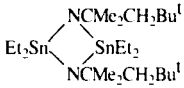
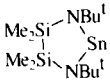
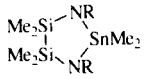
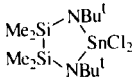
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in C_6D_6	+295.0	(v)
	in C_6D_6	+271.4	(v)
	in C_6D_6 50% in C_6D_6	+310.4 +310.7	(v) (w)
	in C_6D_6	+313.8	(v)
	in C_6D_6	+192.9	(v)
	in C_6D_6		
R			
Bu^t		+317.8	(v)
Pr^i		+336.3	(w)
$Bu^tCH_2CMe_2$		+316.0	(w)
	in C_6D_6	+300.8	(v)
$Me_3SiN(Bu^t)SnMe_3$	in C_6D_6	+324.1	(w)
$Me_3SiN(SnMe_3)_2$	in C_6D_6	+374.4	(w)

Table 6. —*cont.*

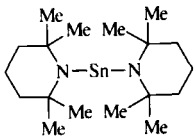
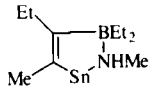
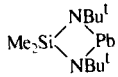
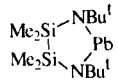
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$N(SnMe_3)_3$	in C_6D_6	+396.0	(x)
$Me_2Sn(NEt_2)_2$	in C_6D_6	+341.1	(w)
$Me_2Sn[N(Me)Ph]_2$	in C_6D_6	+322.7	(w)
$Me_3SnNHBu^t$	in C_6D_6	+329.0	(w)
$Me_3SnNHPh$	in C_6D_6	+326.7	(w)
$(Et_3Sn)_2NH$	in C_6D_6	+414.7	(w)
Me_3SnNEt_2	in C_6D_6	+330.1	(w)
$Me_3SnN(Me)Ph$	in C_6D_6	+329.9	(w)
$(Me_3Sn)_2NMe$	in C_6D_6	+362.0	(w)
$(Me_3Sn)_2NPr^i$	in C_6D_6	+347.6	(w)
$(Me_3Sn)_2NBu^t$	in C_6D_6	+330.5	(w)
$(Me_3Sn)_2NPh$	in C_6D_6	+332.7	(w)
$(Me_3Sn)_2NGeMe_3$	in C_6D_6	+380.5	(w)
$Sn[N(SiMe_3)_2]_2$	in C_6D_6	+243.0	(x)
$Sn[N(Bu^i)SiMe_3]_2$	in C_6D_6	+227.7	(x)
$Sn[N(Bu^t)SiMe_3]_2$	in C_6D_6	+224.7	(y)
$Bu^tN(SnMe_3)_2$	in C_6D_6	+330.5	(x)
	in C_6D_6	+205.4	(y)
	in C_6D_6	+363.8	(w)
other Sn-bound amino groups		see ref. 5, p. 284	
$Pb[N(SiMe_3)_2]_2$	in C_6D_6	+192.9	(x)
$Pb[N(Bu^t)SiMe_3]_2$	in C_6D_6	+144.7	(y)
$Pb[N(SiMe_3)CMe_2CH_2Bu^t]_2$	in C_6D_6	+151.4	(y)
	in C_6D_6	+187.1	(x)
	in C_6D_6	+119.8	(x)
$(Me_3Pb)_3N$	in C_6D_6	+354.1	(x)

Table 6. *—cont.*

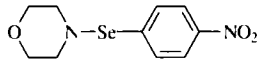
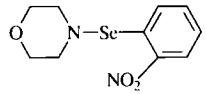
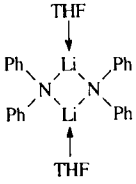
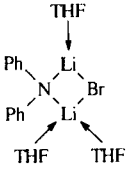
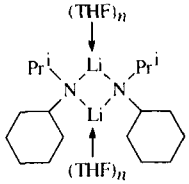
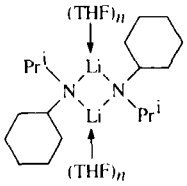
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+335.2 (N—Se) +10.1 (NO_2)	(z) (z)
	in $CDCl_3$	+337.6 (N—Se) +9.9 (NO_2	(z) (z)
$N(SCF_3)_3$	neat + 10% C_6D_6	+364.0	(A)
$HN(SCF_3)_2$	neat + 10% C_6D_6	+377.1	(A)
	same + $Cr(acac)_3$	+375.8	(A)
	gel in CH_2Br_2	+376.0	(A)
	gel in MeOH	+370.0	(A)
$H_2N—SCF_3$	neat + 10% C_6D_6	+381.1	(A)
$(CF_3S)_2NMe$	neat + 10% C_6D_6	+372.8	(A)
$CF_3SNHSiMe_3$	neat + 10% C_6D_6	+376.1	(A)
$CF_3SN(SiMe_3)_2$	neat + 19% C_6D_6	+369.2	(A)
$(CF_3S)_2NSiMe_3$	neat + 10% C_6D_6	+359.0	(A)
$(CF_3S)_2NSnMe_3$	neat + 10% C_6D_6	+377.4	(A)
$[(CF_3S)_2N]_2Hg$	neat + 10% C_6D_6	+361 ± 5	(A)
$[(Me_3Si)_2N]_2Ge(OMe)$ $NHSi(OBu^t)_3$	in $CDCl_3$	+332 (NH) +335 (N)	(B) (B)
	0.05 M in toluene +0.05 M THF, −90°C	+251.4	(C)
	0.05 M in toluene +0.1 M THF, −90°C	+251.0	(C)

Table 6. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	0.20 M in toluene + 0.41 M THF −40°C	+308.9	(D)
	in THF		(E)
R			
none		+286.2	
2-Me		+289.6	
3-Me		+287.5	
4-Me		+291.3	
2-OMe		+299.2	
3-OMe		+285.2	
4-OMe		+297.9	
2,6-Me_2		+290.7	

(a) Data from ref. 129, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 0.1 M nitromethane on $CHCl_3$, +3.8 ppm fron neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(b) Data from ref. 903, 18.24 MHz ^{15}N spectra field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) Data from ref. 905, ^{15}N-labelled samples, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 907, ^{15}N label, 30.4 MHz ^{15}N spectra, other details as in footnote (b).

(e) Data from ref. 757, INEPT spectra, other details as in footnote (a).

(f) Data from ref. 120, details as in footnote (e).

(g) Data from ref. 1045, 14.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to aqueous $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

Table 6. —*cont.*

(h) Data from ref. 1046, 5.8 MHz ^{14}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(i) Data from ref. 1047, 25.4 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(j) Data from ref. 1048, 25.4 MHz ^{15}N spectra, details as in footnote (i).

(k) Data from ref. 788, 25.36 and 40.52 MHz ^{15}N spectra, and 18.07 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to liquid NH_3 + 10% C_6D_6, and also to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(l) Data from ref. 1049, 25.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added to the sample as a relaxation reagent.

(m) Data from ref. 135, details as in footnote (i).

(n) Data from ref. 1050, 25.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(o) Data from refs 150 and 899, details as in footnote (p).

(p) Data from ref. 51, 36.5 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(q) Data from ref. 1024, details as in footnote (a), but originally recalculated to neat nitromethane reference, uncorrected for bulk susceptibility effects.

(r) Data from ref. 134, 30–50% solutions, INEPT spectra, other details as in footnote (a).

(s) Data from ref. 154, details as in footnote (p); the paper contains a value for $N(SiMe_3)_3$ quoted from ref. 130, which is erroneously mixed together with those referred to neat nitromethane; actually, the quoted value was measured with respect to 0.1 M nitromethane in $CDCl_3$, +3.8 ppm from neat nitromethane, see footnotes (a) and (x).

(t) Data from ref. 150, details as in footnote (p).

(u) Data from ref. 1051, 10.14 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to NO_3^- in aqueous ND_4NO_3, +40 ppm fron neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(v) Data from refs. 941 and 943, 10.14 MHz ^{15}N spectra, field perpendicular to sample tube, other details as in footnote (a); some of the values have been misprinted in the paper, and the correct ones, those marked with (*), are reported here, owing to the authors' advice.

(w) Data from ref. 134, INEPT spectra, other details as in footnote (a).

(x) Data from refs. 130, 151 and 931, details as in footnote (a); the value reported in the second reference for $Pb[N(SiMe_3)_2]_2$ corrects that misprinted in the first.

(y) Data from ref. 153, 10–20% solutions, details as in footnote (a).

(z) Data from ref. 1052, 40.56 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(A) Data from ref. 776, details as in footnote (k).

(B) Data from ref. 795, 25.3 MHz ^{15}N spectrum, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(C) Data from ref. 1053, 40.53 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 0.15 M aniline in THF (tetrahydrofuran), and recalculated to fictitious ammonia standard, taken at +50.0 ppm from the reference employed, and +380.2 ppm (uncorrected) from neat nitromethane, conversion scheme IVd (Table 1).

(D) Data from ref. 949, details as in footnote (C).

(E) Data from ref. 775, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to nitromethane, uncorrected for bulk susceptibility effects; reported originally vs. fictitious ammonia standard taken at +380.2 ppm from nitromethane; the latter value (uncorrected for bulk susceptibility effects) comes form measurements where the field was perpendicular to sample tube (see Table 2).

Table 7. Nitrogen shieldings in arylamines and arylammonium ions

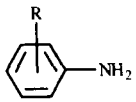
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 R			
none	in THF	+328.1	(a)
	in aqueous MeCN	+325.7	(b)
	in acetone	+325.6	(c)
	in DMSO	+320.0	(d)
	in DMSO	+320.8	(e)
	in DMSO	+320.1	(f)
3-NH_2	in aqueous MeCN	+324.2	(b)
4-OH	in DMSO	+325.9	(d)
2-OMe	in THF	+338.5	(a)
	in DMSO	+330.3	(g)
3-OMe	in THF	+327.6	(a)
4-OMe	in THF	+333.6	(a)
	in acetone	+330.7	(c)
	in DMSO	+324.8	(d)
	in DMSO	+326.2	(e)
2-Me	in THF	+330.1	(a)
	in DMSO	+321.2	(g)
3-Me	in THF	+328.7	(a)
4-Me	in THF	+330.8	(a)
	in acetone	+327.7	(c)
	in DMSO	+321.6	(d)
	in DMSO	+323.0	(e)
2,6-Me_2	in THF	+332.7	(a)
2-Et	in DMSO	+322.4	(g)
2-Pr^i	in DMSO	+322.6	(g)
2-F	in DMSO	+331.2	(g)
4-F	in acetone	+328.5	(c)
	in DMSO	+323.4	(d)
	in DMSO	+323.6	(e)
2-Cl	in DMSO	+320.0	(g)
4-Cl	in acetone	+325.3	(c)
	in DMSO	+318.7	(d)
	in DMSO	+320.7	(e)
4-Br	in DMSO	+318.2	(d)
4-($PhCH_2CONH$)	in DMSO	+318.0	(d)
4-CF_3	in acetone	+319.9	(c)
	in DMSO	+313.5	(e)
4-SCF_3	in acetone	+319.0	(c)
	in DMSO	+313.0	(e)

Table 7. *—contd.*

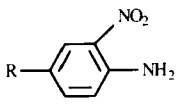
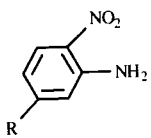
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
2-$CONH_2$	in DMSO	+313.4	(g)
4-COOEt	in acetone	+317.2	(c)
	in DMSO	+310.1	(e)
4-COOMe	in acetone	+316.9	(c)
	in DMSO	+309.7	(e)
4-SO_2Me	in acetone	+315.8	(c)
	in DMSO	+309.0	(e)
2-COMe	in DMSO	+307.4	(g)
4-COMe	in acetone	+316.1	(c)
	in DMSO	+307.9	(d)
	in DMSO	+308.8	(e)
2-CN	in DMSO	+310.5	(g)
4-CN	in acetone	+314.9	(c)
	in DMSO	+306.8	(d)
	in DMSO	+307.6	(e)
2-NO_2	in DMSO	+301.3	(g)
	in DMSO	+302.4	(e)
4-NO_2	in acetone	+310.2	(c)
	in DMSO	+299.8	(d)
	in DMSO	+301.3	(e)
4-SO_2CF_3	in DMSO	+299.2	(e)
	in DMSO		(e)
R			
H		+302.4	
OMe		+305.2	
Me		+304.5	
F		+303.6	
Cl		+300.5	
CF_3		+295.5	
SCF_3		+294.8	
COOEt		+293.7	
COOMe		+293.4	
COMe		+292.5	
SO_2Me		+292.0	
CN		+291.2	
NO_2		+286.6	
	in DMSO		(b)

Table 7. —*contd.*

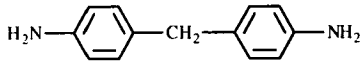
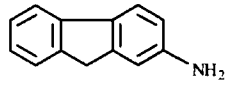
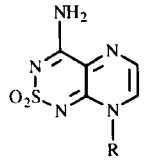
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
R			
H		+302.4	
OMe		+299.8	
Me		+302.4	
F		+299.2	
CF_3		+299.3	
COOEt		+301.0	
COMe		+300.8	
SO_2Me		+298.4	
NO_2		+297.6	
$PhNH_3^+$	various	+329 to +333	(h)
	in DMSO	+330	(i)
	solid state	+326	(i)
NH_2 groups in oxazole and pyrazole derivatives	in DMSO and CF_3COOH	+378 to +341	(j)
NH_2 groups in 2-aminothiazole derivatives	in DMSO and CF_3COOH	+307 to +291	(k)
NH_2 and NH groups in thiazole derivatives	in DMSO	+320 to +292	(l)
NH_2 groups in 5-amino-1,2,4-triazole derivatives	in DMSO	+334 to +327	(m)
	in DMSO	+318.7	(f)
NH group in 8-(*N*-fluoren-2-ylamino)--2′-deoxyguanosine -5′-monophosphate	in DMSO	+295.9	(f)
	in DMSO	+284 to +280 (NH_2)	(n)

Table 7. —*contd.*

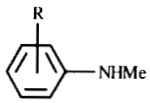
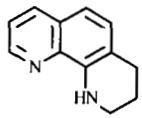
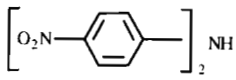
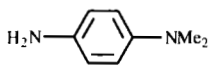
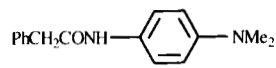
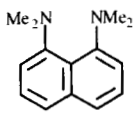
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
			
R			
4-($PhCH_2CONH$)	in DMSO	+324.2 ($NHMe$)	(d)
2-NO-4-NO_2	in DMSO	+297.0 ($NHMe$)	(o)
2-NO-4,6-$(NO_2)_2$	in $CDCl_3$	+290.1 ($NHMe$)	(p)
	sat. in $CDCl_3$	+321.6 (NH) +84.1 (N)	(q) (q)
$PhNHCH_2CHOHCH_2OPh$	in aqueous MeCN	+328.1	(b)
Ph_2NH	in DMSO	+288.5	(f)
	in DMSO	+276.4	(f)
$PhNMe_2$	in DMSO	+338.2	(r)
	in CF_3COOH	+332.5	(r)
$PhNHMe_2^+ Cl^-$	in DMSO	+328.9	(r)
	in CF_3COOH	+331.1	(r)
$PhNMe_3^+ I^-$	in DMSO	+322.5	(r)
	in CF_3COOH	+325.0	(r)
	in DMSO	+342.7 (NMe_2)	(s)
		+329.1 (NH_2)	(s)
	in $CDCl_3$	+342.6 (NMe_2)	(s)
		+331.4 (NH_2)	(s)
	in DMSO	+337.9 (NMe_2)	(d)
	in CD_3CN	+338.1	(t)
	solid state	+329.7	(t)

Table 7. *—contd.*

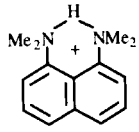
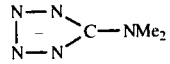
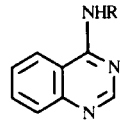
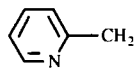
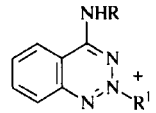
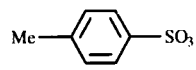
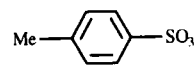
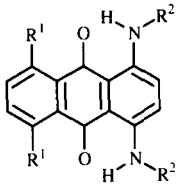
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in CD_3CN	+343.7	(t)
	solid state	+340.0	(t)
	in DMSO	+343.3 (NMe_2)	(u)
	in DMSO (*ca.* 100% amino tautomer)		(v)
R			
Bu^n		+292.0 (NH)	
$MeOCH_2CH_2$		+295.9 (NH)	
		+293.3 (NH)	
p-tolyl		+278.7 (NH)	
	in DMSO		(w)
R R^1 X			
Bu^n Pr^n I		+269.3 (NH)	
$MeOCH_2CH_2$ Pr^n I		+272.6 (NH)	
p-tolyl Pr^n I		+261.4 (NH)	
p-tolyl Pr^n Br		+259.4 (NH)	
p-tolyl Pr^n 		+261.1 (NH)	
p-tolyl Me $MeSO_3$		+269.1 (NH)	
p-tolyl Me 		+261.4 (NH)	

Table 7. —*contd.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Arylamino groups in resin from diglycidyl ether of bisphenol A (DGEBA) and *m*-phenylenediamine	in aqueous MeCN	+323.8 +323.0 +322.9 +322.8 +322.6 +322.6 +322.6 +322.6 +321.7 +321.3	(b) (b) (b) (b) (b) (b) (b) (b) (b) (b)
Arylamino groups in trimethoprim, free and enzyme-bound	in H_2O	+290 to +295	(x)
			(y)

R^1	R^2			
H	H	in DMSO		+297.6
H	$CH_2CH_2NHCH_2CH_2OH$	in DMSO		+291.8 (arylamine)
OH	$CH_2CH_2NEt_2$	in $CDCl_3$		+287.9 (arylamine)
OH	$CH_2CH_2NHCH_2CH_2OH$	in $CDCl_3$		+287.9 (arylamine)
H	Ph	in DMSO,	+27°C	+278.3
			+97°C	+278.6
		in $CDCl_3$,	−33°C	+277.1
			+27°C	+278.4
OH	Ph	in DMSO,	+27°C	+272.7
			+97°C	+272.9
		in $CDCl_3$,	+27°C	+274.5
			+57°C	+275.2

NH groups in polyaniline	solid state	+302 to +294	(z)

(a) Data from ref. 775, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; originally reported vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane (actually, the latter value was measured under conditions where the field was perpendicular to sample tube, Table 2). The corresponding lithium derivatives, —NHLi, are presented in Table 6.

Table 7. *—contd.*

(b) Data from ref. 131, 25.34 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to liquid ammonia via a calibrated sample of HNO_3, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(c) Data from ref. 711, details as in footnote (e).

(d) Data from ref. 1054, *ca.* 2 M solutions, 9.04 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to aqueous NH_4NO_3 and converted to liquid NH_3 standard taken at +380.2 ppm fron neat nitromethane, conversion scheme IVa (Table 1).

(e) Data from ref. 1055, 1.7 M solutions, 10.1 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat formamide, +267.8 ppm from neat nitromethane (uncorrected, see Table 2), conversion scheme IVa (Table 1).

(f) Data from ref. 693, 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to saturated aqueous $NaNO_3$, +3.7 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); originally reported vs fictitious ammonia standard taken at +376.5 ppm from the reference employed or +380.2 ppm from neat nitromethane, see comments in footnote (a); we retrieved the original data and converted them as indicated above.

(g) Data from ref. 1056, details as in footnote (d).

(h) See ref. 5, p. 311, and references therein.

(i) Data from ref. 1057, 50.7 MHz ^{15}N solution spectra, field parallel to sample tube, and 20.3 MHz ^{15}N CPMAS spectra, referenced to liquid NH_3, +381.9 ppm fron neat nitromethane (Table 2), conversion scheme II (Table 1).

(j) Data from ref. 1058, see Table 17, footnote (x).

(k) Data from ref. 805, see Table 17, footnote (dd).

(l) Data from ref. 1059, see Table 17, footnote (cc).

(m) Data from ref. 1060, see Table 17, footnote (T).

(n) Data from ref. 1061, see Table 20, footnote (b).

(o) Data from ref. 1062, ^{15}N-labelled amino group, 10.09 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(p) Data from ref. 360, details as in footnote (o).

(q) Data from ref. 1051, 10.14 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(r) Data from ref. 142, 20.28 MHz ^{15}N INEPT spectra, other details as in footnote (a).

(s) Data from ref. 904, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane via a calibrated sample of aqueous KNO_3, uncorrected for bulk susceptibility effects; reported originally vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane, see comments in footnote (a).

(t) Data from ref. 356, 50.7 MHz solution ^{15}N spectra, field parallel to sample tube, and 27.3 MHz ^{15}N CPMAS spectra, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; the genenion in the case of the cation was the tetrazolate anion.

(u) Data from ref. 1034, 30.5 MHz ^{15}N spectra, field parallel to sample tube, calibration as in footnote (q), conversion scheme IIb (Table 1).

(v) Data from ref. 1063, 36.51 MHz proton-coupled ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(w) Data from ref. 1064, details as in footnote (v).

(x) Data from ref. 94, see Table 19, footnote (w).

(y) Data from ref. 783, ^{15}N-labelled arylamino group, details as in footnote (o).

(z) Data from ref. 376, see Table 24, footnote (w).

Table 8. Nitrogen shieldings in hydroxylamines, hydrazines, hydrazides and related structures

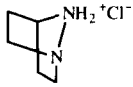
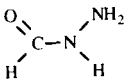
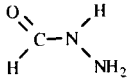
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitomethane	Notes
Hydroxylamines			
NH_2OH	aqueous	+271 to +274	(a)
NH_3^+OH	aqueous	+294 to +296	(a)
NH_2O^-	aqueous	*ca.* +284	(a)
R_2N—OR (R = alkyl, aryl)	various	+194 to +241	(a)
Me_3Si—NHOSiMe_3	in C_6D_6	+255.6	(b)
Hydrazines			
H_2N—NH_2	various	+331 to +335	(c)
R_2N—NR_2 (R = alkyl)	various	+285 to +328	(c)
$PhNHNH_2$	various	*ca.* +295 (NH)	(c)
		ca. +320 (NH_2)	(c)
$(Me_3Sn)_2N$—$N(SnMe_3)_2$	in benzene	+316.6	(d)
$(Me_3Sn)_2N$—NMe_2	in benzene	+304.1 (NSn)	(d)
		+282.9 (NMe)	(d)
$Me_3SnN(Me)$—$N(Me)SnMe_3$	in benzene	+308.0	(d)
$(Me_3Sn)_2N$—$N(Me)SnMe_3$	in benzene	+293.5 (NMe)	(d)
		+317.2 (NSn_2)	(d)
$(Me_3Sn)_2N$—$N(Ph)SnMe_3$	in benzene	+266.7 (NPh)	(d)
		+313.4 (NSn_2)	(d)
$(Me_3Sn)_2N$—NHPh	in benzene	+270.7 (NHPh)	(d)
Me_3SnNH—$N(Ph)SnMe_3$	in benzene	+309.3 (NH)	(d)
	in D_2O	+257.2 (NH_2)	(e)
		+276.0 (N)	(e)
	in $CDCl_3$ + $Cr(acac)_3$	+198.0 (NCl)	(e)
		+241.5 (N)	(e)
Hydrazides			
	in DMSO (*Z*-isomer)	+244.7 (NH)	(f)
		+329.5 (NH_2)	(f)
	in DMSO (*E*-isomer)	+247.9 (NH)	(f)
		+326.2 (NH_2)	(f)

Table 8. —*contd.*

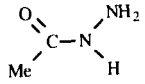
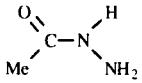
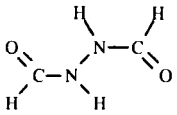
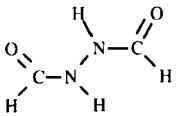
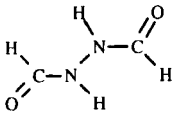
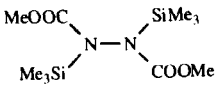
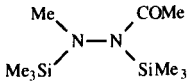
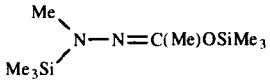
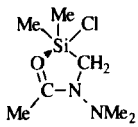
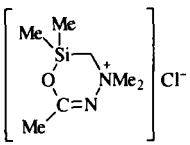
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitomethane	Notes
	in DMSO (*Z*-isomer)	+248.7 (NH) +326.4 (NH_2)	(f) (f)
	in DMSO (*E*-isomer)	+250.9 (NH) +320.6 (NH_2)	(f) (f)
	in DMSO (*Z*,*Z*-isomer)	+250.9	(f)
	in DMSO (*Z*,*E*-isomer)	+249.6 (HN) +252.1 (NH)	(f) (f)
	in DMSO (*E*,*E*-isomer)	+247.9	(f)
$CF_3CONHNH_2$	in DMSO	+243.8 (NH) +323.5 (NH_2)	(f) (f)
$CF_3CONHNHCOCF_3$	in DMSO	+256.0	(f)
$[CF_3CONH—NCOCF_3]^-$ $[H_3NNH_2]^+$	in DMSO	+205.3, +331.6	(f)
MeCONHNHCOMe	in DMSO	+251.5 (*Z*,*Z*-isomer) +247.4, +251.1 (*E*,*Z*-isomer) +245.4 (*E*,*E*-isomer)	(f) (f) (f)
	in $CDCl_3$, +50°C	+250.4	(g)
MeOOCNHNHCOOMe	in $CDCl_3$	+278.3	(g)
	in $CDCl_3$	+258.0 (*Z*,*Z* or *E*,*E*) +257.2, +255.6 (*E*,*Z*) +254.9 (*E*,*E* or *Z*,*Z*)	(g) (g) (g)

Table 8. —*contd.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitomethane	Notes
$Me_3SiO(Me)C{=}N{-}N{=}C(Me)OSiMe_3$			
	in CH_2Cl_2, +1°C	+92.8	(g)
	in $CDCl_3$	+91.7	(g)
			
	0.02 M in CH_2Cl_2		(h)
		+241.0 (NCO)	
		+348.2 (NSi)	
		+289.0 (NSi)	
		+87.6 (N=C)	
$Me_2N{-}N{=}C(Me)OSiMe_3$	0.02 M in CH_2Cl_2		(h)
	syn-isomer	+93.7 (N=C)	
	anti-isomer	+81.5 (N=C)	
		+302.9 (NMe_2)	
$H_2NCSNHNH_2$	in DMSO	+316.8 (NH_2)	(i)
		+278.5 ($C{-}NH_2$)	(i)
		+256.6 (NH)	(i)
$H_2NCSNHNHCSNH_2$	in DMSO	+251.6 (NH)	(i)
		+273.2 (NH_2)	(i)
	in CD_2Cl_2	+209.9 (N—CO)	(j)
	in CD_2Cl_2	+114.4 (N=CO)	(j)

Hydrazido complexes

		N_α	N_β	
trans-$[MoF(N_2H_2)(dppe)_2]BF_4$	in DMF	+75.7	+233.3	(k)
trans-$[MoBr(N_2H_2)(dppe)_2]Br$	in DMF	+75.1	+231.5	(k)
trans-$[MoI(N_2H_2)(dppe)_2]I$	in DMF	+76.4	+233.7	(k)

Table 8. *—contd.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitomethane		Notes
trans-[$MoHSO_4(N_2H_2)(dppe)_2$]HSO_4	in DMF	+45.2 +54.1	+215.6 +224.6	(k)
	in MeOH			
	291 K	+55.8	+229.0	(k)
	270 K	+55.9	+229.8	(k)
trans-[$MoBr(N_2HMe)(dppe)_2$]Br	in DMF	+69.2	+227.7	(k)
trans-[$MoBr(N_2HEt)(dppe)_2$]Br	in DMF	+71.8	+215.3	(k)
	in THF	?	+209.6	(k)
trans-[MoBr(NN )$(dppe)_2$]Br	in CH_2Cl_2	+64.3	+208.8	(k)
[$MoCl_2(N_2H_2)(PMe_2Ph)_3$]	in DMF	+67.9	+236.2	(k)
[$MoI_2(N_2H_2)(PMe_2Ph)_3$]	in DMF	?	+221.3	(k)
	in THF	+68.8	+244.9	(k)
trans-[$WF(N_2H_2)(dppe)_2$]BF_4	in DMF	+95.6	+247.5	(k)
trans-[$WCl(N_2H_2)(dppe)_2$]Cl	in DMF	+96.2	+245.0	(k)
trans-[$WBr(N_2H_2)(dppe)_2$]Br	in DMF	+96.5	+246.1	(k)
trans-[$WI(N_2H_2)(dppe)_2$]I	in DMF	+97.8	+248.3	(k)
trans-[$WHSO_4(N_2H_2)(dppe)_2$]HSO_4	in DMF	+80.2	+242.3	(k)
trans-[$W(PrCN)(N_2H_2)(dppe)_2$]$[HSO_4]_2$	in MeOH	+63.2	+229.8	(k)
trans-[$WBr(N_2HMe)(dppe)_2$]Br	in DMF	+88.7	+243.4	(k)
trans-[$WBr(N_2HEt)(dppe)_2$]Br	in DMF	+90.1	+228.8	(k)
	in THF	+92.6	+230.2	(k)
trans-[WBr(NN )$(dppe)_2$]Br	in THF	+81.1	+222.3	(k)
[$WCl_2(N_2H_2)(PMe_2Ph)_3$]	in DMF	+86.2	+249.5	(k)
[$WI_2(N_2H_2)(PMe_2Ph)_3$]	in DMF	+87.4	+243.1	(k)

(a) See ref. 5, p. 312, and references therein.

(b) Data from refs 150 and 899, 36.5 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) See ref. 5, p. 316, and references therein.

(d) Data from refs. 833 and 931, 30.4 MHz and 20.3 MHz ^{15}N INEPT spectra (via $^3J_{NSnCH}$ = 1.5 Hz or $^2J_{NCH}$ = 2 Hz), field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; 40% to 60% solutions in C_6D_6.

(e) Data from ref. 1031, 40.55 MHz ^{15}N spectra, reference as in footnote (d).

(f) Data from ref. 203, 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported vs fictitious

Table 8. —*cont.*

ammonia standard, taken at +380.2 ppm from nitromethane (the latter value was actually obtained for a field which was perpendicular to sample tube, see Table 1).

(g) Data from ref. 750, ^{15}N-labelled samples, 20.24 MHz ^{15}N spectra, field parallel to sample tube, referencing method as in footnote (d).

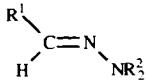
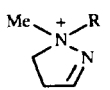
(h) Data from ref. 141, ^{15}N-labelled and unlabelled samples, 9.1 MHz ^{15}N INEPT spectra, field perpendicular to sample tube, referencing as in footnote (d).

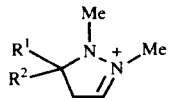
(i) Data from ref. 760, 20.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(j) Data from ref. 133, 9.1 MHz ^{15}N INEPT spectra, field perpendicular to sample tube, referencing as in footnote (d).

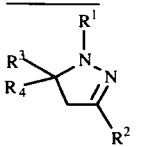
(k) Data from ref. 745, ^{15}N-labelled ligand, 18.24 MHz ^{15}N spectra, field parallel to sample tube, reference as in footnote (d); DMF = dimethylformamide, THF = tetrahydrofuran, dppe = $Ph_2PCH_2CH_2PPh_2$.

Table 9. Nitrogen shieldings in some hydrazones and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
Non-tautomeric hydrazones and related ions				
	in $CDCl_3$			(a)
R^1	R^2_2	(=N—)	(NR_2)	
5-NO_2-2-furyl	Me_2	+19.7	+261.6	
4-NO_2-phenyl	Me_2	+21.3	+268.5	
4-Cl-phenyl	Me_2	+30.3	+276.0	
Ph	Me_2	+30.5	+276.9	
4-OMe-phenyl	Me_2	+36.9	+279.0	
5-NO_2-2-furyl	—$(CH_2)_4$—	+26.6	+234.5	
4-NO_2-phenyl	—$(CH_2)_4$—	+27.9	+242.1	
4-Cl-phenyl	—$(CH_2)_4$—	+35.8	+251.0	
Ph	—$(CH_2)_4$—	+36.5	+252.1	
Me	—$(CH_2)_4$—	+38.2	+257.5	
Ph	—$(CH_2)_5$—	+36.0	+251.0	
Ph	—$(CH_2)_6$—	+33.2	+255.0	
Ph	(cyclohexyl)$_2$	+43.5	+237.4	
				(b)
R = Me	in DMSO	+46.6	+252.1	
	in CF_3COOH	+49.0	+254.3	
R = Ph	in DMSO	+48.9	+239.0	

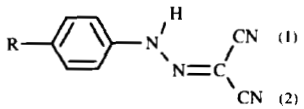
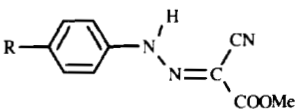


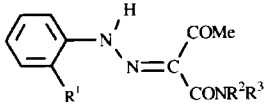
R^1	R^2			
H	H	in DMSO	+151.5	+244.3
Me	Me	in DMSO	+153.2	+232.2
		in CF_3COOH	+153.6	+232.7
H	Ph	in DMSO	+153.7	+233.1



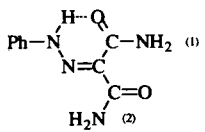
R^1	R^2	R^3	R^4			
H	H	H	H	neat liquid	+34.6	+251.5
				in CF_3COOH	+67.8	+269.6
H	Me	H	H	neat liquid	+49.6	+255.0
				in CF_3COOH	+80.3	+270.6
H	Me	Me	Me	neat liquid	+48.9	+228.2
				in CF_3COOH	+80.7	+253.1
H	Me	H	Ph	neat liquid	+49.6	+242.2
				in CF_3COOH	+81.4	+257.8
Me	H	H	H	neat liquid	+24.8	+250.9
				in CF_3COOH	+48.2	+263.9
Me	Me	H	H	neat liquid	+32.2	+254.8
				in CF_3COOH	+63.2	+264.1
Me	Me	Me	Me	neat liquid	+34.8	+228.5
				in CF_3COOH	+62.2	+247.1
Me	Me	H	Ph	neat liquid	+33.8	+244.6
				in CF_3COOH	+62.7	+254.2
Ph	Me	H	H	neat liquid	+57.2	+231.6
				in CF_3COOH	+79.6	+248.6

Table 9. *—cont.*

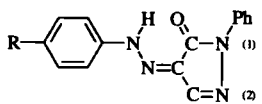
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
	in DMSO					(c)
R		(=N—)	(NH)	(1-CN)	(2-CN)	
H		+2.2	+192.2	+118.9	+98.2	
F		+2.8	+194.4	+119.0	+98.2	
NO_2		+3.6	+194.5	+118.5	+99.0	
	in DMSO					(c)
R		(=N—)	(NH)	(CN)		
H	*E*-isomer	+4.5	+204.5	+99.8		
	Z-isomer	+8.1	+200.6	+122.6		
F	*E*-isomer	+4.5	+205.0	+100.1		
	Z-isomer	+8.0	+202.4	+122.9		
NO_2	*E*-isomer	+7.4	+206.4	+98.2		
	Z-isomer	+11.0	+203.0	?		



R^1	R^2	R^3		(=N—)	(NH)	(CONR)	
H	H	H	in DMSO	+2.4	+204.6	+270.3	
			in $CDCl_3$	−1.0	+201.6	+274.5	
H	Ph	H	in $CDCl_3$	−0.4	+201.3	+245.6	
H	Me	Me	in $CDCl_3$	+27.6	+224.9	?	
H	Ph	Me	in $CDCl_3$	+30.1	+227.2	?	
OH	Ph	H	in DMSO	+4.1	+206.7	+246.0	



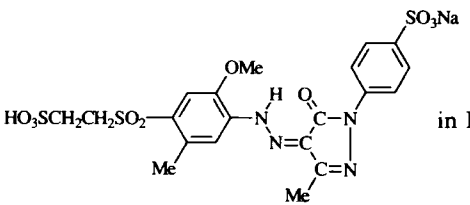
in DMSO	+20.3 (=N)	(d)
	+213.7 (NH)	(d)
	+269.1 (1-N)	(d)
	+281.0 (2-N)	(d)



R		(=N—)	(NH)	(1-N)	(2-N)	
NH_2	in $CDCl_3$	+17.4	+199.9	+191.3	+80.2	(e)
OMe	in $CDCl_3$	+19.0	+204.4	+192.4	+79.2	(e)
			+203.6			

Table 9. *—cont.*

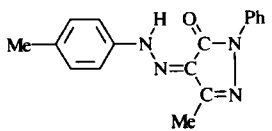
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
Me	in $CDCl_3$	+19.8	+205.8 +204.5	+192.9	+78.1	(e)
H	in DMSO, 300 K	+18.6	+202.8	–	–	(f)
	in DMSO, 330 K	+16.5	+202.2	–	–	(f)
	in pyridine, 300 K	+21.8	+208.3	–	–	(f)
	in pyridine, 330 K	+19.4	+206.4	–	–	(f)
	solid state, 305 K	+25.5	+211.4	–	–	(g)
	solid state, 358 K	+25.4	+211.3	–	–	(g)
	in $CDCl_3$	+18.9 +17.4	+206.4 +205.4	+192.4 +191.5	+76.1 +75.3	(e)
F	in $CDCl_3$	+19.8	+208.6 +207.6	+192.1	+75.8	(e)
Cl	in $CDCl_3$	+20.8	+209.4 +208.7	+192.3	+74.2	(e)
Br	in $CDCl_3$	+20.8	+209.3 +208.2	+192.5	+74.7	(e)
I	in $CDCl_3$	+21.3	+209.2 +208.6	+192.1	+73.9	(e)
MeCOO	in $CDCl_3$	+22.7	+210.8 +209.8	+192.9	+72.3	(e)
CF_3	in $CDCl_3$	+22.2	+212.1 +210.9	+192.8	+72.1	(e)
NO_2	in $CDCl_3$	+22.7 +22.4	+213.2 +212.9	+191.9	+67.4	(e)



in DMSO

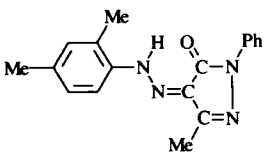
+24.7 (=N, hydrazone)
+216.8 (NH)

(m)



in $CDCl_3$

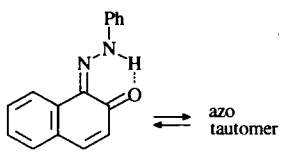
+19.6 (=N, hydrazone) (n)
+206.0 (NH) (n)
+193.3 (NPh) (n)
+78.7 (=N, ring) (n)



in $CDCl_3$

+19.4 (=N, hydrazone) (n)
+205.7 (NH) (n)
+193.0 (NPh) (n)
+79.2 (=N, ring) (n)

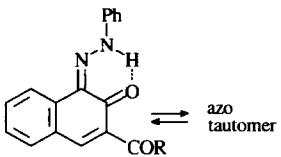
Hydrazones involved in azo–hydrazone tautomerism (see also Table 28)



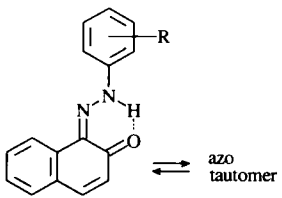
solid

	(=N—)	(NH)	
−79°C (88% NH)	+4.5	+174.4	(g)
	+8.8	+178.7	
−70°C (87% NH)	+3.1	+172.4	
	+7.6	+177.1	
−30°C (83% NH)	−3.0	+161.4	
	+1.5	+166.7	

Table 9. —*cont.*

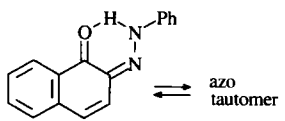
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	+33°C (76% NH)	−11.7	+144.9	
		−7.8	+150.7	
	+85°C (73% NH)	−18.5	+132.5	
		−15.1	+138.2	
	solid state and solution			(h)
R				
OH (*ca.* 97% NH)	solid		+179.3	
	$CDCl_3$, +27°C	−16.6	+173.8	
	+57°C	−16.5		
	benzene, +27°C	−16.2	+178.0	
	CD_3NO_2, +27°C	−16.3		
OMe (*ca.* 70% NH)	solid		+129.7, +148.3	
	$CDCl_3$, +27°C	−16.9	+140.5	
	+57°C	−16.7	+131.4	
	benzene, +27°C	−16.8	+112.5	
	+57°C	−16.5	+101.9	
	CCl_4, +27°C	−16.6		

NHPh (*ca.* 97% NH)	solid		+188.4	
	$CDCl_3$, +27°C	−16.8	+178.1	
	+57°C	−16.8	+175.9	
	benzene, +27°C	−16.5	+180.5	
	+57°C	−16.5	−176.2	
	CCl_4, +27°C	−16.9		



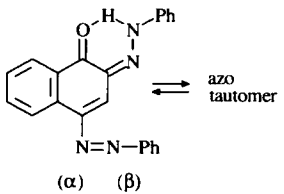
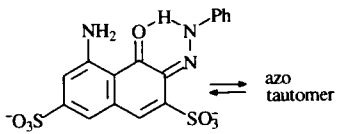
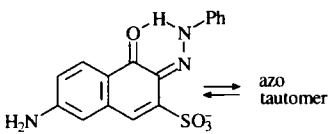
in $CDCl_3$

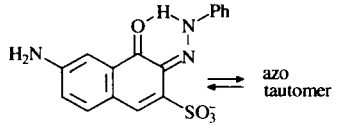
R				
2,4,6-Me_3		−38.6 to −65.7	+111.0 to +121.6	(i)
2,4-Et_2		−30.3 to −36.9	+140.6 to +126.3	(i)
2,4-*i*-Pr_2		−28.6	?	(i)
4-F	(*ca.* 50% NH)	−47.0	+78.7	(j)



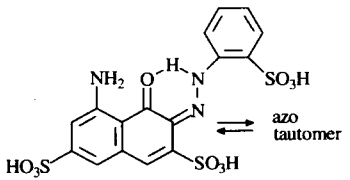
in $CDCl_3$			(k)
+57°C	−22.2	+137.4 (74% NH)	
+27°C	−16.3	+148.1 (78% NH)	
−3°C	−11.5	+157.1 (81% NH)	
+27°C	−4.8	+169.2 (85% NH)	

Table 9. —*cont.*

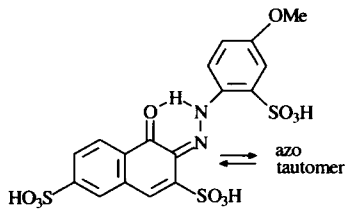
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 (α) (β)	in $CDCl_3$		(k)
	+57°C	−30.7 +126.0 (69.4% NH) (−121.6 N-α,β)	
	+27°C	−26.5 +139.1 (72% NH) (−120.1 N-α,β)	
	−3°C	−21.9 +143.3 (75% NH) (−119.5 N-α,β)	
	+27°C	−15.9 +154.8 (79% NH) (−118.8 N-α,β)	
			(l)
	in DMSO, +27°C	+7.6 +200.6 (96% NH)	
	+87°C	+5.3 +199.3 (95% NH)	
			(l)
	in DMSO, +27°C	−4.6 +184.4 (88% NH)	
	+87°C	−7.7 +180.4 (87% NH)	



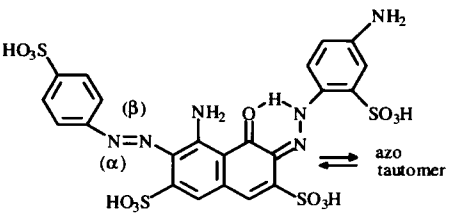
in DMSO,	+27°C	−10.2	+174.7 (85% NH)	(l)
	+87°C	−17.9	+163.4 (80% NH)	



in DMSO		−15.1	+202.8

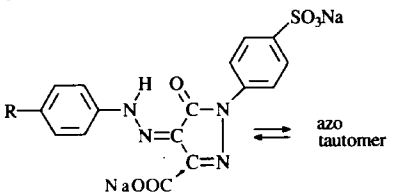


in DMSO		+3.2	+194.1



in DMSO		+4.4	+195.2	(m)
		−138.8 (N-α)		
		−83.2 (N-β)		

Table 9. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
				
R		(=N—)	(NH)	
H	H_2O, pH = 7	+15.2	+172.9	
	pH = 12	−93.0	−48.9	
SO_3Na	H_2O, pH = 12	−93.5	−36.5	

(a) Data from ref. 828, 30.4 MHz ^{15}N INEPT spectra (via ^2J(NH) of *ca.* 7 Hz), field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(b) Data from ref. 142, 20.3 MHz ^{15}N INEPT spectra, other details as in footnote (a).

(c) Data from ref. 855, ^{15}N-labelled and unlabelled samples, 10.095 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(d) Data from refs. 721 and 727, details as in footnote (c).

(e) Data from ref. 724, details as in footnote (c); the data set in *italics* were obtained without the use of $Cr(acac)_3$.

(f) Data from ref. 727, ^{15}N-labelled hydrazone moiety, no relaxation reagent used, other details as in footnote (c).

(g) Data from ref. 412, 20.28 MHz ^{15}N CPMAS spectra, originally referenced to solid NH_4Cl, taken at +352.5 ppm from neat nitromethane, this is erroneous, since the resonance of solid ammonium chloride lies at +341.0 ppm (uncorrected) from neat nitromethane, see ref. 5, p. 224, and references therein; we used the latter value in recalculations.

(h) Data from ref. 726, ^{15}N-labelled and unlabelled samples, 10.095 MHz solution ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; 20.28 MHz ^{15}N CPMAS spectra of solids, referenced originally to solid NH_4Cl, taken at +352.5 ppm from neat nitromethane, and reported vs the latter standard; this is erroneous, as shown in footnote (g), and we recalculated the data for solids according to footnote (g).

(i) Data from ref. 1065, ^{15}N-labelled and unlabelled samples, 40.55 MHz ^{15}N conventional PFT and INEPT spectra, field parallel to sample tube, referenced originally to neat formamide, +268.6 ppm from neat nitromethane (Table 2), conversion scheme IVb (Table 1); originally reported to a fictitious ammonia reference, taken at +112.4 ppm from formamide; this is erroneous, since the latter value refers to a field which is perpendicular to sample tube; we retrieved the original values and performed the recalculation as above.

(j) Data from ref. 728, 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(k) Data from ref. 720, details as in footnote (c).

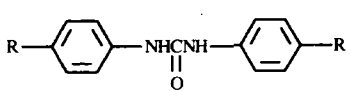
(l) Data from ref. 723, details as in footnote (c).

(m) Data from ref. 725, 27.2 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 50% nitromethane in DMSO, about −1.0 ppm from neat nitromethane (see Table 26), conversion scheme IIb (Table 1).

(n) Data from ref. 548, 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(o) Data from ref. 729, 40.6 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

Table 10. Nitrogen shieldings in ureas, thioureas, guanidines, amidines, amidoximes and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$H_2N-\underset{\underset{O}{\|}}{C}-NH_2$ (urea)	20% in DMSO	+302.5	(a)
	solid	+302.3	(b)
$H_2NCNHCH_2NHCNH_2$ (O, O)	20% in DMSO	+303.9 (NH_2)	(a)
		+284.9 (NH)	(a)
	solid	+304.1 (NH_2)	(b)
		+285.8 (NH)	(b)
$H_2NCNHCH_2OH$ (O)	20% in DMSO	+302.8 (NH_2)	(a)
		+277.7 (NH)	(a)
$HOCH_2NHCNHCH_2OH$ (O)	20% in DMSO	+277.9	(a)
	solid	+280.3	(b)
$HOCH_2NHCN(CH_2OH)_2$ (O)	20% in DMSO	+256.5 (N)	(a)
$MeOCH_2NHCNHCH_2OMe$ (O)	solid	+288.2	(b)
			
R = H	in DMSO	+276	(c)
	solid state	+276	(c)

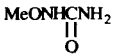
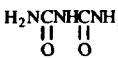
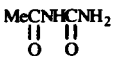
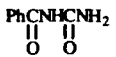
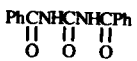
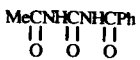
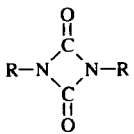
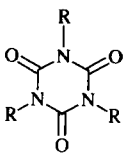
R = Me	in DMSO	+275	(c)
	in H_2O	+214.8 (NH)	(d)
 (biuret)	in H_2O	+260.9 (NH)	(d)
	in DMSO	+292.6 (NH_2) +230.7 (NH)	(e) (e)
	in DMSO	+291.2 (NH_2) +237.6 (NH)	(e) (e)
			
R = Ph	in acetone	+266 (NH) +239 (N)	(c) (c)
R = *p*-tolyl	in acetone	+268 (NH) +239 (N)	(c) (c)
	in DMSO	+230.5	(e)
	in DMSO	+237.3	(e)
	in DMSO	+239.8 (NHCOPh) +228.2 (NHCOMe)	(e) (e)

Table 10. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Urea moieties in melamine-formaldehyde adducts	in DMSO		(f)
$H_2NCONH-$ (chain end)		+303.3 (NH_2)	
		+278.3 (NH)	
$-NHCONHCH_2NHCONH-$		+284.5 ($NHCH_2$)	
$-NHCH_2NH-$ (within chains)		+285.1	
$-NHCH_2-O-CH_2NH$		+285.5	
			
R = Ph	in benzene	+237	(c)
R = *p*-tolyl	in benzene	+237	(c)
	solid state	+237	(c)
 (isocyanurates)			
R = Ph	in acetone	+233	(c)
	in acetone	+233	(c)
R = *p*-tolyl	solid state	+233	(c)

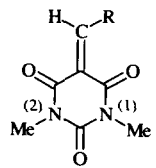
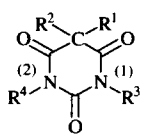
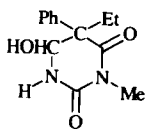
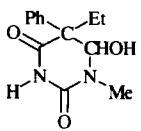
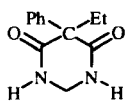
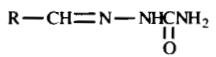
Poly(isocyanurate) resins	solid state		(c)
isocyanurate moieties		+232	
urea and biuret moieties		+262 to +283	
isocyanate moieties (see Table 15)		+336	
Biuret resins from 4,4′-methylene-bis(PhNCO)	solid state		(c)
imide nitogens (?)		+218	
biuret moieties		+272 (terminal N)	
		+245 (central N)	
urea moieties		+282	
isocyanate moieties (see Table 15)		+340	
	0.8–2.0 M in $CDCl_3$		(g)
R = Ph		+235.1 (N-1)	
		+237.2 (N-2)	
R = *p*-Cl-phenyl		+234.8 (N-1)	
		+237.0 (N-2)	
R = *p*-Br-phenyl		+234.4 (N-1)	
		+236.6 (N-2)	
	in DMSO		(h)

Table 10. *—cont.*

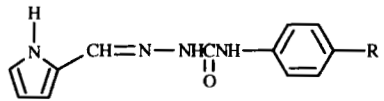
Compound				Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
R^1	R^2	R^3	R^4			
Ph	Et	H	H		+226.1	
Ph	Et	Me	H		+231.0 (N-1) +226.7 (N-2)	
Ph	Et	Me	Me		+231.2	
$PhCH_2CH_2$	H	Me	Me		+232.6	
$CH_2{=}CHCH_2$	$MeCH(OH)CH_2$	H	H		+225.7, +227.7	
$CH_2{=}CHCH_2$	$MeCH(OH)CH_2$	Me	H		+232.8 (N-1) +225.7 (N-2)	
$CH_2{=}CHCH_2$ (other diastereomer)	$MeCH(OH)CH_2$	Me	H		+230.9 (N-1) +227.7 (N-2)	
				in DMSO	+236.0 (NMe) +270.1 (NH)	(h)
				in DMSO	+279.2 (NMe) +231.3	(h)
				in DMSO	+263.9	(h)



in DMSO

(i)

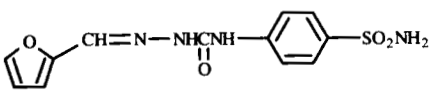
R	N-*N*H	NH_2	=N
2-furyl	+227.6	+307.1	+80.6
2-(2-furyl)-ethyl	+215.8	+307.0	+71.4



in DMSO

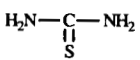
(i)

R	N-*N*H	NHPh	ring NH
H	+233.8	+279.9	+231.4
OMe	+232.4	+282.8	+231.8
Cl	+232.3	+280.7	+231.2



+277.5 (NHPh) (i)
+226.8 (NH) (i)

in DMSO



(thiourea)

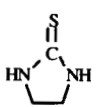
various

+219 to +237

(j)

in DMSO

+250.2 (NHPh) (k)
+269.2 (NH_2) (k)



in H_2O/D_2O

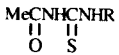
+266

(l)

Table 10. *—cont.*

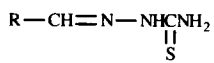
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$H_2NC(=S)NHNH_2$	in DMSO	+278.5 ($C\text{-}NH_2$) +256.6 (NH) +316.8 ($N\text{-}NH_2$)	(m) (m) (m)
$H_2NC(=S)NHNHC(=S)NH_2$	in DMSO	+273.2 (NH_2) +251.6 (NH)	(m) (m)
$MeC(=O)NHC(=S)NH_2$	in DMSO	+254.3 (NH_2) +217.5 (NH)	(n) (n)
$PhC(=O)NHC(=S)NH_2$	in DMSO	+253.1 (NH_2) +244.0 (NH)	(n) (n)
$MeC(=O)NHC(=S)NHC(=O)Me$	in DMSO	+210.7	(n)
$PhC(=O)NHC(=S)NHC(=O)Ph$	in DMSO	+216.9	(n)
$MeC(=O)NHC(=S)NHC(=O)Ph$	in DMSO	+207.6 (NHCOMe) +221.2 (NHCOPh)	(n) (n)
$MeC(=O)NRC(=S)NH_2$	in DMSO		(o)

R	NR	NH_2
p-nitrophenyl	+205.5	+243.9
p-chlorophenyl	+206.4	+247.0
phenyl	+203.5	+246.3
p-NMe_2-phenyl	+204.8	+247.6



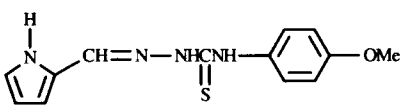
in DMSO (o)

R	NH	NHR
p-nitrophenyl	+213.3	+235.3
p-chlorophenyl	+214.6	+237.0
phenyl	+214.8	+235.3
p-NMe_2-phenyl	+215.7	+235.7



in DMSO (p)

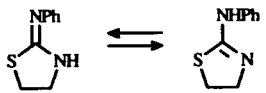
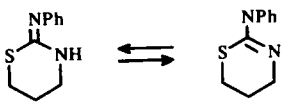
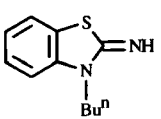
R	N-*N*H	NH_2	=N
2-furyl	+211.0	+274.9	+69.6
2-thiophyl	+212.0	+274.0	?
2-pyrrolyl	+213.7	+275.1	+73.8



in DMSO

+257.8 (NHPh) (p)
+212.2 (NH) (p)
+75.0 (=N) (p)
+232.0 (pyrrole) (p)

Table 10. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in DMSO	+278.5 (C-NH_2) +316.8 (N-NH_2) +256.6 (NH)	(q) (q) (q)
	in DMSO	+272.3 (NH_2) +251.6 (NH)	(q) (q)
	in $CDCl_3$	+206.0 (NPh) +242.5 (ring N)	(r) (r)
	in $CDCl_3$	+182.6 (NPh) +253.9 (ring N)	(r) (r)
	in $CDCl_3$	+307.6 (NBu^n) +193.2 (=NH)	(s) (s)

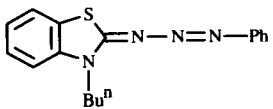
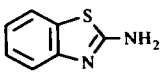
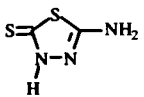
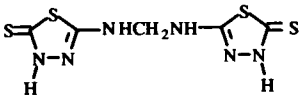
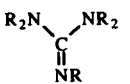
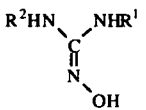
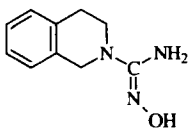
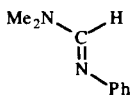
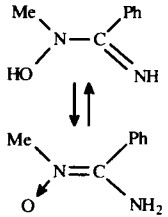
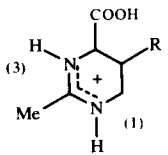
	in acetone	+242.7 (NBu^n)	(s)
	in DMSO	+301.5 (NH_2) +143.0 (=N)	(s) (s)
	in DMSO	+167.4 (NH) +117.4 (=N) +315.6 (NH_2)	(t) (t) (t)
	in DMSO	+167.9 (N*N*H) +116.2 (=N) +299.3 (CH_2NH)	(t) (t) (t)
 (guanidines)	various	+175 to +221 (=NR) +312 to +354 (NR_2)	(u) (u)
Guanidinium ions	various	+265 to +308	(u)
	in DMSO		(v)

Table 10. —*cont.*

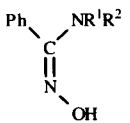
Compound		Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
R^1	R^2		NR^1	NR^2	=N	
H	$Bu^tCH_2CMe_2$— its hydrochloride		+323.5	+296.0	+133.5	
			+303.1	+279.3	+243.4	
H	Bu^t		+322.6	+295.1	+131.8	
Ph	Ph		+295.6	+290.0	+106.7	
		in DMSO	NH_2	N	=N	(v)
		parent compound	+323.0	+319.9	+125.8	
		hydrochloride	+302.8	+297.7	+237.6	
			NH_2	=N	NO_2	(w)
$(NH_2)_2C{=}N{-}NO_2$		solid	+294	+144	+11	
		in DMSO	+297	+139	+10	
		in DMF, −47°C	+301	+141	+11	
			NMe_2	=NPh		(x)
		neat liquid	+299.4	+147.3		
		in cyclohexane	+304.3	+147.4		
		in acetone	+301.4	+151.2		
		in chloroform	+301.7	+153.5		
		in MeOH	+298.4	+163.1		
		in EtOH	+298.4	+165.0		
(amidine structure)		in CF_3COOH	+293.1	?		



in DMSO	+294.7 (N—H)	(y)
	+183.3 (N—O)	(y)
in aqueous HCl	+270.1 (N—H)	(y)
(protonated form)	+216.8 (N—O)	(y)



in aqueous KCl, extract of metabolites from bacteria cultures		(z)
R = H	+268.5 (N-1)	
	+274.0 (N-3)	
R = OH	+265.1 (N-1)	
	+269.7 (N-3)	



in DMSO (A)

R^1	R^2	NR^1R^2	=NOH
H	H (*Z*-isomer)	+317.0	+92.4
its hydrochloride		+278.3	+211.6
H	H (*p*-nitro, *Z*-isomer)	+316.4	+84.4
Ph	H (*Z*-isomer)	+287.4	+71.5
its hydrochloride		+262.2	+192.2
Me	H (*Z*-isomer)	+304.3	+91.2
—$(CH_2)_5$—	(*Z*-isomer)	+308.8	+71.1
	(*E*-isomer)	+301.5	+75.2
Me	Me (*E*-isomer)	+324.6	+78.1
Ph	Me (*E*, *Z*-isomers)	+303.1	+36.5

Table 10. —*cont.*

(a) Data from ref. 1066, 10.09 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to NH_4^+ of NH_4NO_3 in DMSO, +388.1 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(b) Data from ref. 440, 20.3 MHz CPMAS ^{15}N spectra, ^{15}N-labelled and unlabelled samples, referenced to liquid ammonia, +381.9 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(c) Data from refs 441 and 1057, 20.3 MHz ^{15}N CPMAS spectra, and 50.7 MHz ^{15}N solution spectra, referenced originally to liquid NH_3, +381.9 ppm fron neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(d) Data from ref. 515, 25.34 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(e) Data from ref. 777, saturated solutions, 10.09 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(f) See footnote (a).

(g) Data from ref. 1026, 25.36 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effect.

(h) Data from ref. 753, 10.095 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to nitromethane containing some $Cr(acac)_3$ as a relaxation reagent and originally corrected for the presence of the latter vs neat nitromethane, uncorrected for bulk susceptibility effects, samples doped with $Cr(acac)_3$.

(i) Data from ref. 1067, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(j) See ref. 5, p. 356, and references therein.

(k) Data from ref. 730, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(l) Data from ref. 1068, 18.059 MHz ^{14}N spectrum, other details as in footnote (d).

(m) Data from ref. 760, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, +6.2 ppm fron neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(n) See footnote (e).

(o) Data from ref. 822, details as in footnote (e).

(p) See footnote (i).

(q) Data from ref. 760, details as in footnote (m).

(r) Data from ref. 851, 10.09 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to aqueous KNO_3 and recalculated to neat nitromethane, uncorrected for bulk susceptibilty effects, 0.5–1.0 M solutions.

(s) See footnote (k).

(t) See footnote (m).

(u) See ref. 5, pp. 322–327, and references therein.

(v) Data from ref. 755, 10.09 MHz ^{15}N spectra, proton-coupled, field perpendicular to sample tube, referenced originally to ammonium nitrate but reported vs liquid ammonia, +380.2 ppm from neat nitromethane, conversion scheme IVa (Table 1); assignments are based on ^{1}H–^{15}N splitting patterns.

(w) Data from ref. 414, ^{15}N-labelled compound, 20.3 MHz ^{15}N CPMAS and solution spectra, field parallel to sample tube for the latter, referenced originally to NO_3^- in aqueous ammonium nitrate, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table I).

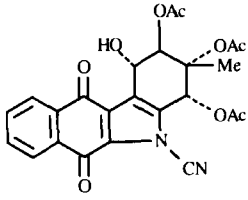
(x) Data from ref. 1069, 30.4 MHz and 50.7 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(y) Data from ref. 121, 10.09 MHz ^{15}N conventional PFT, proton decoupled, and INEPT spectra, proton-coupled, optimized for $^{2}J(NH) = 2.5$ Hz; *ca.* 1 M solutions, field perpendicular to sample tube, referenced originally to aqueous ammonium nitrate and recalculated to liquid ammonia standard, taken at +380.2 ppm from neat nitromethane conversion scheme IVa (Table 1).

(z) Data from ref. 618, ^{15}N-labelled substances from *Streptomyces parvus* cell cultures grown on ^{15}N-labelled L-glutamate, extracts in aqueous HCl; 27.37 MHz ^{15}N spectra with and without ^{1}H gated decoupling, referenced originally to "HNO_3", probably 1 M aqueous HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); the conversion is uncertain in view of the large range of nitrogen shieldings in nitric acid as a function of its concentration (see Table 2).

(A) See footnote (v).

Table 11. Nitrogen shieldings in cyanamide and carbodiimide structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Cyanamide structures			
$R_2N—C{\equiv}N$	various	+335 to +372 (NR_2)	(a)
		+185 to +196 (CN)	(a)
	in $CDCl_3$	+35.7 (ring N)	(b)
		+138.6 (CN)	(b)
Dicyanamido anions			
$(Ph_4As)_2\{M[N(CN)_2]_4\}$	in $CDCl_3$	amido-N CN	(c)
M			
Zn		+366.7 +220.2	
Cd		+345.3 +212.6	
Hg		+367.5 ?	
$K[N(CN)_2]$	in H_2O	+367.7 +223.5	(c)
	in EtOH	+330 +230	(d)
$[Fe(dipy)_2][N(CN)_2]$	in CH_2Cl_2	+230 +90	(d)
Carbodiimide structures			
$R—N{=}C{=}N—R$	various	+270 to +297	(a)

(a) See ref. 5, p. 335, and references therein.

(b) Data from ref. 870, 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to HNO_3 and reported vs liquid ammonia taken at +380.2 ppm from neat nitromethane, conversion scheme IVd (Table 1).

(c) Data from ref. 1070, 10% ^{15}N-labelling, 20.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^-, probably aqueous $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(d) Data from ref. 1071, low-precision 14.4 MHz ^{14}N measurements, referenced to the nitrate ion, *ca.* +4 ppm from neat nitromethane (Table 2).

Table 12. Nitrogen shieldings in amides, thioamides, sulphonamides and related structures

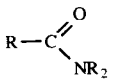
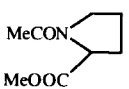
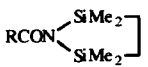
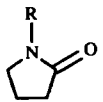
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Amide structures			
$HCONH_2$	neat liquid	+268.1	(a)
(formamide)	various solvents	+264 to +272	(a)
	in DMSO	+268.1	(b)
HCONHMe	in DMSO	+271.8 (*Z*)	(b)
		+273.8 (*E*)	(b)
$HCONMe_2$	neat liquid	+277.01	(a)
(dimethylformamide, DMF)	various solvents	+275 to +283	(a)
$HCON(SiMe_3)_2$	50% in CH_2Cl_2	+245	(c)
$MeCONH_2$ (acetamide)	in acetone	+274.7	(a)
	in H_2O	+268.0	(a)
MeCONHMe	in DMSO	+276.0 (*Z*)	(b)
		+277.8 (*E*)	(b)
$MeCONMe_2$	in acetone	+282.1	(a)
$MeCONHNCH_2CH_2Ph$	in $CDCl_3$	+258.8	(d)
	in $CDCl_3$	+262.9	(d)
	in $CHCl_3$	+275.9 (*Z*, 70%)	(e)
		+274.6 (*E*, 30%)	(e)
	in $CHCl_3$	+250.3 (*Z*, 70%)	(e)
		+250.5 (*E*, 30%)	(e)
MeCONHPh	solid state	+248.0	(f)
	in H_2SO_4	+227.1	(f)

Table 12. —*cont.*

Compound		Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$MeCO(SiHMe)_2$		50% in CH_2Cl_2	+253	(c)
$CF_3CONHCH_2CH_2Ph$		in $CDCl_3$	+264.5	(d)
$EtCO(SiHMe)_2$		50% in CH_2Cl_2	+262	(c)
		50% in CH_2Cl_2		(c)
		R = H	+245	
		R = Me	+247	
		R = CF_3	+253	
	R = H	in CCl_4	+263.8	(a)
		in H_2O	+256.8	(a)
		in $CHCl_3$	+269.2	(e)
			+268.7	(g)
	R = Me	neat liquid	+269.4	(g)
		in DMSO	+268.9	(g)
		in MeOH	+265.1	(g)
		in CF_3CH_2OH	+263.7	(g)
	R = Et	neat liquid	+256.6	(g)
		in DMSO	+255.6	(g)
		in $CHCl_3$	+254.6	(g)
		in EtOH	+254.2	(g)
		in MeOH	+253.3	(g)
		in CCl_3CH_2OH	+252.4	(g)
		in H_2O	+251.8	(g)
		in CF_3CH_2OH	+251.3	(g)

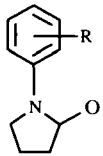
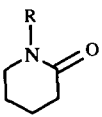
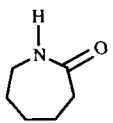
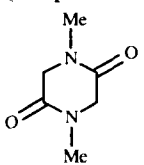
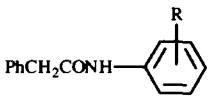
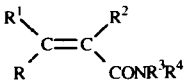
		sat. solutions	amido NPh group			
			para	*meta*	*ortho*	
	R = none	in DMSO	+245.7	+245.7	+245.7	(i)
		in acetone	+247.4	+247.4	+247.4	
	R = OMe	in DMSO	+247.5	+244.5		
		in acetone	+248.6			
	R = Me	in DMSO	+246.6	+244.7	+248.1	
		in acetone	+248.4	+247.1		
	R = Et	in DMSO	+244.4			
	R = Cl	in DMSO	+245.9	+245.9	+251.4	
		in acetone	+248.2			
	R = Br	in DMSO		+245.9		
	$R = NO_2$	in DMSO	+245.2			
	R = H	in CCl_4	+264.4			(a)
		in H_2O	+257.7			(a)
	R = Me	in $CHCl_3$	+270.3			(e)
 (ε-caprolactam)		in $CDCl_3$	+265.3			(h)
		in $CHCl_3$	+276.9			(e)

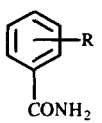
Table 12. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
	30% in DMSO	NH group			(j)
		para	*meta*	*ortho*	
R = NH_2		–	+244.1	+251.7	
	(*NH_2*)	–	+*318.0*	+*322.3*	
NHMe		–	+243.8	–	
	(*NHMe*)	–	+*324.2*	–	
NMe_2		–	+244.2	+251.2	
	(*NMe_2*)	–	+*337.9*	+*349.8*	
OH		+246.9	+244.3	+252.7	
OMe		+246.7	–	+255.9	
Et		+245.5	+244.7	+250.4	
i-Pr		–	–	+250.9	
Me		+245.3	+244.9	+249.2	
none		+244.6	+244.6	+244.6	
F		+245.7	+244.7	+258.2	
Cl		+245.7	+245.1	+246.5	
Br		+245.5	–	+248.6	
CN		+242.6	+245.3	+248.6	
COMe		+242.7	+245.4	+250.9	
NO_2		+242.0	+245.0	+252.0	
$CONH_2$		–	–	+250.6	
	(*NH_2*)	–	–	+*269.9*	



(k) 1 M in $CDCl_3$

R	R^1	R^2	R^3	R^4	
H	H	H	H	Me	+276.4
H	Me	H	H	Me	+277.6
Me	Me	H	H	Me	+276.0
H	H	Me	H	Me	+284.5
H	Me	Me	H	Me	+284.8
H	Br	H	H	Me	+277.5
H	Br	H	H	t-Bu	+242.3
H	Br	H	i-Pr	i-Pr	+235.6
Br	H	H	H	Me	+275.9
Br	H	H	H	t-Bu	+240.1
Br	H	H	i-Pr	i-Pr	+233.0
H	Cl	H	H	Me	+275.0
H	Cl	H	H	t-Bu	+241.3
Cl	H	H	H	Me	+277.8
Cl	H	H	H	t-Bu	+239.1

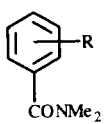


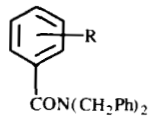
(benzamides)

(l) 0.4 M in DMSO

	$CONH_2$	
	para	*meta*
R = NMe_2	+282.0	+278.6
NH_2	+282.6	+278.7
OMe	+280.0	+278.1
NHCOMe	+279.6	+277.9
Me	+279.2	+278.5
none	+278.4	+278.4
F	+278.5	+277.5

Table 12. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
	Cl	+277.8	+277.4			
	Br	+277.8	+277.4			
	I	+277.9	+277.6			
	$CONH_2$	+277.1	+277.6			
	$CSNH_2$	+277.2	+277.5			
	COMe	+276.6	+277.5			
	COOMe	+276.5	+277.4			
	CF_3	+276.4	+277.2			
	CN	+276.1	+277.0			
	NO_2	+275.5	+276.6			
PhCONHMe	solid state	+279.4				(f)
	in H_2SO_4	+232.4				(f)
		$CONMe_2$				(m)
	sat. solutions	$CDCl_3$	Pyridine	DMSO	CD_3OD	
	R = none	+278.8	+278.6	+275.0	+271.9	
	4-OMe	+280.2	+280.7	+276.3	+272.8	
	4-Me	+280.6	+281.5	+275.4	+272.5	
	4-Cl	+278.9	+281.2	+274.3	+271.4	
	2-OMe	+275.4	+276.5	+272.2	+268.9	
	2-OH	+277.1	+276.8	+271.6		
	2-Me	+275.9	+277.3	+272.3	+268.7	
	2-Cl	+275.1	+275.5	+271.4	+268.6	
	2-OH-5-Cl	+276.5	+276.8	+272.0		
	2-OH-5-NO_2		+275.9	+271.0		
	2-OH-5-OMe	+273.5	+276.8	+271.9	+267.6	
	2-OH-5-Me	+276.0	+277.2	+271.5	+268.8	
	2-OH-3,5-Me_2	+277.2	+276.6	+271.9	+268.0	

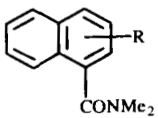


sat. solutions

R = none
4-OMe
4-Me
4-Cl
2-OMe
2-OH
2-Cl

$CON(CH_2Ph)_2$ (m)

$CDCl_3$	Pyridine	DMSO	CD_3OD
+254.5	+255.6	+251.4	–
+256.3	+256.0	+252.7	+248.6
+255.3	+256.6	+252.3	+248.3
+254.3	+255.9	+251.2	–
+250.9	+252.2	+248.9	+248.7
+253.6	+256.4	+249.6	–
+250.2	+251.8	+247.7	+244.1

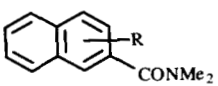


sat. solutions

R = none
2-OMe
2-OH

$CONMe_2$ (m)

Benzene	$CDCl_3$	Pyridine	DMSO	CD_3OD
+277.5	+274.4	+276.4	+270.4	+266.8
+276.2	+256.3	+256.0	+252.7	+248.6
–	+255.3	+256.6	+252.3	+248.3



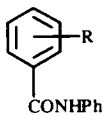
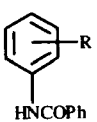
sat. solutions

R = none
1-OMe
1-OH
3-OMe
3-OH

$CONMe_2$ (m)

Benzene	$CDCl_3$	Pyridine	DMSO	CD_3OD
+282.3	+278.3	+280.5	+274.6	+271.5
–	+274.5	+276.4	+270.8	+266.8
–	+278.3	+275.8	+271.0	+267.3
+278.8	+275.3	+277.5	+271.6	+267.5
–	+276.6	+276.2	+271.0	+269.4

Table 12. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
		CONHPh				(m)
	sat. solutions	$CDCl_3$	Pyridine	DMSO	CD_3OD	
	R = none	+253.1	+250.8	+246.3	+247.1	
	4-NMe_2		+254.7	+249.9		
	4-OMe	+254.8	+252.9	+248.1	+248.5	
	4-OH		+253.0	+248.4		
	4-Me	+253.4	+252.0	+247.2	+247.8	
	4-Cl	+253.6	+251.2	+245.6	+247.0	
	4-NO_2		+248.0	+244.0		
	3-Me		+251.0	+246.1		
	3-Cl		+250.4	+245.6		
	2-OMe	+245.9	+245.0	+239.0	+240.7	
	2-OH	+255.3	+248.9	+244.2	+246.7	
	2-Me	+245.2	+243.5	+239.1	+239.1	
	2-Cl	+244.4	+242.4	+237.6	+238.4	
		PhCONH				(m)
	sat. solutions	Pyridine	DMSO			
	R = none	+250.8	+246.3			
	4-NMe_2	+259.5	+253.2			
	4-OMe	+254.6	+248.1			

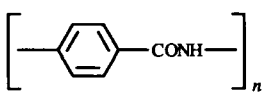
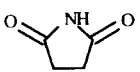
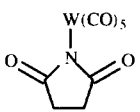
	4-OH	+254.2	+250.9	
	4-Me	+251.6	+246.8	
	4-Cl	+252.1	+247.0	
	4-NO_2	+246.5	+243.4	
	3-Me	+250.8	+246.1	
	3-Cl	+251.1	+246.5	
	3-NO_2	+251.9	+246.7	
NH amido moieties in manumycin	in H_2O	+227.5 (C-2″-N) +237.6 (C-1′-N)		(n) (n)
Amide polymers				
Poly(oxoamides) —[NH—$(CH_2)_n$—NH—CO—CO—]$_x$—	in CF_3COOH			(o)
n = 2		+265.3		
n = 3		+261.3		
n = 4		+259.3		
n = 6		+257.9		
n = 12		+257.0		
n = 2 and 3 (alternating)		+265.2, +261.3		
n = 2 and 4 (alternating)		+265.2, +259.3		
n = 2 and 6 (alternating)		+265.2, +257.8		
n = 2 and 12 (alternating)		+265.1, +256.9		
poly(p-benzamide) 	solid state	+252.6		(f)
poly(p-benzamide-*alt*-caproamide}				
	solid state	+246.7, +267.4		(f)
	in H_2SO_4	+230.2, +235.3		(f)

Table 12. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
nylon-6	in CF_3COOH	+259.2	(h)
	solid state		
	α-crystal form	+263.8	(p)
	amorphous form	+260.2	(p)
	extracted with NaOH	+266.4 (isotropic)	(p)
		+343 (σ_{11})	(p)
		+288 (σ_{22})	(p)
		+168 (σ_{33})	(p)
nylon-6 (annealed)	solid state	+264.6	(f)
	in H_2SO_4	+234.5	(f)
nylon-6 (quenched)	solid state	+264.2, +259.2	(f)
	in H_2SO_4	+234.5	(f)
3-arm star nylon-6	solid state	+261.0	(f)
	in H_2SO_4	+234.5	(f)
nylon-11	solid state		
	α-crystal form	+263.8	(q)
	amorphous form	+261.3	(q)
Imide structures R—CO—NR—CO—R			
	in H_2O	+218	(r)
	in H_2O, its K^+ salt	+322	(r)
	in CH_2Cl_2	+239	(r)

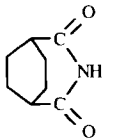
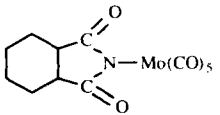
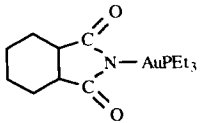
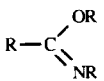
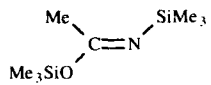
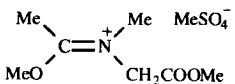
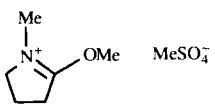
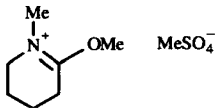
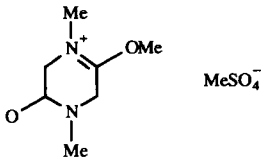
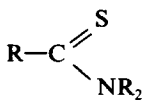
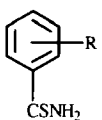
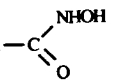
	in acetone	+228	(r)
	in H_2O, its Na^+ salt	+276	(r)
	in acetone	+262	(r)
Saccharin	in DMSO	+153	(r)
$KW(CO)_5$-saccharate	in DMSO	+201	(r)
	solid state	+176.2	(s)
	0.1 M in $CDCl_3$	+176.2	(s)
Polypyromellitimide	solid state	+246 (amide)	(t)
		+206 (imide)	(t)
Isoamide structures and their derivatives			
	50% in CH_2Cl_2	+120	(c)
	in $CHCl_3$	+242.5	(e)
	in $CHCl_3$	+233.1	(e)

Table 12. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CHCl_3$	+235.3	(e)
	in $CHCl_3$	+240.9 (MeN^+=) +282.5 (MeN)	(e) (e)
Thioamide structures 			
$MeCSNH_2$	in H_2O	+272.9	(a)
MeCSNHPh	in $CDCl_3$	+211.7 (*Z*) +210.0 (*E*)	(u) (u)
MeCSN(Me)Ph	in $CDCl_3$	+215.4, +215.6 *Z,E*	(u) (u)
	0.4 M in DMSO	$CSNH_2$	(l)

	para	*meta*
R = NMe_2	+241.4	+232.8
NH_2	+242.1	+233.1
OMe	+235.9	+232.2
NHCOMe	+235.5	+231.8
Me	+234.1	+232.7

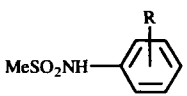
	none	+232.5	+232.5	
	F	+232.7	+231.3	
	Cl	+231.8	+231.0	
	Br	+231.9	+231.0	
	I	+232.2	+231.1	
	$CONH_2$	+231.0	+231.4	
	$CSNH_2$	+231.2	+231.4	
	COMe	+230.1	+231.3	
	COOMe	+229.8	+231.0	
	CF_3	+229.6	+230.6	
	CN	+229.0	+230.2	
	NO_2	+228.1	+229.9	

Hydroxamic acid structure 

MeCONHOH	0.67 M in DMSO	+209 (*Z*, major)	(v)
		+207 (*E*, minor)	(v)

Sulphonamide structures $R—SO_2—NR_2$

$MeSO_2NH_2$	in acetone	+288.7	(w)
$MeSO_2NMe_2$	in DMSO	+300.7	(w)
	in $CHCl_3$	+301.6	(w)
	in CF_3CH_2OH	+302.3	(w)

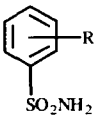


2 mol% in DMSO — NH group — (x)

R = none

		para	*meta*	*ortho*	
	(in acetone)	+257.3	+257.3	+257.3	
		+260.0	+260.0	+260.0	(w)
OMe		+260.8			
Me		+260.3	+257.8	+265.1	
2,6-Me_2				+271.2	
Cl		+256.7	+256.5	+264.9	
Br		+257.6		+261.0	
OSO_2Me		+257.0			
NO_2		+250.8	+255.9	+265.3	

Table 12. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
$MeSO_2NPh_2$	in acetone	+281.5			(w)
		NH group			
		para	*meta*	*ortho*	
R = none	in DMSO	+285.7	+285.7	+285.7	(x)
		+284.3	+284.3	+284.3	(w)
	in acetone	+288.0	+288.0	+288.0	(w)
R = NH_2	in DMSO	+284.0	+285.8		(x)
R = OH	in DMSO	+284.6			(x)
R = OMe	in DMSO	+284.7			(x)
R = NHCOMe	in DMSO	+285.1			(x)
R = Me	in DMSO	+287.6			(w)
		+285.5	+285.7		(x)
	in acetone	+284.3			(w)
R = F	in DMSO	+285.2			(x)
R = Cl	in DMSO	+284.3			(w)
		+285.6	+285.6		(x)
	in acetone	+287.8			(w)
R = Br	in DMSO	+284.2			(w)
		+285.7			(x)
	in acetone	+287.8			(w)
R = CN	in DMSO	+286.0			(x)
R = NO_2	in DMSO	+284.4	+284.6		(w)
		+285.8	+285.6		(x)
R = COOH	in acetone	+288.4	+288.3	+285.6	(w)
	in DMSO	+285.9			(x)

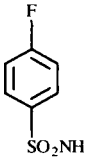
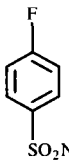
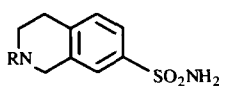
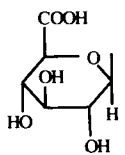
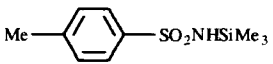
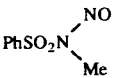
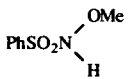
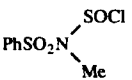
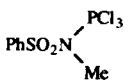
		in DMSO-d_6	+288.9 (triplet)	(y)
		in H_2O	+294.0 (singlet)	(y)
	0.05 M in H_2O + enzyme, pH = 8.5 (neutral)		+291.0 (singlet)	(y)
		(anion)	+299.2 (doublet)	(y)
	(enzyme = ^{111}Cd-substituted bovine carbonic anhydrase)			
		in DMSO-d_6	+224.8 (doublet)	(y)
		in H_2O	+224.4 (singlet)	(y)
	0.10 M in H_2O + enzyme, pH = 7.5		+223.6 (singlet)	(y)
	(enzyme = ^{111}Cd-substituted bovine carbonic anhydrase)			
$PhSO_2NHMe$		neat liquid	+295.3	(w)
		in acetone	+296.3	(w)
$PhSO_2NMe_2$		in acetone	+298.3	(w)
		in DMSO	+298.1	(w)
		in $CHCl_3$	+298.9	(w)
		in CF_3CH_2OH	+299.4	(w)
$PhSO_2NHPh$		in acetone	+259.4	(w)
$PhSO_2NPh_2$		in acetone	+281.0	(w)
		in DMSO	SO_2NH_2	(z)
	R = H, hydrochloride ("SK&F29661")		+290.6 (triplet)	
	R = 		+290.6 (triplet)	

Table 12. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+283.1	(A)
	in $CHCl_3$	+94.4 (NMe)	(B)
	in DMSO	+196.2	(B)
	in $CHCl_3$	+217.6	(B)
	in $CHCl_3$	+260.0	(B)
Sulphinamide structures R—SO—NR_2			
$MeSONH_2$	in acetone	+285.4	(w)
MeSONHMe	neat liquid	+302.7	(w)
	in acetone	+303.4	(w)
$MeSONMe_2$	neat liquid	+308.9	(w)
	in acetone	+309.2	(w)
	in $CHCl_3$	+309.5	(w)
	in DMSO	+309.0	(w)
	in $PhCH_2OH$	+309.9	(w)
	in MeOH	+310.0	(w)

	in CCl_3CH_2OH	+310.1	(w)
	in CF_3CH_2OH	+311.1	(w)
	in $(CF_3)_2CHOH$	+312.0	(w)
$PhSONMe_2$	neat liquid	+305.1	(w)
Sulphenamide structures R—S—NR_2			
$PhSNMe_2$	neat liquid	+335.1	(w)
	in $CHCl_3$	+334.4	(w)

(a) See ref. 5, pp. 336–350, and references therein.

(b) Data from ref. 203, 40.6 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported originally vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane (the latter value refers actually to a perpendicular field-to-sample axis arrangement, Table 2); we retrieved the original data.

(c) Data from ref. 1072, 6.41 MHz ^{14}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane via a calibrated sample of aqueous NH_4Cl, uncorrected for bulk susceptibility effects.

(d) Data from ref. 1073, 9.04 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(e) Data from ref. 1074, 25.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(f) Data from refs. 359, 374 and 1075, 20.3 MHz ^{15}N solution spectra (field parallel to sample tube) and CPMAS spectra, referenced originally to NH_4^+ in aqueous ammonium nitrate, +359.6 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1); reported vs solid glycine, −11.3 ppm from the reference employed.

(g) Data from ref. 1076, 10.04 MHz ^{15}N spectra, other details as in footnote (b); $Cr(acac)_3$ added as a relaxation reagent.

(h) Data from ref. 1077, 40.6 MHz ^{15}N spectra (NOE-suppressed), field parallel to sample tube, referenced originally to liquid ammonia, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(i) Data from ref. 889, 10.04 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(j) Data from refs. 1054 and 1056, 9.04 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to liquid ammonia (at +380.2 ppm from neat nitromethane) via a calibrated sample of aqueous ammonium nitrate, conversion scheme IIIa (Table 1).

(k) Data from ref. 512, 36.506 MHz ^{15}N DEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(l) Data from ref. 509, 20.22 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; actually, only unsubstituted benzamide nitrogen shielding was calibrated as above, shieldings of the derivatives were measured by frequency readout upon sample replacement.

Table 12. —*cont.*

(m) Data from refs. 890 and 1078, ^{15}N-labelled amido groups, 9.04 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to liquid ammonia, +380.2 ppm from neat nitromethane (uncorrected, Table 2), conversion scheme IIa (Table 1).

(n) Data from ref. 878, ^{15}N-labelled sample (by feeding *Streptomyces parvus* with labelled glycine), spectrometer not reported, ^{15}N spectra referenced to saturated aqueous NH_4Cl, +252.9 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(o) Data from ref. 1079, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to NO_3^- in aqueous ammonium nitrate, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(p) Data from refs. 327, 368–371, and 1006, ^{15}N-labelled samples, 20.287 MHz ^{15}N CPMAS and powder spectra, referenced to solid glycine, +348.0 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects.

(q) Data from ref. 372, details as in footnote (p).

(r) Data from ref. 1080, 10.09 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to saturated aqueous $NaNO_3$, +3.7 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(s) Data from refs. 155 and 413. ^{15}N-labelled imide, 15.24 MHz ^{15}N CPMAS spectrum, referenced originally to solid ammonium sulphate, +355.7 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects; also ^{15}N solution spectrum at the same frequency; ^{31}P–^{15}N coupling was observed across P—Au—N.

(t) Data from ref. 443, ^{15}N-labelled and unlabelled samples, 30.4 MHz ^{15}N CPMAS spectra, referenced originally to solid ammonium sulphate, +355.7 ppm from neat nitromethane (Table 2), conversion scheme III (Table 1).

(u) Data from ref. 1081, 8.059 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported vs liquid ammonia standard taken at +380.2 ppm from neat nitromethane.

(v) Data from ref. 787, 27.4 MHz ^{15}N proton-coupled spectrum, field parallel to sample tube, referenced originally to nitromethane +20% C_6D_6, *ca.* +0.2 ppm from neat nitromethane (Table 2).

(w) Data from refs. 770, 1082, 1083 and 1084, details as in footnote (i); concentrated (*ca.* 50 mol%) solutions.

(x) Data from ref. 1085, 20.28 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane via a calibrated sample of aniline; originally reported vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane, see comments in footnote (b).

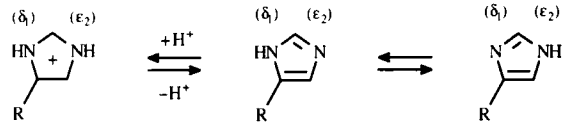
(y) Data from ref. 761, ^{15}N-labelled samples, 40.56 MHz ^{15}N spectra (proton-coupled), field parallel to sample tube, referenced originally to NO_3^-, probably in aqueous $NaNO_3$, +3.5 ppm from neat niromethane (Table 2), conversion scheme IIb (Table 1).

(z) Data from ref. 1086, ^{15}N-labelled sulphonamide moiety, 8.059 MHz ^{15}N spectra (proton-coupled), field perpendicular to sample tube, referenced originally to NH_4^+ in aqueous ammonium nitrate, +359.6 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(A) Data from ref. 154, 36.5 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(B) Data from ref. 515, details as in footnote (e).

Table 13. Nitrogen shieldings in amino acids, peptides proteins, and related structures

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Free amino acids	See ref. 5, p. 365 and references therein	
Free amino acids from cell suspensions of green alga *Chlorella fusa* (ca. 10^8 *cells/ml in* H_2O)	+255.2, +261.1 amido-moieties +266.5 (γ-Gln) +294.4 (δ-Arg) +307.0 (ω,ω'-Arg) +313.4 (Pro) +335.7 (Ala) +337.8 (Glu) +338.1 (Gln) +340.3 (Ser) +346.2 (Lys)	(a)
Histidine		

R = —CH(NH_3^+)COO^-	N_{δ_1}	N_{ε_2}	
in H_2O, *protonated*	+205.2	+208.3	(b)
in H_2O, *neutral species*	+148.0	+203.1	(b)
	+188.7	+161.5	(b)
in 80% EtOH, protonated	+203.6	+206.2	(b)
in 80% EtOH, δ_1*-NH tautomer*	+213.1	+136.4	(b)
in 80% EtOH, ε_2*-NH tautomer*	+133.4	+216.0	(b)
δ_1-*N*-Me-histidine			
in H_2O, *protonated*	+208.4	+208.8	(b)
in H_2O, *neutral species*	+215.6	+139.2	(b)
ε_2-*N*-Me-histidine			
in H_2O, *protonated*	+202.8	+209.4	(b)
in H_2O, *neutral species*	+133.4	+217.0	(b)
His-57 in Asp–His–Ser triad of α-lytic protease			
in H_2O, *protonated*	+196.4	+209.0	(b)
neutral species	+204.2	+142.8	(b)
in H_2O + *phenylmethanesulphonyl fluoride, protonated*	+212.8	+206.3	(b)
neutral species	+204.5	+132.4	(b)

Table 13. —*cont.*

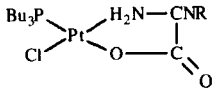
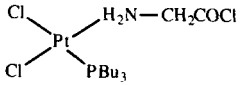
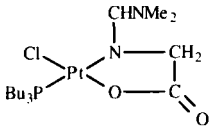
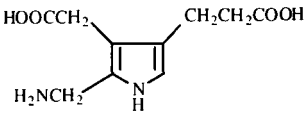
Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
in H_2O + diisopropylfluorophosphate,			
protonated	+203.3	+206.9	(b)
neutral species	+210.7	+137.8	(b)
in H_2O, complexed with peptide boronic acid inhibitors:			
Boc-Ala-Pro-boroVal-OH	+198.5	+195.1	(c)
pH = 4	+198.6	+195.9	(c)
pH = 9			
MeOSuc-Ala-Ala-Pro-boroVal-OH			
pH = 4	+198.0	+195.7	(c)
pH = 9	+198.2	+195.5	(c)
*MeOSuc-Ala-Ala-Pro-*D,L*-boroAla-OH*			
pH = 4	+198.4	+196.6	(c)
pH = 9	+198.3	+197.2	(c)
Ac-Pro-boroVal-OH			
pH = 4	+198.4	+196.7	(c)
pH = 9	+198.5	+196.4	(c)
*MeOSuc-Ala-Ala-Pro-*D,L*-boroPhe-OH*			
pH = 4	+202.4	+171.1	(c)
pH = 9	+202.4	+171.1	(c)
*Boc-Ala-Pro-*D*-boroVal-OH*			
pH = 9	+201.6	+171.2	(c)
Benzeneboronic acid			
pH = 9	+201.9	+171.2	(c)
solid state, complex with (MeOSuc-Ala-Ala-Pro-boroPhe-OH)(boroPhe-OH)			
His-57 and His-51	+202.2	+170.4	(d)
amide backbone	+259		
lyophilized solid state, 64% w/w suspension in solvent			(e)
δ_1-His, in acetone, pH = 8.6	+201 +259		
δ_1-His, in acetone, reclaimed from DMSO	+124 +259		
δ_1,ε_2-His, in acetone, reclaimed from DMSO		+194 +202 +259	
			(f)
R = H (glycine) *in $CDCl_3$*	+402.7 (singlet)		
R = Me (alanine) *in DMSO*	+387.6 (doublet)		

Table 13. —*cont.*

Substance *and its state*		Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	*in acetone*	+401.1 (doublet)	(f)
	*in $CDCl_3$*	+244.1 (doublet)	(f)
$H_2N-CH_2-CO-CH_2CH_2COOH$ (5-aminolevulinic acid, "ALA")			(g)
in H_2O			
pH 2		+354.9	
pH 7		+355.0	
pH 11.6		+368.4	
in H_2O, adduct with hydroxylamine Schiff base			
pH 7		+352.2	
pH 9.7		+362.2	
in H_2O, adduct with hydroxylamine Schiff base			
pH 7		+352.9	
pH 9.7		+360.2	
ALA bound to porphibilinogen synthetase Schiff-base complex		+356.3	
	(porphobilinogen, PBG)		(g)
in H_2O		+229.0 (NH) +340.1 (NH_2)	
in D_2O		+230.9 (NH) +343.4 (NH_2)	

N-acetyl-amino acids

	Ac-N moieties				(h)
in DMSO	Ala (A)	+256.2	Leu (L)	+258.6	
	Arg (R)	+255.8	Lys (K)	+256.4	
	Asn (N)	+258.7	Met (M)	+260.3	
	Asp (D)	+260.3	Phe (F)	+259.6	
	Cys (C)	+261.3	Pro (P)	+249.5	
	Gln (Q)	+258.2	Ser (S)	+264.9	
	Glu (E)	+259.9	Thr (T)	+270.0	

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
	Gly (G)	+271.2	Trp (W)	+258.3	
	His (H)	+258.7	Tyr (Y)	+258.5	
	Ile (I)	+261.3	Val (V)	+262.6	
Bovine pancreatic trypsin inhibitor (BPTI, a 58-residue protein)					
	Peptide nitrogen atoms				(i)
in H_2O, pH = 4.6, +68°C	D3	+258.3	N24	+256.1	R42	+266.1
	F4	+266.0	A25	+255.1	N43	+265.5
	C5	+261.0	K26	+265.2	N44	+260.6
	L6	+267.7	A27	+263.4	F45	+259.3
	E7	+261.1	G28	+275.0	K46	+261.4
	Y10	+258.8	L29	+267.3	S47	+273.1
	T11	+254.6	C30	+263.1	A48	+256.3
	G12	+274.8	Q31	+258.7	E49	+262.1
	C14	+264.0	T32	+273.0	D50	+261.9
	K15	+266.4	F33	+262.5	C51	+262.1
	A16	+258.2	V34	+263.0	M52	+260.6
	R17	+263.6	Y35	+252.0	R53	+261.4
	I18	+256.6	G36	+267.8	T54	+268.4
	I19	+253.5	G37	?	C55	+267.1
	R20	+252.1	C38	+266.7	C56	+274.1
	Y21	+266.0	R39	+268.4	G57	+273.1
	F22	+261.7	A40	+263.6	A58	+252.4
	Y23	+256.8	K41	+260.7		

Apamin *in H_2O*

Peptide nitrogen atoms (i)

	pH 2.2	pH 3.4	pH 4.0	pH 4 + 2M NaCl
Cys-1	?	?	?	?
Asn-2	+254.5	+253.2	+252.3	+253.4
Cys-3	+261.4	+261.5	+261.9	+262.1
Lys-4	+262.1	+262.3	+262.5	+262.2
Ala-5	+262.0	+262.0	+262.1	+262.7
Pro-6	?	?	?	?
Glu-7	+259.7	+258.6	+257.9	+258.1
Thr-8	+274.5	+275.4	+276.1	?
Ala-9	+255.4	+255.7	+256.0	+255.0
Leu-10	+262.5	+262.4	+261.9	+262.1
Cys-11	+264.8	+264.2	+264.7	+265.1
Ala-12	+258.4	+258.7	+259.1	+258.8
Arg-13	+264.4	+264.2	+264.3	+264.3
Arg-14	+261.2	+260.8	+261.0	+261.1
Cys-15	+265.2	+265.0	+265.2	+265.5
Gln-16	+262.5	+262.7	+262.9	+262.7
Gln-17	+262.4	+262.6	+263.0	+263.3
His-18	+262.3	+262.6	+263.3	+263.5

Table 13. *—cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane							Notes
Staphylococcal nuclease (Nase) from *Escherichia coli*								
	Peptide nitrogen atoms							(j)
in H_2O, pH = 7.4			T41	+262.3	R81	+261.7	H121	+268.7
			P42	?	T82	+274.1	E122	?
			E43	?	D83	+260.3	Q123	?
			T44	?	K84	?	H124	+261.8
			K45	?	Y85	+261.3	L125	+263.7
	K6	?	H46	+256.4	G86	+272.6	R126	+263.3
	L7	+259.7	P47	?	R87	+260.3	K127	+259.6
	H8	+262.3	K48	?	G88	+273.6	S128	+263.9
	K9	+258.0	K49	?	L89	+255.8	E129	+256.8
	E10	+258.7	G50	+272.8	A90	+261.8	A130	+262.3
	P11	?	V51	+259.6	Y91	+259.2	Q131	+263.6
	A12	+261.9	E52	+255.1	I92	+259.9	A132	+258.9
	T13	+273.1	K53	+256.3	Y93	+255.6	K133	+264.7
	L14	+256.8	Y54	+266.1	A94	+256.1	K134	+259.6
	I15	+257.3	G55	+273.5	D95	+254.4	E135	+265.3
	K16	+267.5	P56	?	G96	+278.8	K136	+265.3
	A17	+252.5	E57	?	K97	+260.6	L137	+264.8
	I18	+257.6	A58	+257.7	M98	+255.3	N138	+263.3
	D19	+262.9	S59	+270.2	V99	+245.7	I139	+257.5
	G20	+278.1	A60	+259.6	N100	+273.7	W140	+262.7
	D21	+270.1	F61	+260.5	E101	+269.3	S141	+265.7
	T22	+264.3	F62	+261.6	A102	+258.8		
	V23	+261.2	K63	+261.8	L103	+266.4		
	K24	+254.6	K64	+264.6	V104	+264.9		
	L25	+254.6	M65	+265.6	R105	+259.4		
	M26	+259.8	V66	+274.1	Q106	+269.8		
	Y27	+252.3	E67	+260.7	Q107	+275.1		
	K28	+254.4	N68	+268.5	L108	+266.6		
	G29	+279.5	A69	+260.6	A109	+268.8		
	Q30	+262.6	K70	+256.3	K110	+264.6		
	P31	?	K71	+260.5	V111	+257.8		
	M32	+256.2	I72	+252.8	A112	+250.6		
	T33	+257.7	E73	+258.6	Y113	+271.6		
	F34	+256.1	V74	+264.7	V114	+262.5		
	R35	+257.2	E75	+255.1	Y115	+251.4		
	L36	+257.1	F76	+255.3	K116	?		
	L37	+260.0	N77	+258.7	P117	?		
	L38	+270.3	K78	+262.8	N118	+253.3		
	V39	+278.1	G79	+271.1	N119	+264.2		
	D40	+262.7	Q80	+257.1	T120	+257.7		

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Ferrocytochrome c_2 from *Rhodobacter capsulatus*		
0.002 M *in* H_2O, *pH* = 6	Peptide nitrogen atoms	(k)

G1	?	A31	+256.5	G61	+271.0	K91	+263.4
D2	+258.4	K32	+266.5	A62	+255.5	A92	+257.6
A3	+252.5	T33	+264.0	S63	+268.4	K93	+263.0
A4	+259.6	G34	+276.9	G64	+270.8	S94	+265.2
K5	+261.1	P35	?	F65	+259.0	G95	+284.1
G6	+272.2	N36	+262.3	A66	+250.2	M96	+255.6
E7	+257.6	L37	+256.0	W67	+263.1	A97	+246.4
K8	+264.7	Y38	+257.7	T68	+269.4	F98	+261.1
E9	+260.0	G39	+263.6	E69	+258,3	K99	+260.9
F10	+263.2	V40	+263.8	E70	+262.9	L100	+257.4
N11	+263.3	V41	+259.7	D71	+262.3	A101	+251.5
K12	+263.4	G42	+262.7	I72	+260.0	K102	+266.4
C13	+264.6	R43	+256.0	A73	+261.1	G103	+271.4
K14	+261.1	T44	+257.1	T74	+267.0	G104	+269.1
T15	+268.3	A45	+246.5	Y75	+255.4	E105	+260.5
C16	+266.8	G46	+274.5	V76	+272.8	D106	+258.2
H17	+265.0	T47	+278.2	K77	+262.2	V107	+259.4
S18	+269.3	Y48	+250.9	D78	+275.3	A108	+257.2
I19	+262.5	P49	?	P79	?	A109	+261.7
I20	+251.4	E50	+266.2	G80	+276.8	Y110	+260.8
A21	+250.7	F51	+259.4	A81	+257.1	L111	+261.3
P22	?	K52	+252.3	F82	+262.7	A112	+261.2
D23	+267.3	Y53	+254.1	L83	+263.4	S113	+267.9
G24	+272.4			K84	+264.6	V114	+265.5
T25	+262.9			E85	+262.8	V115	+265.6
E26	+252.0	S56	+263.9	K86	+263.2	K116	+250.9
I27	+251.2	I57	+257.4	L87	+265.5		
V28	+265.2	V58	+257.6	D88	+260.3		
K29	+250.8	A59	+256.7	D89	+266.4		
G30	+264.2	L60	+260.3	K90	+256.7		

Cytochrome c^{553} *in* H_2O	Ala +263.1, +264.8, +256.0 His +223.4, +208.5 (ring)	(o)
Calmodulin from *Drosophila*		(l)
0.0015 M *in* H_2O, *complexed with* Ca^{+2}, *pH* = *6.3*	Peptide nitrogen atoms	

A1	?	Q41	+263.5	S81	+265.2	V121	+261.1
D2	+261.4	N42	+265.4	E82	+261.0	D122	+262.3
Q3	+262.3	P43	+266.3	E83	+263.1	E123	+262.7
L4	+259.1	T44	+269.3	E84	+261.7	M124	+262.5

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane								Notes
	T5	+269.0	E45	+261.2	I85	+260.6	I125	+263.7	
	E6	+261.4	A46	+261.4	R86	+260.3	R126	+263.5	
	E7	+262.6	E47	+263.3	E87	+263.5	E127	+266.1	
	Q8	+262.1	L48	+261.7	A88	+260.1	A128	+262.8	
	I9	+262.5	Q49	+263.8	F89	+263.4	N129	+264.6	
	A10	+260.6	D50	+261.9	R90	+266.5	I130	+254.5	
	E11	+262.3	M51	+262.9	V91	+263.8	D131	+264.8	
	F12	+262.3	I52	+263.9	F92	+265.5	G132	+273.6	
	K13	+258.8	N53	+264.4	D93	+265.0	D133	+261.3	
	E14	+261.7	E54	+265.5	K94	+256.1	G134	+269.7	
	A15	+259.7	V55	+273.0	D59	+267.7	Q135	+266.5	
	F16	+262.9	D56	+260.3	G96	+272.8	V136	+256.7	
	S17	+269.5	A57	+250.2	N97	+262.5	N137	+252.9	
	L18	+261.1	D58	+268.0	G98	+269.1	Y138	+263.7	
	F19	+266.9	G59	+273.7	F99	+266.3	E139	+263.7	
	D20	+264.4	N60	+263.5	I100	+254.6	E140	+261.8	
	K21	+257.5	G61	+268.6	S101	+258.1	F141	+257.9	
	D22	+267.9	T62	+272.9	A102	+258.9	V142	+262.5	
	G23	+272.8	I63	+257.9	A103	+263.8	T143	+265.4	
	D24	+261.1	D64	+253.6	E104	+262.5	M144	+260.1	
	G25	+268.8	F65	+262.9	L105	+261.1	M145	+267.1	
	T26	+269.0	P66	+264.7	R106	+264.6	T146	+271.9	
	I27	+254.8	E67	+264.5	H107	+263.3	S147	+264.1	
	T28	+265.3	F68	+258.6	V108	+263.2	K148	+254.2	
	T29	+269.1	L69	+263.1	M109	+265.4			
	K30	+261.5	T70	+267.0	T110	+267.5			
	E31	+260.6	M71	+260.5	N111	+260.0			
	L32	+261.5	M72	+265.5	L112	+263.2			
	G33	+276.6	A73	+260.1	G113	+275.6			
	T34	+264.1	R74	+265.4	E114	+261.6			
	V35	+259.7	K75	+263.2	K115	+258.4			
	M36	+264.0	M76	+263.5	L116	+257.7			
	R37	+263.0	K77	+261.6	T117	+267.9			
	S38	+263.5	D78	+260.5	D118	+259.4			
	L39	+261.8	T79	+267.9	E119	+262.1			
	G40	+275.5	D80	+259.1	E120	+263.2			
Bacteriophage T4 lysozyme									(m)
in H_2O/D_2O, *pH = 5.6, +20°C*	Peptide nitrogen atoms								
	M1	+342.0	A41	+256.7	N81	+258.9	L121	+262.1	
	N2	+265.0	A42	+259.7	A82	+251.6	Q122	+260.0	
	I3	+263.0	K43	+264.0	K83	+267.1	Q123	+267.1	
	F4	+257.6	S44	+266.2	L84	+264.9	K124	+266.6	

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
E5	+262.7	E45	+260.3	K85	+257.6	R125	+260.7	
M6	+262.6	L46	+258.5	P86	?	W126	+262.1	
L7	+262.9	D47	+261.0	V87	+264.9	D127	+264.1	
R8	+258.0	K48	+259.9	Y88	+258.9	E128	+260.1	
I9	+261.1	A49	+259.5	D89	+263.1	A129	+258.3	
D10	+262.8	I50	+266.1	S90	+267.9	A130	+261.9	
E11	+262.9	G51	+271.9	L91	+258.6	V131	+262.6	
G12	+271.6	R52	+264.6	D92	+266.2	N132	+262.5	
L13	+261.8	N53	+264.6	A93	+261.1	L133	+258.7	
R14	+253.4	C54	+255.4	V94	+263.1	A134	+261.3	
L15	+257.8	N55	+260.5	R95	+261.8	K135	+262.6	
K16	+266.2	G56	+278.8	R96	+262.5	S136	+267.5	
I17	+260.5	V57	+260.2	C97	+265.5	R137	+257.2	
Y18	+252.9	I58	+264.1	A98	+259.7	W138	+260.2	
K19	+260.0	T59	+271.7	L99	+262.0	Y139	+262.9	
D20	+256.0	K60	+259.3	I100	+262.2	N140	+269.9	
T21	+270.7	D61	+263.3	N101	+262.0	Q141	+262.3	
E22	+260.6	E62	+259.0	M102	+265.5	T142	+274.2	
G23	+273.8	A63	+259.4	V103	+260.6	P143	?	
Y24	+259.7	E64	+260.1	F104	+256.9	N144	+264.0	
Y25	+257.8	K65	+259.4	Q105	+263.7	R145	+259.9	
T26	+259.3	L66	+262.3	M106	+267.7	A146	+261.7	
I27	+259.6	F67	+261.8	G107	+269.3	K147	+265.0	
G28	+268.6	N68	+262.6	E108	+260.7	R148	+261.3	
I29	+249.9	Q69	+261.9	T109	+268.5	V149	+255.8	
G30	+271.6	D70	+257.3	G110	+271.5	I150	+260.5	
H31	+264.3	V71	+255.7	V111	+259.0	T151	+263.1	
L32	+248.2	D72	+261.1	A112	+262.1	T152	+258.7	
L33	+254.9	A73	+260.7	G113	+279.1	F153	+260.7	
T34	+271.0	A74	+257.3	F114	+256.8	R154	+261.8	
K35	+255.8	V75	+261.2	T115	+266.3	T155	+276.7	
S36	+261.1	R76	+262.9	N116	+261.7	G156	+269.2	
P37	?	G77	+275.1	S117	+262.2	T157	+272.7	
S38	+264.5	I78	+258.0	L118	+260.7	W158	+263.1	
L39	+247.5	L79	+266.6	R119	+262.0	D159	+261.1	
N40	+263.7	R80	+264.6	M120	+264.2	A160	+261.9	
P37, 86, 143	+241.0 +243.0 +246.9					Y161	+267.2	
						K162	+261.4	
						N163	+264.1	
						L164	+255.1	

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	Other nitrogen atoms	
	H31 +193.6 (N_{δ_1}), +207.5 (N_{ε_2})	
	W126 +249.9 (N_{ε_1})	
	W138 +250.5 (N_{ε_1})	
	W158 +252.2 (N_{ε_1})	
2-Fe-2S*-ferrodoxin from *Anabaena* species strain PC 7120 (oxidized form)		(n)
0.007 M *in* H_2O, *ph = 7.1*	Peptide nitrogen atoms	
	A1 +341.1 I26 +261.3 G51 +268.8 Y76 +261.8	
	T2 +267.4 L27 +265.2* K52 +258.8 V77 +262.8	
	F3 +257.2 D28 +264.0 K53 +251.6 L78 ?	
	K4 +257.8 A29 +258.5 V54 +255.5 T79 ?*	
	V5 +252.8 A30 +260.0 S55 +269.2 C80 ?	
	T6 +255.2 E31 +261.9 G56 +271.4 V81 ?	
	L7 +253.5 E32 +259.5 T57 +274.5 A82 +259.3	
	I8 +254.2 Q33 +265.0 V58 +271.7 Y83 +256.7	
	N9 +255.2 G34 +274.5 ?59 ? P84 +244.1	
	E10 +255.6 Y35 +258.8 D60 +260.0 T85 +270.2	
	A11 +259.1 D36 +258.9 Q61 +256.8 S86 +263.1	
	E12 +266.9 L37 +254.9 S62 +263.1 D87 +262.6	
	G13 +271.5 P38 +247.6 D63 +261.6 V88 +255.3	
	T14 +273.0 F39 ?* Q64 +258.2 V89 +253.4	
	K15 +258.2 S40 ? S65 ? I90 +253.1	
	H16 +256.6 C41 ? F66 ?* Q91 +254.6	
	E17 +256.6 R42 ?* L67 +259.5* T92 +265.2	
	I18 +260.8 A43 ? D68 +258.1 H93 +268.1	
	E19 +258.3 G44 ? D69 +263.9 K94 +266.6	
	V20 +254.5 A45 ? D70 +259.8 E95 +259.0	
	P21 +242.6 C46 ? Q71 +257.7 E96 +267.2	
	D22 +264.2 S47 ? I72 +259.8 D97 +261.5	
	D23 +263.7 T48 ? E73 +256.9 L98 +262.8	
	E24 +259.1 C49 ? A74 +261.4 Y99 +256.7	
	Y25 +260.6 A50 ?* G75 +277.3	
	Other nitrogen atoms	
	K4 +348.8 (N_ζ); K52 +346.9 (N_ζ); K94 +348.4 (N_ζ)	
	D9 +270.1 (N_δ)	
	H16 +168.1 (N_{δ_1}), +198.7 (N_{ε_2})	
	H93 +138.8 (N_{δ_1}), +213.3 (N_{ε_2})	
	Q61 +273.3 (N_ε); Q64 +270.0 (N_ε); Q71 +271.1 (N_ε)	
	Q91 +271.0 (N_ε)	

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Anabaena 7120 flavodoxin		(o)
in H_2O	Ala +259.1, +260.3, +259.8, +253.3, +257.0, +260.1, +263.2	
	His +204.4, +150.4 (ring)	

Escherichia coli thioredoxin (p)

0.001 to 0.005 M *in H_2O*

Peptide nitrogen atoms

Arg, R	+247.0
Asx, D, N	+251.3, +248.8, +255.9, +259.8, +255.9, +256.3, +251.3, +255.3, +259.2, +255.3, +259.2, +246.9, +254.3, +258.6, +262.6
Gly, G	+263.2, +253.7, +271.2, +260.4, +269.3, +261.2, +266.5, +267.1, +267.1
His, H	+248.6
Ile, I	+251.7, +248.4, +253.7, +253.7, +262.1, +253.9, +265.6, +256.4, +258.0
Leu, L	+248.3, +244.7, +253.3, +251.3, +252.1, +249.9, +251.3, +255.1, +255.9, +255.9, +256.3, +259.2, +255.8
Met, M	+257.6
Phe, F	+247.0, +246.6, +255.9, +250.1
Tyr, Y	+260.0, +260.6
Val, V	+245.8, +248.6, +252.1, +249.4, +261.2

Turkey ovomucoid third domain (OMTKY 3) (q)

0.05 M *in H_2O/D_2O*

Peptide nitrogen atoms

A15	+274.5	E19	?	S26	+263.9	T30	+268.9
C16	+268.7	Y20	?	D27	+258.7	Y31	+257.8
T17	+265.4	R21	+263.0	N28	?	G32	+264.4
L18	+275.5	G25	+262.1	K29	?	N33	+264.5

Pf1 filamentous bacteriophage coat protein (r)

in H_2O, pH = 4.3, +75°C

Peptide nitrogen atoms

L30	+270.0	L33	+267.1	A36	+264.6	I39	+266.8
V31	+268.9	A34	+266.0	G37	+281.7	Y40	+266.7
I32	+267.9	V35	+269.7	L38	+262.0		

Coliphage *λ-cro* repressor protein (s)

in H_2O, pH = 4.6

	Free	Increment upon complexation with O_R3 DNA
Lys-units	+268.9	+0.09
	+269.9	−0.43

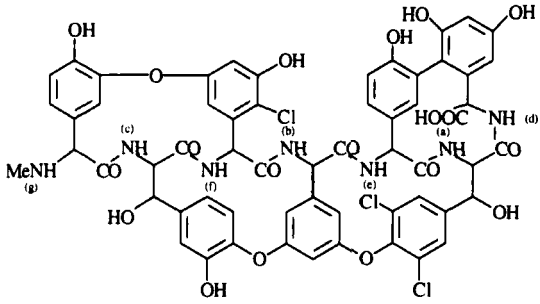
Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	+266.0	?	
	+264.6	−0.37	
	+271.2	−0.03	
	+263.9	−0.06	
	+261.4	−0.14	
	+260.5	−0.70	
Human N-ras p21 protein			(t)
in H_2O, pH = 7.5	Normal p21	Mutant p21	
S17	?	?	
K16	+255.4	+254.9	
G15	+271.6	+270.9	
V14	+267.9	+266.9	
G13	+266.4	+265.9	
G12/D12	+274.9	+262.3	
A11	?	?	
G10/G115	+273.9	+273.6	
G115/G10	+267.8	+267.8	
V9	+255.7	+255.2	
Ribonuclease A (RNase A)			(u)
N-terminal pentadecapeptide moiety ("S-peptide") units 1–15, *in H_2O, pH 6.02*	+347.4 (Lys-7, ε-NH_2) +267.9 (Gln-11, γ-amide) +215, +208 (His-12, ring)		
Synthetic S-peptide in complex with RNaseS′ (RNase A21–124), *in H_2O, values from titration sources for cationic species*	+267.9 (Gln-11, γ-amide) +207.1 (His-12, N_{δ_1}) +206.9 (His-12, N_{ε_2})		
Synthetic S-peptide in complexes, *in H_2O, pH 5.0*			
with 2′-CMP	+263.6 (Gln-11, γ-amide) +199.7 (His-12, N_{δ_1}) +206.1 (His-12, N_{ε_2})		
with 3′-CMP	+264.8 (Gln-11, γ-amide) +204.3 (His-12, N_{δ_1}) +206.2 (His-12, N_{ε_2})		
with 5′-AMP	+265.5 (Gln-11, γ-amide) +203.7 (His-12, N_{δ_1}) +207.3 (His-12, N_{ε_2})		
Streptomyces subtilisin inhibitor (SSI)			(v)
in H_2O	+257.1 (Met^{70}–Cys^{71}) +259.4 (Met^{73}–Val^{74}) +264.4 (Met^{103}–Asn^{104})		

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
Silk fibroins	from *Bombyx mori*	from *Philosamia cynthia ricini*	(w)
in H_2O	+256.5 (Ala) +260.1 (Tyr) +264.7 (Ser) +269.3 (Ser-*Gly*-Ala) +272.0 (Ala-*Gly*-Ser, Ala-*Gly*-Ala) +272.6 (Gly)	+256.6 (Ala) +258.6 (Ala) +260.2 (Tyr) +264.8 (Ser) +269.5 (Gly) +270.1 (Gly) +271.9 (Gly) +273.4 (Gly)	

Aridicin aglycon (x)



in 1 : 1 H_2O/DMSO

	Free +	Complexed with tripeptide	Free +	Complexed with pentapeptide
NH(a)	+274.6	+274.6	+274.6	+275.2
NH(b)	+261.9	+264.2	+262.1	+264.3
NH(c)	+272.2	+268.5	+272.2	+268.5
NH(d)	+251.9	+251.9	+253.7	+253.4
NH(e)	+258.1	+256.3	+258.1	+256.4
NH(f)	+262.1	+257.7	+261.8	+257.6

tripeptide = di-*N*-Ac—L-Lys—D-Ala—D-Ala
pentapeptide = *N*-Ac—L-Ala—γ-D-Gln—L-Lys(Ac)—D-Ala—D-Ala

Gramicidin A
HCO—L-Val—Gly—L-Ala—D-Leu—L-Ala—D-Val—L-Val—D-Val—L-Trp
$HOCH_2CH_2$—NH—L-Trp—D-Leu—L-Trp—D-Leu

0.05 M in DMSO	V1	+255.7	V6	+267.7	W11	+259.2	(y)
	G2	+270.7	V7	+263.3	L12	+258.8	
	A3	+259.0	V8	+263.6	W13	+259.2	
	L4	+262.0	W9	+257.7	L14	+258.1	
	A5	+259.6	L10	+258.6	W15	+269.3	

$NHCH_2CH_2OH$ +269.3

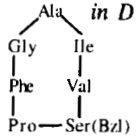
Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane					Notes
solid state	isotropic	σ_{11}	σ_{22}	σ_{33}	oriented	(z)
V1	+256	+315	+297	+156	+162	
G2	+270	+338	+309	+163	+247	
A3	+255	+320	+294	+151	+162	
L4	+262	+327	+296	+163	+215	
A5	+256	+322	+293	+153	+162	
V6	+261	+323	+298	+158	+215	
V7	+260	+323	+300	+157	+164	

Cyclosporin A

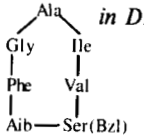
MeBmt[1]—Abu[2]—Sar[3]—MeLeu[4]—Val[5]
MeLeu[10]—MeLeu[9]—D-Ala[8]—Ala[7]—MeLeu[6]

in $CDCl_3$		*in C_6D_6*		(A)
A7	+252.7	A7	+252.1	
Abu	+259.5	Abu	+259.1	
	+260.9		+260.7	
A8	+261.3	A8	+260.9	
	+262.0		+262.3	
V5	+262.6		+263.2	
	+263.2	V5	+264.4	
	+264.1		+265.8	
	+268.2		+267.9	
	+269.2		+269.1	



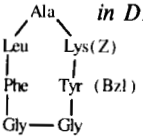
in DMSO

Ala	+264.2	(B)
Ile	+272.0	
Val	+267.7	
Ser	+258.7	
Pro	?	
Phe	+264.2	
Gly	+279.0	



in DMSO

Ala	+267.1	(B)
Ile	+272.1	
Val	+271.7	
Ser	+266.7	
Aib	+254.1	
Phe	+275.0	
Gly	+277.6	



in DMSO

Ala	+267.4	(B)
Lys	+260.0	
Tyr	+275.8	
Gly	+279.3	
Gly	+265.1	
Phe	+269.3	
Leu	+270.0	

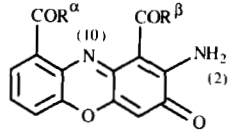
Table 13. —*cont.*

Substance *and its state*		Nitrogen shielding (ppm) referred to neat nitromethane		Notes
Antamanide from mushroom *Amanita phalloides*				(C)
0.07 M *in* $CDCl_3$		Val	+266.4	
		Pro	+243.3	
		Pro	+252.3	
Val^1—Pro^2—Pro^3—Ala^4—Phe^5		Ala	+252.6	
| |		Phe	+266.6	
Phe^{10}—Phe^9—Pro^8—Pro^7—Phe^6		Phe	+263.9	
		Pro	+243.8	
		Phe	+260.2	
		Phe	+271.2	
Toxins from *Amanita phalloides*				(D)
Various solutions				

X^1—Hyp^2—X^3
| |
Cys^8———X^4
| |
Gly^7—Ile^6—Gly^5

	α-amanitin	β-amanitin	γ-amanitin	amaninamide
X^1 =	Asn	Asp	Asn	Asn
X^2 =	γ,δ-$(OH)_2$-Ile	γ,δ-$(OH)_2$-Ile	γ-OH-Ile	γ,δ-$(OH)_2$-Ile
X^4 =	6-OH-Trp	6-OH-Trp	6-OH-Trp	Trp
NH (X-1)	+268.9	+266.3	+270.0	+269.8
NH_2 (X-1)	+262.1	–	+260.9	+262.3
NH (X-3)	+273.2	+275.5	+273.2	+273.2
NH (X-4)	+263.7	+263.2	+263.7	+263.6
Indole (X-4)	+257.7	+257.1	+257.6	+255.7
NH (Gly-5)	+283.8	+282.1	+284.5	+283.3
NH (Ile-6)	+260.5	+259.4	+260.6	+260.6
NH (Gly-7)	+270.2	+269.4	+270.3	+270.2
NH (Cys-8)	+268.2	+267.2	+268.1	+268.0

Actinomycin D (E)



R = —(N_α)—L-Thr—D-Val—L-Pro—Sar—L-(NMe)Val
|
O———————————┘

Solvent		$CDCl_3$	C_6D_6	CD_3OD	CD_3CN	*acetone-*d_6
Pro	(α)	+238.7	+238.8	+233.7	+232.9	+233.5
	(β)	+239.2	+239.1	+234.0	?	?

Table 13. —*cont.*

Substance *and its state*		Nitrogen shielding (ppm) referred to neat nitromethane					Notes
Val	(α)	+259.1	+258.3	+256.2	+254.9	+255.4	
	(β)	+260.0	+259.2	+257.4	+255.7	+256.0	
Thr	(α)	+266.7	+265.9	+262.1	+261.2	+260.9	
	(β)	+267.2	+267.0	+262.6	+262.8	+262.9	
MeVal	(α)	+271.2	+272.3	+265.9	+265.7	+266.3	
	(β)	+271.3	?	?	?	?	
Sar	(α)	+278.9	+280.7	+272.1	+274.0	+275.0	
	(β)	+279.0	?	?	?	+275.1	
N-10		+95.2	+98.6	+91.3	+88.2	+90.3	
2-NH_2		+298.4	+297.6	+293.8	+294.8	+292.9	
		+299.0				+293.5	

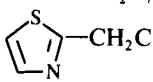
Oxytocin (F)
0.002 M
in H_2O

	Free			Bound to bovine neurophysin		
pH	6	2.3–6	2	6	2.3–6	2
Asn-5	+264.1	+264.1	+264.2	+266.0	+265.8	+265.1
Tyr-2	?	+256.7	+256.5	+255.2	+255.5	+255.6

8-Arginine-vasopressin (F)
0.002 M
in H_2O

	Free			Bound to bovine neurophysin		
pH	6	2.3–6	2	6	2.3–6	2
Asn-5	+264.3	+264.5	+264.3	+265.1	+264.5	+264.3
Tyr-2	?	+257.1	?	+255.5	+255.8	?
Phe-3	+260.2	+259.4	+259.0	+256.3	+256.8	+257.2
Cys-6	?	+260.5	?	+259.3	?	?

Bleomycin A_2 (G)
0.07 M *in* H_2O/D_2O, *pH = 3.9, +20°C*



+262.5 (NH) ("BIT" unit)

Me_2S^+—CH_2CH_2NHCO— +265.0
Thr +264.0
Val +248.1
His *(pH 1.24, +30°C)* +261.9 (NH)

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
Angiotensin				(H)
in H_2O, pH = 4.5		*0.3* M	*0.02* M	
	Arg-2	+307.7	+304.4	
	Val-3	+258.2	+257.9	
	Tyr-4	+255.7	+254.8	
	Val-5	+258.2	+256.2	
	Phe-8	+258.2	+256.2	
Leu-enkephalin, Tyr^1—Gly^2—Gly^3—Phe^4—Leu^5				(I)
0.04 M *in DMSO*		*+30°C*	*+60°C*	
	Gly-2	?	?	
	Gly-3	+271.3	+271.3	
	Phe-4	+259.5	+260.1	
	Leu-5	+257.0	?	
0.01 M *in H_2O, pH = 5.2*				(J)
	Tyr	+343.0 (NH_3^+)		
Vancomycin				(K)
0.14 M *in DMSO, +65°C*		Free	Complex with Ac—D-Ala—D-Ala	
	1-NH_2Me	+346.2	+339.9	
	2-NH	+268.7	+262.0	
	3-NH	+261.6	+260.6	
	4-NH	+261.2	+262.9	
	5-NH	+252.0	+252.7	
	6-NH	+272.7	+273.0	
	7-NH	+255.3	+254.1	
	8-$CONH_2$	+269.3	+271.4	
	9-NH_3^+	+322.8	+323.0	
Ac—D-Ala—D-Ala				(K)
in DMSO		Free	Complex with vancomycin	
	AcAla	+254.7	+252.3	
	Ala	+260.9	+259.0	
Ala—*Ala	+259.9 (*Ala, isotropic)			(L)
solid state	*+314.2* (σ_{11})			
	+301.4 (σ_{22})			
	+164.0 (σ_{33})			

Table 13. *—cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Gly—*Gly · HCl · H_2O	+264.5 (*Gly, isotropic)	(M)
solid state	+319.9 (σ_{11})	
	+309.3 (σ_{22})	
	+164.3 (σ_{33})	
Gly-Tyr	+338 (Gly, NH_2)	(N)
solid state	+258 (Tyr, NH)	(N)
Asp—Phe—OMe	+240.0 (Phe, free peptide)	(O)
in H_2O, pH = 6.0	+239.6 (Phe, complex with β-cyclodextrin)	
Boc—L-Ala—L-Pro—OCH_2Ph	+251 (Pro, isotropic)	(P)
(Boc = $PhCH_2OCO$)	+351 (σ_{11})	
solid state	+250 (σ_{22})	
	+154 (σ_{33})	
Ac—Gly—Ala—NH_2	+256.7 (NH, isotropic)	(Q)
solid state	+334.9 (σ_{11})	
	+294.4 (σ_{22})	
	+150.1 (σ_{33})	
in D_2O	+255.5 (NH)	(Q)
Ac—Gly—Tyr—NH_2	+262.2 (NH, isotropic)	(Q)
solid state	+327.4 (σ_{11})	
	+302.4 (σ_{22})	
	+170.2 (σ_{33})	
in D_2O	+259.8 (NH)	(Q)
Ac—Gly—Gly · HCl	+268.0 (NH, isotropic)	(Q)
solid state	+322.2 (σ_{11})	
	+320.6 (σ_{22})	
	+169.5 (σ_{33})	
in D_2O	+270.7 (NH)	(Q)
Ac—Gly—Gly—NH_2	+270.1 (NH, isotropic)	(Q)
solid state	+338.8 (σ_{11})	
	+315.3 (σ_{22})	
	+168.9 (σ_{33})	
in D_2O	+270.8 (NH)	(Q)
Ac—Gly—Phe—NH_2		
solid state	+256.2, +258.1 (NH, isotropic)	(Q)
in D_2O	+259.2 (NH)	(Q)
Alanine polymers and copolymers	[Ala*, Ala, X]$_n$	
solid state		(R)

Table 13. *—cont.*

Substance *and its state*					Nitrogen shielding (ppm) referred to neat nitromethane				Notes
					Ala*-NH nitrogen atoms				
X	% Ala*	% Ala	% X	Confor-mation	Isotropic	σ_{11}	σ_{22}	σ_{33}	
None	20	80	0	*α-helix*	+260.8	+155.6	+305.6	+321.6	
				β-sheet	+257.4	+158.6	+297.9	+315.6	
D-Ala	5	0	95	*a_L-helix*	+262.9	+162.6	+302.5	+323.6	
	20	0	80	*α_L-helix*	+263.1	+161.6	+304.5	+323.6	
Gly	20	60	20	*α-helix*	+261.0	+157.6	+302.2	+323.6	
	20	0	80	*β-sheet*	+260.8	+159.6	+300.0	+322.6	
Leu	5	0	95	*α-helix*	+261.0	+154.9	+303.6	+324.6	
	20	0	80	*α-helix*	+261.0	+155.6	+302.7	+324.6	
	5	75	20	*α-helix*	+261.5	+156.6	+302.5	+325.6	
	5	45	50	*α-helix*	+261.3	+152.6	+305.4	+325.6	
Val	5	0	95	*β-sheet*	+252.6	+149.6	+296.6	+312.6	
	20	0	80	*β-sheet*	+259.9	+157.6	+297.2	+324.6	
	5	25	70	*α-helix*	+261.0	+158.6	+306.5	+317.6	
Ile	20	0	80	*β-sheet*	+258.6	+159.6	+296.6	+319.6	
Asp(OBz)	5	0	95	*α-helix*	+258.3	+149.6	+304.9	+320.6	
	10	0	90	*α-helix*	+258.5	+149.6	+303.6	+322.6	
	20	0	80	*α-helix*	+258.1	+151.6	+300.9	+321.6	
Glu(OBz)	20	0	80	*α-helix*	+259.2	+153.6	+302.9	+320.6	
Glu(OMe)	20	0	80	*α-helix*	+259.7	+154.6	+301.5	+322.6	
Sar	20	0	80	*?*	+260.6	+161.6	+297.4	+322.6	

Boc—(L-Ala)$_7$—NHBu *solid state, β-sheet*	+257.8 (isotropic)	(S)
Poly(L-Leu) *solid state, α-helix*	+262.6 (isotropic)	(S)
Boc—(L-Leu)$_6$OEt *solid state, β-sheet*	+252.6 (isotropic)	(S)
Poly(*β*-benzyl-L-aspartate) *solid state, α-helix* *β-sheet*	+260.4 (isotropic) +259.2 (isotropic)	(S) (S)
Poly(*β*-benzyl-L-glutamate) *solid state, α-helix*	+262.0 (isotropic)	(S)
o-NO_2—CH_6H_4—SO—[L-Glu(OMe)]$_6$—NHBu *solid state, β-sheet*	+260.1 (isotropic)	(S)
Poly(*γ*-Me—L-glutamate) *solid state, α-helix*	+262.0 (isotropic)	(S)
o-NO_2—C_6H_4—SO—[L-Glu(OBz)]$_4$—OH *solid state, β-sheet*	+260.1 (isotropic)	(S)

Table 13. —*cont.*

Substance *and its state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Poly(L-Val)		
solid state, β-sheet	+253.7 (isotropic)	(S)
Poly(L-Ile)		
solid state, β-sheet	+253.5 (isotropic)	(S)
Ala residues in elastin	+244 (*β-sheet*)	(T)
solid state	+259 (*α-helix*)	(T)
Ala, Gly, Val-copolypeptides		(U)
in CF_3COOH Ala–Gly	+270.7	
Gly–Gly	+269.8	
Val–Gly	+266.9	
Ala–Val	+258.3	
Gly–Val	+257.5	
Ala–Ala	+254.4	
Gly–Ala	+254.1	
Val–Val	+252.8	
$MeCH(NH_2)PO_3H_2$ ("Ala-P")		(V)
lyophilized solid, pH 7.5	+339.2	
pH 13.5	+345.7	
$^{--}O_3P—CH_2—NH_2^+—CH_2—COOH$ (glyphosphate, *N*-phosphonomethylglycine)		(W)
in H_2O pH −1	+345	
pH 4.5 to 7.0	+341	
pH 13	+353	

(a) Data from ref. 1087, ^{15}N-labelled algae, by feeding with $K^{15}NO_3$, 30.416 MHz ^{15}N spectra, field parallel to sample tube, referenced originally, via a calibrated sample of 90% formamide, to 1 M HNO_3, +4.4 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(b) Data from refs. 390, 1088 and 1089, ^{15}N-labelled histidine moiety (at imidazole ring), 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, +4.4 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(c) Data from refs. 392 and 1090, details same as in footnote (b).

(d) Data from ref. 392, 32 MHz ^{15}N CPMAS spectra, other details as in footnote (b).

(e) Data from refs 389 and 390, 20.27 MHz ^{15}N CPMAS spectra, other details as in footnote (b).

(f) Data from ref. 918, ^{15}N-labelled substances, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous ammonium nitrate, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); ^{15}N–^{195}Pt coupling observed.

(g) Data from ref. 1091, ^{15}N-labelled sample, 60.8 MHz ^{15}N spectra, referenced originally to *internal* NH_4^+, probably *ca.* 358 ppm from neat nitromethane.

(h) Data from ref. 1092, 50.7 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported originally vs liquid ammonia taken at +381.9 ppm from neat nitromethane. The reference quoted contains corrections and additions to an earlier paper, ref. 197.

Table 13. —*cont.*

(i) Data from ref. 197, with additions and corrections in ref. 1092, details as in footnote (h), but $^1H\{^{15}N\}$ multiple-quantum (HMQC) COSY spectra.

(j) Data from ref. 215, ^{15}N-labelled enzyme, 500/50.7 MHz and 600/60.8 MHz 2-D $^1H\{^{15}N\}$ spectra, HMQC (heteronuclear multiple-quantum shift correlation), HMBC (heteronuclear multiple-bond correlation), and PS-COSY (pseudo-single-quantum COSY), field parallel to sample tube, referenced originally to liquid NH_3, + 381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1). See also ref. 630, where $^{13}C/^{15}N$-labelled Phe (F) units were examined, using 500/50.7 MHz $^1H\{^{15}N\}$ 2-D forbidden echo spectra, referenced indirectly to liquid NH_3; the relative shieldings for F4, F67, F104, F114, and F153 were essentially the same as those quoted in the present table, but they showed a systematic shift of about + 3.8 ppm from the latter, probably due to some errors in the calibration technique. See also ref. 388, where only valine (V) units were examined, for Nase TDP–Ca^{2+} complex both in the solid state (25 MHz ^{15}N CPMAS spectra) and in an aqueous solution (pH = 7.7, 500/50.7 MHz $^1H/^{15}N$ HMQC spectra); the relevant nitrogen shieldings were essentially the same, for both states, as those shown in the present table, within 0.2 ppm, with the only exception for valine in *N*-terminal extension, + 262.2 in the solid and + 250.9 in solution.

(k) Data from ref. 1093, ^{15}N-labelled cytochrome, details as in footnote (j), but 2-D HMQC-TOCSY and 2-D HMQC-NOESY spectra.

(l) Data from ref. 245, $^{15}N/^{13}C$-labelled sample, 500/125/50.7 MHz 3-D $^1H/^{13}C/^{15}N$ spectra, field parallel to sample tube, referenced originally as in footnote (j). See also references 496, 518, 519, and 628, where 50.7 MHz ^{15}N spectra were employed in observations of nitrogen shieldings of cytochrome c_3 at various pH values; the latter were referenced to 1 M HNO_3 (+ 4.4 ppm from neat nitromethane), but only some approximate values were reported, + 120 to + 210 ppm (after recalculation) for His and haeme units, + 230 to + 270 ppm for peptide nitrogen atoms and those in sidechains of TRP (T), Gln (E), and Asn (N), + 330 to + 350 ppm for *N*-terminus and Lys (L) sidechain nitrogen atoms.

(m) Data from ref. 199, details as in footnote (j), uniformly and selectively ^{15}N-labelled lysozyme, HMQC, ^{15}N-edited COSY and NOESY spectra; unlabelled lysozyme, double-quantum-filtered (DQF) COSY and TOCSY spectra.

(n) Data from refs 201, 202, and 1008, ^{15}N-labelled protein, experimental details as in footnote (m); the numbers with asterisks (*) represent resonance signals which showed appreciable broadening, owing to paramagnetic interactions, but could be discerned from the background.

(o) Data from ref. 231, ^{13}C and ^{15}N randomly labelled samples, 500/50.7 MHz $^1H\{^{15}N\}$ COSY spectra, calibration as in footnote (v).

(p) Data from ref. 204, ^{15}N-labelled amino acid residues, 500/50.7 MHz $^1H\{^{15}N\}$ COSY spectra, field parallel to sample tube, referenced originally to aqueous NH_4Cl, + 352.5 ppm from neat nitromethane (Table 2), conversion scheme IIb, (Table 1); the sequence of nitrogen shieldings in each of the groups follows the increasing shielding for the corresponding proton resonances.

(q) Data from ref. 98, natural-abundance 30.4 MHz ^{15}N INEPT spectra and 300/30.4 MHz $^1H\{^{15}N\}$ 2-D HMPQ spectra, field parallel to sample tube, referenced originally, via a transmitter frequency, to liquid NH_3, + 381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(r) Data from ref. 160, ^{15}N-labelled amino acid residues, 40.5/400 MHz and 50.7/500 MHz $^1H\{^{15}N\}$ COSY spectra, field parallel to sample tube, referenced originally to a fictitious standard taken + 90.4 ppm from a sample of *N*-acetylglycine, probably NH_4^+ in aqueous ammonium nitrate, + 359.6 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(s) Data from ref. 1094, ^{15}N-labelled lysine residues, 40.508 MHz ^{15}N DEPT spectra and 40.508/400 MHz $^1H\{^{15}N\}$ COSY spectra, other details as in footnote (r); the sequence of nitrogen shieldings follows that of the decreasing shielding of the corresponding protons.

Table 13. *—cont.*

(t) Data from ref. 210, ^{15}N-labelled protein, 500/50.7 MHz ^{1}H{^{15}N} 2-D HMQC spectra, calibration as in footnote (j).

(u) Data from ref. 1095, ^{15}N-labelled amino acid residues, 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4^+ in 4 M NH_4NO_3 in 2 M HNO_3, + 359.1 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(v) Data from ref. 873, ^{13}CO/^{15}N-labelled protein at methionine residues, 100.6/40.5 MHz ^{13}C{^{15}N} COSY spectra, field parallel to sample tube, referenced indirectly, via aqueous ammonium sulphate, to liquid NH_3, + 381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(w) Data from refs 35, 110, and 477, labelled samples, by feeding with [^{15}N] glycine, 9.08 MHz INEPT spectra, field perpendicular to sample tube, referenced originally to NH_4^+ in aqueous NH_4NO_3, + 359.6 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(x) Data from ref. 218, ^{15}N-labelled aglycon, 500/50.7 MHz zero- and double-quantum ^{1}H{^{15}N} COSY spectra, field parallel to sample tube, referenced originally to neat nitromethane, *corrected* for bulk susceptibility effects.

(y) Data from refs 170 and 171, natural-abundance 40.5/400 MHz ^{15}N{^{1}H} COSY spectra, field parallel to sample tube, referenced originally to NH_4^+ in 5 M NH_4NO_3 in 2 M HNO_3, + 359.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(z) Data from refs 343 and 344, ^{15}N specifically labelled gramicidin, 20.3 MHz powder and CPMAS ^{15}N spectra of dispersed and oriented solid samples, referenced originally to NH_4^+ in aqueous NH_4NO_3, + 359.6 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1). Essentially the same values for Val^7-unit were obtained in ref. 189, from 20.3 MHz ^{15}N powder spectra of ^{15}N selectively labelled sample, referenced originally to NH_4^+ in solid ammonium nitrate, + 358.4 ppm from neat nitromethane (Table 2).

(A) Data from ref. 174, 30.4 MHz ^{15}N INEPT and 30.4/300 MHz ^{15}N{^{1}H} COSY spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, + 4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(B) Data from ref. 175, 30.4/300 MHz ^{15}N{^{1}H} COSY spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(C) Data from ref. 172, 50.7 MHz ^{15}N INEPT spectra and 500/50.7 MHz ^{1}H{^{15}N} COLOC-COSY spectra, field perpendicular to sample tube, referenced originally to formamide, + 268.6 ppm from neat nitromethane (Table 2), conversion scheme IVb (Table 1); reported originally vs. fictitious ammonia standard taken at + 112.4 ppm from the reference employed; we retrieved the original data, and carried out recalculation as indicated above.

(D) Data from ref. 220, details as in footnote (C).

(E) Data from ref, 181, *ca.* 0.02 M solutions, ^{15}N-labelled actinomycin, 50.1/500 MHz and 30.4/300 MHz ^{15}N{^{1}H} COSY spectra, field parallel to sample tube, referenced originally to 4 M NH_4Cl in 2 M HCl, + 352.5 ppm from neat nitromethane (Table 2) conversion scheme IIb (Table 1).

(F) Data from ref. 97, ^{15}N-labelled amino acid residues, details as in footnote (A), referenced originally, indirectly, to fictitious ammonia standard taken at + 380.2 ppm from neat nitromethane, conversion scheme IVb (Table 1); for formulae and more data, see ref. 5, p. 404.

(G) Data from ref. 192, natural-abundance 50.7/500 MHz ^{15}N{^{1}H} 2-D HMQC spectra, calibration as in footnote (j).

(H) Data from ref. 794, ^{15}N selectively labelled angiotensins, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(I) Data from ref. 190, 400/40.4 MHz ^{1}H{^{15}N} 2-D HMQC spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

Table 13. —*cont.*

(J) Data from ref. 1096, 28.9 MHz ^{14}N spectrum, other details as in footnote (I).

(K) Data from ref. 109, details as in footnote (y).

(L) Data from ref. 346, $^{13}CO/^{15}N$-labelled peptide bond, 20.27 MHz ^{15}N CP-MRCV-8 solid-state measurements, referenced originally to solid NH_4Cl, + 341.0 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects; originally reported vs fictitious ammonia standard taken at + 38.5 ppm from the reference employed; we retrieved the original data, and recalculated them as indicated above.

(M) Data from ref. 320, ^{15}N selectively labelled sample, 29.8 MHz ^{15}N CPMAS spectra, referenced originally to aqueous NH_4Cl, + 352.9 ppm from neat nitromethane (Table 2).

(N) Data from ref. 387, 29.8 MHz ^{15}N CPMAS spectra, referenced originally to a fictitious ammonia standard taken at + 380.2 ppm from neat nitromethane.

(O) Data from ref. 763, ^{15}N-labelled Phe moiety, 40.4 MHz ^{15}N spectrum, calibration as in footnote (z).

(P) Data from ref. 325, ^{15}N-labelled Pro moiety, 15 MHz ^{15}N CPMAS and powder spectra, referenced originally to solid ammonium sulphate, + 355.7 ppm from neat nitromethane (Table 2, conversion scheme II (Table 1).

(Q) Data from ref. 324, $^{13}C/^{15}N$-labelled peptide bonds, 20.3 MHz ^{15}N CPMAS and powder spectra, referenced originally to solid NH_4Cl, + 341.0 ppm from neat nitromethane (Table 2); also 36.5 MHz ^{15}N solution spectra, field parallel to sample tube, referenced originally to *internal* NH_4Cl, *ca.* + 252.9 ppm from neat nitromethane (Table 2); originally reported vs fictitious ammonia standard taken at + 21 ppm from the references used; we retrieved the original data and carried out recalculation as indicated above.

(R) Data from refs 71 and 1097, ^{15}N-labelled alanine residues (Ala*), 27.4 MHz ^{15}N CPMAS spectra, referenced originally to solid glycine, + 348.0 ppm from neat nitromethane (Table 2), but originally reported vs NH_4^+ standard taken at + 11.6 ppm from the actual reference employed; this corresponds to aqueous NH_4NO_3, see Table 2.

(S) Data from ref. 74, details as in footnote (R), but natural-abundance spectra.

(T) Data from ref. 364, 30.4 MHz ^{15}N CPMAS spectra, referenced originally to NO_3^- in aqueous NH_4NO_3, + 4.0 ppm from neat nitromethane (Table 2).

(U) Data from ref. 111, 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally as in footnote (T), conversion scheme IIb (Table 1).

(V) Data from ref. 1074, ^{15}N-labelled sample, 32.2 MHz ^{15}N CPMAS spectra, referenced originally to solid NH_4Cl, + 341.0 ppm from neat nitromethane.

(W) Data from ref. 517, ^{15}N-labelled sample, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4^+ in aqueous ammonium nitrate, + 359.6 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

Table 14. Nitrogen shieldings in some azides

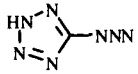
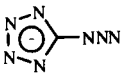
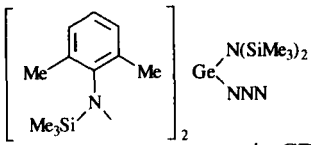
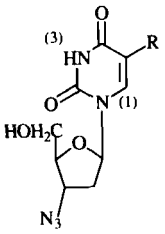
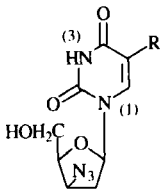
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
Azide ion					
$Na^+[^-N{=}N^+{=}N^-]$	0.3 M in H_2O		+280.6 (=N^-)		(a)
			+131.5 (=N^+=)		(a)
	0.6 M in 0.1 M phosphate buffer		+256(?) (=N^-)		(b)
	as above, complex with chloroperoxidase		+264(?) (=N^-)		(b)
Covalent azides					
$R{-}N{=}N^+{=}N^-$		RN	=N^+=	=N^-	
various	various	+243 to +325	+124 to +149	+114 to +159	(a)
Ph—NNN	in $CDCl_3$	+292.7	+134.4	+147.0	(c)
	in DMSO	–	+145.7	+146.5	(d)
	in DMSO	–	+140.7	+151.2	(d)
$(Bu^tO)_3Si$—NNN	in $CDCl_3$	+316	+145.4	+205.8	(e)
	in $CDCl_3$	+204	+143	+204	(e)
	0.4 M in acetone				(f)
	"AZU", R = H	+35°C	+308.4	+135.7	+165.8
			+232.9 *(N-1)*		
			+233.9 *(N-3)*		
	"AZT", R = Me	+30°C	+303.3	+134.6	+167.0
			+237.8 *(N-1)*		
			+227.7 *(N-3)*		
		−10°C	+303.5	+135.5	+164.0
			+238.0 *(N-1)*		
			+228.1 *(N-3)*		

Table 14. *—cont.*

Compound	Solution or state		Nitrogen shielding (ppm) referred to neat nitromethane			Notes
	0.4 M in acetone					(f)
	"AZU", R = H	+35°C	+305.7	+135.9	+168.4	
			+231.9 *(N-1)*			
			+244.0 *(N-3)*			
	"AZT", R = Me	+30°C	+305.9	+135.2	+169.3	
			+237.1 *(N-1)*			
			+227.7 *(N-3)*			
		−10°C	+306.6	+135.2	+170.4	
			+237.1 *(N-1)*			
			+228.1 *(N-3)*			
		−20°C	+306.7	+136.2	+170.6	
			+237.1 *(N-1)*			
			+228.2 *(N-3)*			
$(CF_3S)_2N{-}B\langle^{NNN}_{NNN}$	neat		+298.8	+150.6	+173.8	(g)
	+ 10% C_6D_6		+335.2 *(N-B)*			
$[(CF_3S)_2N]_2B{-}NNN$	neat		+294.8	+151.6	+168.6	(g)
	+ 10% C_6D_6		+340.0 *(N-B)*			
N_3^- as ligand to Co^{3+}		in H_2O	+239 (N-1)			(h)
			+333 (N-2)			(h)
			+334 (N-3)			(h)

(a) See ref. 5, p. 430, and references therein.

(b) Data from ref. 1017, ^{15}N-labelled terminal atom in the azide ion, 36.5 MHz ^{15}N spectra, referenced to NO_3^- in aqueous ammonium nitrate, +4.0 ppm from neat nitromethane (Table 2); however, the values depart significantly from the data quoted in footnote (a), and probably there was some error in the referencing technique employed.

(c) Data from ref. 648, 40.56 MHz ^{15}N spectrum, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(d) Data from ref. 668, selectively ^{15}N-labelled azido group, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 10 M HNO_3, +18.2 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(e) Data from ref. 795, 25.5 MHz ^{15}N spectra and 18.1 MHz ^{14}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(f) Data from ref. 703, 27.4 MHz ^{15}N spectra, calibration as in footnote (e); the substances are potential inhibitors of replication of human immunodeficiency virus (HIV) and Moloney murine leukaemia virus (MuLV).

(g) Data from ref. 788, 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(h) Data from ref. 732, 18.059 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

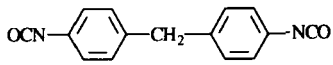
Table 15. Nitrogen shieldings in cyanates, isocyanates, thiocyanates, isothiocyanates and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Covalent isothiocyanates, R—N=C=S			
Me—NCS	0.3 M in DMSO	+287.02	(a)
	neat liquid	+289.90	(a)
	0.3 M in acetone	+290.91	(a)
	0.3 M in dioxane	+290.93	(a)
	0.3 M in $CHCl_3$	+291.61	(a)
	0.3 M in CH_2Cl_2	+291.66	(a)
	0.3 M in MeOH	+292.08	(a)
	0.3 M in benzene	+292.58	(a)
	0.3 M in CCl_4	+293.68	(a)
	0.3 M in Et_2O	+294.42	(a)
	0.3 M in n-hexane	+296.90	(a)
Bu—NCS	0.2 M in DMSO	+276.8	(b)
	0.2 M in THF	+276.8	(b)
	0.2 M in $MeNO_2$	+276.9	(b)
	0.2 M in MeCN	+278.4	(b)
	0.2 M in $(Me_2N)_3$ PO	+278.5	(b)
	0.2 M in dioxane	+278.8	(b)
	neat liquid	+279.0	(b)
	0.2 M in CH_2Cl_2	+279.0	(b)
	0.2 M in MeOH	+279.4	(b)
	0.2 M in $CHCl_3$	+280.0	(b)
	0.2 M in Et_2O	+281.1	(b)
Ph—NCS	in $CDCl_3$	+271.3	(c)
$R^2CH=CH(R^1)$—NCS	neat liquids or in $CHCl_3$		(b)
R^1 / R^2			
Pr / H		+268.4	
t-Bu / H		+271.5	
n-hexyl / H		+268.4	
H / Ph		+275.6	
Et / Et		+264.3	
SMe / Et	(stereoisomers)	+271.5 +268.1	
Me_3Si—NCS	in $CDCl_3$	+265.3	(d)
$Si(NCS)_4$	in pyridine-d_5	+237.2	(d)
Covalent thiocyanates R—S—C≡N			
Me—SCN	neat liquid	+105	(b)
Bu—SCN	0.2 M in Et_2O	+101.8	(b)

Table 15. —*cont.*

Compound		Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
		neat liquid	+102.5	(b)
		0.2 M in dioxane	+103.7	(b)
		0.2 M in $(Me_2N)_3PO$	+104.2	(b)
		0.2 M in CH_2Cl_2	+104.9	(b)
		0.2 M in MeCN	+105.4	(b)
		0.2 M in DMSO	+105.6	(b)
		0.2 M in THF	+105.6	(b)
		0.2 M in $MeNO_2$	+106.5	(b)
		0.2 M in MeOH	+107.9	(b)
Ph—SCN		neat liquid	+97.0	(b)
$R^2CH{=}CH(R^1){-}SCN$		neat liquids or in $CHCl_3$		(b)
R^1	R^2			
H	H		+95.6	
Pr	H		+93.9	
t-Bu	H		+93.6	
n-hexyl	H		+93.1	
H	Ph		+97.2	
SMe	Et	(stereoisomers)	+97.0 +100.2	
(Iso)thiocyanate ions and ligands				
$K^+[NCS]^-$		0.3 M in H_2O	+174.1	(e)
		sat. in H_2O	+170.0	(e)
$NH_4^+[NCS]^-$		solid state	+170.9 (NCS)	(f)
			+345.8 (NH_4)	(f)
$Li^+[NCS]^-$		in H_2O	+160.1	(g)
$Bu_4N^+[NCS]^-$		in H_2O	+167.0 (NCS)	(g)
$(cyclohexyl)_3Sn(NCS)$		0.15 M in toluene	+264.2	(h)
$[Ge(NCS)_6]^{2-}$		in acetone	+225.0	(i)
$[Ge(NCS)_5Cl]^{2-}$		in acetone	+222.0	(i)
$[Ge(NCS)_4Cl_2]^{2-}$		in acetone	+219.0	(i)
$Ge(NCS)_4 \cdot dipy$		in acetone	+237.2	(i)
$Ge(NCS)_3Cl \cdot dipy$		in acetone	+231.5	(i)
$Ge(NCS)_2Cl_2 \cdot dipy$		in acetone	+229.9	(i)
$Ge(NCS)_nCl_{4-n}$		in acetone	+269 to +275	(i)
$K_4[Nb_2(S_2)_2(NCS)_8]$		in acetone	+217	(j)
$Cs_4[Nb_2(S_2)_2(NCS)_8]$		in MeCOOH	+209	(j)
$[Bu_4N]_4[Nb_2(SSe)_2(NCS)_8]$		in acetone	+221	(j)
$[Hg(SCN)_4]^{2-}$		in H_2O	*ca.* +139	(k)
$[Cd(SCN)_4]^{2-}$		in H_2O	*ca.* +171	(k)
$[Zn(NCS)_4]^{2-}$		in H_2O	*ca.* +200	(k)

Table 15. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Covalent isocyanates			
R—N=C=O	various	+338 to +365	(l)
SF_5—NCO	neat liquid	+275.8 (^{14}N)	(m)
TeF_5—NCO	neat liquid	+307.9 (^{14}N)	(m)
		+305.9 (^{15}N)	(m)
	solid	+336	(n)
Covalent cyanates			
R—O—C≡N	various	+190 to +222	(l)
SeF_5—OCN	neat liquid	+193.2	(m)
(Iso)cyanate ion			
$K^+[NCO]^-$	0.3 M in H_2O	+302.6	(l)
	sat. in H_2O	+302.9	(l)

(a) Data from ref. 32, high-precision 4.33 MHz ^{14}N spectra in CW mode, differential saturation technique combined with lineshape fitting, $+35 \pm 0.2$°C, referenced to neat nitromethane in concentric spherical sample and reference containers in order to eliminate bulk susceptibility effects.

(b) Data from ref. 1098, 25.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) Data from ref. 730, 9.12 MHz ^{15}N spectrum, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 154, 36.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 0.1 M nitromethane in $CDCl_3$, +3.8 ppm from neat nitromethane (Table 26), conversion scheme IIb (Table 1).

(e) See ref. 5, pp. 433–436, and references therein.

(f) Data from ref. 351, 20.3 MHz ^{15}N CPMAS and static powder spectra, rotation rate 1.63 kHz, referenced originally to liquid NH_3, +381.99 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(g) See footnote (b).

(h) Data from ref. 939, 4.33 MHz ^{14}N spectrum, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(i) Data from refs. 654 and 1099, 26.0 MHz ^{14}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; dipy = 2,2′-dipirydyl.

(j) Data from ref. 1100, 21.68 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to NO_3^-, probably in aqueous $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(k) Data from ref. 1101, 7.14 MHz ^{14}N spectra, referenced to *internal* NH_4^+ in NH_4NCS which was present in the solutions, probably about +355 ppm from neat nitromethane if one assumes that the NCS resonance observed appears at +170 ppm from nitromethane, as shown in this table.

(l) See footnote (e).

(m) Data from ref. 938, 6.43 MHz ^{14}N spectra and 9.03 MHz ^{15}N spectrum, field perpendicular to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

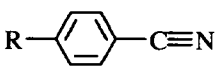
(n) Data from ref. 1057, 20.3 MHz ^{15}N CPMAS spectrum, referenced originally (uncorrected) to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2).

Table 16. Nitrogen shieldings in cyanides, isocyanides, fulminates and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Covalent cyanides (nitriles)			
Me—C≡N (acetonitrile)	0.05 M in cyclohexane	+125.81	(a)
	0.25 M in CCl_4	+127.22	(a)
	0.25 M in benzene	+129.66	(a)
	0.25 M in Et_2O	+129.75	(a)
	0.25 M in dioxane	+132.21	(a)
	0.25 M in acetone	+133.52	(a)
	0.25 M in DMSO	+133.99	(a)
	0.25 M in $CHCl_3$	+134.53	(a)
	0.25 M in CH_2Cl_2	+134.58	(a)
	neat liquid	+135.29	(a)
	0.25 M in EtOH	+138.34	(a)
	0.25 M in MeOH	+139.62	(a)
	0.25 M in H_2O	+145.47	(a)
	0.25 M in CF_3CH_2OH	+148.82	(a)
Et—C≡N	0.25 M in cyclohexane	+128.22	(a)
	0.25 M in CCl_4	+129.25	(a)
	0.25 M in Et_2O	+131.03	(a)
	0.25 M in benzene	+131.28	(a)
	0.25 M in dioxane	+133.66	(a)
	0.25 M in acetone	+134.54	(a)
	0.25 M in DMSO	+134.89	(a)
	0.25 M in CH_2Cl_2	+136.46	(a)
	0.25 M in $CHCl_3$	+136.58	(a)
	0.25 M in EtOH	+138.59	(a)
	0.25 M in MeOH	+140.63	(a)
	0.25 M in H_2O	+146.96	(a)
	0.25 M in CF_3CH_2OH	+151.40	(a)

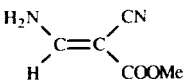
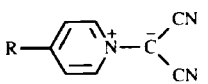
$Pr^i—C\equiv N$	0.25 M in cyclohexane	+129.80	(a)
	0.25 M in CCl_4	+131.03	(a)
	0.25 M in Et_2O	+132.23	(a)
	0.25 M in benzene	+132.78	(a)
	0.25 M in dioxane	+134.76	(a)
	0.25 M in acetone	+135.81	(a)
	0.25 M in DMSO	+136.05	(a)
	0.25 M in CH_2Cl_2	+137.78	(a)
	0.25 M in $CHCl_3$	+138.39	(a)
	0.25 M in EtOH	+139.58	(a)
	0.25 M in MeOH	+141.74	(a)
	0.25 M in H_2O	+148.36	(a)
	0.25 M in CF_3CH_2OH	+151.83	(a)
$Bu^t—C\equiv N$	0.25 M in cyclohexane	+131.51	(a)
	0.25 M in CCl_4	+132.70	(a)
	0.25 M in Et_2O	+134.02	(a)
	0.25 M in benzene	+134.46	(a)
	0.25 M in dioxane	+136.30	(a)
	0.25 M in acetone	+137.33	(a)
	0.25 M in DMSO	+137.51	(a)
	0.25 M in CH_2Cl_2	+139.78	(a)
	0.25 M in $CHCl_3$	+140.56	(a)
	0.25 M in EtOH	+140.84	(a)
	0.25 M in MeOH	+143.07	(a)
	0.25 M in H_2O	+149.89	(a)
	0.25 M in CF_3CH_2OH	+153.87	(a)
Me—CN	neat + 10% benzene-d_6	+136.0	(b)
	in CH_2Cl_2 + $Ph_3Si^+ClO_4^-$	+134.5	(c)
	absorbed on decationated zeolite NaY activated at 300 K and 400 K	+155	(d)
	as above, after heating	+150	(d)

Table 16—*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
Pr^i—CN	neat + 10% benzene-d_6	+137.0		(b)
Bu^t—CN	neat + 10% benzene-d_6	+139.0		(b)
Me_3Si—CN	neat + 10% benzene-d_6	+77.7		(b)
Ph—CN	in $CDCl_3$	+123.8		(e)
		+123.5		(f)
substituted Ph—CN	in $CDCl_3$			
2,4,6-Me_3		+123.5		(f)
2,4,6-Et_3		+115.2		(f)
2,4,6-i-Pr_3		+114.8		(f)
2,4,6-t-Bu_3		+100.3		(f)
3-CF_3		+117.8		(e)
	solid state			(g)
R		static	MASS	
NMe_2	(isotropic)	+129.4	+129	
	(σ_{11})	−14.7	−23	
	(σ_{22})	+26.2	+34	
OMe	(σ_{33})	+376.6	+375	
	(isotropic)	+128.9	+129	
	(σ_{11})	−11.1	−9	
	(σ_{22})	+22.8	+23	
	(σ_{33})	+374.9	+379	

Me	(isotropic)	+127.2	+127
	(σ_{11})	+14.2	−3
	(σ_{22})	+14.6	+11
	(σ_{33})	+381.1	+373
F	(isotropic)	+126.4	+125
	(σ_{11})	−12.0	−3
	(σ_{22})	+11.4	+5
	(σ_{33})	+379.8	+376
Cl	(isotropic)	+124.5	+124
	(σ_{11})	−13.6	−6
	(σ_{22})	+10.5	0
	(σ_{33})	+376.5	+380
Br	(isotropic)	+123.7	+123
	(σ_{11})	−16.3	−9
	(σ_{22})	+7.7	+4
	(σ_{33})	+377.4	+378
Bu^t	(isotropic)	+123.5	+124
	(σ_{11})	−16.4	−11
	(σ_{22})	+7.2	0
	(σ_{33})	+379.6	+382
CN	(isotropic)	+122.1	+120
	(σ_{11})	−11.7	−11
	(σ_{22})	+1.7	−2
	(σ_{33})	+376.2	+373
$NMe_3^+ I^-$	(isotropic)	+115.9	+117
	(σ_{11})	−21.5	−21
	(σ_{22})	−0.8	−4
	(σ_{33})	+369.8	+373
NO_2	(isotropic)	+118.9	+117
	(σ_{11})	−16.0	−8
	(σ_{22})	−4.9	−6
	(σ_{33})	+377.6	+371

Table 16—*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$H-C\equiv N$	acidic aqueous	+145 (NCN) +116 (CN ion)	(h) (h)
$HOOC-CH_2-CN$	in $CDCl_3$ in $CDCl_3$ + HBA	+137.1 +139.6	(i) (i)
$(^-OOC-CH_2-CN)_2Mg^{2+}$	in $CDCl_3$	+143.5	(i)
	in DMSO	+121.8 (CN)	(j)
Cyano group			
in cyanamides, R_2N-CN		see Table 11	
in cyanates, R—O—CN		see Table 15	
in cyanohydrazones, RC(CN)=NNHR		see Table 9	
in cyano-azo cpds., R—N=N—CN		see Table 28	
in $[N(CN)_2]^-$ ion		see Table 11	
in $[R-C(NO)CN]^-$ ions		see Table 29	
 (R = CN, COOMe, COMe, COPh, H, CH_2Ph, Bu^t, Pr, Pr^i, Et, Me, NO_2)	in DMSO + $Cr(acac)_3$	+88.3 to +89.1	(k)
Nitrilium ions			
$R-C\equiv N^+-R$	various	+215 to +252	(l)
$H-C\equiv N^+-KrF$	in BrF_5, −57°C	+200.8	(m)

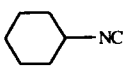
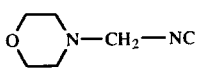
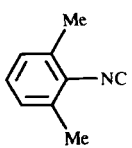
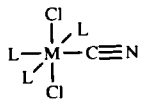
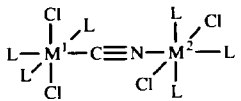
$H—C{\equiv}N^+—XeF$	in anhydrous HF, −10°C	+235.4	(n)
$Me—C{\equiv}N^+—XeF$	in anhydrous HF, −10°C	+251.1	(n)
$Et—C{\equiv}N^+—XeF$	in anhydrous HF, −10°C	+251.9	(n)
$FCH_2—C{\equiv}N^+—XeF$	in anhydrous HF, −10°C	+229.2	(n)
$[HCN—Ag—NCH]^+ SbF_6^-$	in liquid SO_2	+157.8	(o)
Fulminates and nitrile *N*-oxides			
$R—C{\equiv}N{\rightarrow}O$	various	+160 to +189	(p)
$Na^+(CNO)^-$	in H_2O	+180	(p)
MeHg—CNO	1 M in DMSO	+161.4	(q)
	0.87 M in THF	+161.1	(q)
PhHg—CNO	1.3 M in DMSO	+159.3	(q)
	0.35 M in THF	+168.6	(q)
$Hg(CNO)_2$	0.8 M in DMSO	+163.3	(q)
	0.03 M in THF	+161.8	(q)
Covalent isocyanides (isonitriles)			
$R—N^+{\equiv}C^-$	neat liquids	+185 to +220	(r)
$Pr^i—NC$	0.1 M in CH_2Cl_2	+194	(s)
Bu—NC	0.1 M in CH_2Cl_2	+210	(s)
$Bu^t—NC$	0.1 M in CH_2Cl_2	+186	(s)
	0.1 M in CH_2Cl_2	+197	(s)
$PhCH_2—NC$	0.1 M in CH_2Cl_2	+212	(s)
	0.1 M in CH_2Cl_2	+206	(s)
	0.1 M in CH_2Cl_2	+211	(s)

Table 16—*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
CF_3—NC	neat liquid, −102°C	+207.6	(t)
(R—NC)$Mo(CO)_5$	in CH_2Cl_2		(s)
R			
Bu^t		+180	
Pr^i		+188	
cyclohexyl		+191	
2,4-Me_2-phenyl		+200	
cis-(R—NC)$_2Mo(CO)_4$	in CH_2Cl_2		(s)
R			
Bu^t		+182	
Pr^i		+190	
cyclohexyl		+193	
2,4-Me_2-phenyl		+202	
fac-(R—NC)$_3Mo(CO)_3$	in CH_2Cl_2		(s)
R			
Bu^t		+184	
Pr^i		+190	
cyclohexyl		+196	
2,4-Me_2-phenyl		+202	

cis-(R—NC)$_4$Mo(CO)$_2$	in CH_2Cl_2		(s)
R			
Bu^t		+187, +183	
Pr^i		+194, +193	
cyclohexyl		+198, +196	
2,4-Me$_2$-phenyl		+196	
R = 2,6-Me$_2$-phenyl	in CH_2Cl_2		(s)
Mo(CO)(R—NC)$_5$		+203	
Mo(R—NC)$_6$		+197	
(R—NC)W(CO)$_5$		+202	
cis-(R—NC)$_2$W(CO)$_4$		+203	
fac-(R—NC)$_3$MW(CO)$_3$		+203	
cis-(R—NC)$_4$W(CO)$_2$		+206	
W(CO)(R—NC)$_5$		+197	
W(R—NC)$_6$		+197	
Cyanide ion and cyano complexes			
K^+CN^-	0.3 M in H_2O	+106.1	(u)
	8.5 M in H_2O	+102.5	(u)
$[Mn_2H(CN)(CO)_5(dppm)_2]$	in CD_2Cl_2, +22°C	+57.6	(v)
$[Mn_2H(CNH)(CO)_5(dppm)_2]^+$	in CD_2Cl_2 + $HBF_4 \cdot Et_2O$		
	+22°C	+183.4	(v)
	−80°C	+172.4 (doublet)	(v)
$[Mn_2H\{\mu\text{-}\eta^2\text{-}CN\}(CO)_4(dppm)_2]$	in CD_2Cl_2, +22°C	+139.7	(v)
$[Mn_2H\{\mu\text{-}\eta^2\text{-}CNH\}(CO)_4(dppm)_2]^+$	in CD_2Cl_2 + $HBF \cdot Et_2O$		
	−80°C	+235.6	(v)

Table 16—*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in CH_2Cl_2 (L = PMe_2Ph)		(w)
M = Ir		+95.9	
M = Rh		+85.3	
	in CH_2Cl (L = PMe_2Ph)		(w)
M^1 M^2			
Ir Ir		+204.6	
Ir Rh		+178.1	
Rh Ir		+196.1	
Rh Rh		+169.9	
$K_4[Re(CN)_7] \cdot 2\ H_2O$	in D_2O	+99	(x)
$K_4[Re(CN)_6] \cdot 3\ H_2O$	in D_2O	+98	(x)
$K_4[Co(CN)_6]$	in D_2O	+98	(x)

CN^- ions coordinated in cyano-haemoprotein units			
Horseradish peroxidase	in H_2O, pH = 7.0	−572	(y)
	in D_2O, pD = 7.3	−574	(y)
Lactoperoxidase	in H_2O, pH = 7.3	−419	(y)
Chloroperoxidase	in H_2O, pH = 6.1	−408	(y)
Coprinus cinereus peroxidase	in H_2O	−574	(z)
Cytochrome *c*	in D_2O, pH = 7.8	−843	(y)
Cytochrome *c* haemopeptide-11	in D_2O, pD = 7.4	−745	(y)
Myoglobin	in D_2O, pD = 8.0	−932	(y)
Haemoglobin	in D_2O, pD = 7.7	−981 (α)	(y)
		−1051 (β)	(y)
Cyano Fe(III) porphyrin complexes (Prot = protohemin) (Prot DME = its dimethyl ester)			(y)
$(CN)_2$Fe $Prot^{3-}$	in H_2O, pH = 9.2	−444	
$(CN)_2$Fe Prot DME^-	in DMSO	−770	
	in benzene	−765	
	in benzene + N-Me-imidazole	−683	
(N-Me-imidazole)(CN)Prot DME	in DMSO	−922	
(imidazole)(CN)Prot DME	in DMSO	−1011	
(imidazole anion)(CN) Prot DME	in DMSO	−734	
Cyano ligands in ferricytochrome *c* derivatives	in D_2O		(A)
Bovine	(pD = 6.4)	−855	
Chicken		−858	

Table 16—*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Dog		−857	
Horse	(pD = 6.07)	−852	
Pigeon		−861	
Porcine		−857	
Rabbit		−851	
Sheep		−856	
Tuna	(pD = 6.3)	−854	
C. brusei		−880	
S. cerevisiae		−882	
Cyano ligand in cytochrome P-450$_{cam}$	in H_2O		(B)
without *d*-camphor		−437 (*)	
with *d*-camphor		−504	
without *d*-camphor, upon addition of the latter		−517	
without *d*-camphor, in the presence of the latter and putidaredoxase		−481 (*)	
Cyano ligands low-spin Fe(III) porphyrins			(C)
$[FeL(CN)_2]^-$	aqueous detergent micelles, pH = 9.6	−580 to −450	

[FeL(py)(CN)]	detergent micelles in aqueous pyridine	−920 to −880
Free CN^- in the systems		+118

(a) Data from ref. 33, high-precision ^{14}N measurements at 36.141524 MHz, +35.0 ± 0.2°C, field parallel to sample tube, referred to neat nitromethane via 0.3 M nitromethane in deuterioacetone, +0.77 ppm from neat nitromethane; Lorentzian lineshape fitting was employed, and the standard deviations of the shieldings estimated were smaller than 0.1 ppm; the results are corrected for bulk susceptibility effects.

(b) Data from ref. 877, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) Data from ref. 1102, ^{15}N spectra, spectrometer not specified, referenced originally to liquid ammonia taken at +380.2 ppm from neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 1103, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane via a calibrated sample of neat acetonitrile, uncorrected for bulk susceptibility effects.

(e) Data from ref. 879, 30.45 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to aqueous NH_4Cl, +352.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); the results were originally reported vs fictitious ammonia standard taken at +25.0 ppm from the actual reference employed, and we retrieved the original data and recalculated them as indicated above.

(f) Data from ref. 1104, 36.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4^+ in aqueous ammonium nitrate, +359.6 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); originally reported vs fictitious ammonia standard taken at +20.7 ppm from the reference employed, neglecting the fact that the latter value refers to a field which is perpendicular to sample tube; we retrieved the original data and recalculated them as indicated above; $Cr(acac)_3$ was employed as a relaxation reagent for the samples.

(g) Data from ref. 331, ^{15}N-labelled CN group, 20.3 MHz ^{15}N static-powder and MASS spectra, referenced originally to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects; the data from static powder spectra are accurate, on the average, within ±0.5 ppm; those obtained from the spinning sidebands (SSB) in the MASS spectra (rotation rate 1.0–2.5 kHz) are less precise, from ±1 ppm to +6 ppm.

(h) Data from ref. 1105, 28.9 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to 0.1 M nitromethane in $CDCl_2$ + 3.8 ppm from neat nitromethane (Table 26), conversion scheme IIb (Table 1).

(i) Data from ref. 108, 40.0 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat formamide, +268.6 ppm from neat nitromethane (Table 2), conversion scheme IVb (Table 1); see Table 24 for HBA structure.

(j) Data from ref. 193; see Table 4, footnote (d) therein.

(k) Data from refs. 1106 and 1107, 9.1 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

Table 16—*cont.*

(l) See ref. 5, p. 439, and references therein.

(m) Data from ref. 824, 50.7 MHz ^{15}N spectrum, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; Kr–N spin–spin coupling was observed in the ion.

(n) Data from ref. 868, 18.075 MHz ^{14}N spectra, other details as in footnote (m); Xe–N spin–spin coupling was observed in the ions.

(o) Data from ref. 826, spectrometer not reported, ^{15}N spectra, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(p) See ref. 5, p. 440, and references therein.

(q) Data from ref. 951, 5.72 MHz ^{14}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; ^{14}N–^{199}Hg spin–spin coupling was observed in the fulminates concerned.

(r) See ref. 5, p. 439, and references therein.

(s) Data from ref. 1108, 21.7 MHz ^{14}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(t) Data from ref. 829, 6.47 MHz ^{14}N spectrum, field perpendicular to sample tube, referenced originally to NO_3^- in aqueous ammonium nitrate, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(u) See ref. 5, p. 438, and references therein.

(v) Data from ref. 758, ^{15}N-labelled cyanide, 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4^+ in aqueous ammonium nitrate, +359.6 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); dppm = $Ph_2CH_2PPh_2$.

(w) Data from ref. 597, ^{15}N-labelled cyanide, 20.3 MHz and 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(x) Data from ref. 1109, 28.88 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to aqueous $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(y) Data from ref. 1110, ^{15}N-labelled cyanide, 36.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous ammonium nitrate, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); 1.0 μM to 3.0 μM solutions containing 10 μM phosphate buffer or 5 μM acetate buffer in the case of chloroperoxidase.

(z) Data from ref. 1111, details as in footnote (y).

(A) Data from ref. 1112, details as in footnote (y).

(B) Data from ref. 1113, *Pseudomonas putida* cytochrome, pH = 7.4, 2 μM solutions, 0.1 M phosphate buffer at +22°C for data marked with an asterisk (*), 0.05 M Tris-HCl buffer with 5% glycerol at +13°C for other samples; other details as in footnote (y).

(C) Data from ref. 659, 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; 0.0012 M solutions, three detergents were used - ctab, sds, and TX-100 (Merck and Sigma); L = protoporphyrin IX (3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropionic acid).

Table 17. Nitrogen shieldings in azole ring systems and related structures

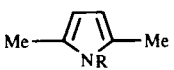
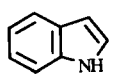
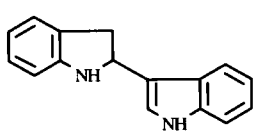
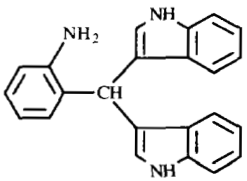
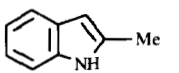
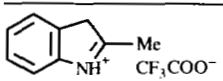
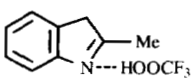
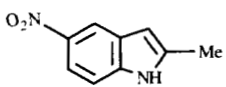
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Pyrrole ring systems			
 (pyrrole)	various	+224 to +233	(a)
	in DMSO	+255.1	(b)
	various	+230 to +232	(a)
	in DMSO		(c)
	R = CH_2CMe_3	+223.1	
	R = CH_2CHMe_2	+223.9	
 (indole)	in DMSO	+245.5	(b)
	in $CDCl_3$	+259.1	(d)
	in $CDCl_3$/pyridine	+253.6	(d)
products of its protonation with CF_3COOH	in $CDCl_3$ + CF_3COOH		(e)
		+256.0 (indole NH) +306.1 (amino NH)	

Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
		+261.1 (indole NH) +338.2 (NH_2)	
	in $CDCl_3$	+253.1	(d)
products of protonation of methylindole with CF_3COOH	in $CDCl_3$ + CF_3COOH		(e)
		+168.3	
		+74.6	
	in DMSO	+238.7 (NH)	(b)

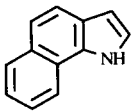
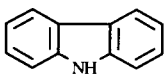
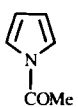
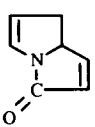
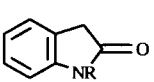
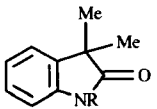
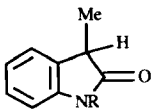
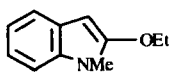
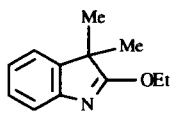
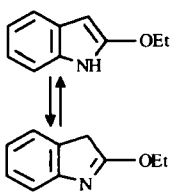
	in $CDCl_3$ in pyridine	+254.1 +246.0	(d) (d)
 (carbazole)	in DMSO	+262.8	(b)
	0.5 M in DMSO	+212.4	(f)
	in $CDCl_3$	+183.8	(g)
	in $CDCl_3$	+194.0	(g)
Pyrrole and indole moieties in natural and synthetic melamines	solid state	*ca.* +200	(h)
	in DMSO R = H (dominant tautomer) R = Me	 +238.6 +245.6	(i)

Table 17. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in DMSO		(i)
	R = H (dominant tautomer)	+245.3	
	R = Me	+252.0	
	in DMSO		(j)
	R = H (dominant tautomer)	+242.1	
	R = Me	+248.5	
	in $CDCl_3$		(j)
	R = H (dominant tautomer)	+242.1	
	R = Me	+248.6	
	in DMSO	+267.3	(i)
	in $CDCl_3$	+266.3	(j)
	in DMSO	+140.6	(i)
	in DMSO	+257.8 (averaged)	(j)
	in $CDCl_3$	+264.6 (NH)	(j)
		+133.9 (=N)	(j)

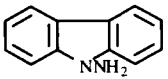
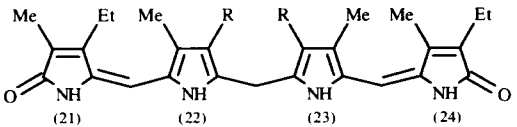
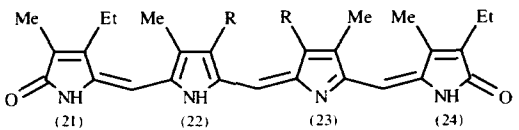
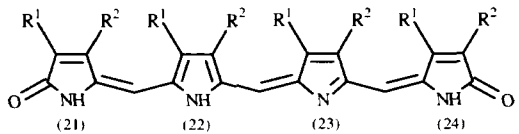
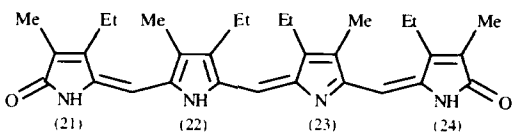
	in DMSO	+209.8 (N) +306.4 (NH_2)	(k) (k)
	in DMSO	+249.2 (N) +322.9 (NH_2)	(k) (k)
	0.03 M in DMSO		
(bilirubin IX-a)	R = CH_2CH_2COOH	+249.8 (N-21) +231.3 (N-22) +231.6 (N-23) +249.2 (N-24)	(l) (l) (l) (l)
		+249.6 (N-21) +231.1 (N-22) +231.4 (N-23) +249.0 (N-24)	(m) (m) (m) (m)
(bilirubin IX-a dimethyl ester)	R = CH_2CH_2COOMe	+249.7 (N-21) +230.8 (N-22) +231.2 (N-23) +249.1 (N-24)	(m) (m) (m) (m)
(bilirubin IX-a ditauride)	R = $CH_2CH_2CONHCH_2CH_2SO_3Na$	+249.6 (N-21) +231.5 (N-22) +231.8 (N-23) +249.0 (N-24)	(m) (m) (m) (m)
bilirubin + dilysine		+249.5 (N-21) +231.0 (N-22) +231.3 (N-23) +249.0 (N-24)	(m) (m) (m) (m)

Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
			
(biliverdin IX-a)	$R = CH_2CH_2COOH$ in DMSO	+246.2 (N-21) +245.4 (N-22) +249.0 (N-24)	(m) (m) (m)
			
Coprobiliverdin III tetramethyl esters (including isomers obtained by permutations of R^1 and R^2 within the rings)			
	in H_2O $R^1 = CH_2COOMe$ $R^2 = CH_2CH_2COOMe$	+244.2 (N-21) +255.2 (N-24) +178.5 (averaged N-22, 23)	(n)
			
	in $CDCl_3$	+249.9 (N-21, 24) +172.4 (averaged N-22, 23)	(o) (o)

in $CDCl_3$	+252.7 (N-21)	(o)
	+226.7 (N-22)	(o)
	+131.4 (N-23)	(o)
	+229.5 (N-24)	(o)
in HMPT	+250.4 (N-21)	(p)
	+211.9 (N-22)	(p)
	+218.4 (N-24)	(p)

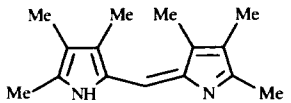
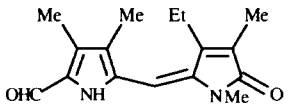
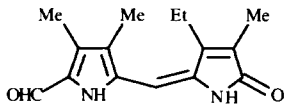
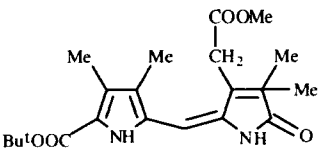
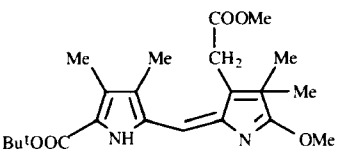
		(q)
in $CDCl_3$	+221.1 (NH–CO)	
	+245.9 (central NH)	

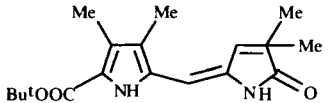
in $CDCl_3$	+315.6	(o)

in $CDCl_3$	+264.4	(o)

in $CDCl_3$	+273.0	(o)

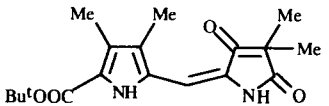
Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+165.5 (averaged)	(o)
	protonated in $CDCl_3$	+212.7	(o)
	in $CDCl_3$	+233.5 (NH)	(o)
		+256.6 (NMe)	(o)
	in $CDCl_3$	+237.9 (pyrrole NH)	(o)
		+256.6 (lactam NH)	(o)
	in $CDCl_3$	+235.1 (pyrrole NH)	(o)
		+240.2 (lactam NH)	(o)
	in $CDCl_3$	+232.2 (pyrrole NH)	(o)
		+140.2 (=N)	(o)



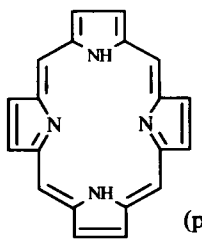
in $CDCl_3$

+235.9 (pyrrole NH) (o)
+235.6 (lactam NH) (o)



in $CDCl_3$

+242.6 (pyrrole NH) (o)
+228.8 (lactam NH) (o)

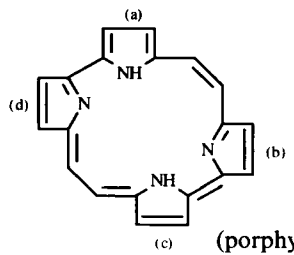


(porphin)

solid state
−81°C
+89°C

+234 (NH)
+126 (=N)
+180 (averaged)

(r)

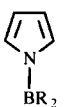


(porphycen)

solid state
−166°C
+93°C

+180 (four sharp peaks)
+180 (single sharp peaks)

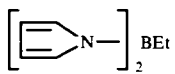
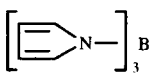
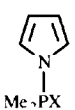
(r)

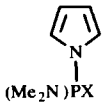


in C_6D_6

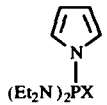
(s)

Table 17. —*cont.*

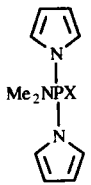
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	R = Bu^t	+201	
	Pr^i	+196	
	Et	+193	
	(*in* $CDCl_3$)	+185	(t)
	Me	+190	
	(*in* $CDCl_3$)	+187	(t)
	R_2 = $-SCH_2CH_2S-$ (*in* $CDCl_3$)	+201	(t)
	in $CDCl_3$	+195	(t)
	in $CDCl_3$	+207	(t)
			(t)
X			
Me_3Si	in C_6D_6	+216.0	
Me_3Sn	in $CDCl_3$	+216.2	
Me_3Pb	in C_6D_6	+206.7	
Me_3P	in C_6D_6	+219.3	
$Me_2P(S)$	in C_6D_6	+212.6	
	in C_6D_6		(u)
	X = lone pair	+219.3	
	S	+212.6	
	Se	+216.9	
	BH_3	+213.0	



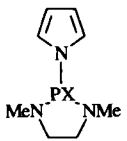
	in C_6D_6	N—P	NMe_2	(u)
	X = lone pair	+203.3	+345.9	
	S	+207.6	+346.5	
	Se	+207.6	+345.4	



	in C_6D_6	N—P	NEt_2	(u)
	X = lone pair	+204.2	+317.5	
	Se	+203.9	+321.3	

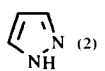


	in C_6D_6	N—P	NMe_2	(u)
	X = lone pair	+207.6	+348.7	
	Se	+210.8	+345.4	



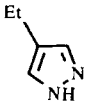
	in C_6D_6	N—P	NMe	(u)
	X = lone pair	+187.0	+338.9	
	S	+199.6	+337.5	
	Se	?	+336.1	
	BH_3	?	+338.3	

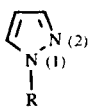
Pyrazole (1,2-diazole) ring systems

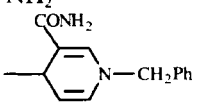


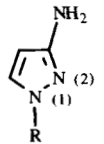
	0.5 M in $CDCl_3$	+132.2 (averaged)	(v)
	0.01 M in phosphate buffer	+138.2 (averaged)	(w)
	5 M in MeCN	+131.7 (averaged)	(w)
LADH—NAD^+—pyrazole	0.0011 M in phosphate buffer	+148.2 (N-1)	(w)
		+124.0 (N-2)	(w)

Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$ZnCl_2$—pyrazole (1 : 2)	3 M in MeCN	+154.4 (averaged)	(w)
$ZnCl_2$—pyrazole (1 : 1)	1 M in DMSO	+144.3 (averaged)	(w)
	0.01 M in phosphate buffer	+139.8 (averaged)	(w)
LADH—NAD^+—4-Et-pyrazole	0.001 M in phosphate buffer	+152.2 (N-1) +125.2 (N-2)	(w) (w)
	in $CDCl_3$	+180.8 (N-1) +76.5 (N-2)	(a) (a)
N-Me-pyrazole—$ZnCl_2$ (2 : 1) in $CHCl_3$		+182.1 (N-1) +127.3 (N-2)	(w) (w)

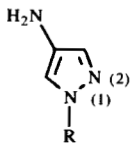


R		N-1	N-2	
CH_2Ph	2 M in MeCN	+167.7	+73.5	(w)
$Me_2C(OH)$—	0.1 M in acetone, −50°C	+140.3	+80.6	(v)
CH_2COOEt	2 M in MeCN	+179.5	+72.6	(w)
	2 M in MeCN + $ZnCl_2$	+181.1	+127.5	(w)
$CONH_2$	3 M in DMSO	+158.8	+87.4	(w)
NO_2	0.5 M in acetone	+107.8	+82.9	(v)
NH_2	in DMSO	+162.1	+72.4	(k)
		(+*295.1*, NH_2)		(k)
	2 M in $CHCl_3$	+142.5	+82.9	(w)



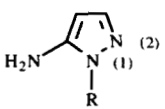
(x)

		N-1	N-2	NH_2
R = Me	in DMSO	+221.5	+128.9	+357.7
	in CF_3COOH	+219.3	+208.6	+353.9
	hydrochloride in DMSO	+205.3	+115.6	+351.3
R = Ph	in DMSO	+207.0	+144.1	+357.4
	in CF_3COOH	+203.7	+198.8	+351.9
	hydrochloride in DMSO	+188.5	+116.5	+351.4



(x)

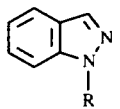
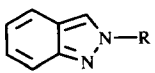
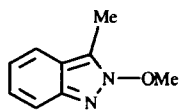
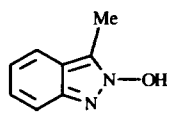
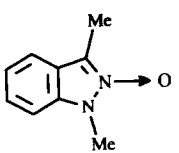
		N-1	N-2	NH_2
R = Me	in DMSO	+211.3	+99.8	+375.7
	in CF_3COOH		decomposition	
	hydrochloride in DMSO	+202.6	+ 96.7	+368.7
R = Ph	in DMSO	+192.4	+103.6	+371.2
	in CF_3COOH	+186.4	+148.6	+370.0
	hydrochloride in DMSO	+183.6	+99.2	+361.7

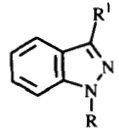


(x)

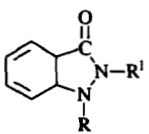
		N-1	N-2	NH_2
R = Me	in DMSO	+225.2	+119.6	+362.5
	in CF_3COOH	+230.5	+242.6	+352.5
	hydrochloride in DMSO	+220.2	+244.3	+344.6
R = Ph	in DMSO	+203.6	+115.1	+355.6
	in CF_3COOH	+228.3	+232.0	+350.6
	hydrochloride in DMSO	+208.2	+227.1	+343.3

Table 17. *—cont.*

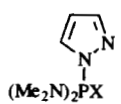
Compound		Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	R = H	in DMSO	+195 (NH) +65 (=N)	(a) (a)
	R = Me	in DMSO	+203 (NMe) +57 (=N)	(a) (a)
	R = NH_2	in DMSO	+184.6 (NR) +56.3 (=N) +305.9 (NH_2)	(k) (k) (k)
	R = Me	in DMSO	+162 (NMe) +92 (=N)	(a) (a)
	R = NH_2	in DMSO	+145.5 (NMe) +94.8 (=N) +289.1 (NH_2)	(k) (k) (k)
			N—O N	(y)
		in DMSO	+115.4 +115.8	
		in MeOH	+117.8 +124.9	
		in CF_3COOH	+120.0 +133.7	
			N—O N	(y)
		in DMSO	+121.0 +123.3	
		in MeOH	+118.5 +164.5	
		in CF_3COOH	+117.9 +214.1	
			N—O N	(y)
		in DMSO	+96.1 +208.5	
		in MeOH	+105.0 +211.8	
		in CF_3COOH	+113.3 +214.1	



R	R^1		N—R	=N	
Me	OMe	in DMSO	+232.7	+104.8	(z)
		in MeOH	+232.4	+108.9	
		in CF_3CH_2OH	+235.5	+116.6	
H	OMe	in DMSO	+226.1	+115.4	
		in MeOH	+226.8	+121.4	
		in CF_3CH_2OH	+232.1	+129.4	
		in CF_3CH_2OH/DMSO	+225.6	+115.5	
Me	OH	in DMSO	+237.1	+112.0	
		in MeOH	+247.4	+161.4	
		in CF_3CH_2OH	+248.5	+161.4	
H	OH	in DMSO	+237.1	+132.6	
		in MeOH	+252.9	+190.1	
		in DMSO/MeOH	+240.2	+152.7	
		in CF_3CH_2OH	+257.4	?	
		in CF_3CH_2OH/DMSO	+238.5	+162.2	
		in CF_3COOH	+250.3	+214.9	

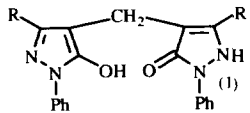
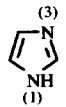
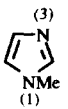
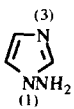


R	R^1		N—R	N—R^1	
H	Me	in DMSO	+255.0	+229.2	(z)
Me	Me	in DMSO	+260.1	+217.8	
		in MeOH	+259.1	+216.0	
		in CF_3CH_2OH	+258.0	+214.4	



		N—P	=N	NMe_2	
in C_6D_6					(u)
X =	lone pair	+147.3	+66.0	+344.1	
	S	+153.4	+67.8	+346.2	
	Se	+153.3	+68.2	+345.1	

Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	tautomers		(A)
(R = $NHCOC_{17}H_{35}$)	in $CDCl_3$	N—Ph N-2	
m.p. 110°C, after dissolving		+222.3 +257.0 (NH) +221.3 +255.0 (NH) +199.0 +138.0 (=N)	
m.p. 61°C, after dissolving		+212.0 ?	
both cases, upon standing		+221.8 +257.8 (NH) +221.4 +255.2 (NH) +199.4 +137.7 (=N)	
Imidazole (1,3-diazole) ring systems			
	in DMSO	+168 (averaged)	(a)
	in D_2O	+177.2 (averaged)	(B)
	protonated in D_2O	+208.2 (averaged)	(B)
	in DMSO	+219 (N-1) +118 (N-2)	(a) (a)
	in D_2O	+217.7 (N-1) +134.7 (N-2)	(B) (B)
	protonated in D_2O	+210.3 (N-1) +209.8 (N-2)	(B) (B)
	in DMSO	+198.7 (N-1) +72.4 (N-2) +311.4 (NH_2)	(k) (k) (k)

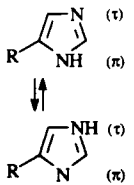
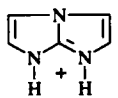
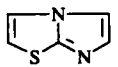
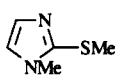
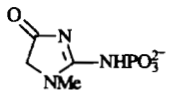
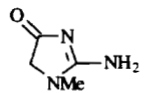
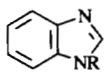
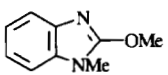
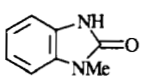
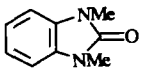
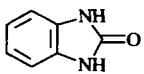
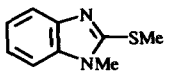
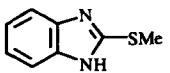
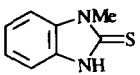
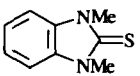
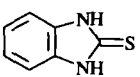
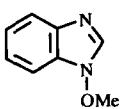
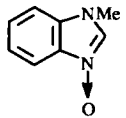
Imidazole moieties in His-57 in α-lytic protease	lyophilized powder prepared from solutions at various pH		(C)
	N(τ), pH = 4.9 pH = 8.1 N(π), pH = 5.0 pH = 9.6	+202 +213 +215 +148	
	in DMSO	+257.4 (NH) +199.7 (N)	(D) (D)
	in DMSO	+176.4 (central N) +147.2 (=N—)	(E) (E)
	in DMSO in $CDCl_3$	+218.6 (NMe) +213.4 (NH) +218.0 (NMe) +210.7 (NH)	(F) (F) (F) (F)
	in $CDCl_3$	+220.4	(F)
	in DMSO in $CDCl_3$	+218.7 (NMe) +117.6 (=N) +220.7 (NMe) +121.9 (=N)	(F) (F) (F) (F)

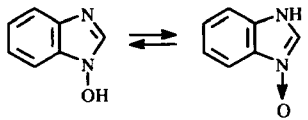
Table 17. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 (phosphocreatinine)	in H_2O, pH = 9.0	+175.0 (=N) +274.8 (NHP)	(G) (G)
 (creatinine)	in H_2O,	=N NH$_2$	(G)
	pH = 11.0	+179.3 +306.0	
	pH = 2.0	+236.7 +303.7	
 R = Me	in DMSO	+236.4 (NMe) +136.3 (=N)	(a) (a)
R = NH$_2$	in DMSO	+215.8 (NNH$_2$) +143.6 (=N) +317.8 (NH$_2$)	(k) (k) (k)
		NMe =N	(H)
	in DMSO	+264.5 +186.8	
	in MeOH	+261.8 +195.5	
	in CF_3CH_2OH	+263.2 +200.8	
		NMe NH	(H)
	in DMSO	+268.5 +262.7	
	in MeOH	+265.4 +261.0	
	in CF_3CH_2OH	+266.2 +263.0	
	in CF_3CH_2OH/DMSO	+268.8 +263.1	

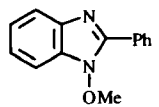
	in DMSO	+269.7	(H)
	in MeOH	+269.2	(H)
	in CF_3CH_2OH	+268.7	(H)
	in DMSO	+259.9	(H)
	in MeOH	+259.5	(H)
	in CF_3CH_2OH	+266.9	(H)
	0.5 M in DMSO	+243.9 (NMe)	(I)
		+145.9 (=N)	(I)
	in DMSO	+241.0 (NMe)	(F)
		+143.0 (=N)	(F)
	0.5 M in DMSO	+186.4 (averaged)	(I)
	in DMSO	+233.0 (NMe)	(F)
		+227.0 (NH)	(F)
	in DMSO	+235.5	(F)
	0.5 M in DMSO	+227.4	(I)
	in DMSO	+225.8	(F)
		NOMe =N	(J)
	in DMSO	+174.0 +145.0	
	in acetone	+174.3 +145.6	
	in MeOH	+174.0 +145.0	
	in CF_3CH_2OH	+167.6 +145.1	



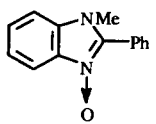
	NO	NMe	
in DMSO	+140.5	+261.8	(J)
in MeOH	+155.9	+255.1	
in CF_3CH_2OH	+156.0	+254.0	



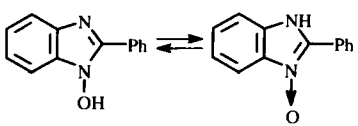
	NO/NOH	=N/NH	
in DMSO (61% NH)	+153.4	+190.8	(J)
in MeOH (52% NH)	+167.8	+198.0	
in CF_3CH_2OH (16% NH)	+159.5	+237.0	



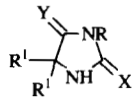
	NOMe	=N	
in DMSO	+179.4	+149.8	(J)
in acetone	+179.4	+147.6	
in MeOH	+179.4	+161.3	
in CF_3CH_2OH	+176.6	+163.0	



	NO	NMe	
in DMSO	+149.2	+260.0	(J)
in MeOH	+160.5	+255.1	
in CF_3CH_2OH	+160.3	+254.1	

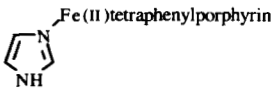


	NO/NOH	=N/NH	
in DMSO	+184.5	+192.8	(J)
in DMSO/phenol	+186.6	+191.2	
in MeOH	+182.0	?	
in CF_3CH_2OH	+170.0	?	



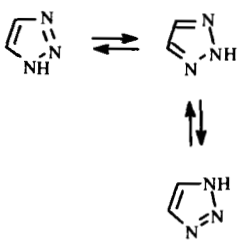
in DMSO/actetone (1 : 1) (K)

X	Y	R	R^1	NH	NR
O	O	H	H	+298.1	+235.1
O	O	Me	H	+272.8	+238.0
O	O	Ph	H	+272.5	+234.7
O	O	Me	Me	+274.7	+234.0
S	O	H	H	+252.9	+211.1
S	O	Me	H	+233.9	+216.7
S	O	Ph	H	+245.1	+215.2
O	S	Me	H	+265.7	+200.7
S	S	Me	H	+227.5	+186.5
S	S	Me	Me	+229.3	+190.9



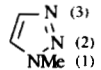
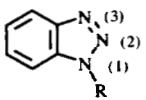
in $CDCl_3$ +2115.2 (=N) (L)
−124.8 (NH) (L)

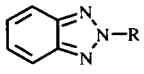
1,2,3-Triazole and 1,2,5-triazole ring systems



	central N	flanking N	
neat liquid	+85.5	+57.2	(M)
in DMSO	+77.8	+68.8	(M)
in acetone	+80.9	+64.8	(M)
in $CDCl_3$	+79.0	+61.9	(M)
in MeOH	+89.7	+70.5	(M)
in H_2O	+86.0	+56.6	(M)
in CF_3CH_2OH	+85.5	+53.0	(M)

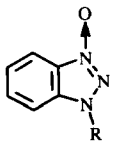
Table 17. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
		N-1	N-2	N-3	(M)
	neat liquid	+144.0	+12.0	+30.0	
	in DMSO	+143.3	+16.2	+28.4	
	in acetone	+144.9	+14.1	+27.1	
	in $CDCl_3$	+145.0	+16.3	+30.7	
	in MeOH	+144.3	+19.1	+41.7	
		N-1	N-2,5		(M)
	neat liquid	+132.0	+53.0		
	in DMSO	+135.0	+54.0		
	in acetone	+135.0	+54.0		
	in $CDCl_3$	+132.8	+51.1		
	in MeOH	+132.8	+51.1		
	R = H, solvent?	+103.8 (N-1, 3)			(N)
		+12.0 (N-2)			(N)
	R = Me, solvent?	+162.0 (N-1)			(N)
		+4.2 (N-2)			(N)
		+40.0 (N-3)			(N)
	R = OH, solvent?	+125.4 (N-1)			(N)
		+18.5 (N-2)			(N)
		+69.6 (N-3)			(N)
	R = NH_2, in DMSO	+148.2 (N-1)			(k)
		+2.3 (N-2)			(k)
		+50.8 (N-3)			(k)
		+307.7 (NH_2)			(k)
	R = 5′-phosphoribosyl, in DMSO	+145.0 (N-1)			(O)
		+2.9 (N-2)			(O)
		+37.2 (N-3)			(O)



R = Me, in — +103.8 (N-1,3); +12.0 (N-2); +99.9 (N–NH_2); +83.6 (=N); +275.3 (NH_2) — (a); (a); (k); (k); (k)

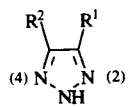
R = NH_2, in DMSO



solvent? — (N)

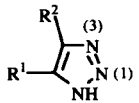
R = —CH(Me)CH_2COOMe — +190.8 (NR); +58.7 (=N—); +76.0 (NO)

R = —COCH=CHCH=CHMe — +174.4 (NR); +54.6 (=N—); +67.6 (NO)



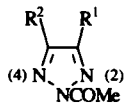
in $CDCl_3$ — (P)

R^1 = —CO—(2-NHCOMe-phenyl), R^2 = Ph — +31.8, +47.8 (N-2,4)



in $CDCl_3$ — (P)

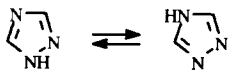
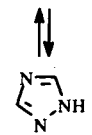
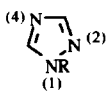
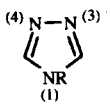
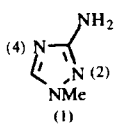
R^1 = —CO—(2-NHCOMe-phenyl), R^2 = Ph — +140.6, +63.3 (N-1,3)

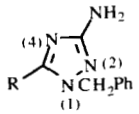


in $CDCl_3$ — (P)

R^1 = —CO—(2-NHCOMe-phenyl), R^2 = Ph or 4-Pr^i-phenyl — +60.5, +47.9 (N-2,4)

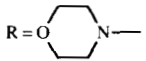
Table 17. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
1,2,4-Triazole and 1,3,4-triazole ring systems			
	in DMSO	+135.7 (N) +123.3 (NN)	(M) (M)
	0.5 M in DMSO	+136.5 (N)	(Q)
 R = Me	in DMSO	+171.3 (N-1) +81.9 (N-2) +127.4 (N-4)	(M) (M) (M)
R = NH_2,	in DMSO	+155.7 (N-1) +79.8 (N-2) +131.6 (N-4) +303.0 (NH_2)	(k) (k) (k) (k)
 R = Me,	in DMSO	+217.8 (N-1) +59.8 (N-3,4)	(M) (M)
R = NH_2,	in DMSO	+198.2 (N-1) +66.1 (N-3,4) +315.5 (NH_2)	(k) (k) (k)
		N-1 N-2 N-4 NH_2	(R)
	in DMSO	+187.4 +130.4 +156.6 +334.1	
	in H_2O	+186.1 +137.7 +166.1 +337.0	
	hydrochloride in H_2O	+178.5 +139.7 +228.2 +332.8	

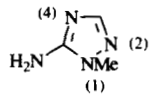


in DMSO

R = MeS

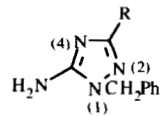


N-1	N-2	N-4	NH_2	(T)
+181.6	+125.6	+153.9	+330.2	
+201.0	+136.9	+171.0	+331.5	



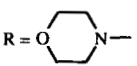
N-1	N-2	N-4	NH_2	(R)
+187.4	+130.4	+156.6	+334.1	
+186.1	+137.7	+166.1	+337.0	
+178.5	+139.7	+228.2	+332.8	

in DMSO
in H_2O
hydrochloride in H_2O



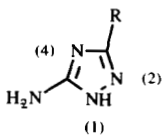
in DMSO

R = MeS



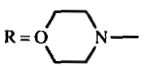
N-1	N-2	N-4	NH_2	(T)
+188.0	+108.8	+166.0	+327.0	
+212.2	+142.8	+187.2	+327.9	

(+*319.7, morpholine moiety*)



in DMSO

R = MeS



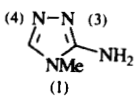
N-1	N-2	N-4	NH_2	(T)
+200.4	+118.8	+166.3	+328.5	
+216.0	+151.3	+187.2	+327.7	

(+*319.9, morpholine moiety*)

R = PhNH

+216.4	+149.8	+184.1	+329.7	

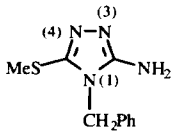
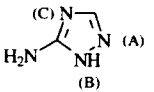
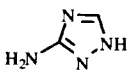
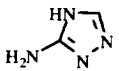
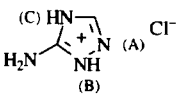
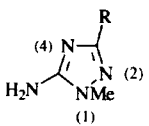
(+*292.2, PhNH*)



N-1	N-3	N-4	NH_2	(R)
+241.6	+112.0	+75.4	+339.6	
+238.8	+128.7	+95.9	+340.6	
+240.4	+207.9	+119.9	+325.3	

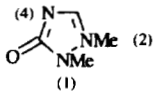
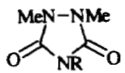
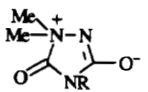
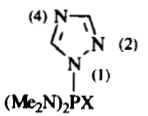
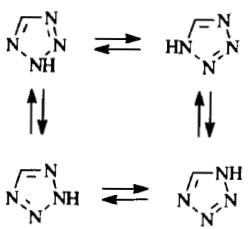
in DMSO
in H_2O
hydrochloride in H_2O

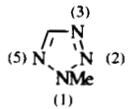
Table 17. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
		N-1	N-3	N-4	NH_2	(T)
	in DMSO	+227.1	+109.4	+72.4	+333.9	
 	*ca.* 35%					
	in H_2O	+138.7 (N_A)				(R)
		+183.9 (N_B)				(R)
		+175.6 (N_C)				(R)
	*ca.* 65%	+336.1 (NH_2)				(R)
 (dominant tautomer)	in H_2O	+116.9 (N_A)				(R)
		+208.1 (N_B)				(R)
		+236.6 (N_C)				(R)
		+325.3 (NH_2)				(R)
	0.5 M in DMSO					
	R = OMe	+184.4 (N-1)				(Q)
		+128.2 (N-2)				(Q)
		+157.8 (N-4)				(Q)
	R = SMe	+160.8 (N-1)				(S)
		+96.9 (N-2)				(S)
		+125.0 (N-4)				(S)

(1)	0.5 M in DMSO		
	R = OMe	+207.7 (N-1)	(Q)
		+91.7 (N-2)	(Q)
		+166.8 (N-4)	(Q)
	R = SMe	+174.0 (N-1)	(S)
		+72.9 (N-2)	(S)
		+134.4 (N-4)	(S)
(1)	0.5 M in DMSO		
	R = OMe	+243.0 (N-1)	(Q)
		+112.0 (N-3)	(Q)
		+75.0 (N-4)	(Q)
	R = SMe	+218.9 (N-1)	(S)
		+65.3 (N-3)	(S)
		+60.9 (N-4)	(S)
(1)	0.5 M in DMSO		
	X = O	+238.2 (N-1)	(Q)
		+214.1 (N-3)	(Q)
		+116.9 (N-4)	(Q)
	X = S	+206.8 (N-1)	(S)
		+176.0 (N-3)	(S)
		+99.1 (N-4)	(S)
(1)	0.5 M in DMSO		
		+244.4 (N-1)	(Q)
		+214.3 (N-3)	(Q)
		+118.0 (N-4)	(Q)
(1)	0.5 M in DMSO	+245.0 (N-1)	(Q)
		+220.6 (N-3)	(Q)
		+112.3 (N-4)	(Q)

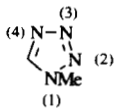
Table 17. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	0.5 M in DMSO	+202.7 (N-1) +216.8 (N-2) +138.4 (N-4)	(Q) (Q) (Q)
	in DMSO, R = Ph R = α-naphthyl	NMe NR +315.7 +241.7 +316.4 +242.2	(U)
	in DMSO, R = Pr^i R = α-naphthyl	NR =N NMe_2 +235.0 +167.9 +263.0 +238.6 +163.7 +261.5	(U)
	in C_6D_6 X = lone pair X = S	N-1 N-2 N-3 NMe_2 +141.3 +81.1 +124.8 +342.5 +145.6 +82.3 +124.2 +345.9	(u)
Tetrazole ring systems			
	0.5 M in DMSO	+98.3 (flanking N) +5.8 (central NN)	(a) (a)



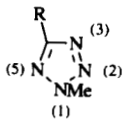
0.5 M in DMSO

+101.8 (N-1)	(a)
+0.8 (N-2)	(a)
+46.8 (N-3)	(a)
+72.8 (N-5)	(a)



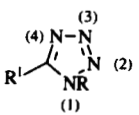
0.5 M in DMSO

+151.4 (N-1)	(a)
+10.8 (N-2)	(a)
−12.3 (N-3)	(a)
+49.9 (N-4)	(a)



in acetone-d_6

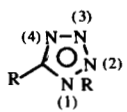
R =	N-1	N-2	N-3	N-5	
Me	+104.5	+50.3	0.0	+78.1	(V)
CH_2COOEt	+102.5	+46.4	+2.0	+74.6	
CH_2CH_2OMe	+104.1	+48.0	−1.2	+78.0	
CN	+96.3	+36.9	−6.1	+61.1	
	(+*110.3, CN*)				



R = Me, Et, Me

in acetone-d_6

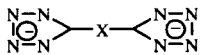
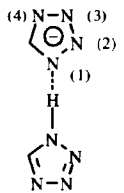
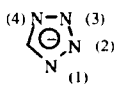
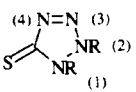
R^1 =	N-1	N-2	N-3	N-4	
Me	+154.8	+9.8	−7.7	+65.8	(V)
CH_2COOEt	+152.7	+6.9	−9.8	+53.5	
CH_2CH_2OMe	+153.7	+8.7	−9.6	+52.7	

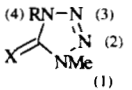


in D_2O

R =		N-1,4	N-2,3	
CN		+52.4	+14.5	(V)
CF_3	(pH 7.49)	+69.1	−1.6	
Ph	(pH 6.51)	+77.9	+5.0	
CH_2Ph	(pH 9.58)	+72.0	−3.2	
H	(pH 9.55)	+71.8	+5.0	
Me	(pH 10.63)	+73.3	+4.5	
NMe_2	(pH 7.83)	+102.4	+7.7	
$CH_2CH_2NMe_2$	(pH 10.77)	+72.8	−3.4	

Table 17. *—cont.*

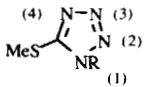
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in D_2O		(V)
X		N-1,4 N-2,3	
none		+71.0 −0.5	
CH_2CH_2		+79.2 +4.4	
$CH_2CH_2CH_2CH_2$		+79.2 +5.0	
$CH_2CH_2OCH_2CH_2$		+84.1 +5.5	
$CH_2CH_2NHCH_2CH_2$		+72.8 −3.0 (+247.3, *NH*)	
	in CD_3CN	+78.8 (N-1,4) +1.6 (N-2,3)	(W) (W)
	solid state	+56.4 (N-1,4) +11.4 (N-2,3)	(W) (W)
	in DMSO	N-1 N-2 N-3 N-4	(X)
	R = H	+82.2 +70.4 −3.9 +50.4	
	R = Me	+97.3 +70.9 −4.5 +47.7	



in DMSO

R = H, X = S
R = Me, X = O

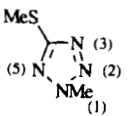
N-1	N-2	N-3	N-4	(X)
+151.9	+25.4	+17.4	+145.7	
+193.2	+39.1	+39.1	+193.2	



in DMSO

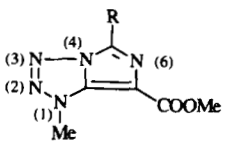
R = H
R = Me

N-1	N-2	N-3	N-4	(X)
+100.5	+4.5	+4.5	+100.5	
+158.1	+7.1	−11.1	+55.6	



in DMSO

N-1	N-2	N-3	N-5	(X)
+101.4	−2.3	+53.4	+81.6	



in $CDCl_3$,
R = Me

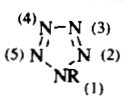
(Z)

+194.2 (N-1)
+4.6 (N-2)
+57.4 (N-3)
+120.7 (N-4)
+108.4 (N-6)

R = Ph

+194.0 (N-1)
+4.8 (N-2)
+54.8 (N-3)
+124.5 (N-4)
+110.9 (N-6)

Pentazole ring system

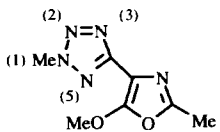
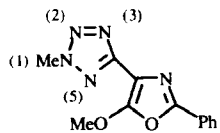
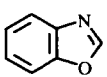
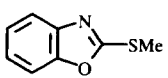
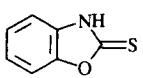


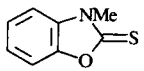
in $CDCl_3$, −35°C

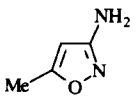
R = 4-NMe_2-phenyl

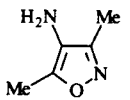
N-1	N-2,5	N-3,4	NMe_2	(Y)
+80.0	+27.5	−4.9	+324.6	

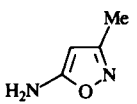
Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Oxazole and oxadiazole ring systems			
 (1,3-oxazole)	in DMSO	+123.7	(a)
	in $CDCl_3$	+132.8 (oxazole) +107.7 (N-1) +1.5 (N-2) +57.1 (N-3) +85.0 (N-5)	(Z)
	in $CDCl_3$	+134.9 (oxazole) +107.4 (N-1) +1.3 (N-2) +56.8 (N-3) +84.9 (N-5)	(Z)
	0.5 M in DMSO	+131.5	(a)
	in DMSO	+114.3	(F)
	in DMSO	+223.2	(F)

	in DMSO	+230.4	(F)
 (1,2-oxazole, isoxazole)	in DMSO	−2.7	(a)

		=N—	NH_2	
	in DMSO	+76.8	+367.1	(x)
	in CF_3COOH	+189.7	+341.0	

		=N—	NH_2	
	in DMSO	+37.4	+378.2	(x)
	in CF_3COOH	+57.7	+372.7	
	hydrochloride in DMSO	+30.9	+363.4	

		=N—	NH_2	
	in DMSO	+54.3	+344.7	(x)
	in CF_3COOH	+188.5	+333.4	

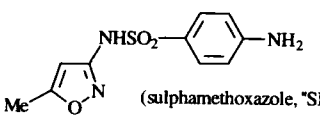
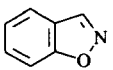
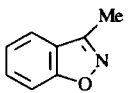
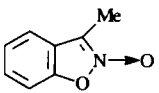
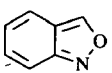
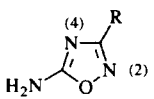
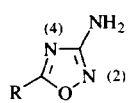
		=N—O	NSO_2	NH_2	
 (sulphamethoxazole, "SM2")	in DMSO	+34.7	+263.9	+307.9	(aa)
	solid state	+34.3	+264.6	+310.0	
$SM2^- Na^+$	in DMSO	+54.1	+254.1	+323.1	

Table 17. *—cont.*

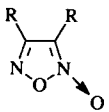
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
SM2 complex with trimethoprim	in DMSO	+36.5	+259.7	+309.7	
	solid state	+49.0	+245.4	+316.0	
	in $CDCl_3$	+0.2			(bb)
	0.5 M in DMSO	−3.3			(a)
	in $CDCl_3$	+9.0			(bb)
	in $CDCl_3$	+59.5			(bb)
	0.5 M in DMSO	+7.5			(a)
 (1, 2, 4-oxadiazole)	in Et_2O	+20 (N-2)			(a)
		+140 (N-4)			(a)
	in $CDCl_3$	N-2	N-4	NH_2	(R)
	R = Me	+44.3	+189.9	+320.3	
	R = SMe	+50.9	+192.8	+318.2	
	R = OMe	+82.1	+208.3	+317.2	
	in $CDCl_3$	N-2	N-4	NH_2	(R)
	R = OMe	+71.8	+199.8	+331.9	
	R = OEt	+72.5	+199.9	+331.9	

(1,3,4-oxadiazole)

in Et_2O | +81 | (a)

(1,2,5-oxadiazole, furazan)

in DMSO | −33.8 | (a)

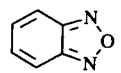


(furoxan structure)

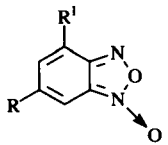
in DMSO

	=N—	=NO—
R = Me	+13.5	+25.9
R = Et	+12.4	+24.8
R = I	−0.3	+23.9
R = Ph	−12.5	+24.7

(ee)



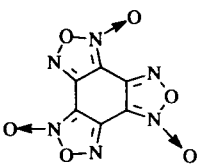
in DMSO | −35.6 | (a)



in DMSO

	=N—	=NO—	NO_2
R = R¹ = H	+7.2	+19.2	
R = H, R¹ = NO_2	+5.5	+19.8	+17.9
R = R¹ = NO_2	+5.2	+21.2	+16.9
			+18.8

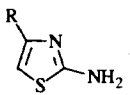
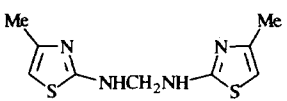
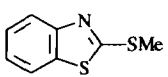
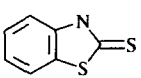
(ee)



in DMSO

+5.5 (=N—) (ee)
+24.3 (=NO—) (ee)

Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Thiazole and thiadiazole ring systems			
 (1,3-triazole)	in DMSO	+57.4	(a)
	in DMSO	=N— NH$_2$	
	R = Me	+124.7 +311.5	(cc)
	R = CH_2COOEt	+123.6 +307.0	(dd)
	its hydrochloride	*+216.9* *+287.1*	(dd)
	R = C(=NOMe)COOEt	+137.5 +305.2	(dd)
	R = C(=NOMe)COOH	+138.8 +306.2	(dd)
	its solution in CF_3COOH	*+236.2* *+297.1*	(dd)
	its hydrochloride	*+222.2* *+284.5*	(dd)
	R = C(=NOH)COOEt	+135.5 +306.2	(dd)
	its hydrochloride	*+196.6* *+291.5*	(dd)
	in DMSO	+124.9 (=N—)	(cc)
		+294.4 (NH)	(cc)
	in DMSO	+83.9	(F)
	in DMSO	+196.8	(F)

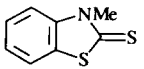
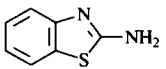
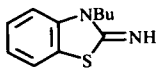
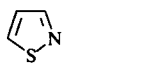
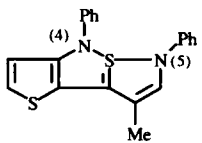
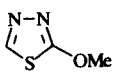
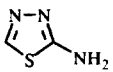
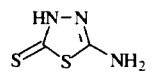
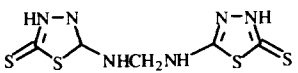
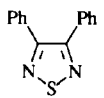
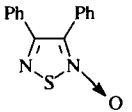
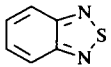
	in DMSO	+205.3	(F)
	in pyridine-d_6	+143.0 (=N) +301.5 (NH_2)	(gg) (gg)
	in pyridine-d_6	+307.6 (NBu) +193.2 (=NH)	(gg) (gg)
 (1,2-thiazole, isothiazole)	in acetone	+81.8	(a)
	in $CDCl_3$	+165.8 (N-4) +184.4 (N-5)	(ff) (ff)
 (1,2,4-thiadiazole)	in Et_2O	+106 (N-2) +70 (N-4)	(a) (a)
 (1,3,4-thiadiazole)	in DMSO	+7.9	(a)
	in $CDCl_3$	+69.8 (N-3) +18.0 (N-4)	(R) (R)
	in $CDCl_3$	+65.0 (=N—) +190.0 (NH)	(R) (R)

Table 17. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+56.8 (=N—) +195.5 (NMe)	(R) (R)
	in DMSO	+81.2 (N-3 ?) +319.2 (NH_2)	(cc) (cc)
	in DMSO	+82.0 (N-3,3′?) +301.7 (NH)	(cc) (cc)
	in DMSO	+117.4 (=N—) +167.6 (NH) +319.2 (NH_2)	(cc) (cc) (cc)
	in $CDCl_3$	+117.4 (=N—) +167.4 (NH) +315.6 (NH_2)	(cc) (cc) (cc)
	in $CDCl_3$	+116.2 (=N—) +167.9 (NH) +299.3 ($NHCH_2$)	(cc) (cc) (cc)
 (1,2,5-thiadiazole)	in Et_2O	+31	(a)
	in DMSO	+37.7	(ee)

	in DMSO	+27.7 (=N—) +100.5 (=N—)	(ee) (ee)
	0.5 M in DMSO	+49.1	(a)
 (1,2,3-thiadiazole)	in DMSO	−30.3 (N-2) −56.2 (N-3)	(a) (a)

Phosphazole ring systems

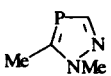
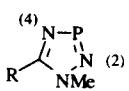
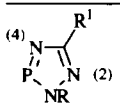
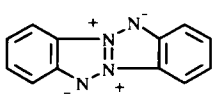
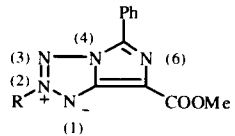
	in C_6D_6	+146.7 (NMe) +13.7 (=N)	(hh) (hh)
	in C_6D_6	+154.1 (NMe) +35.4 (=N)	(hh) (hh)
	in C_6D_6	+150.9 (NMe) +20.9 (=N)	(hh) (hh)
	in C_6D_6	+105.5 (averaged)	(hh)
	in C_6D_6 or $CDCl_3$		(ii)

Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
R		NMe	N-2	N-4	
Me		+157.5	+12.1	+88.5	
Me, complex with BF_3		+154.9	+22.8	+142	
Bu, complex with BF_3		+151.1	+21.0	+138	
i-Pr		+159.5	+14.9	+95.2	
CH_2Ph		+156.4	+11.8	+86.5	
Ph		+156.5	+10.4	+87.0	
	in C_6D_6 or $CDCl_3$				(ii)
R R^2		NMe	N-2	N-4	
Me Me		+120.4	+42.7	+93.5	
	its complex with BF_3	+120.2	+42.8	+147	
Me i-Pr		+122.0	+44.5	+97.7	
Me CH_2Ph		+119.4	+41.6	+93.1	
	its complex with BF_3	+119.1	+39.6	?	
Me Ph		+117.8	+42.7	+99.0	
Ph Ph		+100.3	+56.3	+100.3	
	its complex with BF_3	+101.4	+48.7	+146	
Mesoionic structures					
	in CH_2Cl_2	+105 (N^+)			(jj)
		+159 (N^-)			(jj)

(*trans*-pentalene)



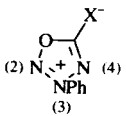
in $CDCl_3$,
R = Me

+99.4 (N-1)
+103.6 (N-2)
+68.9 (N-3)
+137.7 (N-4)
+102.5 (N-6)

(Z)

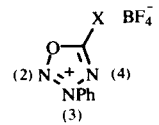
R = Et

+100.8 (N-1)
+89.0 (N-2)
+69.3 (N-3)



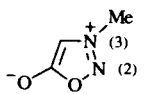
in acetone-d_6

	N-2	N-3	N-4	
X = O	+39.6	+74.2	+95.2	(kk)
X = S	−12.9	+64.5	+107.5	



in acetone-d_6

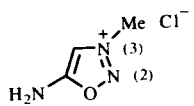
	N-2	N-3	N-4	
X = O—Et	+39.4	+74.2	+95.1	(kk)
X = S—Et	−22.3	+62.9	+101.4	



(sydnone structure)

in acetone

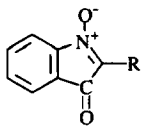
+36.2 (N-2) (a)
+112.5 (N-3) (a)



in CD_3OD/H_2O

+15.0 (N-2) (a)
+104.9 (N-3) (a)
+309.2 (NH_2) (a)

Table 17. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Thiazole and thiadiazole ring systems			
	in $CDCl_3$		(ll)
	R = 2-pyridyl	+71.0	
	2-pirymidyl	+74.4	
	COOMe	+52.6	
	1-Et-2-benzimidazolyl	+66.6	
	phenyl	+77.3	

(a) See ref. 5, pp. 444–447, and references therein.

(b) Data from ref. 693, 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to sat. aqueous $NaNO_3$, +3.7 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); originally reported vs fictitious ammonia standard taken at +376.5 ppm from the reference employed (i.e. +380.2 ppm from nitromethane), but the latter value corresponds to a perpendicular field-to-sample arrangement; we retrieved the original data and performed recalculations as shown above.

(c) Data from ref. 1020, details as in footnote (f).

(d) Data from ref. 772, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); $Cr(acac)_3$ added as a relaxation reagent.

(e) Data from ref. 773, details as in footnote (d).

(f) Data from ref. 27, 30.4 MHz ^{15}N spectrum, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(g) Data from ref. 1114, 36.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(h) Data from ref. 363, 30.4 MHz ^{15}N CPMAS spectra, referenced originally to aqueous NH_4Cl, +352.9 ppm from neat nitromethane (Table 2).

(i) Data from ref. 1115, 50.7 MHz ^{15}N spectra, other details as in footnote (f); also CPMAS spectra for the solid state, ref. 357.

(j) Data from ref. 1116, details as in footnote (i).

(k) Data from ref. 807, 25.35 and 20.29 MHz ^{15}N spectra, other details as in footnote (f).

(l) Data from ref. 99, 30.41 MHz ^{15}N INEPT and SINEPT-2 spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(m) Data from ref. 173, details as in footnote (l).

(n) Data from ref. 1117, ^{15}N-labelling, 25.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to aqueous NO_3^-, + 3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1.)

(o) Data from refs 127 and 1118, 36.54 MHz ^{15}N INEPT and DEPT spectra, field parallel to sample tube, referenced originally to 0.5 M KNO_3, + 3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(p) Data from ref. 1119, details as in footnote (o).

(q) Data from ref. 1120, details as in footnote (o).

(r) Data from ref. 435, ^{15}N label, 9.12 MHz ^{15}N CPMAS spectra, referenced originally to solid NH_4Cl, + 341.0 ppm from neat nitromethane (Table 2), conversion scheme IV (Table 1). Porphin shows dynamic NMR effects upon temperature variation while porphycen shows a sharp peak at high temperatures which splits into four sharp peaks whose spacing grows with the decreasing temperature; the former reflects changes in the rate of intramolecular proton migration, and the latter indicates at two independent migration pathways and fast migration even at the lowest temperatures examined. See also refs. 427, 432, 434, 439 and 545 for dynamic effects in ^{15}N spectra in porphyrin systems.

(s) Data from ref. 1045, 14.4 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to sat. aqueous $NaNO_3$, + 3.7 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(t) Data from ref. 1121, details as in footnote (u), but neat nitromethane as reference, uncorrected for bulk susceptibility effects.

(u) Data from ref. 83, 20.3 MHz ^{15}N spectra and 14.4 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to 0.1 M nitromethane in $CDCl_3$, + 3.8 ppm from neat nitromethane (Table 26), conversion scheme IIb (Table 1).

(v) Data from ref. 812, ^{15}N doubly labelled pyrazole, 25.36 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; originally reported vs fictitious ammonia standard taken at + 380.2 ppm from nitromethane (actually, the latter value corresponds to a perpendicular field-to-sample arrangement, see Table 2).

(w) Data from ref. 1122, ^{15}N-labelled pyrazole, 50.68 and 18.25 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, + 6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1)

(x) Data from ref. 1058, 27.25 and 20.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane via a calibrated sample of 6 M NH_4NO_3 in 2 M HNO_3, uncorrected for bulk susceptibility effect.

(y) Data from ref. 1123, 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced ot neat nitromethane, uncorrected for bulk susceptibility effects.

(z) Data from ref. 20, details as in footnote (y).

(A) Data from ref. 754, ^{15}N double label, 20.282 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, + 6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); reported originally vs liquid ammonia taken at + 375.8 ppm from the reference employed.

(B) Data from ref. 1088, 40.55 MHz ^{15}N spectra, other details as in footnote (w).

(C) Data from ref. 391, ^{15}N-labelled imidazole moieties in histidine, 29.82 MHz ^{15}N CPMAS spectra, referenced originally to 1 M HNO_3, (+ 6.2 ppm from neat nitromethane (Table 2) conversion scheme, II, Table 1), via a calibrated sample of solid ammonium sulphate, see also ref. 5, p. 372, and references therein.

Table 17. —*cont.*

(D) Data from ref.1124, 25.35 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; originally reported vs fictitious ammonia standards, see comments in footnote (v).

(E) Data from ref. 665, 50.7 MHz ^{15}N spectra, other details as in footnote (g).

(F) Data from ref. 1081, 8.059 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported originally vs liquid ammonia taken at +380.2 ppm from nitromethane.

(G) Data from ref. 774, ^{15}N selective labelling, 24.426 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4^+ in aqueous NH_4NO_3, +259.6 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(H) Data from ref. 22, details as in footnote (y), proton-coupled and decoupled spectra.

(I) Data from ref. 542, details as in footnote (g).

(J) Data from ref. 24, details as in footnote (y).

(K) Data from ref. 798, 25.33 MHz ^{15}N spectra, other details as in footnote (y).

(L) Data from ref. 1125, ^{15}N-labelled imidazole, 27.4 MHz ^{15}N spectra, other details as in footnote (y).

(M) Data from ref. 1126, details as in footnote (g).

(N) Data from ref. 1127, 25.352 MHz ^{15}N spectra, calibration as in footnote (v); $Cr(acac)_3$ added as a relaxation reagent, solutions in what was termed as "common solvents", probably DMSO and $CDCl_3$.

(O) Data from ref. 1128, 40.5 MHz ^{15}N spectra, calibration as in footnote (v); $Cr(acac)_3$ added as a relaxation reagent.

(P) Data from ref. 800, ^{15}N doubly labelled triazole moiety, 20.3 MHz ^{15}N spectra, calibration as in footnote (w).

(Q) Data from ref. 25, details as in footnote (y).

(R) Data from ref. 1036, 40.55 MHz ^{15}N spectra, other details and comments as in footnote (v).

(S) Data from ref. 26, details as in footnote (y).

(T) Data from ref. 1060, 40.544 MHz ^{15}N spectra, referenced originally to *internal* nitromethane in the solvent employed (DMSO), −2.0 ppm from neat nitromethane (Table 2), conversion scheme I (Table 1).

(U) Data from ref. 1129, 50.7 MHz ^{15}N spectra, other details as in footnote (f).

(V) Data from ref. 1034, 30.4 MHz ^{15}N spectra, field parallel to sample tube, and 10.13 MHz ^{15}N sepctra, field perpendicular to sample tube; for non-aqueous solutions, the original reference was nitromethane + 10% C_6D_6, *ca.* +0.4 ppm from neat nitromethane, as can be reckoned from the data in Table 26, conversion scheme II (Table 1): for aqueous solutions, the nitrate ion in aqueous ammonium nitrate, +4.0 ppm from neat nitromethane (Table 2), was employed as an external reference, conversion as above, $Cr(acac)_3$ was added as a relaxation reagent for non-aqueous solutions.

(W) Data from ref. 356, 50.7 MHz ^{15}N solution spectra, field parallel to sample tube, and 27.3 MHz ^{15}N CPMAS spectra, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; the gegenion was the nonprotanated form of *N,N,N,N*-tetramethyl-1,8-diaminonaphthalene.

(X) Data from refs 23 and 29, 40.5 MHz ^{15}N spectra, other details as in footnote (f).

(Y) Data from ref. 648, ^{15}N selective labelling, 40.56 MHz ^{15}N spectra, other details as in footnote (g).

(Z) Data from ref. 1130, 25.35 MHz ^{15}N DEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; reported originally vs fictitious ammona standard taken at + 380.2 ppm from neat nitromethane, see comments in footnote (v).

(aa) Data from ref. 523, 27.25 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4^+ in 6 M NH_4NO_3 in 2 M HNO_3, + 359.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); also 30.42 MHz ^{15}N CPMAS spectra, referenced to solid NH_4NO_3, + 358.4 ppm from neat nitromethane, uncorrected for bulk susceptibility effects. For the structure of trimethoprim, see Table 19.

(bb) Data from ref. 1131, details as in footnote (y).

(cc) Data from refs 760 and 1059, 20.3 MHz ^{15}N spectra, other details as in footnote (w).

(dd) Data from ref. 805, details as in footnote (U).

(ee) Data from ref. 1132, details as in footnote (U); $Cr(acac)_3$ added as a relaxation reagent.

(ff) Data from ref. 881, 30.454 MHz ^{15}N proton-coupled spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(gg) Data from ref. 730, ^{15}N-labelled compounds, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(hh) Data from ref. 818, 20.3 MHz ^{15}N spectra and 14.4 MHz ^{14}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

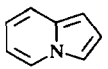
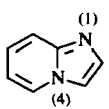
(ii) Data from ref. 910, 30.416 MHz ^{15}N spectra, other details as in footnote (hh); $Cr(acac)_3$ added as a relaxation reagent.

(jj) Data from ref. 90, 4.33 MHz ^{14}N spectra, concentric spherical sample/reference containers in order to eliminate bulk susceptibility effects, differential saturation techniques combined with lineshape fitting, referenced to external neat nitromethane, + 35°C.

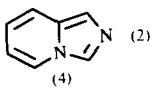
(kk) Data from ref. 1133, 50.7 MHz ^{15}N spectra and 36.15 MHz ^{14}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; see also ref. 1134.

(ll) Data from ref. 1135, 30.42 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to aqueous $NaNO_3$, + 3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); $Cr(acac)_3$ added as a relaxation reagent.

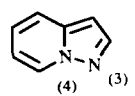
Table 18. Nitrogen shieldings in azolo-azine systems and related heterocycles

Compound	Solution or state	Nitrogen shieldings (ppm) referred to neat nitromethane		Notes
Indolizine structures				
 (indolizine)	0.25 M in			
	cyclohexane	+190.90		(a)
	Et_2O	+190.69		(a)
	CCl_4	+191.04		(a)
	benzene	+190.74		(a)
	dioxane	+189.97		(a)
	acetone	+189.93		(a)
	DMSO	+189.04		(a)
	CH_2Cl_2	+190.02		(a)
	$CHCl_3$	+189.99		(a)
	EtOH	+190.07		(a)
	MeOH	+189.93		(a)
	H_2O (0.01 M)	+189.19		(a)
	CF_3CH_2OH	+189.75		(a)
	0.25 M in	N-1	N-4	
	cyclohexane	+132.85	+180.06	(a)
	Et_2O	+134.97	+179.77	(a)
	CCl_4	+135.44	+180.21	(a)
	benzene	+136.03	+180.14	(a)
	dioxane	+136.74	+179.00	(a)
	acetone	+138.42	+179.00	(a)
	DMSO	+139.19	+178.04	(a)
	CH_2Cl_2	+141.60	+179.41	(a)

$CHCl_3$	+143.92	+179.59	(a)
EtOH	+153.03	+179.54	(a)
MeOH	+155.85	+179.46	(a)
H_2O	+159.03	+178.92	(a)
CF_3CH_2OH	+164.60	+180.45	(a)

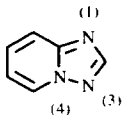
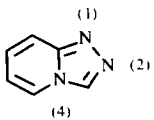
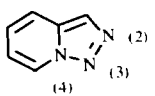
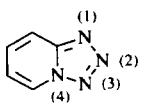


0.25 M in	N-2	N-4	
cyclohexane	+102.07	+187.47	(a)
Et_2O	+104.14	+187.07	(a)
CCl_4	+104.49	+187.44	(a)
benzene	+104.85	+187.17	(a)
dioxane	+105.88	+186.42	(a)
acetone	+106.58	+186.03	(a)
DMSO	+107.32	+185.27	(a)
CH_2Cl_2	+109.54	+186.31	(a)
$CHCl_3$	+112.16	+186.43	(a)
EtOH	+119.50	+186.09	(a)
MeOH	+123.17	+186.00	(a)
H_2O	+125.16	+185.64	(a)
CF_3CH_2OH	+132.8	+186.73	(a)



0.25 M in	N-3	N-4	
cyclohexane	+89.54	+144.33	(a)
Et_2O	+90.98	+144.30	(a)
CCl_4	+91.65	+144.78	(a)
benzene	+92.24	+144.66	(a)
dioxane	+92.05	+144.07	(a)
acetone	+93.15	+144.40	(a)
DMSO	+93.23	+144.09	(a)
CH_2Cl_2	+95.51	+144.25	(a)

Table 18. —*cont.*

Compound	Solution or state	Nitrogen shieldings (ppm) referred to neat nitromethane	Notes
	$CHCl_3$	+97.43 +144.50	(a)
	EtOH	+103.68 +145.05	(a)
	MeOH	+105.98 +146.08	(a)
	H_2O (0.1 M)	+110.18 +146.08	(a)
	CF_3CH_2OH	+115.79 +147.20	(a)
	0.5 M in DMSO	+139.8 (N-1) +102.0 (N-3) +148.1 (N-4)	(b) (b) (b)
	0.5 M in DMSO	+80.9 (N-1) +49.5 (N-2) +183.6 (N-4)	(b) (b) (b)
	0.2 M in DMSO	+24.9 (N-2) +44.2 (N-3) +120.6 (N-4)	(b) (b) (b)
	0.5 M in DMSO	+67.8 (N-1) −18.3 (N-2) +34.4 (N-3) +128.3 (N-4)	(b) (b) (b) (b)

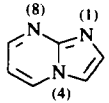
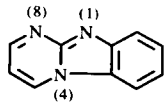
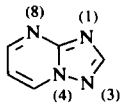
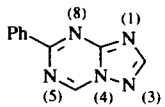
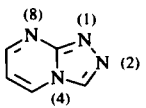
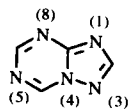
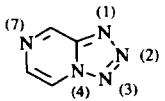
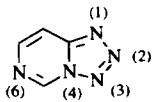
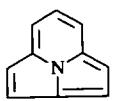
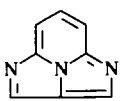
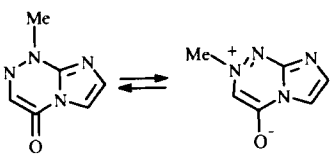
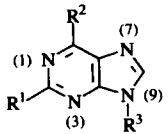
	0.5 M in DMSO	+141.5 (N-1) +190.8 (N-4) +100.3 (N-8)	(c) (c) (c)
	0.5 M in DMSO	+158.8 (N-1) +206.1 (N-4) +100.5 (N-8)	(d) (d) (d)
	0.5 M in DMSO	+149.4 (N-1) +102.1 (N-3) +153.3 (N-4) +105.0 (N-8)	(e) (e) (e) (e)
	in DMSO	+149.7 (N-1) +108.6 (N-3) +153.4 (N-4) +135.3 (N-5) +137.5 (N-8)	(f) (f) (f) (f) (f)
	0.5 M in DMSO	+84.3 (N-1) +49.4 (N-2) +196.9 (N-4) +103.5 (N-8)	(e) (e) (e) (e)
	0.5 M in DMSO	+66.6 (N-1) −15.9 (N-2) +27.5 (N-3) +117.2 (N-4) +57.3 (N-5) +84.5 (N-8)	(e) (e) (e) (e) (e) (e)

Table 18. —*cont.*

Compound	Solution or state	Nitrogen shieldings (ppm) referred to neat nitromethane	Notes
	0.5 M in DMSO	+63.0 (N-1) −19.5 (N-2) +30.9 (N-3) +124.8 (N-4) +53.7 (N-7)	(c) (c) (c) (c) (c)
	0.5 M in DMSO	+69.8 (N-1) −20.6 (N-2) +34.6 (N-3) +127.9 (N-4) +109.0 (N-6)	(e) (e) (e) (e) (e)
	0.5 M in DMSO	+192.4	(d)
	0.5 M in DMSO	+102.1 (N=) +165.4 (central N)	(e) (e)
	in DMSO	+53.6 (2-N=) +159.4 (2-N$^+$)	(g) (g)

Purines and related structures (see also Table 22)



in DMSO (h)

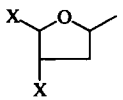
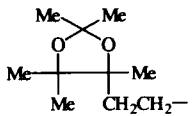
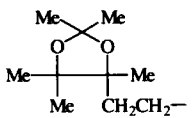
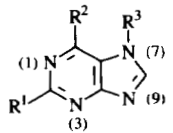
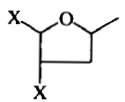
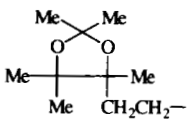
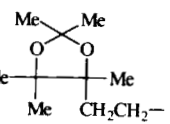
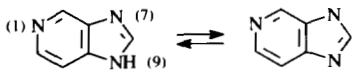
R^1	R^2	R^3		N-1	N-3	N-7	N-9	NH_2
H	Cl			+106.6	+130.4	+139.6	+207.2	–
			(*in $CDCl_3$*)	+107.6	+132.8	+140.1	+210.0	–
NH_2	H			+139.8	+179.8	+140.2	+225.0	+300.6
NH_2	Cl	$MeCO(CH_2)_4$—		+146.4	+182.6	+141.1	+221.1	+298.4
NH_2	Cl	$Me(CH_2)_4$—		+146.5	+182.5	+141.6	+220.6	+298.5
NH_2	Cl			+146.9	+182.9	+141.6	+222.3	+298.4
			(+*TFA*)	+144.4	+183.2	+162.2	+220.2	+297.1

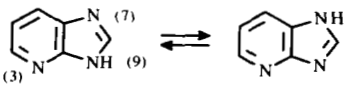
Table 18. —*cont.*

Compound	Solution or state	Nitrogen shieldings (ppm) referred to neat nitromethane					Notes
	in DMSO						(h)
R^1 R^2 R^3		N-1	N-3	N-7	N-9	NH_2	
H Cl 	(*in* $CDCl_3$)	+105.7	+112.2	+217.6	+138.4	–	
NH_2 H 		+141.1	+160.6	+230.0	+138.4	+303.4	
NH_2 Cl $MeCO(CH_2)_4$—		+143.3	+163.8	+227.8	+141.0	+301.3	
NH_2 Cl $Me(CH_2)_4$—		+143.1	+163.7	+227.3	+141.2	+302.2	
NH_2 Cl 	(+ *TFA*)	+143.8 +141.6	+164.3 +172.6	+229.0 +225.1	+141.5 +167.6	+301.4 +300.2	



(3-deazapurine) (i)

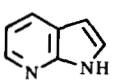
	in H_2O	N-1	N-7	N-9
100%, 1,7-NH	pH = 0.35	+193.7	+206.6	+157.9
	pH = 4.35	+189.2	+206.5	?
	pH = 5.00	+170.4	+206.9	+160.6
70% 7-NH	pH = 5.85	+136.8	+203.5	+163.9
	pH = 6.50	+126.1	+205.2	+168.7
	pH = 9.80	+103.9	+203.0	+171.7



(1-deazapurine) (i)

	in H_2O	N-3	N-7	N-9
3,9-NH + 7,9-NH	pH = 0.3	+161.4	+182.7	+221.6
	pH = 1.7	+156.8	+181.6	+220.2
	pH = 3.1	+138.8	+177.5	+213.8
	pH = 4.3	+120.8	+175.6	+206.0
70% 9-NH	pH = 5.7	+113.2	+175.4	+202.3
	pH = 7.4	+114.3	?	?
	pH = 9.3	+114.9	+175.8	?

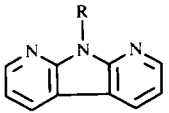
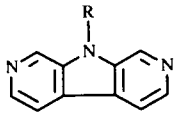
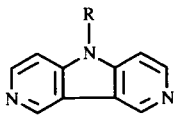
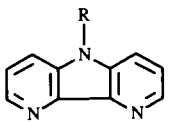
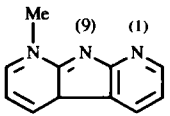
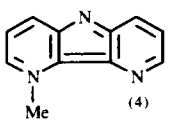
Other azolo-azines without a bridgehead nitrogen atom

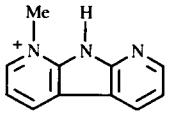


(j)

	NH	—N=
in CCl_4	+241.4	+121.4
in EtOH	+243.9	+123.3
in 0.1 M HCl	+245.7	+214.2

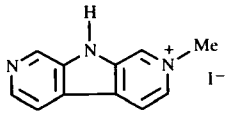
Table 18. *—cont.*

Compound	Solution or state	Nitrogen shieldings (ppm) referred to neat nitromethane	Notes
	0.5 M in DMSO	NR —N=	(k)
	R = H	+251.1 +111.2	
	R = Me	+260.4 +114.9	
	0.5 M in DMSO	NR —N=	(k)
	R = H	+268.3 +64.9	
	R = Me	+276.2 +65.2	
	0.5 M in DMSO	NR —N=	(k)
	R = H	+256.5 +88.3	
	R = Me	+264.3 +88.9	
	0.5 M in DMSO	NR —N=	(k)
	R = H	+271.1 +78.6	
	R = Me	+279.4 +78.9	
	0.5 M in DMSO	+232.2 (NMe)	(k)
		+173.5 (N-9)	(k)
		+105.8 (N-1)	(k)
	0.5 M in DMSO	+209.1 (NMe)	(k)
		+179.9 (N-9)	(k)
		+87.3 (N-4)	(k)



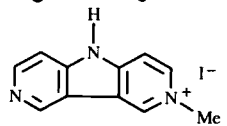
0.5 M in DMSO

+250.5 (NH) (k)
+213.8 NMe) (k)
+101.1 (—N=) (k)



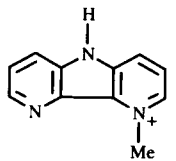
0.5 M in DMSO

+261.6 (NH) (k)
+185.7 (NMe) (k)
+60.7 (—N=) (k)



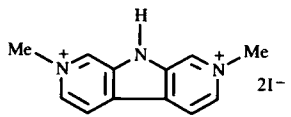
0.5 M in DMSO

+237.8 (NH) (k)
+201.6 (NMe) (k)
+109.3 (—N=) (k)



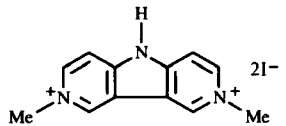
0.5 M in DMSO

+262.0 (NH) (k)
+193.8 (NMe) (k)
+79.2 (—N=) (k)



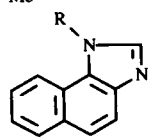
0.5 M in DMSO

+250.2 (NH) (k)
+180.0 (NMe) (k)



0.5 M in DMSO

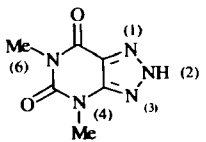
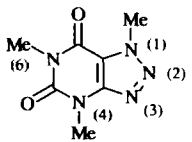
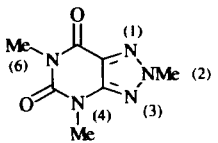
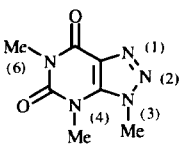
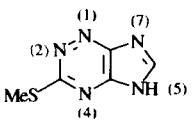
+236.5 (NH) (k)
+196.1 (NMe) (k)

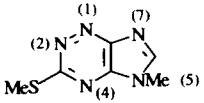
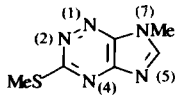


R = H, in $CDCl_3$
in pyridine
R = Me, in $CDCl_3$

NR	—N=	
+244.5	+113.0	(l)
+241.6	+88.5	
+244.9	+88.3	

Table 18. *—cont.*

Compound	Solution or state	Nitrogen shieldings (ppm) referred to neat nitromethane					Notes
		N-1	N-2	N-3	N-4	N-6	(m)
	in DMSO	+55.2	?	+90.2	+276.3	+227.9	
	in DMF	+55.7	+111.7	+89.7	?	+227.9	
	in $CDCl_3$	+150.0	+9.7	+66.5	+275.2	+228.5	(m)
	in $CDCl_3$	+47.0	+134.1	+84.3	+277.8	+228.5	(m)
	in DMSO	+33.3	+18.0	+163.9	+275.1	+231.1	(m)
		N-1	N-2	N-4	N-5	N-7	(n)
	in DMSO (68% 5-NH)	−4.8	+40.2	+131.1	?	?	

	in DMSO	−11.7	+41.1	+139.5	+234.4	+141.0	(n)
	in DMSO	+12.5	+41.3	+117.6	+144.2	+235.3	(n)

(a) Data from ref. 533, high precision ^{14}N spectra, 36.14 MHz, field parallel to sample tube, referenced to neat nitromethane, *corrected* for bulk susceptibility effects; temperature +35.0 ± 0.3°C, Lorentzin lineshape fitting employed.

(b) See ref. 5, pp. 478–481, and ref. 90, and references therein.

(c) Data from ref. 27, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 1136, details as in footnote (e).

(e) Data from ref. 65, 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(f) Data from ref. 835, 30.42 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(g) Data from ref. 827, ^{15}N-labelled N-2, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to what was termed as "concentrated HNO_3"; we assumed that it was 70% HNO_3, +31.3 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1), but a large error is likely to be involved in view of the high sensitivitiy of HNO_3 nitrogen shielding to the concentration of the acid.

(h) Data from ref. 123, 27.4 MHz ^{15}N spectra, NOE suppressed, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; abberviations used − X = *p*-Me-C_6H_4—COO, TFA = CF_3COOH.

(i) Data from ref. 1137, 36.53 MHz ^{15}N spectra (proton-coupled and decoupled), field parallel to sample tube, referenced originally to neat nitromethane via a calibrated sample of formamide, uncorrected for bulk susceptibility effects.

(j) Data from ref. 538, 40.56 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

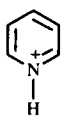
(k) Data from ref. 21, 40.5 MHz ^{15}N spectra, other details as in footnote (e).

(l) Data from ref. 772, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(m) Data from ref. 122, 25.4 MHz ^{15}N spectra (DEPT and conventional), referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported vs fictitious ammonia standard taken at +380.2 ppm from nitromethane (the latter value corresponds actually to a perpendicular field-to-sample arrangement, see Table 1).

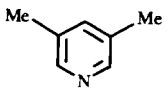
(n) Data from ref. 819, 50.7 MHz ^{15}N spectra (NOE suppressed), field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

Table 19. Nitrogen shieldings in azines and related heterocycles, their ions and *N*-oxides

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 (pyridine)	gaseous	+54.6	(a)
	neat liquid	+62.0	(b)
	inf. dil in		
	cyclohexane	+57.7	(b)
	CCl_4	+60.5	(b)
	benzene	+61.1	(b)
	DMSO	+63.1	(b)
	CH_2Cl_2	+65.3	(b)
	$CHCl_3$	+68.7	(b)
	MeOH	+81.1	(b)
	in H_2O	+84.3	(b)
	CF_3CH_2OH	+96.1	(b)
 (pyridinium ion)	0.5 M in 10 M HCl	+178.96	(a)
	0.5 M in CF_3COOH	+182.5	(a)
	0.5 M in FSO_3H	+186.9	(a)
	solid, NO_3^-	+167 (isotropic)	(c)
		+44 (σ_{xx})	(c)
		+96 (σ_{yy})	(c)
		+360 (σ_{zz})	(c)
	solid, I^-	+175 (isotropic)	(c)
		+86 (σ_{xx})	(c)
		+86 (σ_{yy})	(c)
		+354 (σ_{zz})	(c)
 (pyridine *N*-oxide)	0.008 M in cyclohexane	+76.47	(d)
	0.064 M in Et_2O	+78.78	(d)

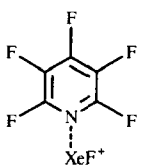
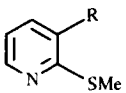
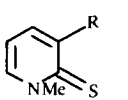
	0.128 M in CCl_4	+80.84	(d)
	0.25 M in benzene	+81.36	(d)
	0.25 M in dioxane	+81.40	(d)
	0.25 M in acetone	+82.85	(d)
	0.25 M in DMSO	+85.64	(d)
	0.25 M in CH_2Cl_2	+85.66	(d)
	0.25 M in $CHCl_3$	+86.78	(d)
	0.25 M in EtOH	+97.06	(d)
	0.25 M in MeOH	+97.53	(d)
	0.25 M in H_2O	+106.47	(d)
	0.25 M in CF_3CH_2OH	+106.61	(d)
Pyridine	*ca.* 1 M in $CDCl_3$		(g)
+ proton donors (CF_3CH_2OH, PhOH, MeCOOH, CCl_3COOH, CF_3COOH)	free pyridine	*ca.* +67	
	H-bonded pyridine	*ca.* +93	
	pyridinium ion	*ca.* +185	
Pyridine adsorbed on HY-zeolites	shallow-bed actived	+168 to +175	(e)
	deep-bed activated	+121 to +145	(e)
Pyridine absorbed on γ-alumina,	solid samples		(f)
partially dehydroxylated		+107, +128	
intermediately hydroxylated		+110, +133	
extensively dehydroxylated		+113, +127	
upon partial exposure to air		+113	
upon prolonged exposure to air		+82	
Pyridine adsorbed on coals:	solid samples		(c)
bituminous			
fresh Illinois No. 6		+78.7 (isotropic)	

Table 19. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
		+98 (σ_{xx})	
		+41 (σ_{yy})	
		+360 (σ_{zz})	
Devco		+79 (isotropic)	
sub-butuminous			
Whitewood and oxidized Illinois No. 6		+79, +150	
	*ca.* 17 mol% in solvents specified:		(h)
	n-hexane	+59.2	
	Et_2O	+60.4	
	$MeOCH_2OH_2OMe$	+61.7	
	tetrahydrofuran	+61.8	
	neat liquid	+62.3	
	acetone	+62.3	
	benzene	+62.3	
	CCl_4	+62.4	
	dimethylformamide	+63.3	
	pyridine	+63.4	
	DMSO	+63.8	
	$MeCOCH_2COMe$	+63.9	
	nitrobenzene	+64.0	
	MeCN	+64.2	
	$MeNO_2$	+65.0	
	PhSH	+66.4	
	CH_2Cl_2	+66.6	
	$CHCl_3$	+69.8	
	MeNHCHO	+73.8	

	EtOH	+77.2	
	H_2O + 10% acetone	+79.0	
	MeOH	+80.0	
	m-cresol	+92.6	
	CF_3CH_2OH	+92.8	
	2-Cl-phenol	+97.7	
	2-Br-phenol	+97.9	
	2-F-phenol	+104.2	
	MeCOOH	+143.7	
	HCOOH	+176.6	
	CF_3COOH	+184.3	
Substituted pyridines; with substituent(s):			
none	in DMSO, +68°C	+63.3	(i)
	1 M in CH_2Cl_2	+63.0	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+147.5	(j)
3-Me	in DMSO, +68°C	+61.8	(i)
	1 M in CH_2Cl_2	+66.8	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+150.7	(j)
4-Me	in DMSO, +68°C	+70.3	(i)
	1 M in CH_2Cl_2	+74.6	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+159.3	(j)
3,5-Me_2	1 M in CH_2Cl_2	+66.6	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+153.5	(j)
2,4-Me_2	1 M in CH_2Cl_2	+75.4	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+161.9	(j)
2,6-Me_2	1 M in CH_2Cl_2	+68.1	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+158.4	(j)
2,4,6-Me_3	1 M in CH_2Cl_2	+75.8	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+168.4	(j)
4-Et	in DMSO, +68°C	+69.6	(i)
4-Pr	in DMSO, +68°C	+68.6	(i)

Table 19. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
4-Bu^t	in DMSO, +68°C	+68.8	(i)
		+104.7 (ring)	(O)
4-NMe_2	in $MeNO_2$, +55°C	+352.0 (NMe_2)	(O)
2-OCH=CH_2	neat + 20% CCl_4	+112.5	(P)
3-CN	1 M in CH_2Cl_2	+65.8	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+100.0	(j)
4-CN	1 M in CH_2Cl_2	+52.1	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+98.1	(j)
3-Br	1 M in CH_2Cl_2	+59.9	(j)
	1 M in CH_2Cl_2 + CF_3COOH	+113.8	(j)
4-COPh	in DMSO, +68°C	+52.3	(i)
4-COOMe	in DMSO, +68°C	+61.7	(i)
2,3,4,5,6-F_5	in acetone-d_6	+145.9	(k)
	in HF, −30°C	+208	(l)
 R = H	0.7 M in DMSO	+78.9	(m)
R = COOH	2 M in DMSO	+71.6	(n)
R = COOMe	2 M in DMSO	+72.1	(n)
 R = H	0.7 M in DMSO	+187.4	(m)
R = COOH	2 M in DMSO	+175.2	(n)
R = COOMe	2 M in DMSO	+178.7	(n)

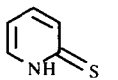
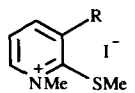
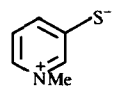
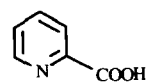
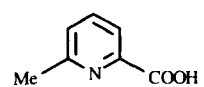
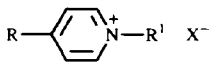
	R = H	0.7 M in acetone	+185.9	(m)
	R = H	0.7 M in $CDCl_3$	+182.5	(m)
	R = COOH	2 M in DMSO	+169.8	(n)
	R = COOMe	2 M in DMSO	+174.1	(n)
	R = COOH	2 M in DMSO	+166.5	(n)
	R = COOMe	2 M in DMSO	+166.0	(n)
		2 M in MeOH	+177.7	(n)
		in DMSO	+66.7	(o)
		its anion complexed with $H_2Rh(PPH_3)_2$, in CH_2Cl_2	+115.3	(o)
		in DMSO	+69.1	(o)
		its anion complexed with $H_2Rh(PPH_3)_2$, in CH_2Cl_2	+111.8	(o)

Table 19. —*cont.*

Compound			Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
			in DMSO		(p)
R	R^1	X			
H	Me	I		+178.2	
Me	Me	I		+182.8	
t-Bu	Me	I		+180	
CN	Me	I		+170.2	
COMe	Me	I		+171.5	
NMe_2	Me	I		+221	
OMe	Me	I		+194	
Br	Me	I		+181	
Me	Et	Br		+171	
CN	Et	Br		+155.8	
H	i-Pr	Br		+153	
Me	i-Pr	Br		+158.6	
t-Bu	i-Pr	Br		+160	
NMe_2	i-Pr	Br		+197	
H	CH_2Ph	Br		+162	
Me	CH_2Ph	Br		+166	
t-Bu	CH_2Ph	Br		+171	
CN	CH_2Ph	Br		+157.3	
NMe_2	CH_2Ph	Br		+196	
H	OH	Cl		+110	
NO_2	OH	Cl		+81	
OMe	OH	Cl		+137	

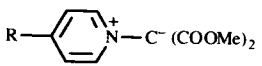
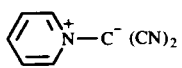
Substituted pyridine *N*-oxides, with substituent(s):	in DMSO, +68°C		(i)
none		+87.6, +84.0 (?)	
3-Me		+87.6	
4-Me		+96.4, +90.1 (?)	
4-Et		+88.4	
4-i-Pr		+88.4	
4-t-Bu		+88.8	
4-Ph		+85.9	
4-COPh		+75.4	
4-COMe		+74.8	
4-COOMe		+74.4	
4-CN		+74.9	
$4\text{-}NO_2$		+70.5	
	in DMSO, +68°C		(i)
R			
H		+160.3	
4-Me		+166.6	
4-Et		+166.3	
4-i-Pr		+165.9	
4-t-Bu		+166.0	
4-Ph		+165.1	
4-COPh		+156.5	
4-CN		+152.9	
Substituted  substituent(s):	in DMSO, +68°C		(i)
none		+161.4	

Table 19. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
3-Me		+162.0	
4-Me		+168.5	
3,5-Me_2		+162.4	
3,4-Me_2		+168.5	
4-Et		+167.9	
4-Pr		+167.9	
4-i-Pr		+167.6	
4-t-Bu		+167.7	
4-CH_2Ph		+166.9	
4-COPh		+155.6	
4-COMe		+155.0	
3-COOMe		+160.2	
4-COOMe		+153.9	
3-CN		+157.9	
4-CN		+153.9	
 (pyridazine: 1,2-diazine)	0.15 M in cyclohexane	−35.31	(q)
	0.15 M in Et_2O	−31.01	(q)
	0.15 M in CCl_4	−29.35	(q)
	0.15 M in benzene	−27.80	(q)
	0.15 M in dioxane	−26.74	(q)
	0.15 M in acetone	−25.85	(q)
	0.15 M in DMSO	−20.93	(q)
	0.15 M in CH_2Cl_2	−20.19	(q)
	0.15 M in $CHCl_3$	−19.01	(q)
	0.30 M in EtOH	−10.50	(q)
	0.15 M in MeOH	−6.32	(q)

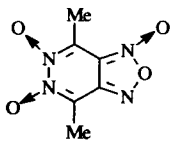
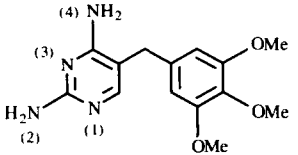
	0.15 M in H_2O	+6.24	(q)
	0.30 M in CF_3CH_2OH	+13.2	(q)
Substituted pyridazines, with substituent(s):			
3-Me	in $CDCl_3$	−17.6 (N-1)	(r)
		−14.3 (N-2)	(r)
3,6-Me_2	in $CDCl_3$	−12.1 (N-1,2)	(r)
3,4,5,6-F_4	in acetone-d_6	+51.6 (N-1,2)	(k)
	in DMSO	+43.4 azine +44.5 ring	(s)
	in acetone	+39.7 azine +40.8 ring	(s)
	0.20 M in cyclohexane	+80.30	(q)
	0.20 M in CCl_4	+81.59	(q)
	0.20 M in Et_2O	+81.81	(q)
	0.20 M in benzene	+82.83	(q)
	0.20 M in dioxane	+82.99	(q)
	0.20 M in acetone	+83.41	(q)
	0.20 M in DMSO	+83.90	(q)
(pyrimidine; 1,3-diazine)	0.20 M in CH_2Cl_2	+85.25	(q)
	0.20 M in $CHCl_3$	+86.21	(q)
	0.20 M in EtOH	+88.67	(q)
	0.20 M in MeOH	+90.84	(q)
	0.20 M in H_2O	+97.14	(q)
	0.30 M in CF_3CH_2OH	+98.2	(q)

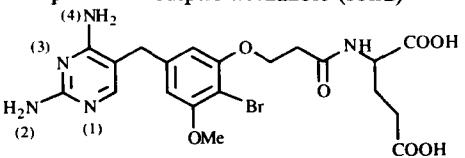
Table 19. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Substituted pyrimidines, with substituent(s):			
2,4-Cl_2-6-Me	0.4 M in $CDCl_3$	+91.5 (N-1)	(t)
		+98.7 (N-3)	(t)
2-Cl-6-Me	0.4 M in $CDCl_3$	+87.3 (N-1)	(t)
		+96.0 (N-3)	(t)
2-Cl-4,6-Me_2	0.4 M in $CDCl_3$	+95.2 (N-1,3)	(t)
4,6-Me_2	0.4 M in $CDCl_3$	+94.6 (N-1,3)	(t)
5-NO_2	in $CHCl_3$	+83.8 (N-1,3)	(u)
		+*19.3* (*NO_2*)	(u)
	in DMSO	+84.6 (N-1,3)	(u)
		+*16.7* (*NO_2*)	(u)
4-OMe-5-NO_2	in $CHCl_3$	+106.1 (N-1)	(u)
		+121.5 (N-3)	(u)
		+*18.8* (*NO_2*)	(u)
2-SMe-5-NO_2	in $CHCl_3$	+97.8 (N-1,3)	(u)
		+*19.2* (*NO_2*)	(u)
2-SO_2Me-5-NO_2	in DMSO	+94.4 (N-1,3)	(u)
		+*18.1* (*NO_2*)	(u)
2,4,5,6-F_4	in acetone-d_6	+152.3	(k)

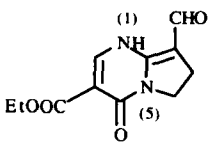


("trimethoprim")

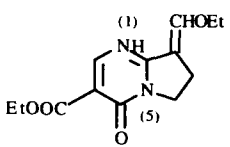
	N-1	N-3	2-NH_2	4-NH_2	(v)
trimethoprim in DMSO	+163.4	+181.3	+305.6	+302.7	
its hydrochloride in DMSO	+246.9	+180.6	+296.6	+275.6	
complex with sulphomethazole in DMSO	+179.1	+173.6	+301.1	+294.7	
triethoprim in solid state	+165.9	+181.3	+302.6	+300.2	
its hydrochloride (solid)	+242.0	+189.5	+301.5	+273.1	
complex with sulphomethazole (solid)	+241.4	+182.3	+294.9	+284.9	



		N-1	N-3	2-NH_2	(w)
monoprotonated	in H_2O, pH = 3.5	+243.3	+179.9	+294.9	
	in DMSO	+240.4	+172.5	+290.1	
complexed with *Lactobacillus casei* dihydrofolate reductase	in H_2O	+241.2	+173.1	+292.7	
as above + NADPH	in H_2O	+242.5	?	+293.4	

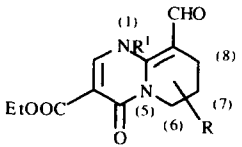
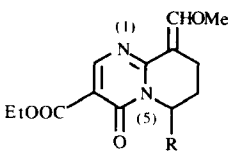


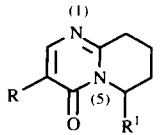
in $CDCl_3$	+181.1 (N-1)	(x)
in DMSO	+167.9 (N-1)	(x)



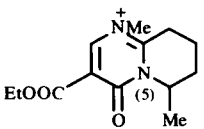
in $CDCl_3$	+167.3 (N-1)	(x)
	+197.8 (N-5)	(x)

Table 19. —*cont.*

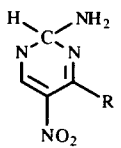
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
				
R R[1]	in $CDCl_3$	N-1	N-5	(x)
none Me		+267.3	+232.2	
	(+CF_3COOH)	+242.0	+196.6	
none H		+247.1	+231.5	
	(+CF_3COOH)	+246.9	+216.4	
6-Me Me		+268.3	+222.5	
6-Me H		+251.6	+221.6	
	(+CF_3COOH)	+244.7	+201.9	
7-Me H		+247.6	+231.8	
8-Me H		+248.5	+231.8	
	(+CF_3COOH)	+245.4	+214.9	
	in $CDCl_3$	N-1	N-5	(x)
	R = H	+161.8	+244.6	
	(+CF_3COOH)	+248.8	+224.6	
	R = Me	+161.2	+193.5	



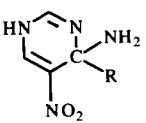
R	R^1	in $CDCl_3$	N-1	N-5	
COOEt	H		+145.5	+194.8	(x)
		(+ *CF_3COOH*)	+229.7	+187.8	
COOEt	Me		+144.9	+183.5	
		(+ *CF_3COOH*)	+222.8	+177.9	
CH_2COOEt	Me		+143.5	+174.2	
		(+ *CF_3COOH*)	+226.3	+168.8	



in $CDCl_3$ + CF_3COOH: +231.0 (N^+Me) (x); +178.0 (N) (x)



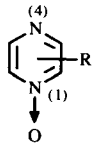
in liquid NH_3 (u)
R = H: +98 (averaged)
R = OMe: +96 (=N), +163 (NH)



in liquid NH_3 (u)
R = H: +92 (=N), +256 (NH)
R = SMe: +141 (=N), +147 (NH)
R = SO_2Me: +130 (=N), +178 (NH)

Table 19. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 (pyrazine; 1,4-diazine)	0.20 M in cyclohexane	+42.17	(q)
	0.20 M in CCl_4	+43.36	(q)
	0.20 M in Et_2O	+43.40	(q)
	0.20 M in benzene	+44.77	(q)
	0.20 M in dioxane	+44.81	(q)
	0.20 M in acetone	+44.88	(q)
	0.20 M in DMSO	+45.34	(q)
	0.20 M in CH_2Cl_2	+46.93	(q)
	0.20 M in $CHCl_3$	+47.80	(q)
	0.20 M in EtOH	+49.51	(q)
	0.20 M in MeOH	+51.70	(q)
	0.20 M in H_2O	+59.02	(q)
	0.30 M in CF_3CH_2OH	+58.0	(q)
Substituted pyrazines, with substituent(s):	in DMSO	N-1 N-4	(y)
none		+48 +48	
2-Me		+56 +54	
2-OMe		+111 +45	
2-NH_2		+115 +54	
2-Cl		+64 +44	
2-COOH		+55 +53	
		+47.4 +45.4	(o)
its complex with $H_2Rh(PPh_3)_2$		+93.7 +49.6	(o)
2-$CONH_2$		+66 +52	
2,3,5,6-F_4	in acetone-d_6	+102.5 +102.5	(k)

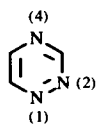


in DMSO

R =	N-1	N-4	
none	+71	?	(y)
2-Me	+84	+82	
3-Me	+83	+78	
2-Cl	+93	+74	
3-Cl	+73	+93	
3-OMe	+75	+132	
$3\text{-}NH_2$	+79	+133	

(1,3,5-triazine)

0.05 M in cyclohexane	+95.36	(q)
0.05 M in CCl_4	+95.92	(q)
0.05 M in Et_2O	+96.57	(q)
0.05 M in benzene	+96.92	(q)
0.05 M in acetone	+97.44	(q)
0.05 M in dioxane	+97.93	(q)
0.05 M in DMSO	+98.06	(q)
0.05 M in $CHCl_3$	+98.07	(q)
0.05 M in CH_2Cl_2	+98.21	(q)
0.05 M in EtOH	+98.69	(q)
0.05 M in MeOH	+100.32	(q)
0.05 M in H_2O	+106.27	(q)
0.10 M in CF_3CH_2OH	+106.1	(q)

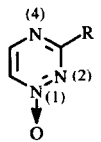
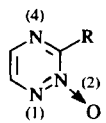
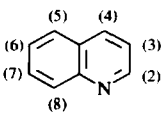


(1,2,4-triazine)

in DMSO

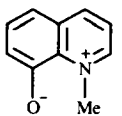
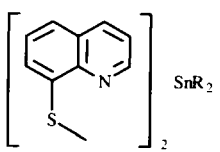
−39.8 (N-1)	(y)
−1.8 (N-2)	(y)
+62.2 (N-4)	(y)

Table 19. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
Substituted 1,2,4,-triazines substituent:	in DMSO	N-1	N-2	N-4	(y)
3-NH_2		−35.5	+61.2	+130.2	
3-OMe		−35.8	+58.2	+126.6	
3-SMe		−31.8	+29.2	+98.2	
	in DMSO	N-1	N-2	N-4	(y)
	R = NH_2	+51.3	+107.2	+151.3	
	R = OMe	+50.2	+97.2	+148.2	
	in DMSO	N-1	N-2	N-4	(y)
	R = NH_2	+39.2	+137.2	+153.2	
	R = Br	+28.8	+71.2	+74.4	
 (1,2,4,5-tetrazine)	in acetone	−4.0			(a)
 (quinoline)	0.05 M in DMSO	+67.2			(a)
	in $CDCl_3$	+74.7			(z)
		+70.9			(A)
	in $CDCl_3$ + CF_3COOH	+165.7			(A)

Substituted quinolines, with substituent(s):			
2-COOH	in DMSO	+66.9	(o)
its complex with $H_2Rh(PPh_3)_2$	in DMSO	+114.1	(o)
2-OCH=CH_2—4-Me	neat + 20% CCl_4	+133.2	(P)
2-Me—4-OCH=CH_2	neat + 20% CCl_4	+88.3	(P)
5-OCH=CH_2	neat + 20% CCl_4	+76.1	(P)
8-OCH=CH_2	neat + 20% CCl_4	+68.0	(P)
2-SCH=CH_2	neat + 20% CCl_4	+89.6	(P)
5-SCH=CH_2	neat + 20% CCl_4	+65.3	(P)
8-SCH=CH_2	neat + 20% CCl_4	+73.8	(P)
8-OH	in $CDCl_3$	+95.7	(B)
its hydrochloride	in 1 M HCl	+200.3	(B)
	in 0.1 M HCl	+192.6	(B)
its hydrobisulphate	in DMSO	+138.3	(B)
8-OMe	in $CDCl_3$	+84.0	(B)
		+82.5	(C)
8-O^-Na^+	0.1 M NaOH	+89.0	(B)
	in CD_3OD	+89.0	(B)
	in $CDCl_3$	+84.0	(B)
8-$OSnBu_3$	neat liquid	+99.0	(C)
	in $CDCl_3$	+99.8	(C)
	in pyridine	+100.1	(C)
5-Me-8-$OSnPh_3$	in $CDCl_3$	+115.5	(D)
	in $CDCl_3$ (240 K)	+120.4	(C)
	$CDCl_3$ (360 K)	+114.4	(C)
	in pyridine (240 K)	+124.3	(C)
	in pyridine (360 K)	+114.2	(C)
	in $(Me_2N)_3PO$ (290 K)	+117.8	(C)
	in $(Me_2N)_3PO$ (370 K)	+113.7	(C)
	solid state	+116.5	(D)
		+118.2	(D)
		+118.9	(D)

Table 19. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
8-S—$SnBu_3$	in $CDCl_3$	+82.1	(E)
8-S—$Sn(CH_2Ph)_3$	in $CDCl_3$	+94.9	(E)
8-S—$SnPh_3$	in $CDCl_3$	+95.1	(E)
8-S—$Sn(CH{=}CH_2)_3$	in $CDCl_3$	+94.5	(E)
	in CD_3OD	+187.7	(B)
Complexes of 8-hydroxyquinoline anion ("Q"), R = Me, Et, Ph:	in $CDCl_3$		(B)
SnR_2Q_2		+120 to +125	
$SbPh_3ClQ$		+114.8	
SnR_3Q		+101 to +119	
SbR_3ClQ		+97 to +99	
SbR_3Q_2		+84	
	in $CDCl_3$		(E)
	R = Bu	+92.3	
	R = CH_2Ph	+116.8	
	R = Ph	+110.8	
	R = $CH{=}CH_2$	+101.4	

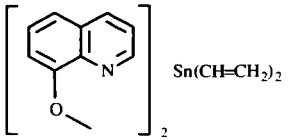
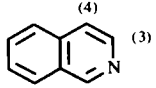
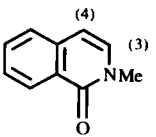
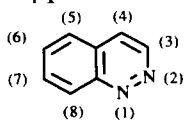
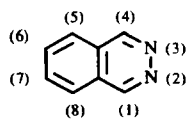
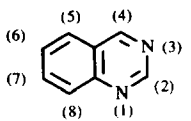
	in $CDCl_3$	+123.0	(E)
6-OMe-3-quinolyl moiety in:			(A)
quinidine	in $CDCl_3$	+82.0	
	in $CDCl_3$ + CF_3COOH	+176.5	
epi-quinidine	in $CDCl_3$	+74.3	
 (isoquinoline)	0.5 M in DMSO	+69.3	(a)
Substituted isoquinolines, with substituent(s):			
1-COOH	in DMSO	+79.0	(o)
its complex with $H_2Rh(PPh_3)_2$	in DMSO	+116.4	(o)
	in $CDCl_3$		(F)
substituent(s):			
none		+234.2	
3-Me		+229.7	
3-SEt		+229.9	
3-SOEt		+241.7	

Table 19. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
3-SO_2Et		+244.1	
3-Cl		+231.0	
3-Br		+230.0	
4-Me		+236.4	
4-COMe		+233.0	
4-COOMe		+231.6	
4-Cl		+235.3	
4-Br		+232.6	
4-I		+228.0	
 (cinnoline)	0.4 M in DMSO	+44.0 (N-1) +40.9 (N-2)	(a) (a)
 (phthalazine)	0.5 M in DMSO	+10.3	(a)
1,4,5,6,7,8-F_6-phthalazine in acetone-d_6		+106.9	(k)
 (quinazoline)	0.5 M in DMSO	+97.8 (N-1) +86.5 (N-2)	(a) (a)

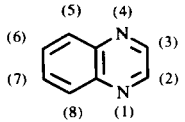
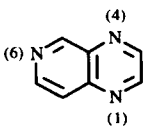
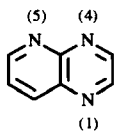
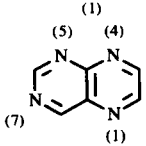
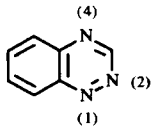
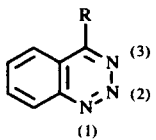
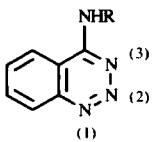
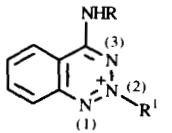
	0.5 M in DMSO	+50.1	(a)
	in benzene-d_6	+51.4	(G)
(quinoxaline)			
Substituted quinoxalines, with substituent(s):			
6-Me	in benzene-d_6	+52.1 (N-1)	(G)
		+52.8 (N-4)	(G)
5-Me	in benzene-d_6	+49.6 (N-1)	(G)
		+54.1 (N-4)	(G)
2-COOH	in DMSO	+47.4 (N-1)	(o)
		+45.4 (N-4)	(o)
its complex with $H_2Rh(PPh_3)_2$	in DMSO	+96.8 (*N-1*)	(o)
		+49.6 (*N-4*)	(o)
2,3,5,6,7,8-F_6	in acetone-d_6	+107.4	(k)
	0.5 M in DMSO	+52.7 (N-1)	(H)
		+51.7 (N-4)	(H)
		+57.7 (N-6)	(H)
	0.5 M in DMSO	+45.0 (N-1)	(a)
		+49.1 (N-4)	(a)
		+62.2 (N-5)	(a)
	0.5 M in DMSO	+46.6 (N-1)	(H)
		+52.2 (N-4)	(H)
		+92.1 (N-5)	(H)
		+73.8 (N-7)	(H)

Table 19. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	0.5 M in DMSO	−68.2 (N-1) −23.4 (N-2) +98.1 (N-4)	(a) (a) (a)
	1 M in DMSO	N-1 N-2 N-3	(I)
	R = Me	+14.6 −68.5 −16.8	
	R = Ph	+14.9 −66.5 −16.5	
	1 M in DMSO (*ca.* 100% of NHR tautomer)		(I)

R	N-1	N-2	N-3	NH	R
n-Bu	+15.4	−67.3	+67.7	+292.0	—
CH_2CH_2OMe	+13.7	−67.6	+67.3	+295.9	—
CH_2(α-pyridyl)	+9.6	−69.9	+67.0	+293.3	+64.5
CH_2(β-pyrydyl)	+10.6	−68.5	+66.3	?	+63.4
p-tolyl	+7.6	−66.3	+65.1	+278.7	—

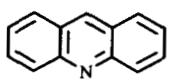


X^-

1 M in DMSO

(I)

R	R^1	X	N-1	N-2	N-3	NH
n-Bu	Pr	I	+40.5	+84.6	+91.8	+269.3
CH_2CH_2OMe	Pr	I	+39.6	+84.4	+91.6	+272.6
p-tolyl	Pr	I	+36.6	+85.5	+90.4	+261.4
p-tolyl	Pr	Br	+36.8	+85.1	+90.2	+259.4
p-tolyl	Pr	(*p*-tolyl)SO_3	+36.4	+85.0	+90.2	+261.1
p-tolyl	Me	$MeSO_3$	+35.8	+88.6	+93.5	+269.1
p-tolyl	Me	(*p*-tolyl)SO_3	+35.3	+88.6	+93.4	+261.4

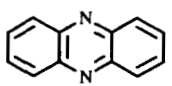


(acridine)

0.5 M in DMSO

+74.4

(a)

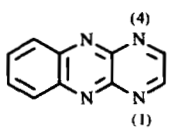


(phenazine)

0.1 M in DMSO

+53.9

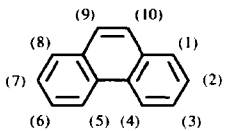
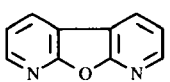
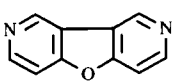
(a)



0.5 M in DMSO

+43.6 (N-1,4) (H)
+49.6 (central N) (H)

Table 19. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Azaphenanthrenes 	0.5 M in DMSO		
N atom(s) at positions:			
1		+67.5	(a)
4		+76.8	(a)
9		+70.8	(a)
1,8		+67.1	(a)
4,5		+69.3	(a)
1,5		+68.2 (N-1)	(a)
		+76.9 (N-5)	(a)
9,10		−59.9	(a)
4,5,9,10		+70.2 (N-4,5)	(J)
		−70.3 (N-9,10)	(J)
3,6,9,10		+46.9 (N-3,6)	(J)
		−84.4 (N-9,10)	(J)
2,7,9,10 (3-Cl substituent)		+54.2 (N-2)	(J)
		+53.2 (N-7)	(J)
		−67.8 (N-9)	(J)
		−62.8 (N-10)	(J)
	0.5 M in DMSO	+79.7	(J)
	0.5 M in DMSO	+75.2	(J)

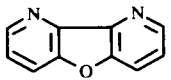
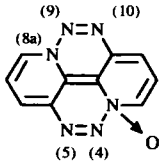
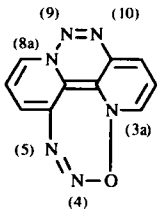
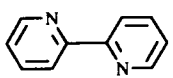
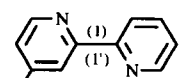
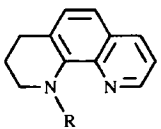
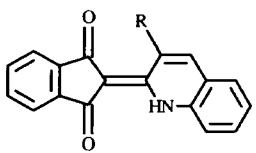
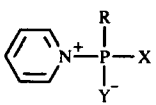
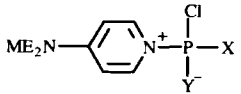
	0.5 M in DMSO	+76.4	(J)
	in $CDCl_3$	+73.8 (NO) −14.3 (N-4) +24.7 (N-5) +79.7 (N-8a) −5.8 (N-9) +31.0 (N-10)	(K) (K) (K) (K) (K) (K)
	in $CDCl_3$	+74.3 (NO) −16.3 (N-4) +23.9 (N-5) +80.0 (N-8a) −5.5 (N-9) +30.4 (N-10)	(K) (K) (K) (K) (K) (K)
 (2,2′-bipyridyl, "bpy")			
$[Fe(bpy)_3]Cl_2$	in D_2O	+2.8	(L)
cis-$[Co(bpy)_2(H_2O)_2](PF_6)_3$	in D_2O	+50.2, +75.1	(L)
 ("fbpy")	in $CDCl_3$	+49.9 (N-1) +40.7 (N-1′)	(L) (L)
mer- and *fac*-$[Fe(fbpy)_3]^{2+}$	in D_2O	+1.91, +2.11, +2.59, +2.73 (N-1′)	(L)

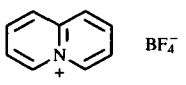
Table 19. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
		+15.21 +15.45 +15.87 +15.94 (N-1)		(L)
	in $CDCl_3$	=N—	NR	(M)
	R = H	+84.1	+321.6	
	R = $SiMe_3$	+74.9	+317.1	
	R = $SiMe_2Cl$	+38.9	+308.6	
	in $CDCl_3$			(N)
	R = H	+240.0		
	R = OH	+230.9		
(*ca.* 100% NH-tautomer)				
	in $MeNO_2$, +55°C			(O)
R X Y				
Cl O O		+144.1		
Cl S O		+134.2		
Cl S S		+126.5		
F S S		+133.1		

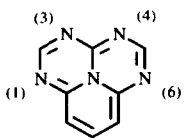


in $MeNO_2$, +55°C (O)

X	Y	ring	NMe_2
O	O	+188.6	+284.8
S	O	+179.2	+283.3
S	S	+123.9	+283.3



0.5 M in DMSO +171.4 (H)



0.5 M in DMSO
+146.1 (N-1,6) (H)
+160.7 (N-3,4) (H)
+185.1 (central) (H)

(a) See ref. 5, pp. 486–511, and ref. 516, and references therein.

(b) See refs 532 and 31, original data from R. Duthaler and J.D. Roberts, *J. Am. Chem. Soc.*, 1979, **100**, 4969, recalculated to neat nitromethane reference, corrected for bulk susceptibility effects.

(c) Data from ref. 424, ^{15}N-labelled pyridine moieties, 18.25 MHz ^{15}N CPMAS and powder spectra, referenced originally to NO_3^- in solid ammonium nitrate, +5.0 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects.

(d) Data from ref. 34, high-precision ^{14}N measurements, 36.14 MHz, Lorentzian lineshape fitting, referenced to neat nitromethane, *corrected* for bulk susceptibility effects, temperature +35.0 ± 0.3°C.

(e) Data from ref. 1138, ^{15}N-labelled pyridine, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(f) Data from ref. 423, ^{15}N-labelled pyridine, 30.4 MHz ^{15}N CPMAS spectra, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(g) Data from ref. 105, 25.357 MHz INEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; the values quoted were computed from the relevant titration curves.

Table 19. —*cont.*

(h) Data from ref. 125, 40.56 MHz ^{15}N INEPT and DEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects, +29°C.

(i) Data from refs 1106 and 1107, 9.1 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(j) Data from ref. 1139, details as in footnote (h) but the reference was neat nitromethane + 20% C_6D_6, *ca.* +0.8 ppm from neat nitromethane, as can be reckoned from Table 26, conversion scheme IIb (Table 1).

(k) Data from ref. 156, 20.3 MHz ^{15}N INEPT spectra (via $^2J_{NF}$ = 2 Hz), field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(l) Data from ref. 952, 18.075 MHz ^{14}N spectrum, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(m) Data from ref. 779, 20.3 MHz ^{15}N spectra, calibration as in footnote (k).

(n) Data from ref. 107, 40.5 MHz ^{15}N INEPT spectra, calibration as in footnote (k).

(o) Data from ref. 140, 20.3 MHz ^{15}N INEPT spectra, calibration as in footnote (k).

(p) Data from ref. 1140, 5.75 MHz asnd 14.46 MHz ^{14}N spectra, field perpendicular and parallel, respectively, to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(q) Original data from ref. 532, high-precision ^{14}N measurements, details as in footnote (d).

(r) Data from ref. 46, ^{15}N doubly labelled molecules, 20.2 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^- in NH_4NO_3 in 2 M HNO_3, +4.6 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(s) Data from ref. 1141, ^{15}N-labelled and unlabelled compound, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(t) Data from ref. 813, ^{15}N-labelled compounds, 20.2 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^-, probably aqueous $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(u) Data from ref. 162, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane via a calibrated sample of $MeNO_2$ in methanol, uncorrected for bulk susceptibility effects; reported vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane (the latter value actually corresponds to a perpendicular field-to-sample axis arrangement, Table 2).

(v) Data from ref. 523, 27.25 MHz ^{15}N solution spectra, field parallel to sample tube, referenced originally to NH_4^+ in 6 M NH_4NO_3 in 2 M HNO_3, +359.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); 30.42 MHz ^{15}N CPMAS spectra, referenced to NH_4^+ in solid NH_4NO_3, +358.4 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects.

(w) Data from refs 94 and 522, 27.4 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced originally to aqueous NH_4Cl, +352.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(x) Data from ref. 128 and ref. 1142, ^{15}N-labelled compounds, 10.04 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane via a calibrated sample of aqueous KNO_3, uncorrected for bulk susceptibility effects.

(y) Data from ref. 1143, 20.27 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; reported vs fictitious ammonia standard, see comments in footnote (u); $Cr(acac)_3$ added as a relaxation reagent.

(z) Data from ref. 772, 20.3 MHz ^{15}N spectra, parallel to sample tube, referenced originally to 1 M HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(A) Data from ref. 1144, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4^+ in 5 M NH_4NO_3 in 2 M HNO_3, +359.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(B) Data from refs 820 and 821, 18.25 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects other than those resulting from the addition of $Cr(acac)_3$ as a relaxation reagent.

(C) Data from refs 940 and 1145, ^{15}N-labelled compounds, 10.095 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(D) Data from ref. 942, ^{15}N-labelled compound, 20.218 MHz ^{15}N solution and CPMAS spectra, referenced to neat nitromethane (in the latter case via a calibrated sample of solid NH_4Cl), uncorrected for bulk susceptibility effects; the three signals observed in the CPMAS spectrum represent unequivalent crystal sites.

(E) Data from refs 144 and 1146, details as in footnote (C).

(F) Data from ref. 1038, 25.32 MHz ^{15}N DEPT spectra, calibration as in footnote (u).

(G) Data from ref. 1147, selectively ^{15}N-labelled molecules, spectrometer not reported, neat nitromethane reference, uncorrected for bulk susceptibility effects.

(H) Data from refs 27 and 665, 30.4 MHz and 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(I) Data from refs 1063, 1064 and 1148, 36.51 MHz ^{15}N spectra, other details as in footnote (H); $Cr(acac)_3$ added as a relaxation reagent.

(J) Data from ref. 21, 50.7 and 40.5 MHz ^{15}N spectra, other details as in footnote (H).

(K) Data from ref. 1149, 40.5 MHz ^{15}N spectra, other details as in footnote (H); assignments are tentative.

(L) Data from ref. 1150, details as in footnote (H).

(M) Data from ref. 1151, 27.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(N) Data from ref. 1036, 40.55 MHz ^{15}N spectra, calibration as in footnote (u).

(O) Data from ref. 913, 28.914 MHz ^{14}N spectra, referenced to *internal* nitromethane used as a solvent; 10–20% solutions (mol %).

(P) Data from ref. 681, 30.41 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects, $Cr(acac)_3$ added as a relaxation reagent; originally reported vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane.

Table 20. Nitrogen shieldings in azine analogues containing the SO_2 moiety

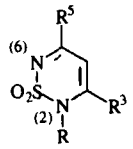
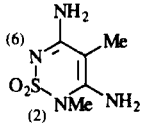
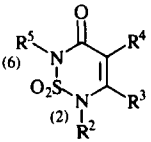
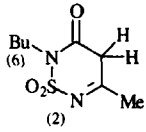
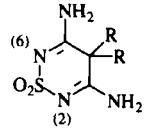
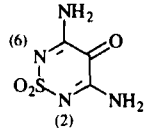
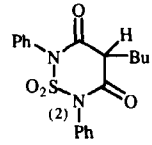
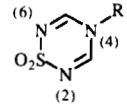
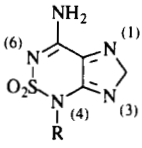
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in DMSO		(a)
	R = H; R^3 = Me; R^5 = Me	N-2: +*184.9 (averaged)*	
	R = Me; R^3 = Me; R^5 = Me	N-2: +240.9; N-6: +143.3	
	R = CH_2Ph; R^3 = Ph; R^5 = Ph	N-2: +241.6; N-6: +130.6	
	R = Bu; R^3 = Me; R^5 = OH	N-2: +234.3; N-6: +176.9	
	R = Bu; R^3 = Me; R^5 = OMe	N-2: +244.9; N-6: +179.8	
	R = H; R^3 = H; R^5 = OH	N-2: +242.7; N-6: +176.5	
	in DMSO	+261.9 (N-2)	(a)
		+214.7 (N-6)	(a)
		+290.6, +302.6 (NH_2)	(a)
	in DMSO		(a)
	R^2 = H; R^3 = H; R^4 = H; R^6 = H	N-2: +242.7; N-6: +176.5	
	R^2 = H; R^3 = Me; R^4 = H; R^6 = Ph	N-2: +241.6; N-6: +209.6	
	R^2 = H; R^3 = Me; R^4 = H; R^6 = Bu	N-2: +242.6; N-6: +220.7	
	R^2 = Me; R^3 = Me; R^4 = H; R^6 = Ph	N-2: +257.1; N-6: +209.5	
	R^2 = Me; R^3 = Me; R^4 = Br; R^6 = Ph	N-2: +258.6; N-6: +209.2	
	R^2 = Me; R^3 = Me; R^4 = H; R^6 = Me	N-2: +259.4; N-6: +232.6	
	in DMSO	+72.3 (N-2)	(a)
		+215.1 (N-6)	(a)
	in DMSO	N-2,6: +164.9; NH_2: +277.6	(a)
	R = $CH_2CH{=}CH_2$	N-2,6: +161.0; NH_2: +283.2	
	in DMSO	N-2,6: +149.6; NH_2: +285.2	(a)
	in DMSO	+204.4 (N-2)	(a)

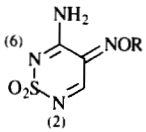
Table 20. —cont.

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	in DMSO	N-2,6	N-4	(a)
	R = H	+141.5	+231.7	
	R = Me	+142.4	+238.7	

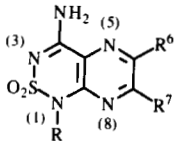


in DMSO (a)

X	R	N-1	N-3	N-4	N-6	NH_2
O	H	−35.7	+6.6	+270.3	+173.9	+273.2
O	Me	−37.9	+7.6	+276.4	+181.8	+270.1
S	Me	+326	+98.8	+258.4	+188.8	+273.4



see Table 24



in DMSO (b)

R^6	R^7	N-1	N-3	N-5	N-8	NH_2
H	Me	+251.5	+178.9	+59.8	+86.1	+284.0
H	Ph	+248.0	+171.1	+54.8	+84.1	+281.9
Me	Me	+260.3	+185.6	+58.5	+86.1	+280.0

(a) Data from refs 1152 and 1153, 30.41 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane via a calibrated sample of 4 M NH_4NO_3 in 2 M HNO_3, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(b) Data from ref. 1061, details as in footnote (a).

Table 21. Nitrogen shieldings in flavin and related pterin ring systems

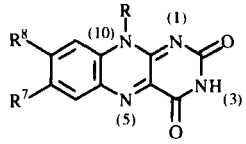
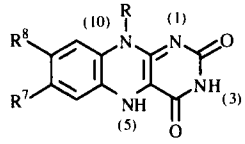
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
		N-1	N-3	N-5	N-10	
Oxidized forms of flavins						
						
R = ribityl-5′-monophosphate, $R^7 = R^8 = H$ ("FMN")						
	0.004 M in D_2O, pD = 7.5	+191.1	+221.4	+47.2	?	(a)
	0.12 M in D_2O, pD = 7.5	+189.0	+220.8	+47.5	+219.4	(a)
FMN in old yellow enzyme	pH = 8.5	+187.6	+217.8	+62.5	?	(a)
Bacterial luciferase from *Vibrio harveyi*	pH = 7.0	+194.8	+219.6	+56.1	+221.1	(c)
FMN from *Azotobacter vinelandii*	pH = 8.0	+195.5	+221.7	+40.5	?	(b)
Megasphaera elsdenii	pH = 8.0	+196.9	+221.0	+32.6	?	(b)
Clostridium MP	pH = 8.0	+197.4	+220.8	+30.4	?	(b)
R = ribityl-5′-monophosphate, R^7 = Me, R^8 = H ("MeIMN")	0.0006 M in D_2O, pD = 7.5	+191.4	+221.5	+46.4	+217.3	(a)
	0.006 M in D_2O, pD = 7.5	+190.8	+221.5	+46.3	+217.6	(a)
MeIMN in old yellow enzyme	pH = 8.5	+187.1	+217.7	+61.1	+220.4	(a)
R = tetraacetylribityl, $R^7 = R^8 = H$ ("TARF")	0.35 M in $CDCl_3$	+182.0	+222.1	+37.6	+231.7	(a)
	same + 10% MeOH	+183.1	+222.1	+38.5	+230.5	(a)
R = tetraacetylribityl, R^7 = Me, R^8 = H ("MeTARI")	in $CDCl_3$	+180.8	+222.2	+35.2	+231.5	(a)
R = tetraacetylribityl, $R^7 = R^8$ = Me ("Me_2TARI")	0.007 M in $CDCl_3$	+182.0	+222.1	+37.6	+231.7	(a)
Desulphovibrio vulgaris apoflavodoxin (oxidized)	in H_2O	+193.9	+222.0	+40.8	?	(a)

Table 21. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Riboflavin bound to riboflavin-binding protein			
from egg white	in D_2O/H_2O		
	pH = 9.0	+190.4 +222.7 +43.7 +216.5	
	pH = 6.4	+190.4 +223.4 +44.2 +216.8	
from egg yolk	pH = 6.2	+190.3 +222.5 +43.7 +216.6	
Anabaena 7120			
flavodoxin	pH = 7.5	+193.4 +218.9 +46.4 +217.9	(d)
Flavodoxin prosthetic group in 6-OH-L-nicotine oxidase (oxidized form)	in H_2O	+189.7 +221.3 +46.6 +219.7	(e)
	(+ D-inhibitor)	*+188.1 +221.8 +51.9 +220.2*	(e)

Reduced forms of flavins



	N-1	N-3	N-5	N-10	
R = ribityl-5′-monophosphate, $R^7 = R^8 = H$					
("$FMNH^-$") in D_2O, pD = 7.8,	+199.3	+232.6	+324.2	?	(a)
$FMNH^-$ in					
old yellow enzyme pH = 8.0	+194.5	+228.7	+333.4	?	(a)
bacterial luciferase					
from *Vibrio harveyi* pH = 6.5–8.5	+205.1	+231.9	+322.0	+287.3	(c)
$FMNH^-$ from					
Azotobacter vinelandii pH = 8.0	+199.9	+231.9	+320.2	?	(b)
Megasphaera elsdenii pH = 8.0	+198.5	+232.2	+320.6	?	(b)
Clostridium MP pH = 8.0	+199.1	+231.8	+320.0	?	(b)
R = ribityl-5′-monophosphate, R^7 = Me, R^8 = H					
("MeIMNH$^-$") in D_2O, pD = 8.5,	+195.0	+231.2	+321.3	+284.7	(a)
MeIMNH$^-$ in					
old yellow enzyme pH = 8.0	+195.2	+229.4	+324.8	+284.3	(a)
protonated (1-NH)					
form, "$MeIMNH_2$" pH = 5.4	+253.8	+231.2	+321.3	+294.6	(a)
R = tetraacetylribityl, $R^7 = R^8$ = Me, protonated (1-NH) form					
("Me_2TARIH_2")	+195.0	+231.2	+321.3	+284.7	(a)
Desulphovibrio vulgaris in H_2O,					
apoflavodoxin					
(reduced) pH = 6–8.5	+195.3	+233.6	+320.7	?	(a)

Table 21. —*cont.*

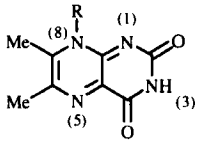
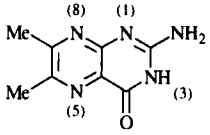
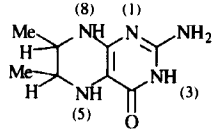
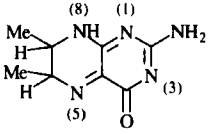
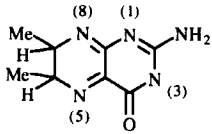
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Anabaena 7120 flavodoxin	pH = 7.0	+198.9 +229.9 +326.4 +285.8	(d)
Flavodoxin prosthetic group in 6-OH-L-nicotine oxidase			
(substrate-reduced)	in H_2O	+189.4 +234.2 +321.4 +279.3	(e)
(dithionite-reduced)	in H_2O	+189.2 +232.7 +329.2 +281.3	(e)
Pterin systems			
		N-1 N-3 N-5 N-8	(f)
R = ribityl,	in H_2O	+198.2 +220.0 +48.1 +183.9	
(6,7-Me_2-8-ribityl-lumazine)	in DMSO	+191.0 +216.5 +34.9 +187.3	
lumazine protein in *Photobacterium phosphoreum*	pH = 7	+193.2 +218.3 +55.4 +182.3	
		N-1 N-3 N-5 2-NH_2	(g)
	pH = 12.8, +4°C	+201.5 +171.5 +66.9 +304.7	
("DMP")			
	in H_2O		(g)
	pH = 8.1, +5°C	+207.8 +241.8 +335.2 ?	
	pH = 7.4, +5°C	? +241.6 +335.2 +311.4	
	pH = 1, +30°C	+240.6 +243.2 +336.2 +301.3	
("$DMPH_4$")			
	in H_2O		(g)
	pH = 8.6, +4°C	+201.2 +186.1 +21.7 ?	
	pH = 2.5–4.5	+205.9 +240.2 +17.1 +276.7	
("Q-$DMPH_2$")			
	in H_2O		(g)
	pH = 13, +4°C	+208.4 +188.1 +106.4 +310.2	
("7,8-$DMPH_2$")			

Table 21.—*cont.*

(a) Data from refs. 158, 524, 525, 527, 528, 1154 and 1155, ^{15}N-labelled and unlabelled compounds 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, *corrected* for bulk susceptibility effects.

(b) Data from ref. 764, details as in footnote (a).

(c) Data from ref. 1156, details as in footnote (a).

(d) Data from ref. 103, ^{15}N-labelled samples, 50.68 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to $(NH_4)_2SO_4$ in 1 M HNO_3, *ca.* + 359.1 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); originally reported vs fictitious ammonia standard taken at + 380.2 ppm from neat nitromethane (the latter value refers actually to a perpendicular field-to-sample axis arrangement), but we retrieved the original data and carried out the recalculation as indicated above; also 2-D $^1H\{^{15}N\}$ COSY spectra.

(e) Data from ref. 1157, ^{15}N-enriched samples, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported originally vs NH_3, + 381.9 ppm from nitromethane (Table 1); 0.001–0.002 M concentrations in phosphate buffer.

(f) Data from ref. 1158, details as in footnote (a).

(g) Data from ref. 526, ^{15}N-labelled (N-1,3,5, and NH_2) compounds, 36.5 and 20.3 MHz ^{15}N spectra, field parallel to sample tube; also 9.11 MHz ^{15}N spectra, field perpendicular to sample tube; referenced originally to NH_4^+ in NH_4NO_3 in 2 M HNO_3, + 359.1 ppm from neat nitromethane (Table 2), as can be reckoned from the reported difference in the shieldings for the two signals in the standard, 353.2 ppm; conversion schemes IIb and IIa, respectively (Table 1).

Table 22. Nitrogen shieldings in nucleosides, nucleotides and related structures

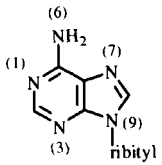
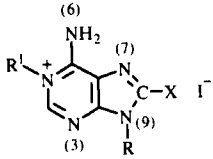
Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane					Notes
 (adenosine)	N-1	N-3	N-7	N-9	6-NH_2	
adenosine						
in DMSO	+144.3	+157.0	+140.1	+209.3	+297.1	(a)
	+144.9	+158.2	+139.9	+211.3	+299.2	(b)
	+145.3	+158.5	+140.3	+211.8	+299.3	(c)
in DMSO + 1 eq. CF_3COOH	+205.9	+157.1	+138.0	+205.2	+292.2	(c)
8-Br-adenosine						
in DMSO	+141.0	+157.7	?	?	+294.2	(a)
2′,3′-*O*-isopropylidene-adenosine						
in DMSO	+142.0	+155.5	+137.0	+207.9	+296.3	(a)
8-Br-2′,3′-*O*-isopropylidene-adenosine						
in DMSO	+141.2	+156.3	?	?	+295.0	(a)
8-Br-6-*N*-Me-2′,3′-*O*-isopropylidene-adenosine						
in DMSO	+145.5	+158.1	?	?	+300.1	(a)
5′-O-[CPh(*p*-anisyl)$_2$]adenosine						
in DMSO	+143.2	+154.5	+136.6	+207.7	+296.5	(a)
5′-*O*-acetyladenosine						
in DMSO	+144.4	+157.5	+139.1	+215.6	+299.3	(c)
in DMSO + 1 eq. CF_3COOH	+203.4	+157.5	+137.2	+209.9	+291.6	(c)
in CH_2Cl_2	+148.5	+156.7	+144.8	+215.1	+307.1	(c)
in CH_2Cl_2 + 1 eq. CF_2COOH	+215.4	+156.6	+141.2	+209.5	+294.0	(c)
6-*N*-5′-O-di[CPh(*p*-anisyl)$_2$]adenosine						
in DMSO	+135.8	+152.5	+141.7	+207.1	+296.7	(a)
5′-O-(CO-*p*-tolyl)adenosine						
in DMSO	+142.2	+154.8	+137.0	+209.0	+296.7	(a)
6-*N*-5′-*O*-di(CO-*p*-tolyl)adenosine						
in DMSO	+118.7	+134.3	+133.3	+209.0	?	(a)
6,6-*N*-5′-*O*-tri(CO-*p*-tolyl)adenosine						
in DMSO	+109.6	+128.3	+137.6	+207.6	?	(a)
6-*N*-benzoyladenosine						
in DMSO	+120.9	+136.4	+136.4	+211.2	+247.6	(c)
in DMSO + 1 eq. CF_3COOH	+128.8	+137.3	+153.2	+208.9	+248.0	(c)
6-*N*-benzoyl-5′-*O*-acetyl-adenosine						
in DMSO	+120.2	+134.9	+136.7	+215.7	+249.3	(c)
in DMSO + 1 eq. CF_3COOH	+126.4	+137.3	+141.6	+214.5	+248.3	(c)
in CH_2Cl_2	+129.0	+139.2	+140.0	+215.9	+252.3	(c)
in CH_2Cl_2 + 1 eq. CF_3COOH	+164.9	+139.4	+153.8	+210.8	+250.9	(c)
6-*N*-acetyl-5′-*O*-acetyl-adenosine						
in DMSO	+125.7	+138.9	+136.9	+215.1	+242 9	(c)

Table 22. —*cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane					Notes
in DMSO + 1 eq. CF_3COOH	+140.6	+139.4	+140.6	+213.4	+242.9	(c)
in CH_2Cl_2	+133.2	+141.8	+143.7	+215.4	+244.1	(c)
in CH_2Cl_2 + 1 eq. CF_3COOH	+166.1	+140.8	+148.3	+211.2	+244.4	(c)
adenosine-1-*N*-oxide						
in DMSO	+143.7	+159.4	+139.9	+206.6	+302.0	(a)
2′,3′-*O*-isopropylidene-adenosine-1-*N*-oxide						
in DMSO	+142.1	+158.8	+140.1	+205.8	?	(a)
2′-deoxy-adenosine						
in DMSO	+145.0	+157.7	+140.3	+207.5	+299.0	(b)
	+145.7	+158.5	+140.7	+208.3	+299.5	(d)
in DMSO + 1 eq. CF_3COOH	+209.1	+157.3	+138.5	+201.1	+292.1	(d)
in H_2O, pH = 6.5	+148.5	?	?	?	+298.3	(f)
3′-*O*-benzoyl-2′-deoxyadenosine						
in DMSO	+145.2	+156.5	+140.0	+208.5	+299.5	(d)
in DMSO + 1 eq. CF_3COOH	+205.7	+156.4	+138.1	+202.1	+292.3	(d)
6,6-*N*,*N*-dimethyl-2′-deoxyadenosine						
in DMSO	+146.0	+160.8	+136.8	+208.7	+303.6	(d)
in DMSO + 1 eq. CF_3COOH	+175.5	+164.0	+135.9	+205.4	+297.1	(d)
6-*N*-(*S*-*O*-nitrophenyl)-2′-deoxyadenosine						
in DMSO	+141.0	+148.3	+141.0	+206.9	+310.4	(d)
in DMSO + 1 eq. CF_3COOH	+147.9	+148.8	+143.2	+205.9	+309.4	(d)
6-*N*-benzoyl-2′-deoxyadenosine						
in DMSO	+121.7	+136.8	+137.8	+207.6	+249.7	(d)
in DMSO + 1 eq. CF_3COOH	+129.2	+137.2	+156.7	+204.8	?	(d)
6-*N*-benzoyl-3′-*O*-acetyl-2′-deoxyadenosine						
in DMSO	+121.2	+137.3	+135.8	+210.0	+248.9	(d)
in DMSO + 1 eq. CF_3COOH	+124.5	+137.5	+143.9	+209.0	+248.6	(d)
6-*N*-benzoyl-3′-*O*-benzoyl-2′-deoxyadenosine						
in DMSO	+121.1	+137.3	+135.9	+210.2	+249.5	(d)
in DMSO + 1 eq. CF_3COOH	+125.8	+137.6	+146.0	+208.7	+248.2	(d)
6-*N*-benzoyl-5′-*O*-benzoyl-2′-deoxyadenosine						
in DMSO	+121.0	+135.7	+136.2	+208.5	+249.6	(d)
in DMSO + 1 eq. CF_3COOH	+125.7	+136.1	+144.4	+207.3	+248.5	(d)
6-*N*-benzoyl-5′-*O*-($COOCH_2$-fluorenyl)-2′-deoxyadenosine						
in DMSO	+121.1	+136.0	+135.9	+208.6	+237.8	(d)
in DMSO + 1 eq. CF_3COOH	+126.9	+136.5	+145.9	+207.2	?	(d)
6-*N*-(*m*-chlorobenzoyl)-2′-deoxyadenosine						
in DMSO	+122.9	+136.4	+136.9	+207.4	+247.3	(d)
in DMSO + 1 eq. CF_3COOH	+124.9	+136.4	+145.7	+206.2	?	(d)
6,6-*N*,*N*-di-benzoyl-2′-deoxyadenosine						
in DMSO	+112.2	+130.6	+141.2	+205.7	+208.3	(d)
in DMSO + 1 eq. CF_3COOH	+112.2	+130.6	+141.5	+205.7	+208.3	(d)
6-*N*-($COOCH_2$-fluorenyl)-2′-deoxyadenosine						
in DMSO	+127.7	+139.5	+139.5	+207.1	+269.8	(d)
in DMSO + 1 eq. CF_3COOH	+136.6	+139.9	+146.4	+205.4	+262.5	(d)

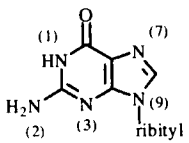
Table 22. —*cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane					Notes
6-*N*-($COOCMe_2CCl_3$)-2′-deoxyadenosine						
in DMSO	+124.8	+138.4	+140.9	+207.0	+269.0	(d)
in DMSO + 1 eq. CF_3COOH	+133.1	+139.1	+147.3	+205.5	+267.4	(d)
3′,5′-phosphoramidatoadenosine derivatives						
(C-3′)—O\ / P(R)=O (C-5′)—O/						
				PNR_2		
R = NH_2	(*R*-P isomer)			+344.3		(e)
	(*S*-P isomer)			+343.6		(e)
R = NHMe	(*R*-P isomer)			+353.6		(e)
	(*S*-P isomer)			+352.8		(e)
R = NMe_2	(*R*-P isomer)			+356.3		(e)
	(*S*-P isomer)			+357.6		(e)



(R = 2′,3′-*O*-isopropylidene-ribityl)

	N-1	N-3	N-7	N-9	6-NH_2	
in DMSO						(a)
R^1 = Me, X = H	+225.5	+153.2	+136.0	+200.5	?	
R^1 = Me, X = Br	+223.9	+153.7	?	?	?	
R^1 = OMe, X = H	+166.4	+152.0	+133.8	+199.0	?	

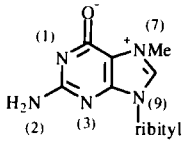


(guanosine)

	N-1	N-3	N-7	N-9	2-NH_2	
guanosine						
in DMSO	+233.3	+214.8	+132.7	+210.6	+307.2	(b)
	+233.4	+214.9	+132.8	+210.7	+307.2	(g)
	+231.8	+213.3	+131.9	+209.1	+305.8	(h)
	+234.4	+215.7	+133.8	+212.6	+308.5	(i)
in DMSO + cytidine	+234.0	+215.4	+134.7	?	+307.0	(i)
in H_2O	+231.5	?	?	?	+306.1	(j)
2′,3′,4′,5′-tetra-*O*-acetylguanosine						
in DMSO	+233.5	+216.1	+131.5	+215.7	+307.0	(k)
guanosine-5′-monophosphate (GMP)						
in D_2O, pD = 7.5	+232.5	+214.4	+144.0	+210.5	+306.5	(l)
in D_2O, pD = 12	+174.3	+214.4	+144.9	+209.9	+307.3	(l)

Table 22. *—cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane					Notes
in D_2O, pD = 8.0	+235.9	+211.0	+143.9	+210.7	+304.9	(m)
same + MeHgOH	+186	+208	+139	+207	+299	(m)
GMP adduct with (diethylenetriamine)nitratopalladium(II) nitrate						
in D_2O	?	?	+206	+229	+302	(l)
cis-$Pt(NH_3)_2(guo)_2Cl_2$						
0.25 M in DMSO	+231.8	+217.3	+235.5	+206.7	+303.4	(n)
				+423.6	*(NH_3)*	(n)
8-OMe-guanosine						
in DMSO	+229.2	+211.6	+186.0	+234.9	+306.0	(h)
8-OH-guanosine						
in DMSO	+232.8	+211.6	+270.3	+237.7	+305.5	(h)
8-OCH_2Ph-guanosine						
in DMSO	+231.5	+211.4	+185.2	+234.3	+306.3	(h)
8-SMe-guanosine						
in DMSO	+231.5	+211.9	+137.7	+214.8	+305.3	(h)
8-SH-guanosine						
in DMSO	+232.1	+212.5	+229.9	+210.2	+303.8	(h)
8-Br-guanosine						
in DMSO	+230.6	+212.7	+126.4	+212.3	+304.1	(h)
8-SO_2Me-guanosine						
in DMSO	+230.9	+213.0	+116.7	+215.0	+301.2	(h)
2′-deoxy-guanosine						
in DMSO	+231.8	+213.1	+132.7	+205.4	+305.7	(h)
2′-deoxy-guanosine-5′-monophosphate						
0.5 M in DMSO	+233.5	+214.8	+133.6	+208.1	+306.4	(t)
as above + CF_3COOH	+233.0	+216.0	+168.1	+205.4	+304.4	(t)
8-OH-2′-deoxyguanosine						
in DMSO	+229.2	+211.5	+271.0	+235.8	+304.4	(h)
1-*N*-Me-guanosine						
pure, in DMSO	+237.8	+216.5	+133.2	+213.0	+301.3	(i)
in DMSO + 1 eq. CF_3COOH	+236.3	+219.1	+193.4	+208.0	+296.6	(i)
commercial, in DMSO	+238.1	+217.0	+134.0	+213.4	+302.4	(g)
cis-$Pt(NH_3)_2$(1-Me-guo)$_2Cl_2$						
0.25 M in DMSO	+237.0	+218.1	+236.6	+208.9	+297.6	(n)
				+424.3	*(NH_3)*	(n)

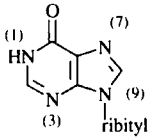


(7-*N*-Me-guanosine)

7-*N*-Me-guanosine	N-1	N-3	N-7	N-9	2-NH_2	
pure, in DMSO	+173.3	+213.0	+222.1	+211.2	+301.3	(i)
	+173.1	+212.8	+222.9	+211.0	+301.1	(h)
in DMSO + 1 eq. CF_3COOH	+233.0	+219.2	+221.8	+208.2	+301.2	(i)
	+230.6	+216.8	+219.4	+205.8	+298.8	(h)

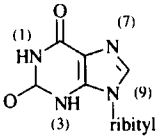
Table 22. —*cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane					Notes
commercial, in DMSO	+200.6	+214.2	+221.2	+208.8	?	(g)
(ca. *60% protonated*)	+201.7	+215.2	+222.2	+209.7	+299.8	(i)



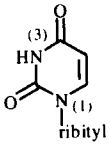
(inosine)

inosine	N-1	N-3	N-7	N-9	
0.25 M *in DMSO*	+173.3	+213.0	+222.1	+211.2	(n)



(xanthosine)

xanthosine	N-1	N-3	N-7	N-9	
0.25 M *in DMSO*	+228.3	+268.3	+132.6	+216.2	(n)
0.25 M *in DMSO + 0.5 eq.* CF_3COOH	+228.2	+268.3	+137.3	+215.8	(n)
cis-$Pt(NH_3)_2(xan)_2Cl_2$					
in DMSO	+228.4	+268.4	+225.8	?	(n)
			+424.6	*(NH_3)*	(n)

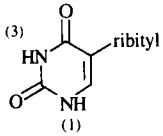


(uridine)

uridine	N-1	N-3	
in DMSO	+236	+222	(o)
3-*N*-(*p*-NO_2-phenyl-SO_2-CH_2CH_2)-uridine			
0.35 M *in DMSO*	+237.2	+222.0	(p)
3-*N*-(*p*-NO_2-phenyl-SO_2-CH_2CH_2)-2′,3′,5′-tri-*O*-acetyluridine			
0.55 M *in DMSO*	+240.6	+221.6	(p)
0.55 M *in* CH_2Cl_2	+242.2	+222.3	(p)
3-*N*-(*p*-NO_2-phenyl-CH_2CH_2)-2′,3′,5′-tri-*O*-benzoyluridine			
0.25 M *in DMSO*	+240.3	+216.9	(p)
0.25 M *in* CH_2Cl_2	+242.6	+217.2	(p)
2′,3′-*O*-isopropylidene-5′-*O*-acetyluridine			
in $CDCl_3$	?	+220.1	(q)
in $CDCl_3$, *paired with adenosine*	?	+214.5	(q)
uridine 2′-monophosphate			
0.01 M *in* H_2O, *pH = 5.5*	+235.0	+221.1	(s)
as above, complexed with RNAase A	+228.8	+220.2	(s)

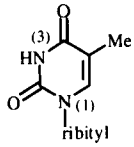
Table 22. —*cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
uridine 3′-monophosphate			
0.01 M *in* H_2O, *pH = 5.5*	+234.1	+221.3	(s)
as above, complexed with RNAase A	+232.3	+220.6	(s)



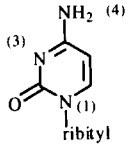
(pseudo-uridine)

	N–1	N–3	
2′,3′,5′-tri-*O*-acetylpseudouridine			
in $CDCl_3$	+242.7	+219.4	(q)



(thymidine)

	N–1	N–3	
thymidine			
in DMSO	+236	+224	(o)
2′,3′,5′-tri-*O*-benzoylthymidine			
in $CDCl_3$	?	+224.2	(q)
in $CDCl_3$, *paired with adenosine*	?	+217.0	(q)

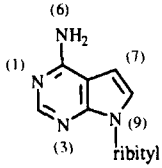


(cytidine)

	N–1	N–3	4–NH_2	
cytidine				
0.5 M *in DMSO*	+229.9	+172.3	+289.0	(i)
0.5 M *in DMSO + 0.5* M *guanosine*	+228.8	+176.2	+286.9	(i)
0.4 M *in DMSO*	+229.3	+171.9	+288.9	(i)
0.5 M *in DMSO + 0.4* M *7-Me-guanosine*	+229.6	+175.7	+287.9	(i)
0.8 M *in DMSO*	+228.4	+172.1	+287.7	(r)
0.8 M *in DMSO + 1 eq.* CF_3COOH	+228.4	+236.9	+266.9	(r)
cytidine-2′-monophosphate				
0.01 M *in* H_2O, *pH = 5.5*	+229.2	+183.3	+284.5	(s)
as above, complexed with RNAase A	+228.4	+177.5	+284.5	(s)
0.01 M *in* H_2O, *pH = 8.4*	+222.1	+179.3	+287.4	(s)

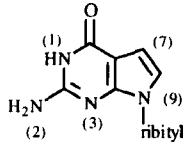
Table 22. —*cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
cytidine-3′-monophosphate				
0.8 M in H_2O, pH = 6.0	+227.1	+187.0	+282.6	(m)
as above + 0.2 eq. MeHgOH	+225.6	+198.6	+281.4	(m)
2′,3′,5′-tri-*O*-acetylcytidine				
0.45 M in DMSO	+232.3	+171.2	+285.2	(c)
0.45 M in DMSO + 1 eq. CF_3COOH	+231.7	+235.2	+272.5	(c)
0.45 M in CH_2Cl_2	+233.6	+177.2	+284.9	(c)
0.45 M in CH_2Cl_2 + 1 eq. CF_3COOH	+232.6	+236.9	+275.3	(c)
4-*N*-acetyl-2′,3′,5′-tri-*O*-acetylcytidine				
0.8 M in DMSO	+218.5	+146.3	+232.2	(c)
0.8 M in DMSO + 1 eq. CF_3COOH	+218.4	+148.9	+232.4	(c)
0.95 M in DMSO	+219.2	+152.4	+234.0	(c)
0.95 M in DMSO + 1 eq. CF_3COOH	+216.0	+206.8	+235.8	(c)
4-*N*-benzoylcytidine				
0.8 M in DMSO	+213.1	+154.1	+238.8	(c)
0.8 M in DMSO + 1 eq. CF_3COOH	+212.2	+157.8	+238.5	(c)
4-*N*-benzoyl-2′,3′,5′-tri-*O*-acetylcytidine				
0.8 M in DMSO	+218.5	+135.6	+239.1	(c)
0.8 M in DMSO + 1 eq. CF_3COOH	+218.6	+135.6	+236.5	(c)
0.8 M in CH_2Cl_2	+219.3	+139.3	+239.5	(c)
0.8 M in CH_2Cl_2 + 1 eq. CF_3COOH	+217.8	+187.0	+240.6	(c)
2′-deoxycytidine-3′-monophosphate				
0.5 M in DMSO	+226.4	+174.7	+286.1	(t)
0.8 M in DMSO + 2.6 eq. CF_3COOH	+225.2	+236.9	+274.3	(t)



(7-deazaadenosine, tubercidin)

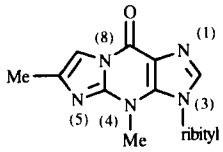
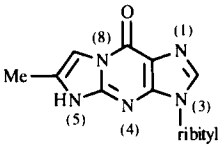
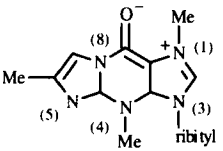
	N–1	N–3	N–9	6–NH_2	
tubercidin					
in DMSO	+148.1	+155.4	+224.4	+296.7	(u)
	+150.4	+157.8	+226.9	+298.2	(b)
5′-*O*-CPh_3-tubercidin					
in DMSO	+148.2	+154.1	+224.1	+296.1	(a)
6-*N*-CPh_3-5′-*O*-CPh_3-tubercidin					
in DMSO	+138.8	+152.5	+224.9	+271.6	(a)
2′-deoxy-tubercidin					
in DMSO	+150.2	+157.7	+223.7	+298.3	(b)

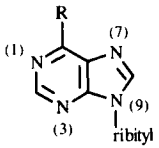


(7-deazaguanosine)

	N–1	N–3	N–9	2–NH_2	
2′-deoxy-7-deazaguanosine					
in DMSO	+218.9	+212.5	+222.5	+309.6	(b)

Table 22. —*cont.*

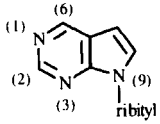
Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane					Notes
 (wyosine)	N-1	N-3	N-4	N-5	N-8	
wyosine	+131.9	+213.2	+287.4	+157.1	+191.2	(g)
in DMSO	+132.0	+213.7	+287.8	+157.2	+191.5	(v)
7-Me-wyosine						
in CH_2Cl_2	+130.0	+221.2	+291.8	+162.3	+194.1	(v)
wyosine 2′,3′,5′-triacetate						
in CH_2Cl_2	+131.9	+213.2	+287.4	+157.1	+191.2	(v)
7-Me-wyosine 2′,3′,5′-triacetate						
in CH_2Cl_2	+131.2	+214.4	+289.7	+161.3	+193.4	(v)
	+134.8	+213.2	+221.7	+243.1	+194.8	(g)
	+226.1	+215.1	+214.2	+159.3	+187.1	(g)

 (purine derivatives, see also Table 18)

	N-1	N-3	N-7	N-9	R	
5′-*O*-acetyl-derivatives						
R = OMe						
in DMSO	+140.4	+142.6	+139.5	+214.3	-	(c)
in DMSO + 1 eq. CF_3COOH	+140.0	+142.7	+140.4	+214.2	-	(c)
in CH_2Cl_2	+141.4	+144.3	+140.8	+215.6	-	(c)
in CH_2Cl_2 + 1 eq. CF_3COOH	+140.8	+145.1 *broad*		+213.3	-	(c)
R = OPh						
in DMSO	+137.0	+138.9	+139.8	+213.6	-	(c)
in DMSO + 1 eq. CF_3COOH	+137.1	+139.0	+141.2	+213.6	-	(c)
in CH_2Cl_2	+138.4	+140.5	+140.4	+215.5	-	(c)
in CH_2Cl_2 + 1 eq. CF_3COOH	+138.3	+141.5	?	+213.3	-	(c)

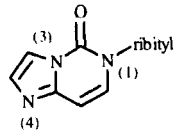
Table 22. —*cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
R = SPh					
in DMSO	+112.8	+140.2	+139.1	+214.3 –	(c)
in DMSO + 1 eq. CF_3COOH	+112.8	+140.2	+139.3	+214.3 –	(c)
in CH_2Cl_2	+113.8	+142.0	+139.5	+216.3 –	(c)
in CH_2Cl_2 + 1 eq. CF_3COOH	+123.1	+142.7	+153.0	+213.8 –	(c)
2′-deoxyderivatives					
R = H					
in DMSO	+101.8	+130.6	+139.1	+208.1 –	(d)
in DMSO + 1 eq. CF_3COOH	+122.6	+130.6	+139.0	+206.4 –	(d)
R = OPh					
in DMSO	+138.2	+138.2	+141.3	+205.5 –	(d)
in DMSO + 1 eq. CF_3COOH	+138.2	+138.9	+141.8	+205.5 –	(d)
R = —N=CHNME$_2$					
in DMSO	+130.4	+147.7	+137.3	+208.9	+170.7 (d)
in DMSO + 1 eq. CF_3COOH	+187.3	+148.9	+137.4	+201.6	+201.6 (d)
R = —N=C—NMe$_2$					
in DMSO	+123.6	+148.4	+136.9	+209.2	+177.3 (d)
in DMSO + 1 eq. CF_3COOH	+190.4	+150.3	+136.0	+201.3	+197.9 (d)



(7-deazapurine derivatives)

	N–1	N–3	N–9	NH_2	
6-Cl-7-deazapurine					
in DMSO, α-anomer	+112.0	+134.1	+222.7	–	(b)
in DMSO, β-anomer	+113.0	+134.6	+222.6	–	(b)
2′-deoxy-6-Cl-7-deazapurine					
in DMSO	+112.2	+134.3	+219.2	–	(b)
2′-deoxy-3′,5′-di-*O*-tolyl-6-Cl-7-deazapurine					
in DMSO	+111.2	+133.6	+222.8	–	(b)
2′-deoxy-3′,5′-di-*O*-tolyl-6-SMe-7-deazapurine					
in DMSO	+119.1	+143.2	+225.2	–	(b)
2-NH_2-6-Cl-7-deazapurine					
in DMSO	+147.4	+183.9	+229.0	+299.4	(b)
2′-deoxy-2-NH_2-6-Cl-7-deazapurine					
in DMSO	+147.2	+184.0	+225.6	+299.6	(b)



(cytidine analogue)

	N–1	N–3	N–4	
0.3 M in DMSO	+232.0	+190.8	+164.0	(r)
hydrochloride, 0.3 M in DMSO	+226.1	+191.7	+205.8	(r)

Table 22. *—cont.*

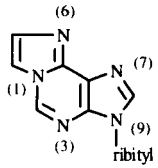
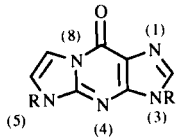
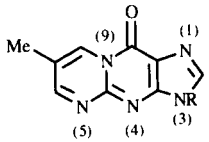
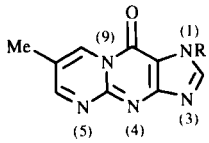
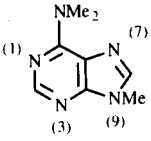
Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 (adenosine analogue)		
	N-1 N-3 N-7 N-9 N-6	
0.4 M in DMSO	+178.5 +152.2 +150.1 +139.1 +207.6	(w)
hydrochloride in DMSO	+182.0 +147.6 +190.5 +139.9 +205.3	(w)
 (R = $CH_2CH_2CH_2CH_2OCOMe$)		
	N-1 N-3 N-4 N-5 N-8	
in DMSO	+136.1 +220.9 +223.7 +245.9 +195.5	(x)
in DMSO + CF_3COOH	+170.3 +218.5 +223.6 +243.7 +194.7	(x)
 (R = $CH_2CH_2CH_2CH_2OCOMe$)		
	N-1 N-3 N-4 N-5 N-9	
in DMSO	+134.4 +216.4 +181.9 +85.7 +191.4	(x)
in DMSO + CF_3COOH	+142.3 +215.9 +182.2 +85.7 +191.1	(x)
 (R = $CH_2CH_2CH_2CH_2OCOMe$)		
	N-1 N-3 N-4 N-5 N-9	
in DMSO	+219.0 +133.8 +161.3 +82.7 +194.3	(x)
in DMSO + CF_3COOH	+217.1 +150.1 +171.4 +85.4 +192.7	(x)
		
	N-1 N-3 N-7 N-9 NMe_2	
in DMSO	+148.2 +160.9 +138.4 +233.1 ?	(y)
in DMSO + 3,5-dichlorophenol	+151.5 +170.4 +141.6 +232.1 ?	(y)

Table 22. —*cont.*

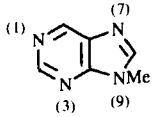
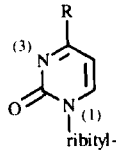
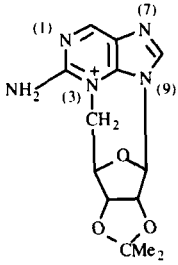
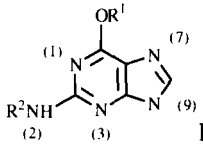
Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
	N–1	N–3	N–7	N–9	
in DMSO	+103.9	+131.1	+140.2	+233.1	(y)
in DMSO + 3,5-dichlorophenol	+114.0	+130.6	+148.7	+230.6	(y)
 (2-pyrimidone derivatives)					
	N–1	N–3	R		
R = OMe					
0.95 M in DMSO	+225.8	+155.9	–		(c)
0.95 M in DMSO + 1 eq. CF_3COOH	+223.8	+162.0	–		(c)
R = OPh					
0.8 M in DMSO	+222.3	+151.5	–		(c)
0.8 M in DMSO + 1 eq. CF_3COOH	+220.3	+158.5	–		(c)
R = O-C_6H_4-*p*-Me					
0.45 M in CH_2Cl_2	+225.6	+155.3	–		(c)
R = O-C_6H_4-*p*-NO_2					
0.5 M in DMSO	+220.7	+152.0	+15.8		(c)
0.5 M in DMSO + 1 eq. CF_3COOH	+219.8	+154.5	+15.8		(c)
R = SPh					
0.5 M in CH_2Cl_2	+222.2	+119.1	–		(c)
0.5 M in CH_2Cl_2 + 1 eq. CF_3COOH	+219.1	+136.7	–		(c)
R = OCH_2CH_2-C_6H_4-*p*-NO_2					
0.3 M in DMSO	+223.2	+154.5	+10.5		(c)
0.3 M in DMSO + 1 eq. CF_3COOH	+223.3	+154.6	+10.6		(c)
0.3 M in CH_2Cl_2	+224.7	+155.3	+12.3		(c)
0.3 M in CH_2Cl_2 + 1 eq. CF_3COOH	+224.2	+157.2	+11.9		(c)
 *in DMSO*					(u)
X	N–1	N–3	N–7	N–9	NH_2
p-Me-$C_6H_4SO_3$	+140.1	+230.9	+131.9	+201.4	+268.8
$MeSO_3$	+144.8	+230.7	?	+217.1	+271.4

Table 22. —*cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes



$R^1 = CH_2CH_2C_6H_4$-*p*-NO_2
$R^2 = CO$-C_6H_4-*p*-Bu^t

in DMSO	N-1	N-3	N-7	N-9	2-NH	
	+165.9	+157.8	+140.9	+210.4	+242.9	(h)

Nucleoside units in RNA

Escherichia coli 5S RNA	N-3 atoms in uridine (U)	(z)
in H_2O, pH = 6.0		
GU base pairs	+225.4, +225.2, +224.7, +225.2, +225.2	
AU base pairs	+223.4, +222.9, +221.7, +221.0	
Escherichia coli tRNA	N-3 atoms in uridine (U)	(A)
in H_2O, pH = 7.0		
$tRNA_f^{Met}$	+229.6, +221.9, +222.2, +221.2, +221.7, +216.6, 198.1	
$tRNA^{Lys}$	+227.9, +222.6, +222.3, +218.9, +221.3, +219.3, +216.9, +217.9, +220.3, +217.3, +217.3, +197.6	
$tRNA^{Phe}$	+229.1, +221.6. +220.0, +214.6, +217.3, +220.5, +196.9	
$tRNA^{Ser}$	+221 to +215; +227 (dihydrouridine); +200 (s^4U9)	
$tRNA^{Tyr}$	+221 to +215; +201 (s^4U9)	
Yeast $tRNA^{Phe}$	(pseudo)uridine and guanosine	(B)
in H_2O, pH = 7		
pseudo-uridine (ψ) and uridine (U) units, N-3 atoms if not stated otherwise		
ψ39	+247 (N-1)	
ψ55	+245 (N-1), +221.1 (N-3)	
T54(m^1A58)	+225.4	
U or D	+224	
U69(G4)	+223.4	
AU12 or AU52	+221	
AU7	+220.4	
AU5	+219.6	
AU29,50; ψ39(A31)	+219.3, +218.7, +218.7	
AU6	+218.3	
AU12 or AU52	+218.2	

Table 22. —*cont.*

Compound *and state*	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
U8(A14)	+217.3	
guanosine N-1 atoms		
G4(U69, m_2^2G26)	+237.4	
GC2,27,50,53; G19	+234.2, +233.2, +232.4	
GC3,28; G15(C48)	+234.3, +234.0, +232.8	
GC13	+233.4	
m^2G10(C25); GC51	+233.6	
m^7G46(G22)	+230.3	
GC11	+235	

(a) Data from ref. 823, 10.1 MHz ^{15}N INEPT spectra, field perpendicular to sample tube, referenced originally to NH_4^+ in aqueous ammonium nitrate, +359.6 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1); 0.1–0.6 M solutions.

(b) Data from refs. 126 and 1159, spectrometer not reported, ^{15}N spectra, referenced originally to nitromethane containing 5% DMSO-d_6, −0.1 ppm from neat nitromethane as can be reckoned from Table 2, conversion scheme II (Table 1).

(c) Data from ref. 1160, 27.4 MHz ^{15}N gated decoupled and INEPT (proton-coupled) spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 1161, details as in footnote (c).

(e) Data from ref. 911, 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous ammonium nitrate, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(f) Data from ref. 157, 1,6-^{15}N-labelled compound, spectrometer not reported, ^{15}N DEPT spectra, referenced originally to ammonium chloride in 10% HCl, +352.5 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(g) Data from ref. 781, details as in footnote (c).

(h) Data from ref. 1162, 50.7 MHz ^{15}N spectra, calibration as in footnote (j), but reported fictitious ammonia standard, taken at +380.2 ppm from neat nitromethane; the latter value refers to a perpendicular field-to-sample axis setup (Table 2).

(i) Data from refs. 1163 and 1164, 30.408 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M HNO_3, +6.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(j) Data from ref. 706, 1,2-^{15}N-labelled guanosine, 30.42 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to aqueous $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(k) Data from ref. 148, details as in footnote (c).

(l) Data from ref. 831, 50.5 and 40.4 MHz ^{15}N spectra, calibration as in footnote (k); proton-coupled spectra, concentration 0.2 M. In the GMP complex, the signal at +206 ppm shows Pd–^{15}N coupling.

(m) Data from ref. 1165, 20.27 MHz ^{15}N spectra (NOE-suppressed), field parallel to sample tube, referenced originally to saturated aqueous NH_4Cl, +352.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); reported vs fictitious ammonia standard taken at +27.3 ppm from the actual reference employed, see footnote (h) for comments; we retrieved the original data and carried out recalculation as above.

(n) Data from ref. 1166, details as in footnote (i).

Table 22.—*cont.*

(o) See ref. 5, pp. 519–524, and references therein.

(p) Data from ref. 1160, details as in footnote (v).

(q) Data from ref. 1167, 36.49/360 MHz $^{15}N/^{1}H$ spectra (FINDS = Fourier internuclear difference spectroscopy; FES = forbidden echo spectroscopy; JIDS = J-modulated internuclear difference spectroscopy), field parallel to sample tube, referenced originally to 2.9 M NH_4Cl in 1 M HCl, +352.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); reported originally to fictitious ammonia standard taken at +24.9 ppm from the actual reference employed, see comments in footnotes (h,m).

(r) Data from ref. 1168, details as in footnote (c).

(s) Data from ref. 1169, ^{15}N-labelled nucleotides from ^{15}N-labelled bacteria, 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to NH_4^+ in 4 M NH_4NO_3 in 3 M HNO_3, +359.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(t) Data from ref. 1170, details as in footnote (i).

(u) Data from ref. 793, 40.5 MHz ^{15}N spectra, field parallel to sample tube, calibration as in footnote (a).

(v) Data from refs 124, 147 and 148, 27.4 MHz ^{15}N spectra (proton-decoupled, NOE-retained; and proton-coupled INEPT), field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; 0.4 M solutions.

(w) Data from ref. 752, details as in footnote (r).

(x) Data from ref. 1171, details as in footnote (c).

(y) Data from ref. 539, 25.35 MHz ^{15}N DEPT spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(z) Data from ref. 208, details as in footnote (q); ^{15}N-labelled N-3 atoms in uridine units.

(A) Data from refs. 205 and 1172, ^{15}N-labelled nucleoside units, details as in footnote (q).

(B) Data from ref. 178, ^{15}N-labelled tRNA, 500/50.7 MHz and 270/27.3 MHz $^{1}H\{^{15}N\}$ INDOR, SPENDOR and FES spectra, field parallel to sample tube, referenced originally to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

Table 23. Nitrogen shieldings in phosphazenes, cyclophosphazenes and phosphazoles

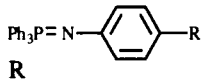
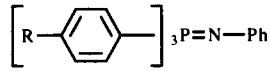
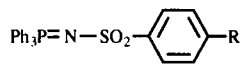
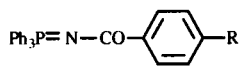
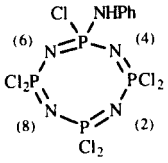
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	1.3–1.8 M in $CDCl_3$		(a)
R		(P=N)	
NO_2		+280.1	
Cl		+302.6	
H		+302.5	
Me		+305.4	
OMe		+308.4	
NMe_2		+310.1	
	1.3–1.8 M in $CDCl_3$		(a)
R		(P=N)	
CN		+304.3	
CF_3		+304.2	
COOMe		+304.0	
F		+302.1	
Cl		+303.2	
H		+302.5	
Me		+302.0	
OMe		+301.7	
	1.3–1.8 M in $CDCl_3$		
R		(P=N)	
NO_2		+283.3	
F		+284.4	
Cl		+284.2	
Br		+284.2	
H		+285.0	
Me		+284.6	
OMe		+284.5	
NH_2		+284.5	
	1.3–1.8 M in $CDCl_3$		
R		(P=N)	
NO_2		+255.3	
CN		+256.1	
F		+259.3	
Cl		+258.6	

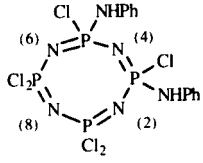
Table 23. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Br		+258.6	
H		+259.0	
Me		+259.6	
OMe		+260.4	
$Bu^tN{=}P{-}N{<}^{Bu^t}_{SiMe_3}$	in $CDCl_3$	+227.4 (P=N) +14.5 (P—N)	(c) (c)
$Me_3SiN{=}P{-}N(SiMe_3)_2$	in $CDCl_3$	+217.2 (P=N) +71.0 (P—N)	(c) (c)
$R^1R^2N{-}P{=}NR^3$	1–1.5 M in $CHCl_3$ or benzene		(d)

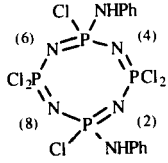
R^1	R^2	R^3		(N=P)	(N—P)	
$SiMe_3$	$SiMe_3$	$SiMe_3$	(benzene?)	+213.6	+67.1	
$SiMe_3$	$SiMe_3$	$SiMe_3$	($CDCl_3$?)	+220.5	+74.2	
Bu^t	$SiMe_3$	$SiMe_3$		+249.9	−9.0	
Bu^t	Bu^t	$SiMe_3$		+224.4	+36.1	
$SiMe_3$	$SiMe_3$	Bu^t		+254.3	?	
$SiMe_3$	$SiMe_3$	Bu^t_2P		+229.4	+59.8	
$SiMe_3$	$SiMe_3$	$Bu^t_2P(S)$		+220.3	+96.4	



in $CDCl_3$ +290.2 (NH) (e)
+260.1 (4,6-N) (e)
+246.7 (2,8-N) (e)

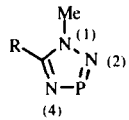
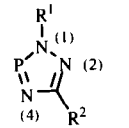
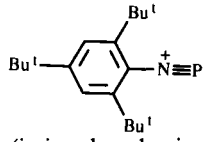


in $CDCl_3$ +289.0 (NH) (e)
+275.5 (4-N) (e)
+259.2 (2,6-N) (e)
+244.5 (8-N) (e)



in $CDCl_3$ +294.0 (NH) (e)
+259.2 (P—N=P) (e)

Table 23. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
	in $CDCl_3$ or benzene				(f)
R		1-N	2-N	4-N	
Me		+157.5	+12.1	+88.5	
its 4-N → BF_3 adduct		+154.9	+22.8	+142	
i-Pr		+159.5	+14.9	+95.2	
$PhCH_3$		+156.4	+11.8	+86.5	
Ph		+156.5	+10.4	+87.0	
n-Bu, 4-N → BF_3 adduct		+151.1	+21.0	+138	
	in $CDCl_3$ or benzene				(f)
R^1	R^2	1-N	2-N	4-N	
Me	Me	+120.4	+42.7	+93.5	
its 4-N → BF_3 adduct		+120.2	+42.8	+147	
Me	i-Pr	+122.0	+44.5	+97.7	
Me	$PhCH_2$	+119.4	+41.6	+93.1	
its 4-N → BF_3 adduct		+119.1	+39.6	?	
Me	Ph	+117.8	+42.7	+99.0	
Ph	Ph	+100.3	+56.3	+100.3	
its 4-N → BF_3 adduct		+101.4	+48.7	+146	
Various structures containing P=N bonds					(g)
 (iminophosphenium cation)	$AlCl_4^-$ solid state	+133.9 (iso) +18 (σ_{11}) +16 (σ_{22}) +403 (σ_{33})			(h)

(a) Data from refs 886 and 904, 20.28 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to aqueous KNO_3 standardized against neat nitromethane, but reported vs fictitious ammonia standard, taken at +380.2 ppm from neat nitromethane (this is erroneous, since the latter value comes from measurements where the field was perpendicular to sample tube, Table 2), conversion scheme IIIb (Table 1).

(b) Data from refs 885, 906, 1173, details as in footnote (a).

Table 23.—*cont.*

(c) Data from ref. 153, 10.14 MHz ^{15}N INEPT spectra (via $^{3}J_{NH}$ = 1–1.5 Hz or 2–2.5 Hz), field perpendicular to sample tube, referenced originally to 0.1 M nitromethane in $CDCl_3$, + 3.2 ppm from neat nitromethane (Table 26), conversion scheme IIa (Table 1).

(d) Data from ref. 910, 30.4 MHz and 25.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added to samples as a relaxation reagent.

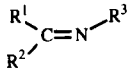
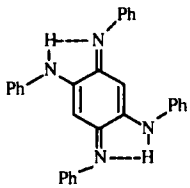
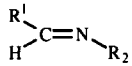
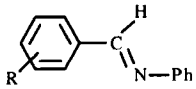
(e) Data from ref. 1174, 9.1 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(f) See footnote (d).

(g) See ref. 5, p. 525, and references therein.

(h) Data from ref. 421, 20.30 MHz CPMAS and powder spectra of ^{15}N-labelled sample, referenced originally to NH_4^+ in solid NH_4NO_3, + 358.4 ppm from neat nitromethane (Table 2); reported originally to fictitious ammonia standard taken at + 23.8 ppm from the actual reference employed, i.e. + 382.2 ppm from nitromethane.

Table 24. Nitrogen shieldings in some imines, nitrones, oximes and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Imines, immonium ions, and imino complexes			
	Solvent?		(a)
R^1 R^2 R^3			
H Ph Ph		+53.2	
H Ph 2-F-phenyl		+67.8	
H Ph 4-F-phenyl		+57.1	
H Ph 2,4-F_2-phenyl		+71.5	
H Ph C_6F_5		+87.9	
H Ph Ph		+53.2	
H C_6F_5 Ph		+29.1	
H C_6F_5 2-F-phenyl		+42.8	
H C_6F_5 4-F-phenyl		+33.3	
H C_6F_5 2,4-F_2-phenyl		+46.3	
H C_6F_5 C_6F_5		+63.5	
C_6F_5 C_6F_5 4-F-phenyl		+27.5	
C_6F_5 C_6F_5 2,3,5,6-F_4-phenyl		+60.8	
C_6F_5 C_6F_5 C_6F_5		+63.9	
	solid state	+62 (=N)	(b)
	+27 to +132°C	+217 (NH)	(b)
	in $CDCl_3$		(c)
R^1	R^2		
2-OH-phenyl	2-Br-phenyl	+87.7	
2-OH-phenyl	4-Me-phenyl	+85.8	
2-OH-phenyl	2,4-Me_2-phenyl	+87.8	
2-OH-phenyl	4-NO_2-phenyl	+90.0 *(+13.0, NO_2)*	
Ph	2-OH-phenyl	+83.6	
2-Br-phenyl	2-OH-phenyl	+78.5	
4-NO_2-phenyl	2-OH-phenyl	+71.0 *(+13.0, NO_2)*	
	in $CDCl_3$		(d)

and their Pd complexes

Table 24. *—cont.*

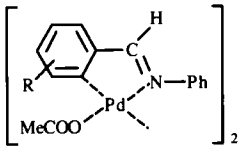
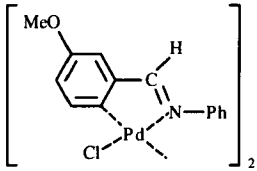
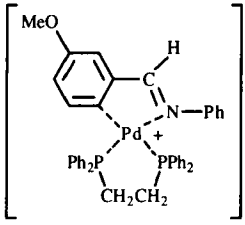
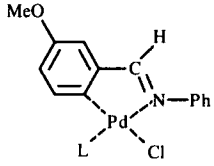
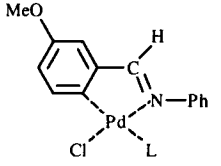
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
			
R	Imine	Complex	
5-OMe	+52.6	+135.0	
4-OMe	+61.5	+147.2	
5-Me	+55.2	+136.1	
4-Me	+56.7	+139.2	
H	+55.0	+135.6	
5-Cl	+49.5	+132.8	
4-Cl	+52.1	+136.2	
5-NO_2	+45.2	+130.2	
4-NO_2	+40.3	+127.8	
	in $CDCl_3$	+129.3	(d)
	in $CDCl_3$ Cl^-	+111.4	(d)
 and 	(*trans*-L,N) in $CDCl_3$ (*cis*-L,N)		(d)

Table 24. *—cont.*

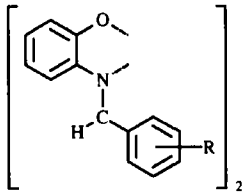
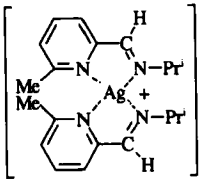
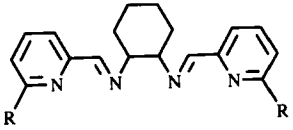
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
L		(=N—Pd)	
Pyridine	*trans, 53%*	+128.0	
	cis, 47%	+131.0	
$NHEt_2$	*trans, 44%*	+126.1	
	cis, 56%	+133.4	
PPh_3		+107.6	
	$TeMe_2$ in $CDCl_3$		(e)
R		(=N—Te)	
4-NO_2		+64	
3-NO_2	*(in DMSO)*	+76	
4-Br		+77	
H		+82	
4-Me		+85	
4-OMe		+92	
4-NMe_2	*(in DMF)*	+97	
	in CD_3OD	+63 (=N—Pr^i)	(f)
	$CF_3SO_3^-$	+102 (ring N)	(f)
			(g)
R	in CD_3OD	(=N)	Ring N
H		+33.6	+78.3
Me		+34.3	+77.5

Table 24. —*cont.*

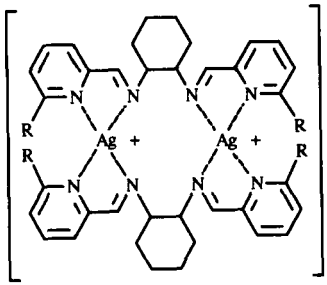
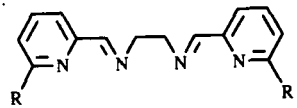
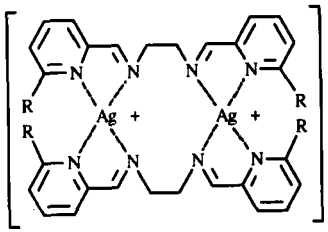
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
				(g)
R	in CD_3OD	(=N)	Ring N	
H	(spatial non-equivalence)	+80.2 +77.1	+102.5 +111.3	
Me	(spatial non-equivalence)	+82.0 +79.0	+104.2 +111.0	
				(h)
R	in CD_3OD	(=N)	Ring N	
H		+47.8	+75.2	
Me		+50.4	+77.9	
				(h)
	in CD_3OD	(=N)	Ring N	
R = Me		+89.4	+107.8	

Table 24. —*cont.*

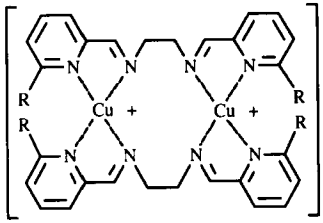
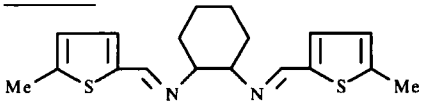
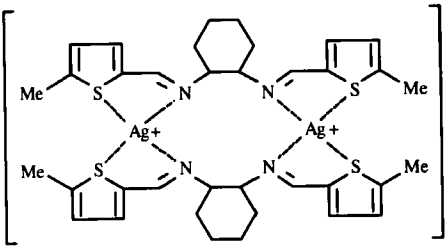
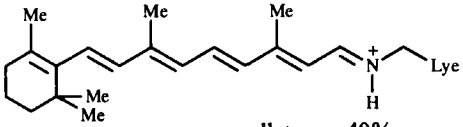
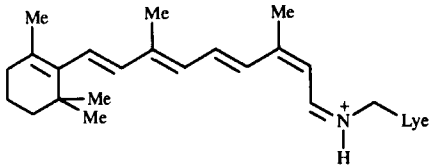
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 $(CF_3SO_3^-)_2$			(h)
R	in CD_3OD	(=N) / Ring N	
H		+94.8 / +111.3	
Me		+95.0 / +113.4	
	in CD_2Cl_2	+54.3	(i)
 $(CF_3SO_3^-)_2$	in CD_2Cl_2	+83.7, +96.6	(i)
Protonated Schiff bases in bacteriorhodopsin retinal	solid state		(j)
 "bR_{568}"	all-*trans*, 40%	+208.0 (=NH^+) +201.3 (=NH^+) +259.3 (amide backbone) +344.5 ($LysNH_3^+$)	
 "bR_{548}"			

Table 24. —*cont.*

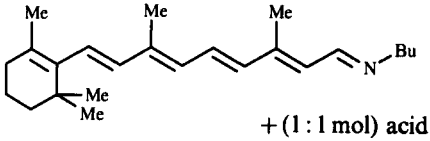
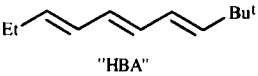
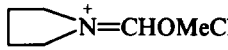
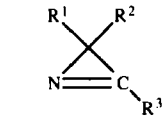
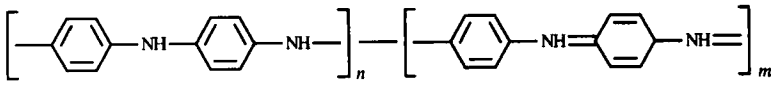
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	solid state		(j)
+ (1 : 1 mol) acid			
Acid (pK_a)			
None		+37.4	
HI (−9.25)		+198.5	
HBr (−8.5)		+186.8	
HCl (−6.1)		+181.2	
2,4,6-trinitrophenol (0.37)		+192.0	
Cl_3CCOOH (0.51)		+198.7	
F_3CCOOH (0.52)		+192.4	
Br_3CCOOH (0.72)		+188.1	
$F_2CHCOOH$ (1.34)		+179.3, +183.2	
$Cl_2CHCOOH$ (1.35)		+178.2	
2-chloro-4,6-dinitrophenol (2.1)		+187.6	
2,4-dibromo-3,6-dinitrophenol (2.9)		+184.5	
2,6-dibromo-4-nitrophenol (3.4)		+183.1	
 "HBA"	in $CDCl_3$ and CD_3OD		(m)
"HBA" + (1 : 1 mol) additive (pK_a)	in $CDCl_3$	in CD_3OD	
None	+31.5	+46.6	
EtCOOH (4.90)	+60 7	+82.6	
$O_2NCH_2CH_2COOH$ (3.90)	+84.6	+148.3	
ICH_2COOH (3.15)	+111.8	+161.3	
$BrCH_2COOH$ (2.95)	+130.2	-	
$ClCH_2COOH$ (2.85)	+131.2	+175.1	
$NCCH_2COOH$ (2.45)	+157.9	-	
HC≡CCOOH (1.85)	+162.4	-	
Cl_3CCOOH (0.66)	+168.5	+176.5	
F_3CCOOH (0.23)	+171.1	+176.7	
HCl (−6.90)	+171.7	+176.9, +176.6	
HI (−9.20)	+192.8	+178.3	
	in H_2O	+218.2	(k)
$MeCCH_2CH_2C{=}NCH_2CMe_3$ (O, Me)	in DMSO	+67.4	(l)

Table 24. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$MeCCH_2CH_2C{=}NCH_2CHMe_2$ (O, Me)	in DMSO	+70.5	(l)
	in $CDCl_3$		(n)

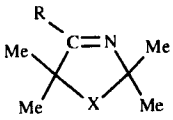
R^1	R^2	R^3	
Ph	Me	Me	+83.5
Ph	H	Me	+98.0
Ph	H	Ph	+104.3
Ph	H	COOEt	+63.2



(o)

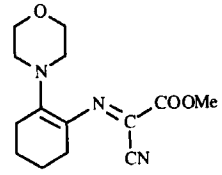
in solid state

NH in amino–amino units	+301
NH in amino–imino units	+294
=N in imino–amino units	+23
=N in imino–imino units	+35 to +54



in acetone-d_6 (p)

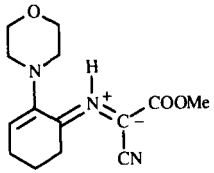
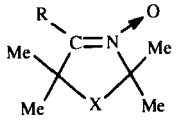
R	X		(=N—)
Me	N—O·	(nitroxyl radical)	+31.6
	N—OH	(hydroxylamino moiety)	+61.7
Ph	N—O·		+23.4
	N—OH		+47.6
Ph	N—O·	*(in CD_3OD)*	+28.7
	N—OH		+54.9



in $CDCl_3$

+17.1 (=N)	(q)
+247.8 (N)	(q)
+120.4 (CN)	(q)

Table 24. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+198.8 (=N) +337.1 (N) +105.9 (CN)	(q) (q) (q)
Imino moieties in guanidines and amidines	see Table 10		
Aromatic imines	see Tables 19, 20		
Ketenimines			
$R_2C{=}C{=}N{-}R$	various	+161 to +186	(r)
Nitrones (imine *N*-oxides)			
$R_2C{=}N(\rightarrow O)R$	see also ref. 5, p. 546		
PhCH=N(O)Ph	solvent?	+118.8	(s)
$(C_6F_5)_2C{=}N(O)R$	solvent?		(s)
R			
Ph		+105.0	
4-fluorophenyl		+98.0	
2,3,5,6-tetrafluorophenyl		+124.3	
C_6F_5		+126.1	
	in acetone-d_6		(t)

R	X		(=NO—)
Me	N—O·	(nitroxyl radical)	+77.2
	N—OH	(hydroxylamino moiety)	+93.7
CH_2Br	N—O·		+69.3
	N—OH		+77.2
Ph	N—O·		+102.4
	N—OH		+84.0
	N—OMe		+85.9
p-tolyl	N—O·		+103.4
	N—OH		+90.1
o-nitrophenyl	N—O·		+77.6
	N—OH		+83.0
Ph	N—O·	*(in CD_3OD)*	+98.5
	N—OH		+90.7

Table 24. *—cont.*

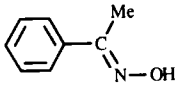
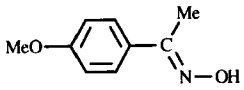
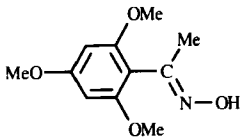
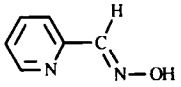
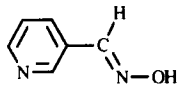
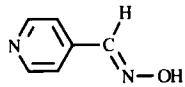
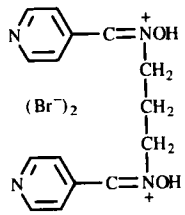
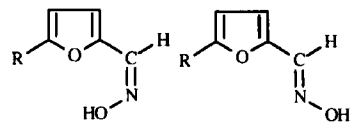
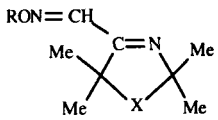
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Oximes and their ethers $R_2C{=}N{-}O{-}R$	see also ref. 5, pp. 544–545		
	solid state		(u)
	(isotropic)	+11	
	(σ_{11})	−200	
	(σ_{22})	+32	
	(σ_{33})	+200	
	solid state		(u)
	(isotropic)	+15	
	(σ_{11})	−195	
	(σ_{22})	+37	
	(σ_{33})	+202	
	solid state		(u)
	(isotropic)	+13	
	(σ_{11})	−199	
	(σ_{22})	+37	
	(σ_{33})	+200	
	in DMSO	−0.6 (NOH) +69.6 (N)	(v) (v)
	in DMSO	+4.7 (NOH) +64.3 (N)	(v) (v)
	in DMSO	−3.2 (NOH) +64.8 (N)	(v) (v)
	in DMSO	−23.9 (NOH)	(v)
 (*E*-isomer) (*Z*-isomer)	in DMSO		(w)

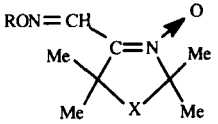
Table 24. *—cont.*

Compound		Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
R				
Me	(*Z*)	−19.4		
H	(*Z*)	−16.8		
$SiMe_3$	(*Z*)	−16.2		
	(*E*)	−9.3		
Br	(*Z*)	−14.5		
	(*E*)	−9.4		
NO_2	(*Z*)	+3.1		
	(*E*)	+7.6		



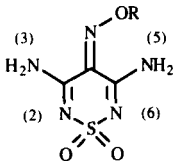
in acetone-d_6 (x)

R	X		(oxime)
H	N—O·	(nitroxyl radical)	−29.9
H	N—OH	(hydroxylamino moiety)	−20.2



in acetone-d_6 (x)

R	X		(oxime)
H	N—O·	(nitroxyl radical)	−57.6
H	N—Me		−9.1
Me	N—O·		−70.8
Me	N—OH		−25.6

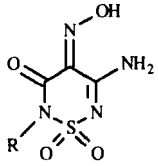


solvent? (y)

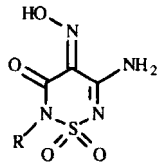
R	=NOR	2,6-N	3-NH_2	5-NH_2
H	−28.0	+159.3	+285.5	+274.3
Me	−30.2	+157.4	+285.7	+275.1

Table 24. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes



(*E*-isomer)

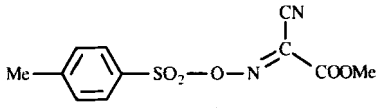


(*Z*-isomer)

solvent?

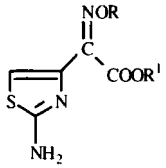
(y)

R		=NOH	N—R	—N=	NH_2
H	(*Z*)	−40.9	+209.5	+174.3	+276.8
CH_2Ph	(*Z*)	−41.8	+209.7	+181.3	+270.5
	(*E*)	−45.2	+206.6	+177.8	+261.0



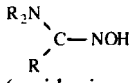
in $CDCl_3$

−31.0 (=N—O) (q)
+95.2 (CN) (q)



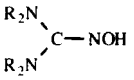
(z)

R	R^1		
Me	Et	in DMSO	−7.2 (=N—O)
Me	H	in DMSO	−11.7 (=N—O)
		in DMSO/HCl	−5.9 (=N—O)
		in CF_3COOH	+14.6
H	Et	in DMSO	−20.7 (=N—O)
		in DMSO/HCl	−14.1 (=N—O)



(amidoximes)

see Table 10



(*N*-hydroxyguanidines)

see Table 10

(a) Data from ref. 574, ^{15}N-labelled samples, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(b) Data from ref. 430, ^{15}N-labelled compound, 9.12 MHz ^{15}N CPMAS spectra, referenced originally to solid $(NH_4)_2SO_4$, +355.7 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects; dynamic nitrogen NMR spectra were observed in the solid, owing to the prototropic tautomerization processes involving the NH and =N moieties.

(c) Data from ref. 548, 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $(Cracac)_3$ added as a relaxation reagent.

(d) Data from ref. 139, ^{15}N-labelled imine, 25.33 MHz ^{15}N spectra, inverse-gated proton decoupling in order to suppress NOE, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; the assignments imine vs its complex are erroneously reversed in the original table in the paper quoted, but they are correct in the text concerned; an INEPT spectrum, via ^2J(NH), was taken in the case of the $NHEt_2$ ligand.

(e) Data from ref. 796, 21.68 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to NO_3^-, probably in aqueous $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(f) Data from ref. 946, 30.4 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced originally to nitromethane containing 20% benzene-d_6, *ca.* +0.8 ppm from neat nitromethane, as can be reckoned from Table 26, conversion scheme IIb (Table 1).

(g) Data from ref. 136, details as in footnote (f).

(h) Data from ref. 137, details as in footnote (f).

(i) Data from ref. 138, details as in footnote (f).

(j) Data from refs 329, 348, 408, 410 and 1175, ^{15}N-labelled samples of retinal in bacteriorhodopsin in the purple membrane of *Halobacterium halobium*, 32.2 MHz ^{15}N MASS and static powder spectra, referenced originally to 5.6 M aqueous NH_4Cl, +352.9 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects.

(k) Data from refs 1074 and 1176, 25.35 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(l) Data from ref. 1020, 30.4 MHz ^{15}N spectra, other details as in footnote (k).

(m) Data from ref. 108, 40.4 MHz ^{15}N spectra, gated-decoupled for C=N, and INEPT for $C{=}NH^+$, field parallel to sample tube, referenced originally to neat formamide, +268.8 ppm from neat nitromethane (Table 2), conversion scheme IVb (Table 1).

(n) Data from ref. 118, 36.5 MHz ^{15}N spectra, other details as in footnote (k).

(o) Data from ref. 376, 15.24 MHz ^{15}N CPMAS spectra, referenced originally to solid $(NH_4)_2SO_4$, +355.7 ppm (uncorrected) from neat nitromethane (Table 2).

(p) Data from ref. 657, ^{15}N-labelled imino moiety, details as in footnote (t).

(q) Data from ref. 1036, 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported originally vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane (the latter value actually comes from measurements where the field was perpendicular to sample tube, see Table 2).

(r) See ref. 5, p. 531, and references therein.

(s) Data from ref. 574, ^{15}N-labelled samples, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to liquid ammonia, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); solvent not reported.

(t) Data from ref. 657, ^{15}N-labelled nitrone moiety, 21.7 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane via a calibrated sample of neat aniline, uncorrected for bulk susceptibility effects; the solutions included, respectively, both the radical and its hydroxylamino diamagnetic analogue.

(u) Data from ref. 330, 20.3 MHz ^{15}N CPMAS and static powder spectra, referenced originally to NH_4^+ in solid $(NH_4)_2NO_3$, +359.6 ppm (uncorrected) from neat nitromethane (Table 2), but reported vs fictitious ammonia standard taken at +23.8 ppm from the reference employed; we retrieved the original data, and carried out the recalculations as noted above.

(v) Data from ref. 815, 9.12 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

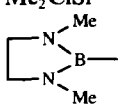
(w) Data from ref. 817, details as in footnote (v).

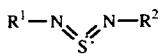
(x) ^{15}N-labelled oxime moiety, see footnote (t).

(y) Data from ref. 797, 30.4 MHz ^{15}N spectra, other details as in footnote (k).

(z) Data from ref. 805, 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

Table 25. Nitrogen shielding in various sulphur–nitrogen compounds containing sulphur–nitrogen bonds

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Bu^t—N=S=O (sulphinylamine structure)	neat liquid	+69	(a)
Ph—N=S=O	neat liquid	+66	(a)
	in CCl_4	+62.5	(b)
Substituted Ph—NSO	in CCl_4		(b)
2-F		+70.8	
3-F		+81.3	
4-F		+81.7	
2,4-F_2		+84.6	
2,6-F_2		+88.1	
2,3,4,5,6-F_5		+89.6	
2,3,5,6-F_4-4-CF_3		+89.9	
R^1—N=S=N—R^2 (sulphurdiimide structure)			
R			
o-tolyl	in benzene	+84.1	(c)
p-tolyl	in benzene	+83.0	(c)
2,4,6-Me_3-phenyl	in benzene	+83.2	(c)
Bu^t	in $CDCl_3$	+54.9	(d)
Me_3Si	neat liquid	+61	(e)
	in $CDCl_3$	+54.2	(d)
Me_2ClSi	in $CDCl_3$	+58.6	(d)
	in $CDCl_3$	+89.5 (N=S) +330.8 (NMe)	(d) (d)



(sulphurdiimide structure)

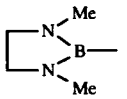
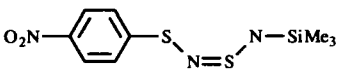
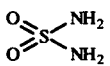
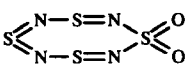
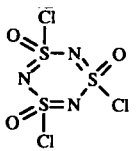
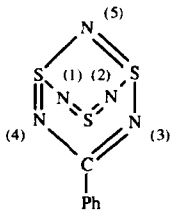
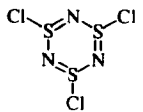
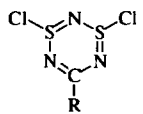
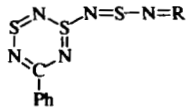
R^1	R^2		NR^1	NR^2	
Me_3Si	Bu^t	neat liquid	+58	+70	(e)
		in $CDCl_3$	–	+68.2	(d)
Me_3Si	Ph	in $CDCl_3$	–	+77.0	(d)
Me_3Si	2,4-Me_2-phenyl	in $CDCl_3$	+67.7	+86.3	(d)
	Bu^t	in $CDCl_3$	+66.5	+86.9 *+330.8 (NMe)*	(d) (d)
		in benzene	+71 (SNS) +100 (SNSi) +12 (NO_2)		(e) (e) (e)
		in D_2O	+289		(e)
		in benzene	+260		(e)
		in tetrahydrofuran	+78 (SNS) +145 ($SNSO_2$)		(e) (e)
		in benzene	+217		(e)

Table 25. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$	+327.0 (5-N) +205.8 (3,4-N) +51.8 (1,2-N)	(f) (f) (f)
	0.25 M in CCl_4 (52 to −70°C) 0.25 M in SO_2	+263 +259	(g) (g)
	in CH_2Cl_2		(h)

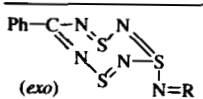
R	CNS	SNS	R
Me_2N	+211	+263	+211
Et_2N	+213	+240	+213
$(i\text{-}Pr)_2N$	+205	+241	+220
CCl_3	+181	+248	–
t-Bu	+191	+242	–
Ph	+196	+237	–



in $CDCl_3$ ($-40°C$)

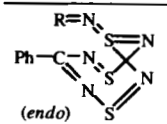
(i)

R	SNR	CNS	CNS	SNS	SNS
PPh_3	+275	+185	+222	+275	+142
P(cyclohexyl)$_3$	+282	–	–	+282	+139
PPh_2Me	+274	+188	+222	+276	+144
P(*o*-tolyl)$_3$	+272	+190	+221	+279	+142



(*exo*)

R	RNS	CNS	SNS
PPh_3	+303.8	+189.6	+224.4
P(cyclohexyl)$_3$	+320.8	+190.2	+223.9
PPh_2Me	+305.8	+190.6	+225.4
P(*o*-tolyl)$_3$	+303.8	+191.7	+223.4
		+189.3	+227.3
$AsPh_3$	+291.5	+187.4	+220.5



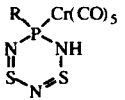
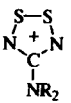
(*endo*)

in $CDCl_3$ ($-40°C$)

(i)

R	RNS	CNS	SNS
PPh_3	+311.2	+196.2	+214.5
P(cyclohexyl)$_3$	+324.5	+195.7	+213.4
PPh_2Me	+318.6	+197.1	+212.6
P(*o*-tolyl)$_3$	+308.3	+196.5, +195.4	+214.7
$AsPh_3$	+308.4	+194.4	+204.9

Table 25. —*cont.*

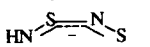
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in acetone		(j)
R			
Bu^t		+259.7 (NH)	
NH_2		+311.4 (NH)	
		+313.4 (NH_2)	
	in CH_2Cl_2		(k)
R		CNS $\quad$ NR_2	
Me		+69 $\quad$ +318	
Et		+62 $\quad$ +250	
Pr^i		+59 $\quad$ +244	
$(SNS)^+AeF_6^-$	in SO_2	+91	(l)
$(NS)^+AeF_6^-$	in SO_2	−202	(l)
N≡S—F	in benzene	+115.5	(m)
	in $SO_2(NS^+F^-?)$	−196	(l)
NSCl	in $SO_2(NS^+Cl^-?)$	−323	(l)
$[N(SCl)_2]^+AeF_6^-$	in SO_2	−19	(l)
$(\overline{HCSNSCH})^+AeF_6^-$	in SO_2	+5	(l)

$(H_2\overline{CSNSCH_2})^+AeF_6^-$	in SO_2	−134	(l)
$(H_2\overline{CSNSCH_2})^+AeF_6^-$ $CH_2—CH_2$	in SO_2	+298	(l)
 $[AeF_6]^-$	in SO_2		(l)

X	SNS	XNS
SF	+27	+173
SCl	+40	+176
CMe	+27	−126
$CNMe_2$	+17	+101

$PPN^+\ S_3N^-$	in MeCN	−235 (S_3N)	(n)
$PPN^+\ S_4N^-$	in MeCN	−106 (S_4N)	(n)
$(Me_2N)_3S^+\ NSO^-$	in MeCN	−139 (NSO)	(n)
		+325 (NMe_2)	(n)
$K(18\text{-}crown\text{-}6)^+\ NSO^-$	in tetrahydrofuran	−134	(n)
$(Me_2N)_3S^+\ SSNSO^-$	in MeCN	−45 (SSNSO)	(n)
$PPN^+\ S_3N_3O_2^-$	in CH_2Cl_2	+165, +28	(n)
$PPN^+\ S_3N_3O^-$	in CH_2Cl_2	+155, +92	(n)
$PPN^+\ S_3N_3^-$	in $CHCl_3$	+232	(n)
$Ph_4P^+\ S_3N_3^-$	in $CHCl_3$	+234	(n)
$PPN^+\ S_4N_5O^-$	in CH_2Cl_2	+276, +251, +225	(n)
S_7NH	in THF (−80°C)	+364	(o)
	in liquid NH_3	+364	(o)
S_7N^-	in THF (+25°C)	+327	(o)
	in liquid NH_3	+324	(o)
S_4N^-	in THF (+25°C)	−106	(o)
	in liquid NH_3	−107	(o)
S_3N^-	in liquid NH_3	−231	(o)

Table 25. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$S_3N_3^-$	in liquid NH_3	+230	(o)
	in liquid NH_3	+148 (doublet) −9 (singlet)	(o) (o)
$S_4N_4H_4$	in liquid NH_3	+321.5	(o)

(a) Data from ref. 1177, 21.692 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to aqueous ammonium chloride and reported vs liquid ammonia, taken at +380.2 ppm from neat nitromethane, conversion scheme IVd (Table 1).

(b) Data from refs. 574 and 1178, 30.414 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to liquid ammonia, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(c) Data from ref. 1179, 40.5 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 1046, 5.6 MHz ^{14}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(e) See footnote (a).

(f) Data from ref. 1180, 40.5 MHz ^{15}N spectra, other details as in footnote (b); originally, the molecule was labelled with ^{15}N at 1,2-N and at 5-N, but internal rearrangement led to the label scrambling over 3,4-N.

(g) Data from ref. 1181, 0.4–1.8 M solutions, 14.45 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(h) Data from ref. 1182, 28.915 MHz ^{14}N spectra, other details as in footnote (g).

(i) Data from ref. 908, 99% ^{15}N-labelling, 40.5 MHz ^{15}N spectra, other details as in footnote (b).

(j) Data from refs 152 and 227, 30.4 MHz ^{15}N INEPT spectra, and 200 MHz $^1H\{^{15}N\}$ 2-D inverse COSY, field parallel to sample tube, referenced to nitromethane containing 10% benzene-d_6, *ca.* +0.4 ppm from neat nitromethane (estimated from data in Table 26), conversion scheme IIb (Table 1).

(k) See footnote (h).

(l) See footnote (g).

(m) Data from ref. 1183, ^{14}N spectrum, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects, spectrometer not reported.

(n) Data from ref. 1184, 28.915 MHz ^{14}N spectra, other details as in footnote (g).

(o) Data from refs. 809 and 810, 36.14 MHz ^{14}N spectra and 50.7 MHz ^{15}N spectra, field parallel to sample tube referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

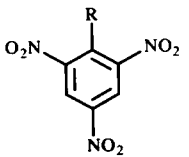
Table 26. Nitrogen shieldings in some nitro compounds, nitramines, nitrates and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$MeNO_2$	0.05 M in cyclohexane	+8.50	(a)
(nitromethane)	0.3 M in CCl_4	+7.10	(b)
	0.3 M in benzene	+4.38	(b)
	0.3 M in Et_2O	+3.91	(b)
	0.3 M in $CHCl_3$	+3.79	(b)
	0.3 M in CH_2Cl_2	+3.21	(b)
	0.3 M in EtOH	+2.70	(b)
	0.3 M in MeOH	+2.01	(b)
	0.3 M in dioxane	+1.82	(b)
	0.3 M in CF_3CH_2OH	+0.88	(a)
	0.3 M in acetone	+0.77	(b)
	0.3 M in MeCN	+0.20	(b)
	neat liquid	0.00	(c)
	0.08 M in H_2O	−1.98	(b)
	0.3 M in DMSO	−2.01	(b)
$^{13}CH_3NO_2$	in nitromethane	−0.019	(B)
CD_3NO_2	in nitromethane	−0.038	(B)
$MeONO_2$	0.2 M in n-hexane	+42.21	(d)
(methyl nitrate)	0.2 M in CCl_4	+41.94	(d)
	0.2 M in Et_2O	+40.46	(d)
	0.2 M in benzene	+40.43	(d)
	0.2 M in $CHCl_3$	+39.99	(d)
	0.2 M in CH_2Cl_2	+39.19	(d)
	0.2 M in dioxane	+38.95	(d)
	0.2 M in acetone	+38.41	(d)
	0.2 M in MeOH	+38.39	(d)
	0.2 M in CF_3CH_2OH	+38.08	(d)

Table 26. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	0.2 M in glycol	+38.06	(d)
	0.2 M in DMSO	+37.14	(d)
$EtNO_2$	various	−11.4 to −4.1	(b)
Pr^nNO_2	various	−10.1 to −3.8	(b)
Pr^iNO_2	various	−19.5 to −14.7	(b)
Bu^tNO_2	various	−28.2 to −21.8	(b)
$CH_2(NO_2)_2$	10% in $CHCl_3$	+25.1	(e)
$CH(NO_2)_3$	10% in $CHCl_3$	+38.2	(e)
$C(NO_2)_4$	neat liquid	+46.6	(b)
	10% in $CHCl_3$	+48.1	(e)
$CF(NO_2)_3$	10% in $CHCl_3$	+40.2	(e)
$(NO_2)_3C—C(NO_2)_3$	10% in $CHCl_3$	+47.0	(e)
$(NO_2)_2CF—CF(NO_2)_2$	10% in $CHCl_3$	+37.8	(e)
$(NO_2)_2O_2CCl—CCl(NO_2)_2$	10% in $CHCl_3$	+32.2	(e)
$MeCF(NO_2)_2$	10% in $CHCl_3$	+17.0	(e)
hexanitrobenzene	10% in CH_2Cl_2	+39.9	(e)
pentanitrobenzene	10% in CH_2Cl_2	+35.5, +33.0, +32.8	(e)
pentanitrotoluene	10% in CH_2Cl_2	+35.3, +34.2, +37.5	(e)
3-NH_2-4-NO_2-furazan	10% in acetone	+32.4 (NO_2)	(e)
3-(*p*-chlorophenyl)-4-NO_2-furazan	10% in $CHCl_3$	+34.3	(e)
3-Me-4-NO_2-furoxan	in DMSO	+31.8 (NO_2)	(D)
3-NO_2-4-Me-furoxan	in DMSO	+35.1 (NO_2)	(D)
3,5-dinitro-isoxazole	10% in $CHCl_3$	+34.7, +39.2	(e)
3-$C(NO_2)_2$Me-4-nitro-5-Me-isoxazole	in DMSO	+25.1 (4-NO_2)	(D)
		+15.9 (other)	(D)

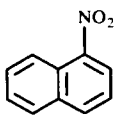
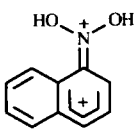
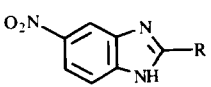
4,4′-dinitro-3,3′-bis-furazan	10% in $CHCl_3$	+39.4	(e)
same, ^{13}C-labelled at 4,4′	10% in $CHCl_3$	+39.6	(e)
4,4′-dinitro-5,5′-bis-isoxazole	in DMSO	+24.1 (NO_2)	(D)
4,4′-dinitro-3,3′-dimethyl-5,5′-bis-isoxazole	in DMSO	+26.7 (NO_2)	(D)
N-Me-tetranitropyrrole	10% in CH_2Cl_2	+39.3 (NO_2)	(e)
$PhNO_2$ (nitrobenzene)	various solvents	+9.5 to +12.2	(b)



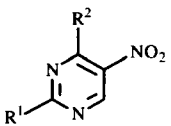
10–20% in DMSO (f)

R	N-2,6	N-4
H	+18.7	+18.7
Me	+12.7	+18.3
OH	+11.8	+14.6
OMe	+18.0	+18.9
OPh	+20.2	+19.6
p-nitrophenoxy	+21.3	+19.8
p-bromophenoxy	+20.4	+19.4
p-Bu′-phenoxy	+19.8	+19.2
NH_2	+14.4	+16.8
NHMe	+13.2	+16.7
NMe_2	+12.6	+17.7
NH(cyclohexyl)	+12.8	+17.4
NHPh	+15.7	+17.7
NH(*p*-CN-phenyl)	+15.8	+17.9

Table 26. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
NH(*p*-OMe-phenyl)		+15.3 +17.4	
COOH		+18.3 +20.0	
COOMe		+20.4 +20.8	
COCl		+18.6 +20.1	
Cl_2		+19.2 +20.4	
SO_3^-		+12.2 +18.9	
	in CF_3SO_3H, −20°C	+5.1	(g)
	in CF_3SO_3H, −20°C	+33.8	(g)
	in MeOH		(h)

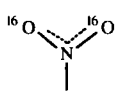
R	(NO_2)
NMe_2	+8.8
NH_2	+8.2
OEt	+9.3
Me	+9.7
Et	+9.8
H	+9.8
Cl	+10.6
COMe	+10.5
CF_3	+11.3
CN	+11.7



(i)

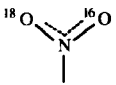
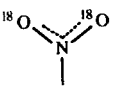
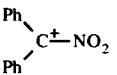
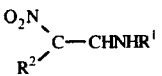
R^1	R^2		(NO_2)
H	H	in DMSO	+16.7
		in $CHCl_3$	+19.3
H	OMe	in $CHCl_3$	+18.8
SMe	H	in $CHCl_3$	+19.2
SO_2Me	H	in DMSO	+18.1

$O_2N—CH_2—CH_2—COOH$ in H_2O(?) (j)



−3.30

Table 26. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
		−3.22	
		−3.16	
	in FSO_3H/SO_2ClF −78°C	+18.3	(k)
			(l)

R^1	R^2		(NO_2)
Me	*p*-tolyl	in CF_3COOH	+38.9 (*Z*)
		in DMSO	−0.8 (*E*)
H	Me	in CF_3COOH	+34.0
		in DMSO	+0.2 (*E*)
Me	4-Me-2-pyridyl	in CF_3COOH	+4.1 (*E*), +4.3 (*Z*)
		in DMSO	−2.2 (*E*), −17.2 (*Z*)
Me	2-pyrimidyl	in CF_3COOH	+4.1, +3.6 (*E*, *Z*)
		in DMSO	−2.5 (*E*)

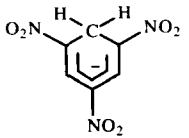
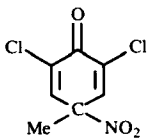
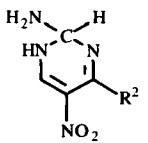
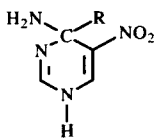
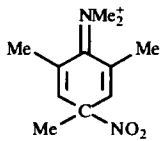
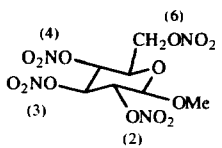
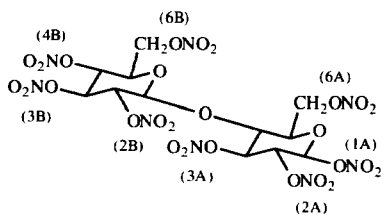
N-Me-2-NO-4-NO_2-aniline	in DMSO	+12.0 (NO_2)	(m)
3,3′-(NO_2)$_2$-4,4′-(NHMe)$_2$-azoxybenzene	in DMSO	+9.8, +11.4 (NO_2)	(m)
N-Me-2-NO-4,6-dinitroaniline	in $CDCl_3$	+16.3 (4-NO_2) +14.5 (6-NO_2)	(n)
 $[NMe_4]^+$	in DMSO	+8.5 (2,6-N) +17.7 (4-N)	(o)
	in $CDCl_3$	−35	(p)
	in liquid NH_3 R = H R = OMe	 +31.2 (NO_2) +31.2 (NO_2)	(q)
	in liquid NH_3 R = H R = SMe R = SO_2Me	 +47.2 (NO_2) +18.2 (NO_2) +11.2 (NO)	(q)

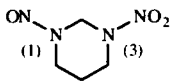
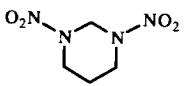
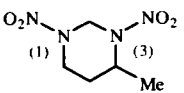
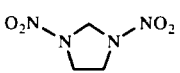
Table 26. *—cont.*

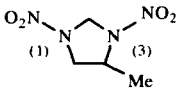
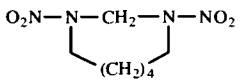
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in 70–80% H_2SO_4	−7 to +3 (NO_2)	(r)
	in acetone-d_6	+45.0 (2-N) +44.9 (3-N) +45.6 (4-N) +39.6 (6-N)	(s) (s) (s) (s)
(methyl-β-D-glucopyranoside tetranitrate)			
	in acetone-d_6	+50.8 (1A-N) +47.4 (2A-N) +45.0 (3A-N) +40.6 (6A-N) +46.5 (2B-N) +45.8 (3B-N) +46.5 (4B-N) +40.1 (6B-N)	(s) (s) (s) (s) (s) (s) (s) (s)
(β-cellobiose octanitrate)			
$HONO_2$	neat liquid	+42.5	(t)

HNO_3/H_2O	3 M in H_2O	+5	(u)
	5 M in H_2O	+18	(u)
	10 M in H_2O	+38	(u)
	(see also Table 2)		
$HNO_3/H_2SO_4/H_2O$	in 3 M H_2SO_4	+5.5	(u)
	in 14 M H_2SO_4	+23	(u)
	in 24 M H_2SO_4	+43	(u)
HNO_3/Bu_3PO_4	0.5–3.5 M in Bu_3PO_4	+26 to +37	(v)
	0.1–2 M in Bu_3PO_4/CCl_4 (1 : 1)	+32 to +38	(v)
N_2O_5/HNO_3	liquid	+46.5 to +49.7	(w)
KNO_3, $NaNO_3$	0.3 M in H_2O	+3.5	(t)
$(Bu_4N^+)_{x-3}L(NO_3)_x$	in CH_2Cl_2		(x)

L	x		NO_3
La	6		+10
Lu	5		+10
Ce	6		+33
	5	(in acetone, Pr_4N^+)	+40
Pr	6		+85
	5	(in acetone, Pr_4N^+)	+100
Nd	6		+105
	5	(in acetone, Pr_4N^+)	+126
Sm	5		+25
Eu	5		−162
Tb	5		−378
Dy	5		−267
Ho	5		−130
Er	5		−50
Tm	5		−46
Yb	5		−2

Table 26. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$UO_2(NO_3)_2 \cdot 2TBP$	in DEHPA + TBP + benzene	+8.3 to +9.5	(y)
$UO_2(NO_3)A \cdot TBP$	in DEHPA + TBP + hexane	+10.3 to +10.8	(y)
$TBP(HNO_3) \cdot xA$	in DEHPA + TBP + benzene	+31.8 to +36.8	(y)
$[(H_2O)_2Lu(NO_3)_2]^+$	in H_2O–acetone–Freon-12 at −115°C	+3.9	(C)
$[(H_2O)_4Lu(NO_3)]^+$	in H_2O–acetone–Freon-12 at −115°C	+4.4	(C)
$Sn(NO_3)_4$	in MeCN	+28	(E)
	in CF_3COOH	+55	(E)
	in $(CF_3CO)_2O$	+82	(E)
	in DMSO	+27.8 (NO_2)	(z)
		+198.3 (3-N, *anti*)	(z)
		+196.6 (3-N, *syn*)	(z)
	in DMSO	+28.7 (NO_2)	(z)
		+200.6 (N)	(z)
	in DMSO	+29.3 (1-NO_2)	(z)
		+30.3 (3-NO_2)	(z)
		+201.4 (1-N)	(z)
		+191.6 (3-N)	(z)
	in DMSO	+31.2 (NO_2)	(z)
		+205.3 (N)	(z)

	in DMSO	+31.0 (1-NO_2) +31.9 (3-NO_2) +206.8 (1-N) +195.5 (3-N)	(z) (z) (z) (z)
	in DMSO	+31.0 (NO_2) +197.3 (N)	(z) (z)
N-nitroguanidine	solid state in DMSO in dimethylformamide	+12 (NO_2) +10 (NO_2) +11 (NO_2)	(A) (A) (A)

(a) Data from ref. 81, high-precision ^{14}N spectra, 36.14 MHz, referenced to neat nitromethane, field parallel to sample tube, lineshape fitting, corrected for bulk susceptibility effects.

(b) See ref. 31; ref. 5, p. 223; ref. 4, p. 385; and references therein.

(c) Arbitrary standard, see also ref. 5, pp. 17–30.

(d) Data from ref. 88, high-precision ^{14}N spectra, 4.33 MHz, references to neat nitromethane, +35°C ± 0.3, lineshape fitting, differential saturation CW technique, concentric spherical sample/reference containers in order to eliminate bulk susceptibility effects.

(e) Data from ref. 859 and 1185, 6.5 MHz ^{14}N spectra, field perpendicular to sample tube, referenced originally to liquid 10% nitromethane in $CHCl_3$, +3.8 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(f) Data from refs 360 and 1186, ^{15}N spectra, 10.095 MHz, field perpendicular to sample tube, $Cr(acac)_3$ added as a relaxation reagent, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(g) Data from ref. 836, ^{15}N spectra, 99% ^{15}N label, 10.095 MHz, field perpendicular to sample tube, referenced originally to liquid NH_3, +381.9 ppm from nitromethane (Table 2), conversion scheme IIa (Table 1).

(h) Data from ref. 273, $^1H\{^{15}N\}$ INDOR spectra, ^{15}N-labelled NO_2, 80 MHz, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility.

(i) Data from ref. 162, ^{15}N spectra, 30.4 MHz, field parallel to sample tube, referenced originally to $MeNO_2$ in MeOH (+1.97 ppm from neat nitromethane) and recalculated to the latter reference, uncorrected for bulk susceptibility.

(j) Data from ref. 164, ^{15}N spectra, ^{15}N and ^{18}O labels, DEPT sequence, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility, solvent not specified.

(k) Data from ref. 1187, ^{15}N spectra, 5% ^{15}N label, 8.1 MHz, field perpendicular to sample tube, referenced originally to liquid NH_3, conversion to neat nitromethane as in footnote (g).

(l) Data from ref. 766, ^{15}N DEPT spectra, 40.5 MHz, field parallel to sample tube, referred to nitromethane with 10% benzene-d_6, *ca.* +0.8 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(m) Data from ref. 1062, 30.405 MHz ^{15}N spectra, other details as in footnote (f).

(n) Data from ref. 360, details as in footnote (f).

Table 26. —*cont.*

(o) Data from ref. 862, ^{15}N spectrum, 10.095 MHz, referred to neat nitromethane, uncorrected for bulk susceptibility.

(p) Data from ref. 1188, ^{15}N spectrum, spectrometer not specified, referenced to 8 M HNO_3, *ca.* +14.5 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1).

(q) Data from ref. 162, see footnote (i).

(r) Data from refs 484 and 486, ^{15}N CINDP spectra, 9.1 MHz, referenced to internal $PhNMe_2^+$, *ca.* +327 ppm from neat nitromethane, as can be reckoned from the position of the resonance of $HONO_2$, which should appear at *ca.* +43 ppm from nitromethane under the experimental conditions involved (Table 2).

(s) Data from ref. 1189, 30 and 20 MHz $^{15}N\{^1H\}$ COSY spectra, field parallel to sample tube, referenced originally to 1 M NH_4Cl in 10 M HCl, +349.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(t) See Table 2.

(u) Data from ref. 1190, 7.2 MHz ^{14}N spectra, field perpendicular to sample tube, referenced originally to aqueous KNO_3, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(v) Data from ref. 742, 6.5 MHz ^{14}N spectra, field perpendicular to sample tube referenced originally to aqueous KNO_3, +3.5 ppm from nitromethane (Table 2), conversion scheme IIa (Table 1).

(w) Data from ref. 743, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility.

(x) Data from ref. 491, 5.74 MHz ^{14}N spectra, referenced originally to internal nitrobenzene (10% + 10% TMS in CH_2Cl_2), *ca.* +10 ppm from neat nitromethane, low-precision measurements, ±2 ppm.

(y) Data from refs 1191 and 1192, 9.1 MHz ^{15}N spectra, field perpendicular to sample tube, ^{15}N-labelled NO_3^-, referenced originally to aqueous $NaNO_3$, +3.5 ppm from nitromethane, conversion scheme IIa (Table 1); see also ref. 1193, 6.5 MHz ^{14}N spectrum, referenced to aqueous KNO_3, conversion as above. The abbreviations employed are DEHPA = HA = bis(2-ethylhexyl) phosphoric acid, A = its anion, TBP = tributyl phosphate.

(z) Data from ref. 373, 20.3 MHz ^{15}N spectra, referenced originally to internal nitromethane, but reported relative to liquid NH_3 (with an assumed conversion constant of 380.2 ppm); this is erroneous, since the latter value is referred to neat nitromethane, and contains bulk susceptibility effects for a field which is perpendicular to sample tube; the actual value of the nitrogen shielding for nitromethane in DMSO (−2.0 ppm from neat nitromethane, this table) was used here for conversion.

(A) Data from ref. 414, 20.272 MHz ^{15}N CPMAS and solution spectra, referenced to NO_3^- in solid and aqueous NH_4NO_3, +5.0 and +4.0 ppm, respectively, from neat nitromethane (Table 2); conversion scheme IIb (Table 1).

(B) Data from ref. 495, ^{15}N-labelled nitromethane isotopomers, 30.4 MHz ^{15}N spectra referenced to *internal* $^{12}CH_3{}^{15}NO_2$.

(C) Data from ref. 1194, ^{15}N-labelled nitrate, 40.561 MHz ^{15}N spectra, referenced originally to internal $NaNO_3$, 3.5 ppm from neat nitromethane (Table 2).

(D) Data from ref. 844, 30.4 MHz ^{15}N spectra and 21.7 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(E) Data from ref. 1195, 7.2 MHz ^{14}N spectra, field perpendicular to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

Table 27. Nitrogen shieldings in diazo compounds, diazonium salts and diazoates

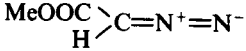
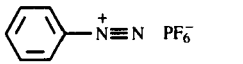
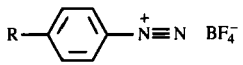
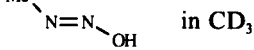
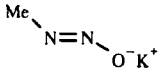
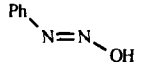
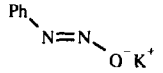
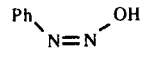
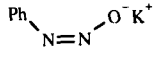
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
Diazo structures		(=$\overset{+}{N}$=)	(=N^-)	
$R_2C{=}N^+{=}N^-$	various	+75 to +155	−60 to +66	(a)
$H_2C{=}N^+{=}N^-$	in CD_3OD	+92.6	−14.0	(b)
$MeCH{=}N^+{=}N^-$	in CD_3OD	+76.5	−45.4	(b)
$EtCH{=}N^+{=}N^-$	in CD_3OD	+78.1	−47.0	(b)
	in $CDCl_3$	+113.6	0.0	(c)
Diazonium salts		(—$\overset{+}{N}$≡)	(≡N)	
$R{-}\overset{+}{N}{\equiv}N\ X^-$	various	+82 to +191	+32 to +166	(d)
	in acetone	+149.7	+66.9	(e)
	in acetone + [18-*crown*-6]	+155.8	+63.4	(e)
	0.05 M in MeCN (if not stated otherwise)			
R		(—$\overset{+}{N}$≡)	(≡N)	
NMe_2		+133.3	+33.1	(f)
OMe		+145.9	+57.2	(f)(g)
	(*0.5 M in 0.1 M HCl*)	–	+57.9	(g)
Me		+147.8	+63.2	(f)
H		+148.2	+65.2	(f)
F		+149.9	+63.3	(f)
Cl		+149.7	+62.7	(f)
Br		+149.2	+62.2	(f)
I		+148.5	+61.6	(f)
CN		+151.3	+64.9	(f)
NO_2		+151.4	+64.3	(f)
			+65.2	(g)
	(+*1 M 18-crown-6*)	–	+62.9	(g)
	(*0.1 M 0.05 M 18-crown-6*)	–	+64.6	(g)
$NMe_3^+\ Cl^-$	(*in MeCN/H_2O, 4 : 1*)	+151.7	+65.4	(f)
SO_3H	(*0.11 M in 0.1 M HCl*)	–	+66.9	(g)
$MeO{-}\overset{+}{N}{\equiv}N$	in SO_2F_2/meF, −100°C	+158.5	+293.4	(h)
$Ph{-}\overset{+}{N}{\equiv}N$	in SO_2F_2/MeF, −100°C	+156.4	+63.4	(h)
$F{-}N{\equiv}\overset{+}{N}$	in SO_2F_2/MeF, −100°C	+166.1	+191.2	(h)
$MeNH{-}N{\equiv}N$	in SO_2F_2/MeF, −100°C	–	+166.3	(h)
Diazotates (diazoates)		(—N=)	(=N—O)	
$R{-}N{=}N{-}O^-$ (*syn, anti*)	various	−6 to +18	−148 to −187	(i)
	in CD_3OD	+33.8	−187.2	(j)

Table 27. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	in CD_3OD	+18.8	−182.9	(j)
	in DMSO	+9.5	−173.5	(j)
	in DMSO	+10.0	−158.7	(j)
	in DMSO	+71.4	−113.2	(j)
	in DMSO	+30.1	−119.9	(j)

(a) See ref. 5, p. 560, and references therein.

(b) Data from ref. 837, see Table 29, footnote (s).

(c) Data from ref. 1074, 25.34 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(d) See ref. 5, p. 561, and references therein.

(e) Data from ref. 900, 36.4 MHz and 18.2 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(f) Data from refs 75 and 482, ^{15}N doubly labelled benzenediazonium ions, 9.12 MHz ^{15}N CINDP spectra, field perpendicular to sample tube; 0.05 M or 0.1 M pyrene was present in the solutions, irradiated with a high-pressure mercury lamp; enhanced absorption was observed for the ^{15}N signals of the diazonium ions, while emission signals of N_2 appeared in the spectra; the latter signals were calibrated (+70.3 ppm) against neat nitromethane, uncorrected for bulk susceptibility effects.

(g) Data from ref. 1196, ^{15}N singly labelled ions, ^{15}N spectra, referenced to neat nitromethane, uncorrected for bulk susceptibility effects, spectrometer not reported, field was probably parallel to sample tube.

(h) Data from ref. 896, ^{15}N-labelled ions, 8.1 MHz ^{15}N spectra, field perpendicular to sample tube, reference not given, probably liquid ammonia at +380.2 ppm from neat nitromethane, uncorrected for bulk susceptibility effects.

(i) See Table 29, footnote (s) therein; see also ref. 5, p. 561, and references therein.

(j) See footnote (b).

Table 28. Nitrogen shieldings in azo, azoxy and azodioxy compounds, diazenes, triazenes, and tetrazenes

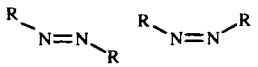
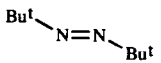
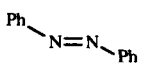
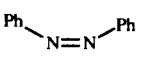
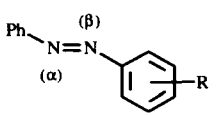
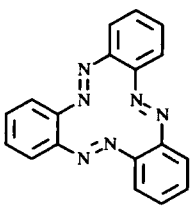
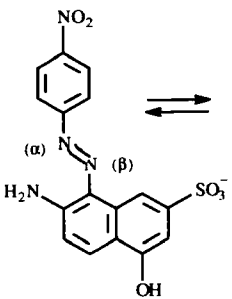
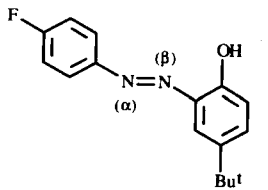
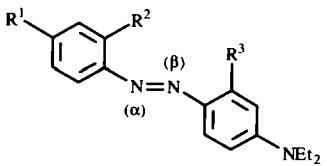
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Azo structures			
 *trans* *cis*	various (R = aryl)	−165 to −80	(a)
Protonated forms of azoarenes	in FSO_3H	−76 to −6	(a)
Azoarenes in equilibria with hydrazone tautomers	various	see Table 9	
	0.5 M in $CHCl_3$	−151.33	(b)
	0.3 M in MeOH	−151.60	(b)
	0.2 M in acetone	−151.73	(b)
	0.2 M in n-hexane	−152.07	(b)
	neat liquid	−152.65	(b)
	0.3 M in CCl_4	−152.91	(b)
	1.0 M in CF_3CH_2OH	−159.0	(b)
	various solvents	−130 to −128	(a)
	solid, +21°C	+127, −126 isotropic	(c)
		−650, −621 (σ_{11})	(c)
		−7, −16 (σ_{22})	(c)
		+275, +259 (σ_{33})	(c)
	various solvents	−151 to −146	(a)
	solid		(d)

Table 28. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
R				
4-OH	+32°C	−95.7, −68.7	(N-α)	
		−114.4, −80.5	(N-β)	
2-OH-4-Bu^t	+33°C	−65.3	(N-α)	
		−129.9	(N-β)	
	+50°C	−65.6	(N-α)	
		−129.9	(N-β)	
4-NMe_2	+29°C	−117.0	(N-β)	
	in $CDCl_3$	−154.7		(e)
 hydrazone tautomer	in DMSO			(f)
	+27°C	−44.1	(N-α)	
		−118.1	(N-β)	
		−48.2	(N-α)	
	+87°C	−121.4	(N-β)	
	(>95% azo form)			



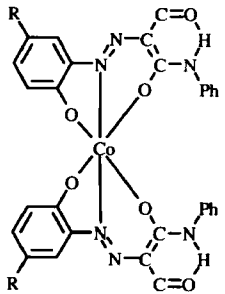


R^1	R^2	R^3	in $CDCl_3$	N-α	N-β	NEt_2	
H	H	H	(ca. 100% azo form)	−63.9	−122.6		(g)
Me	Br	H					
Me	H	H					
Me	Me	H					
NO_2	NO_2	H					
H	H	NHCOMe	in $CDCl_3$	−93.1	−116.6	+295.9	(h)
				−90.6	−115.9	+295.2	
				−93.0	−112.3	+296.8	
				−96.0	−109.6	+297.7	
				−127.6	−54.2	+282.7	
				(+13.9; +16.9, *NO_2*)			
H	Br	NHCOMe		−63.8	−103.6	+289.3	
				(+253.4, *NHCOMe*)			
Me	Br	NHCOMe		−51.4	−114.6	+296.1	
				(+251.5, *NHCOMe*)			
H	H	OH		−59.3	−112.3	+287.8	
				(+251.9, *NHCOMe*)			
Me	H	OH		+23.7	−81.3	+285.4	
Me	Me	OH		+11.7	−84.2	+286.9	
				?	−71.8	+286.0	

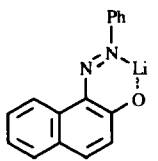
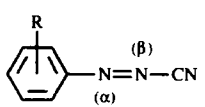
azo structures in tautomeric equilibria with hydrazones

see Table 9

Table 28. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in $CDCl_3$		(i)

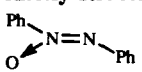
R	(=N—Co)	(=N)	(NHPh)
H	?	−47.9	+249.1
Cl	+113.7	−46.3	+247.8

	in $CDCl_3$	−8.8 (=N—Li)	(j)
Cyanodiazo structures			
	in $CDCl_3$		

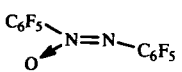
R		N-α	N-β	CN	
4-OMe	*syn*	−162.5	−12.1	-	(k)
	anti	−203.2	−53.3	-	(k)
4-Cl	*syn*	−179.6	−48.8	+105.3	(k)
	anti	−215.7	−81.3	+123.1	(k)
4-Br	*syn*	−183.0	−54.5	+100.9	(l)
	anti	−218.1	−84.0	+119.6	(l)
4-NO_2	*syn*	−187.1	−72.8	-	(k)
	anti	−222.5	−104.2	-	(k)
3-Me	*syn*	−186.1	−49.1	+106.0	(k)
	anti	−220.8	−78.1	+125.4	(k)

Hydroxy-azo structures
R—N=N—OH
and corresponding anions — see Tables 27 and 29

Azoxy structures

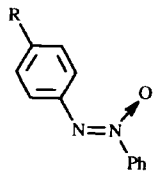
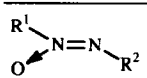


	various	+57 to +64	(NO)	(m)
		+34 to +52	(=N—)	(m)
	in SO_2, −80°C	+67	(NO)	(n)
		+50	(=N—)	(n)
(monoprotonated)	in FSO_3H/SO_2	+53	(NO)	(n)
		+53	(=N—)	(n)
(diprotonated)	in $SbF_5/FSO_3H/SO_2$	+209	(NO)	(n)
		+169	(=N—)	(n)



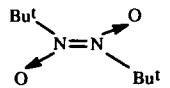
	in SO_2, −80°C	+76	(NO)	(n)
		+63	(=N—)	(n)
(monoprotonated)	in FSO_3H/SO_2	+65	(NO)	(n)
		+65	(=N—)	(n)
(diprotonated)	in $SbF_5/FSO_3H/SO_2$	+176	(NO)	(n)
		+165	(=N—)	(n)

Table 28. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	in DMSO			(o)
R				
H		+57.3	(NO)	
		+52.1	(N)	
OMe		+64.0	(NO)	
		+54.5	(N)	
Me		+59.7	(NO)	
		+52.8	(N)	
Cl		+56.5	(NO)	
		+56.3	(N)	
CF_3		+52.3	(NO)	
		+54.5	(N)	
COMe		+53.2	(NO)	
		+53.2	(N)	
CN		+51.8	(NO)	
		+55.0	(N)	
NO_2		+50.8	(NO)	
		+55.6	(N)	
				
R^1=R^2=2,4-F_2-phenyl	in SO_2 (?)	+65.0	(NO)	(p)

R^1=R^2=2,3,5,6-F_4-phenyl	in SO_2 (?)	+55.9	(=N—)	(p)
		+66.0	(NO)	(p)
R^1=R^2=C_6F_5	in SO_2 (?)	+53.9	(=N—)	(p)
		+76.0	(NO)	(p)
		+62.7	(=N—)	(p)
R^1=2-NHMe-5-NO_2-phenyl R^2=2-NH_2-5-NO_2-phenyl	in DMSO	+60.1	(NO)	(q)
		+56.5	(=N—)	(q)

Azodioxy structures (nitroso dimers)



in n-hexane			(r)
0.5 M	+65.5		
2.0 M	+64.7		
in CCl_4			(r)
0.5 M	+67.6		
2.0 M	+64.1		
in MeOH			(r)
0.5 M	+63.4		
1.5 M	+61.7		
in DMSO, 1.0 M	+54.7		(r)

Diazene structure

R_2N^+=N^-	in solution	*ca.* + 60 (N^+)	(s)
		ca. −530 (N^-)	(s)

Triazene structure (amino-azo type)

		R—N=	=N—	NR_2	
R—N=N—NR_2	various	−29 to	−72 to	+169 to	(s)
	in $CDCl_3$	+38	−31	+225	
	25% v/w				(t)

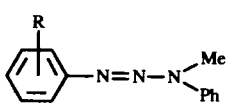
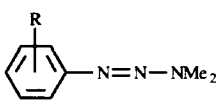
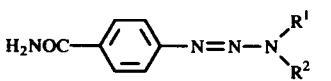


Table 28. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane			Notes
R					
H	*(60%w/v)**	+5.2	−61.5	+205.8	
		+6.7	−60.2	+207.4	
	(3%w/v)	+5.7	−62.4	+205.4	
4-OMe		+6.2	−55.6	+210.0	
4-Me		+6.0	−58.6	+208.7	
4-F		+9.3	−59.7	+207.5	
4-Br		+11.0	−61.2	+205.6	
	*(3%w/v)**	+9.7	−62.6	–	
3-Br		+11.5	−62.5	+204.2	
4-CF_3		+13.0	−64.3	+203.4	
4-SO_2Me		+15.4	−66.5	+199.5	
3-NO_2		+16.2	−64.5	+201.5	
4-NO_2		+16.5	−67.8	+198.4	
	(3%w/v)	+17.1	−67.9	–	
	*(3%w/v)**	–	−68.3	–	
 R	0.4 M in DMSO + $Cr(acac)_3$				(u)
R					
H		+23.5	−71.2	+222.2	
4-OMe		+20.8	−68.4	+226.2	
4-Me		+21.7	−70.1	+224.3	
4-Cl		+29.0	−71.2	+219.8	
4-$CONH_2$		+28.8 (+*276.2, amide*)	−72.6	+218.2	

4-COOH		+30.4	−73.3	+215.7
4-COOMe		+31.4	−73.5	+214.9
4-COOEt		+31.3	−73.4	+214.9
4-CF		+32.4	−73.6	+215.2
4-SO_2NH_2		+32.2	−73.3	+215.2
		(+282.0, *sulphonamide*)		
4-SO_2Me		+34.5	−74.2	+212.8
4-NO_2		+37.3	−75.0	+208.6
		(+7.2, *nitro group*)		
3-$CONH_2$		+26.6	−71.8	+220.4
		(+275.0, *amide*)		
3-COOH		+28.2	−71.8	+218.8
3-COOMe		+29.2	−71.7	+218.8
3,5-$(CF_3)_2$		+40.0	−73.4	+211.3
3-F-4-COOH		+35.9	−74.3	+212.0
2-$COHN_2$		+43.9	−68.2	+212.9
		(+267.2, *amide*)		
2-$CONH_2$	(fully deuteriated Me)	+44.3	−68.3	+212.4
		(+267.2, *amide*)		
2-COOH		+68.6	−61.8	+205.4
2-F-4-COOH		+46.2	−73.4	+210.2



0.4 M in DMSO
+ $Cr(acac)_3$

(u)

R^1	R^2	R—N=	=N—	NR_2	$CONH_2$
Me	Me	+28.8	−72.6	+218.2	+276.2
Me	Et	+29.5	−71.5	+205.1	+276.2
Me	Pr	+29.3	−72.1	+206.2	+276.2
Me	i-Pr	+30.9	−70.8	+196.3	+276.2
Me	t-Bu	+31.5	−72.6	+189.7	+276.2

Table 28. —*cont.*

Compound		Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane				Notes
Me	$(CH_2)_{11}$		+29.7	−72.0	+207.1	+276.2	
Me	CH_2Ph		+25.4	−72.8	+207.0	+275.9	
Et	Et		+31.6	−70.0	+193.4	+276.3	
i-Pr	i-Pr		+33.7	−68.6	+178.0	+276.3	
Me	CH_2CH_2OH		+29.4	−72.8	+209.4	+276.1	
Me	CH_2CF_3		+11.6	−75.2	+225.4	+275.5	
Me	CH_2OH		+20.2	−74.5	+195.3	+275.8	
Et	CH_2OH		+26.6	−71.2	+191.0	+276.0	
Me	COMe		−25.4	−73.9	+166.2	+274.7	
Me	OMe		−2.2	−76.9	+150.7	+273.5	
Triazene structure (imino-azo type)							
$R_2C{=}N{-}N{=}N{-}R$		various	−87 to −22		(C=N)		(s)
			−122 to −40		(—N=)		(s)
			+81 to +92		(=N—R)		(s)
Tetrazene structure							
$R_2N{-}N{=}N{-}NR_2$		in solution	*ca.* −35		(N=N)		(s)
			ca. +220		(NR_2)		(s)

(a) See ref. 5, pp. 563–569, and references therein.

(b) Data from ref. 31, 4.33 MHz high-precision ^{14}N spectra, +35 ± 0.3°C, concentric spherical sample-reference containers in order to eliminate bulk susceptibility effects, Lorentzian lineshape fitting, neat nitromethane as reference.

(c) Data from ref. 332, ^{15}N double label, 20.29 MHz ^{15}N MAS and powder spectra, references to NH_4^+ in aqueous NH_4NO_3, but reported vs liquid ammonia standard taken at +23.8 ppm from the standard employed; in recalculation according to scheme II (Table 1), we retrieved the experimental values and then used the shielding value of +359.6 ppm for the actual reference with respect to neat nitromethane (Table 2); there are two non-equivalent sites of the molecule within the crystal lattice.

(d) Data from ref. 412, 20.28 MHz ^{15}N CPMAS spectra, referenced to solid NH_4Cl, but reported vs neat nitromethane by using a conversion constant (+352.5 ppm) which pertains to aqueous NH_4Cl; this is erroneous, since the shielding for solid NH_4Cl is +341.0 ppm (uncorrected) with

respect to neat nitromethane (Table 2). We retrieved the experimental values and recalculated the latter using the proper constant. The 4-OH derivative shows two non-equivalent positions within the crystal lattice.

(e) Data from ref. 1197, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(f) Data from ref. 722, ^{15}N doubly labelled azo moiety, 10.095 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(g) Data from ref. 728, 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(h) Data from ref. 548, 40.55 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent.

(i) Data from ref. 587, details as in footnote (f).

(j) Data from ref. 586, ^{15}N-monolabelled sample, 20.3 MHz ^{15}N spectrum, other details as in footnote (g).

(k) Data from ref. 854, 20.28 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(l) Data from ref. 893, 9.1 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; originally reported vs liquid ammonia taken at +380.2 ppm from neat nitromethane.

(m) See ref. 5, p. 568, and references therein.

(n) Data from ref. 897, 30.414 MHz ^{15}N spectra, field parallel to sample tube, referencing as in footnote (k).

(o) Data from ref. 1198, 36.5 MHz ^{15}N INEPT spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(p) Data from ref. 574, details as in footnote (n); solvent not reported, but the experimental value for perfluoroazoxybenzene indicates that the solvent was the same as in footnote (n), i.e. liquid SO_2 at −80°C.

(q) Data from ref. 1062, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(r) Data from ref. 30, details as in footnote (b); the substance is a dimer of the corresponding nitroso compound, Bu^{t}NO, in equilibrium with the latter, and both the components are visible in the nitrogen NMR spectra.

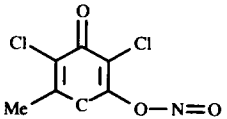
(s) See ref. 5, pp. 570–573, and references therein.

(t) Data from ref. 853, 10.095 MHz ^{15}N spectra, field perpendicular to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; $Cr(acac)_3$ added as a relaxation reagent, with exception of the cases marked with an asterisk (*); at concentrations of 3% w/v, ^{15}N doubly and singly labelled samples were employed.

(u) Data from ref. 806, 25.36 MHz ^{15}N spectra, referenced originally to *internal* nitromethane (0.25 M in DMSO solvent employed), −2.0 ppm from neat nitromethane (Table 26); the conversion does not involve bulk susceptibility effects, because of the internal standard used, but may be affected by interactions between nitromethane and the other solutes.

Table 29. Nitrogen shieldings in some nitroso compounds, nitrosamines, nitrites and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Bu^t—N=O	in n-hexane,		(a)
	2.0 M	−591.9	
	1.5 M	−590.8	
	1.0 M	−590.5	
	0.5 M	−590.5	
	in CCl_4,		(a)
	2.0 M	−592.8	
	1.5 M	−592.3	
	1.0 M	−591.8	
	0.5 M	−591.5	
	in MeOH,		(a)
	1.5 M	−595.2	
	0.5 M	−595.6	
	in DMSO, 1.0 M	−600.7	(a)
Ph—N=O	various	*ca.* −530	(b)
N-Me-2-nitroso-4,6-dinitroaniline	in $CDCl_3$	−485.0 (NO)	(c)
Bu^t—O—N=O	0.5 M in		(d)
(100% *trans*)	$CHCl_3$	−207.16	
	DMSO	−207.12	
	benzene	−205.82	
	Bu^tOH	−204.92	
	CCl_4	−202.43	
	n-hexane	−201.77	
	Et_3N	−201.74	
	Et_2O	−201.63	
	MeOH	−183.07	
	CF_3CH_2OH	−181.44	
Bu^n—O—N=O	0.5 M in		(d)
(*cis*, *trans*)	DMSO	−198.80	

	Et_2O	−190.62	
	CCl_4	−189.76	
Me—O—N=O	in MeCN	−184	(e)
	solvent not reported	−220.1	(f)
Bu^t—S—N=O	0.75 M in n-hexane	−452.4	(g)
$NaNO_2$	0.3 M in H_2O	−227.6	(h)
HONO	in 0.1 M HCl	−180.5	(h)
$Na^+[Co(NO_2)_6]^-$	in H_2O	−91	(i)
cis-$[Co(NO_2)_2(en)_2]^+$	in H_2O	−83.9	(j)
trans-$[Co(NO_2)_2(en)_2]^+$	in H_2O	−93.9	(j)
cis-$[CoCl(NO_2)(en)_2]^+$	in H_2O	−69.9	(j)
trans-$[CoCl(NO_2)(en)_2]^+$	in H_2O	−67.4	(j)
$Na_3[Rh(NO_2)_6]$	in aqueous HCl	−88	(k)
$[Rh(NO_2)_x(H_2O)_{6-x}]^{(3-x)+}$	in aqueous HCl	−44	(k)
$Na_3[Ir(NO_2)_4Cl_2]$	in H_2O	−50.8	(l)
$Na_3[Ir(NO_2)_6]$	in H_2O	−52.4	(l)

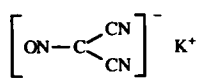
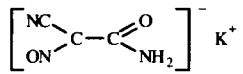
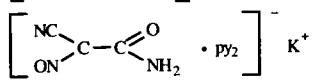
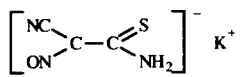
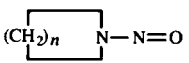
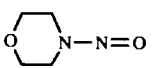
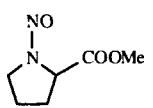
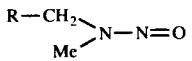
		CN	NO	
	10% in H_2O	+124	−171	(m)
	in H_2O	+130	−195	(n)
	10% in MeOH	+116	−188	(m)
	10% in EtOH	+105	−201	(m)
	in EtOH	+111	−195	(n)
	5% in Pr^nOH	+94	−116	(m)
	4% in Pr^iOH	(+73)??	−379	(m)
	3% in Bu^tOH	(+73)??	−411	(m)

Table 29. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	in H_2O	+88	−210	(n)
	in pyridine	?	−435	(n)
	in H_2O	+85	−225	(o)
	in acetone	+130	−125	(o)
		N	NO	
$Me_2N-N=O$	in acetone-d_6	+148.7	−155.2	(p)
	in $CDCl_3$	+149.7	−154.9	(e)
				
$n = 2$	in Et_2O	+180.6	−280.5	(p)
$n = 3$	in acetone-d_6	+149.9	−160.1	(p)
$n = 4$	in $CDCl_3$	+123.8	−154.0	(p)
		+123.7	−154.9	(e)
$n = 5$	in $CDCl_3$	+133.5	−151.6	(p)
	in $CDCl_3$	+142.1	−153.6	(p)
	in acetone			
	(*Z*, 50%)	+118.6	−152.1	
	(*E*, 50%)	+119.1	−157.9	(q)



R		N	NO	
CH_2CH_2COOMe	in $CDCl_3$	+141.0	−159.4	(q)
$CH_2CH_2CH_2COOMe$	in $CDCl_3$	+139.1	−156.3	(q)
COOMe	(*Z*, 40%) in $CDCl_3$	+147.0	−157.0	(q)
	(*E*, 60%)	+149.3	−162.4	
$CO(NMe)CH_2COOMe$	(*Z*, 50%) in $CDCl_3$	+145.3	−153.9	(q)
	(*E*, 50%)	+148.0	−159.4	(q)
COOH	(*Z*, 50%) in aqueous	+142.1	−152.0	(q)
	(*E*, 50%) acetone	+144.5	−158.2	(q)
CH_2CONH_2	(*E*, *Z*) in	–	−161.3	(r)
	CD_3OD/D_2O (1 : 1)	–	−165.2	(r)
CN	(*E*, *Z*) in	+154.9	−156.4	(r)
	CD_3OD/D_2O (1 : 1)	+149.3	−161.3	(r)

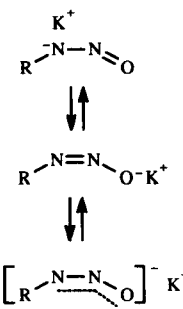
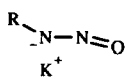
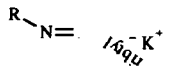
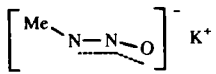
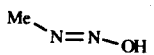
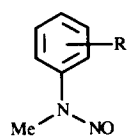
		N	NO	
$MeNH—N{=}O$	in Et_2O	–	−171.7	(s)
	in DMSO,			
	R = Me	+42.4	−133.0	(s)
	R = Et	+36.9	−128.9	(s)
	R = Pr^n	+25.3	−127.4	(s)

Table 29. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
		N	NO	
	in DMSO,			
	R = Me	+18.8	−182.8	(s)
	R = Pr^n	?	−153.5	(s)
	in DMSO,			
	R = Me	+18.8	−182.8	(s)
	R = Pr^n	?	−153.5	(s)
	in CD_3OD	+34.1	−186.8	(s)
	in CD_3OD	+33.8	−187.2	(s)
	33% v/v in $CDCl_3$			(t)
R		N	NO	
4-OMe		+129.9	−161.3	
4-Me		+129.1	−163.5	
4-Pr^i		+129.0	−164.0	
3-Me		+128.6	−164.9	
H		+128.5	−165.4	
4-F		+130.1	−165.0	
3-OMe		+128.7	−165.9	
4-Cl		+130.1	−166.1	

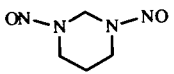
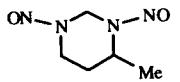
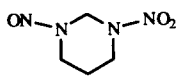
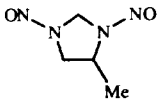
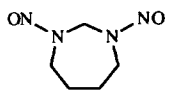
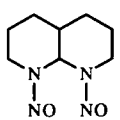
4-Br		+130.0	−166.1	
3-F		+129.2	−167.3	
3-Cl		+129.5	−167.5	
3-Br		+129.8	−167.5	
3-CF_3		+129.8	−168.4	
4-CF_3		+129.2	−169.9	
3-NO_2		+129.8	−169.6	
4-NO_2		+128.5	−173.6	
		N	NO	
	in DMSO			(u)
	anti–anti	+131.1	−169.1	
	anti–(syn)	+133.2	−169.9	
	(anti)–syn	+134.8	−166.1	
	syn–syn	+137.7	−165.1	
	in DMSO			(u)
	anti–anti	+132.9	−165.0	
	(anti)–anti	+123.2	−160.4	
	syn–(anti)	+133.3	−162.7	
	(syn)–anti	+127.5	−157.6	
	anti–(syn)	+135.6	−161.4	
	(anti)–syn	+128.5	−160.4	
	syn–(syn)	+137.3	−158.4	
	(syn)–syn	+131.5	−156.5	
	in DMSO			(u)
	anti	+134.9	−158.4	
	syn	+139.2	−165.6	
	in DMSO			(u)
	anti–anti	+135.9	−168.7	
	anti–(syn)	+136.7	−169.7	

Table 29. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	(*anti*)–*syn*	+137.8	−169.7	
	syn–*syn*	+138.2	−169.1	
	in DMSO			(u)
	anti–(*anti*)	+136.8	−169.4	
	(*anti*)–*anti*	+127.4	−169.4	
	syn–(*anti*)	+137.6	−169.9	
	(*syn*)–*anti*	+125.3	−169.9	
	anti–(*syn*)	+139.8	−168.9	
	(*anti*)–*syn*	+126.6	−168.9	
	syn–(*syn*)	+139.9	−170.3	
	(*syn*)–*syn*	+127.2	−168.3	
	in DMSO			(u)
	anti–*anti*	+128.2	−166.5	
	anti–(*syn*)	+130.0	−158.1	
	(*anti*)–*syn*	+133.5	−164.7	
	syn–*syn*	+136.7	−165.6	
 (*trans* ring junction)	in DMSO			(v)
	anti–*anti*	?	−173.6	
	anti–(*syn*)	?	−169.6	
	(*anti*)–*syn*	?	−156.8	
	syn–*syn* (*skew*)	?	−168.0	
	in $CDCl_3$			(v)
	anti–*anti*	?	−173.2	
	anti–(*syn*)	?	−169.8	
	(*anti*)–*syn*	?	−157.4	
	syn–*syn* (*skew*)	?	−167.1	

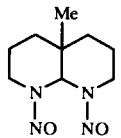
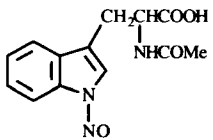
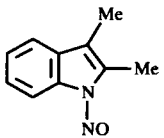
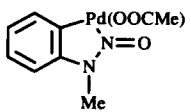
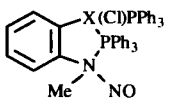
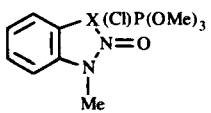
 (*trans* ring junction)	in DMSO			(v)
	anti–anti	?	−185.0	
	anti–(syn)	?	−171.0	
	(anti)–syn	?	−153.7	
	syn–syn (skew)	?	−159.3, −161.3	
	in $CDCl_3$			(v)
	anti–anti	?	−185.7	
	anti–(syn)	?	−172.7	
	(anti)–syn	?	−155.1	
	syn–syn (skew)	?	−161.1, −163.3	
	in $DMSO/H_2O$			(w)
	(*E*, 65%)	+100.7	−169.9	
	(*Z*, 35%)	+101.1	−184.6	
	in $CHCl_3$			
	(*Z*, 100%)	+100.8	−183.0	(w)
	in $CDCl_3$		−34.7 (NO)	(x)
	in $CDCl_3$			
	X = Pt		−164.4 (NO)	(x)
	X = Pd		−156.9 (NO)	(x)
	in $CDCl_3$			
	X = Pt		−40.9 (NO)	(x)
	X = Pd		−58.2 (NO)	(x)

Table 29. —*cont.*

(a) Data from ref. 30, high-precision ^{14}N spectra, 4.33 MHz, referenced to neat nitromethane, + 35°C ± 0.3, lineshape fitting, differential saturation CW technique, concentric spherical sample/reference containers in order to eliminate bulk susceptibility effects.

(b) See ref. 5, pp. 574–590, and references therein.

(c) Data from ref. 360, 10.095 MHz ^{15}N spectrum, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(d) Data from ref. 31, details as in footnote (a).

(e) Data from ref. 1176, 25.35 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(f) Data from ref. 1188, spectrometer not reported, referenced to 8 M HNO_3, + 14.5 ppm from neat nitromethane (Table 2), conversion scheme II (Table 1); originally reported relative to liquid ammonia reference, taken at + 366 ppm from the standard employed.

(g) Data from ref. 89, details as in footnote (a).

(h) See footnote (b).

(i) Data from ref. 1199, 14.46 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to NO_3^- in saturated aqueous NH_4NO_3, + 4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); 0.1–1.1 M solutions, aged for 5 min to 4 h; additional signal of free nitrite ion was observed at − 231 ppm.

(j) Data from ref. 1200, ^{15}N-labelled NO_2^-, 8.104 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to saturated aqueous $NaNO_2$, − 228.9 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 4); Na-aspartate gegenion, en = ethylenediamine ligand.

(k) Data from ref. 1201, low-precision ^{14}N spectra, referenced originally to aqueous $NaNO_3$, *ca.* + 4 ppm from neat nitromethane.

(l) Data from ref. 479, 30.42 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to 1 M $NaNO_3$, + 3.5 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(m) Data from ref. 1202, 14.46 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to NO_3^- in saturated aqueous NH_4NO_3, + 4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); the sharp resonances observed at + 73 ppm are probably those of N_2 dissolved in the samples (see Table 31).

(n) Data from ref. 1203, low-precision ^{14}N spectra, 14.4 MHz, reference not reported, but the resonance of neat pyridine, at + 52 ppm in the original spectrum, + 62 ppm from neat nitromethane according to Table 2, was used here for recalculation.

(o) Data from ref. 1204, details as in footnote (m).

(p) Data from ref. 892, ^{15}N-labelled NO group, 20.28 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; originally reported relative to liquid ammonia reference, taken at + 380.22 ppm from nitromethane; this is erroneous, since latter value was obtained (Table 2) under conditions where the field was perpendicular to the sample tube.

(q) Data from ref. 1074, 25.4 MHz ^{15}N spectra, field parallel to sample tube, $Cr(acac)_3$ added as a relaxation reagent, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; original assignments are erroneously reversed as far as the amino and nitroso moieties are concerned.

(r) Data from ref. 1205, 18.25 MHz ^{15}N spectra, field parallel to sample tube, originally referenced to 0.1 M HNO_3, +6.2 ppm from neat nitromethane, and originally recalculated to the latter, uncorrected for bulk susceptibility effects.

(s) Data from ref. 837, double ^{15}N-labelling, 20.28 MHz ^{15}N spectra, field parallel to sample tube, referred originally to external formamide, but reported vs liquid ammonia; no conversion constant was reported. We use a value of +381.9 ppm for ammonia vs neat nitromethane for recalculation (see Table 2), conversion scheme IIb (Table 1).

(t) Data from ref. 1206, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(u) Data from ref. 373, 20.3 MHz ^{15}N spectra, $Cr(acac)_3$ added as a relaxation reagent, referenced to *internal* nitromethane (solutions in DMSO), −2.0 ppm from neat nitromethane (Table 2).

(v) Data from ref. 1207, 20.28 MHz, 30.4 MHz, 36.5 MHz and 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to formamide in DMSO, +264.7 ppm from neat nitromethane (Table 2), conversion scheme IVd (Table 1); the data were reported originally vs liquid ammonia reference, taken at +108.5 ppm from the actual standard employed.

(w) Data from ref. 1208, 25.3 MHz ^{15}N spectra, other details as in footnote (t).

(x) Data from ref. 1209, ^{15}N labelled NO moiety, 20.3 and 25.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

Table 30. Nitrogen shieldings in nitrogen oxides, nitrogen–oxygen ions and related species

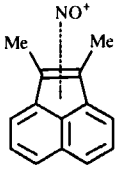
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
$\overset{-}{N}=\overset{+}{N}=O$		N	NO	(a)
	gaseous, 10^5 Pa	+147.3	+235.5	
	adsorbed on Na–Y zeolite, 293 K, 220 μmol g^{-1}	+150.6	+228.8	
	adsorbed on H–Y zeolite, 293 K, 145 μmol g^{-1}	+146.0	+205.6	
	adsorbed on H-ZSM-5 zeolite, 500 μmol/g, 293 K	+120.4	broad	
	353 K	+138.8	+191.2	
	adsorbed on H-ZSM-5 zeolite, 293 K, 180 μmol g^{-1} + 170 μmol g^{-1} CO	+132.4	+227.9	
	adsorbed on 10% H_3PO_4/SiO_2 catalyst, 293 K, 80 μmol g^{-1}	+147.2	+234.2	
	adsorbed on γ-Al_2O_3, 293 K, 120 μmol g^{-1}, pretreated in vacuum at			
	473 K for 4 h	+146.8	+230.2	
	773 K for 8 h	+149.2	+219.5	
	873 K for 8 h	+148.3	+213.0	
NO^+	in 50% D_2SO_4	+28		(b)
	in 98% H_2SO_4	+5		(b)
	in FSO_3H	−1		(b)
$NO^+ AlCl_4^-$	in liquid SO_2, −65°C	+2.6		(c)
	in liquid SO_2, −70°C	+399.1		(c)
N_2O_3	neat liquid	−60 (NO_2)		(d)
		−300 (NO)		(d)
N_2O_4	various	+10 to +20		(d)

Table 30. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
N_2O_5	various	+48 to +64	(d)
	in MeCN	+62	(e)
	in CF_3COOH	+63	(e)
	in $(CF_3CO)_2O$	+66	(e)
NO_2^+	various	*ca.* +133	(d)
$NO_2^+[Sn(OOCCF_3)]^-$	in $MeNO_2$	+124	(e)
HNO_3	neat liquid	+42.5	(d)
	in CF_3COOH	+45	(e)
	in $(CF_3CO)_2O$	+66	(e)
HNO_2	aqueous HCl	−180 to −200	(d)
	in 3–50% D_2SO_4	−183 to −193	(b)
$H_2N_2O_2$	aqueous	*ca.* −32	(d)
$NO_3^-Na^+$	0.3 M in H_2O	+3.5	(d)
$NO_2^-Na^+$	0.3 M in H_2O	−227.6	(d)

(a) Data from refs 1210 and 1211, 30.42 MHz ^{15}N spectra, 60% ^{15}N enrichment at both sites, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(b) Data from ref. 714, ^{15}N-labelled samples, 20.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to liquid NH_3, +381.9 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(c) Data from ref. 1212, referenced to neat nitromethane, uncorrected for bulk susceptibility effects, other experimental details not reported.

(d) See ref. 5, pp. 587–590, and references therein.

(e) Data from ref. 1195, 7.2 MHz ^{14}N spectra, field perpendicular to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

Table 31. Nitrogen shieldings in dinitrogen and its complexes, diazenido complexes and related structures

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
N_2 (dinitrogen)	gaseous, 300 K	+74.2		(a)
	in cyclohexane		+70.2	(b)
	in n-pentane	+71.7		(c)
	in mineral oil	+71.5		(c)
	in acetone,			
	35°C		+70.5	(b)
	−20 to +25°C	+71.5	(+71.2)	(c)
	−40°C	+71.7		(c)
	−60°C	+71.8		(c)
	in DMSO	+70.6	(+69.6)	(c)
			+69.8	(b)
	in MeCN	+71.4		(c)
	in CCl_4		+69.8	(b)
	in $CHCl_3$	+71.3	(+69.9)	(c)
			+69.6	(b)
	in CH_2Cl_2	+71.7	(+70.3)	(c)
			+69.9	(b)
	in benzene		+70.4	(b)
	in toluene	+71.6		(c)
	in Et_2O		+70.6	(b)
	in dioxane		+70.2	(b)
	in tetrahydrofuran	+72.0		(c)
	in MeOH		+70.8	(b)
	in EtOH	+71.6	(+70.8)	(c)
			+70.4	(b)
	in Bu^tOH	+71.6		(c)
	in CF_3CH_2OH		+71.5	(b)
	in MeCOOH	+71.6		(c)

	in H_2O	+71.5	(+70.1) +69.6	(c, d) (b)
Dinitrogen complexes		N_α	N_β	
trans-[Mo(N$_2$)$_2$(dppe)(depe)]	in THF	+45.1	+45.1	(e)
	in THF(?), −3°C	+41.2	+41.2	(f)
trans-[Mo(N$_2$)$_2$(L)(dppe)(depe)] L	in THF			(f)
PhCN	(−3°C)	+19.6	+30.3	
p-OMe-benzonitrile	(+25°C)	+25.0	+30.2	
p-MeCO-benzonitrile	(+25°C)	−3.1	?	
trans-[Mo(N$_2$)$_2$(depe)$_2$]	in THF	+42.0	+43.4	(e)
	in THF(?), −3°C	+42.0	+43.0	(f)
	in toluene, +15°C	+42.5	+43.8	(e)
	in toluene, −30°C	+43.8	+46.1	(e)
trans-[Mo(N$_2$AlMe$_3$)(N$_2$)(depe)$_2$]	in toluene	+45.6	+45.6	(g)
trans-[Mo(N$_2$)$_2$(L)(depe)$_2$] L	in THF, +25°C			(f)
PhCN		+16.4	+31.0	
p-OMe-benzonitrile		+24.0	+30.9	
trans-[Mo(N$_2$)$_2$(dppe)$_2$]	in THF	+43.1	+42.8	(e)
	in THF(?), −3°C	+43.1	+42.8	(f)
	in toluene, −40°C	+45.1	+45.1	(e)
trans-[Mo(N$_2$AlMe$_3$)(N$_2$)(dppe)$_2$]	in toluene	+45.4	+45.4	(g)
trans-[Mo(N$_2$)$_2$(L)(dppe)$_2$] L	in THF(?), −3°C			(f)
MeCN		+31.2	+34.0	
n-PrCN		+32.2	+35.9	

Table 31. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
PhCN		+24.0	+33.0	
p-OMe-benzonitrile		+28.6	+33.7	
p-F-benzonitrile		+24.8	+35.1	
p-MeCO-benzonitrile		+7.0	+34.8	
trans-[$Mo(N_2)_2(L)(PMe_2Ph)_3$] L	in THF/benzene (9:1 v/v)			(i)
N-Me-imidazole		+37.4	+50.3	
4-Me-pyridine		+37.7	+51.7	
3-Me-pyridine		+36.0 +38.4	+50.8 +55.9	
3-PPh_2-pyridine		+37.6 +38.2	+49.2 +52.2	
$PMePh_2$		+37.6	+44.7	
$P(OMe)_3$		+42.9	+45.1	
$Ph_2PCH_2CH_2SMe$		+42.7	+46.8	
trans-[$W(N_2)_2$(dppe)(depe)]	in THF	+59.4	+47.4	(e)
trans-[$W(N_2)_2(depe)_2$]	in THF, +18°C	+63.7	+52.4	(e)
trans-[$W(N_2)_2(dppe)_2$]	in toluene, −40°C	+66.6	+55.5	(e)
	in THF(?), −3°C	+60.1	+48.6	(f)
trans-[$W(N_2AlMe_3)(N_2)(dppe)_2$]	in toluene	+64.3	+82.2	(g)
trans-[$W(N_2)_2(L)(dppe)_2$] L	in THF(?), −3°C			(f)
MeCN		+42.3	+55.5	

n-PrCN		+43.4	+56.3	
PhCN	(+25°C)	+28.1	+56.3	
trans-$[W(N_2)_2(PEt_2Ph)_4]$	in THF	+62.1	+30.5	(h)
trans-$[\{W(N_2)_2(PEt_2Ph)_4\}_2(\mu\text{-}N_2)]$	in THF	+64.6	+44.9	(h)
			+21.3 (μ-N)	(h)
$[W(\eta^6\text{-}C_6H_5PEt_2)(N_2)(PEt_2Ph)_2]$	in THF	+50.9	−9.0	(h)
$[\{W(N_2)_2(PPr^n_2Ph)_3\}_2(\mu\text{-}N_2)]$		+66.7	+48.1	(h)
			+25.9 (μ-N)	(h)
$[W(\eta^6\text{-}C_6H_5PPr^n_2)(N_2)(PPr^n_2Ph)_2]$	in THF	+54.3	+7.2	(h)
trans-$[ReCl(N_2)_2(dppe)_2]$	in CH_2Cl_2	+93.2	?	(e)
trans-$[ReCl(N_2AlMe_3)(dppe)_2]$	in toluene	+88.0	+127.3	(g)
trans-$[ReCl(N_2)_2(dmtpe)_2]$	in CH_2Cl_2	+91.4	+69.1	(e)
trans-$[ReCl(N_2)_2(PMe_2Ph)_4]$	in THF	+86.2	+60.7	(e)
	in toluene, −40°C	+87.2	+63.9	(e)
trans-$[ReCl(N_2AlMe_3)(PMe_2Ph)_4]$	in toluene	+85.4	+129.8	(g)
$[ReCl(N_2)(CO)\{C(OH)Me\}(PPh_3)_2]$	in THF	+111.2	?	(e)
$[Ru(NH_3)_5(N_2)]Br_2$	in HCl_{aq}	+81.3	+43.8	(e)
mer-$[OsCl_2(N_2)(PMe_2Ph)_3]$	in THF	+120.2	+65.2	(e)
mer-$[OsCl_2(N_2AlMe_3)(PMe_2Ph)_3]$	in toluene	+100.6	+136.2	(g)
mer-$[OsHCl(N_2)(PMe_2Ph)_3]$	in THF	+121.0	+67.9	(e)
mer-$[OsHBr(N_2)(PMe_2Ph)_3]$	in THF	+122.6	+67.3	(e)
mer-$[OsCl_2(N_2)(PEt_2Ph)_3]$	in THF	?	+63.4	(e)
mer-$[OsBr_2(N_2)(PEt_2Ph)_3]$	in THF	?	+62.8	(e)
trans-$[RhCl(N_2)\{P(C_6H_{11})_3\}_2]$	in CH_2Cl_2	+90.7	+59.2	(e)
$[Cl_5Nb(N_2)ReCl(PMe_2Ph)_4]$	in CH_2Cl_2	+74.3	+8.7	(g)
$[Cl_5Ta(N_2)ReCl(PMe_2Ph)_4]$	in CH_2Cl_2	+76.7	+24.2	(g)
$[TiCl_4\{(N_2)ReCl(PMe_2Ph)_4\}]$	in CH_2Cl_2	+76.7	+53.2	(g)
$[ZrCl_4\{(N_2)ReCl(PMe_2Ph)_4\}]$	in CH_2Cl_2	+75.9	+95.0	(g)
$[HfCl_4\{(N_2)ReCl(PMe_2Ph)_4\}]$	in CH_2Cl_2	+75.4	+96.8	(g)
$[(THF)Cl_4Ti(N_2)ReCl(PMe_2Ph)_4]$	in CH_2Cl_2	+68.1	+19.0	(g)

Table 31. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
Hexa-coordinate singly-bent diazenido complexes				
M—NN$^{\diagup R}$				
$[ReCl(NNCOPh)(py)(PPh_3)_2]$	in toluene	+55.9	+148.6	(j)
$[RuCl_3(NN\text{-}C_6H_4\text{-}NO_2\text{-}4)(PPh_3)_2]$	in CH_2Cl_2	+47.7	?	(j)
$[RuCl_3(NNPh)(PPh_3)_2]$	in CH_2Cl_2	+46.8	+185.6	(j)
$[RuCl_3(NN\text{-}C_6H_4\text{-}Me\text{-}4)(PPh_3)_2]$	in CH_2Cl_2	+46.4	?	(j)
$[W(NNPh)(S_2CNMe_2)_3]$	in CH_2Cl_2	+38.2	+138.0	(j)
$[MoCl(NNCOMe)(dppe)_2]$	in THF	+35.4	+123.7	(j)
$[WCl(NNCOMe)(dppe)_2]$	in THF	+32.2	+134.5	(j)
$[WBr(NNEt)(dppe)_2]$	in THF	+28.2	+164.7	(j)
$[WBr(NNH)(dppe)_2]$	in THF	+25.9	+187.1	(j)
$[WF(NNH)(dppe)_2]$	in THF	+24.6	+182.6	(j)
$[ReBr_2(NNPh)(NNHPh)(PPh_3)_2]$	in CH_2Cl_2	+3.7	+124.7	(j)
$[MoBr(NNEt)(dppe)_2]$	in CH_2Cl_2	+2.6	+153.6	(j)
$[Mo(PhCN)(NNEt)(dppe)_2][BPh_4]$	in CH_2Cl_2	−13.7	+134.2	(j)
Penta-coordinate singly-bent diazenido complexes				
M—NN$^{\diagup R}$				
$[Fe(CO)_2(NNPh)(PPh_3)_2][PF_6]$	in CH_2Cl_2, 0°C	−15.6	+104.2	(j)
$[Ir(NNPh)(dppe)_2][PF_6]_2$	in CH_2Cl_2, 0°C	−46.4	+38.2	(j)
$[Os(CO)_2(NNPh)(PPh_3)_2][PF_6]$	in CH_2Cl_2, −10°C	−58.5	+21.4	(j)
$[IrCl(NNPh)(PPh_3)_3][BF_4]$	in CH_2Cl_2, −30°C	−59.0	+22.9	(j)
$[IrCl(NNPh)(PMePh_2)_3][BF_4]$	in CH_2Cl_2, 0°C	−64.0	+23.6	(j)
$[OsH(CO)(NNPh)(PPh_3)_3]$	in CH_2Cl_2, 0°C	−98.9	+35.5	(j)
$[RhCl(NNPh)(PMePh_2)_3][PF_6]$	in CH_2Cl_2, 0°C	−109.2	−4.8	(j)
$[Ru(CO)_2(NNPh)(PPh_3)_2][BF_4]$	in CH_2Cl_2, 0°C	−116.8	+25.2	(j)

Tetra-coordinate singly-bent diazenido complexes

$M—NN^{R}$

trans-[IrCl(NNPh)(PPh_3)$_2$][BF_4]	in CH_2Cl_2	+92.1	+239.0	(j)
trans-[RhCl(NNPh)(PPh_3)$_2$][PF_6]	in CH_2Cl_2, −10°C	+89.8	+225.7	(j)

Doubly-bent diazenido complexes

M^{NN-R}

[RhCl(NNPh){PhP($CH_2CH_2CH_2PPh_2$)$_2$}][PF_6]	in CH_2Cl_2	−137.9 −84.6	−40.2 +26.8	(j) (j)
[$ReCl_2$(NNCOPh)(PPh_3)$_2$][PF_6]	in CH_2Cl_2	−157.4	+72.0	(j)
[IrBr(NNPh)(dppe)$_2$][PF_6]	in CH_2Cl_2	−220.5	−158.3	(j)
[RhCl(NNPh)(dppe)$_2$][PF_6]	in CH_2Cl_2, 0°C	−224.6	−135.3	(j)
[$IrCl_2$(CO)(NNPh)(PPh_3)$_2$]	in CH_2Cl_2, −10°C	−241.4	−150.2	(j)
[$RhCl_2$(NNPh)($PEtPh_2$)$_2$]	in CH_2Cl_2	−241.0	?	(j)
[PtCl(NNPh)(PEt_3)$_2$]	in THF	−285.0	−162.0	(j)
[$RhCl_2$(NNPh)(PEt_3)$_2$]	in CH_2Cl_2	−298.4	?	(j)
[$RhCl_2$(NN-C_6H_4-NO_2-4)(PPh_3)$_2$]	in CH_2Cl_2	−327.1	?	(j)
Cyclopentadienyl-diazenido complexes				
[Cp $Re(CO)_2$(NN-C_6H_4-OMe-4)]BF_4	in acetone	+17.0*	−	(k)
		+16.1	+125.5	(k)
[Cp $Re(CO)_2$(NNPh)]BF_4	in acetone	−	+125.1*	(k)
[Cpme $Re(CO)_2$(NN-C_6H_4-OMe-4)]BF_4	in acetone	+7.3*	−	(k)
		+6.7	+123.0	
[Cpme $Re(CO_2)$(NNPh)]BF_4	in acetone	−	+118.5*	(k)
		+8.5	+118.0	(k)
[Cpme Re(CO)(MeCN)(NNC_6H_4-OMe-4)]BF_4	in acetone	+6.1*	−	(k)
		+6.9	+135.1	(k)
[Cpme Re(CO)(PMe_3)(NNC_6H_4-OMe-4)]BF_4	in acetone	+0.6*	−	(k)
		+1.9	+126.0	(k)

Table 31. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
[Cpme Re(CO){P(OMe)$_3$}(NNC$_6$H$_4$-OMe-4)]BF$_4$	in acetone	+2.0*	–	(k)
[Cp Re(CO)$_2$N$_2$)]	in acetone	+121.1*	+58.2*	(k)
[Cpme Re(CO)$_2$(N$_2$)]	in acetone	+111.0*	+28.1*	(k)
		+110.9	+26.1	(k)
[Cpme Re(CO)(PMe$_3$)(N$_2$)]	in acetone	+90.7*	–	(k)
		+90.2	+29.9	(k)
[Cpme Re(CO){P(OMe)$_3$}(N$_2$)]	in acetone	+98.2*	–	(k)
		+98.3	+30.3	(k)

(a) See ref. 5, p. 591, and references therein.

(b) Data from ref. 1213, 36.14 MHz ^{14}N spectra, field parallel to sample/reference tubes, 10 mm/4 mm, referenced to 0.3 M nitromethane in acetone, +0.77 ppm from neat nitromethane (Table 26), +35.0 ± 0.3°C, corrected for bulk susceptibility effects at that temperature and recalculated to neat nitromethane scale, Lorentzian lineshape fitting employed.

(c) Data from ref. 992, 28.9 MHz ^{14}N and 40.5 MHz ^{15}N spectra, field parallel to sample tube, +25°C, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; the numbers in parentheses come from our recalculations by introducing due corrections for bulk susceptibility effect.

(d) Data from ref. 1096, N_2 dissolved in aqueous Leu-enkephalin, 28.9 MHz ^{14}N spectra, other details as in footnote (c).

(e) Data from ref. 891, ^{15}N-labelled N_2, 18.4 MHz and 36.4 MHz ^{15}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; abbreviations, dppe = $Ph_2PCH_2CH_2PPh_2$; depe = $Et_2PCH_2CH_2PEt_2$; dmtpe = $Me_2PCH_2CH_2PMe_2$; THF = tetrahydrofuran.

(f) Data from ref. 894, 18.24 MHz ^{15}N spectra, samples prepared under argon, solvent not reported, probably tetrahydrofuran (THF), other details as in footnote (e).

(g) Data from ref. 954, details as in footnote (e).

(h) Data from ref. 1214, 36.4 MHz ^{15}N spectra, other details as in footnote (e).

(i) Data from ref. 1215, *ca.* 0.05 M solutions, details as in footnote (e).

(j) Data from ref. 900, details as in footnote (e); py = pyridine.

(k) Data from ref. 916, unlabelled and ^{15}N-labelled (*) samples, 40.5 MHz ^{15}N spectra and 28.7 MHz ^{14}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects; abbreviations, Cp = cyclopentadienyl anion, Cpme = pentamethylcyclopentadienyl anion.

Table 32. Nitrogen shieldings in ammino complexes and related structures

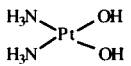
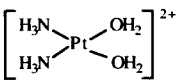
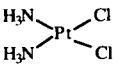
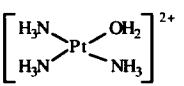
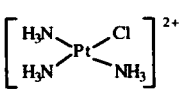
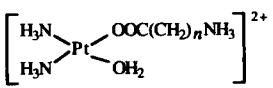
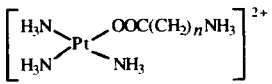
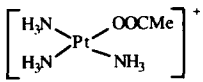
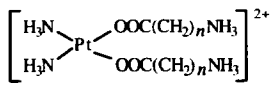
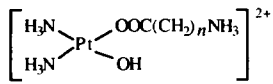
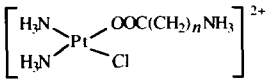
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
Pt(II) complexes				
	in D_2O	+435.9		(a)
	in H_2O	+444.8		(a)
	sat. in D_2O	+430		(b)
	in D_2O,			
	trans to O	+447.6		(c)
	cis to O	+422.8		(c)
	in D_2O,			
	trans to Cl	+428.8		(c)
	cis to Cl	+425.0		(c)
	in D_2O	*trans* to OH_2	*cis* to OH_2	(a)
$n = 1$ (glycine)		+446.6	+441.6	
$n = 2$ (β-alanine)		+446.3	+441.0	
$n = 3$ (γ-aminobutyric acid)		+446.1	+440.7	

Table 32. *—cont.*

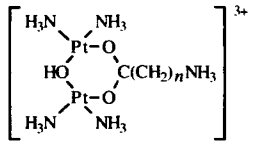
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	in D_2O			(a)
		trans to OOC	*cis* to OOC	
$n = 1$		+444.7	+424.0	
$n = 2$		+444.0	+424.1	
$n = 3$		+443.7	+424.1	
	in D_2O	*trans* to OOC	*cis* to OOC	(a)
		+443.8	+424.3	
	in D_2O			(a)
$n = 1$		+442.9		
$n = 2$		+442.5		
$n = 3$		+442.6		
	in D_2O			(a)
		trans to OH	*cis* to OH	
$n = 2$		+441.9	+437.5	
$n = 3$		+441.6	+437.5	



in D_2O (a)

trans to Cl	*cis* to Cl
+427.2	+444.2
+427.5	+443.6
+427.6	+443.3

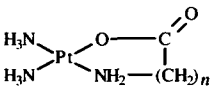
$n = 1$
$n = 2$
$n = 3$



in D_2O (a)

to OH	to OH
+436.1	+442.8
+435.9	+442.5

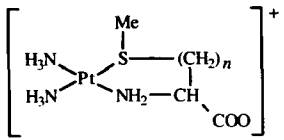
$n = 2$
$n = 3$



in D_2O (a)

trans to O	*cis* to O
+444.4	+416.2
+444.2	+420.2

$n = 2$
$n = 3$

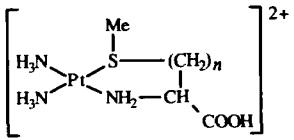
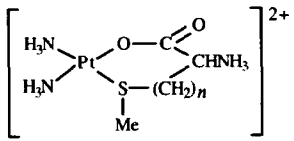
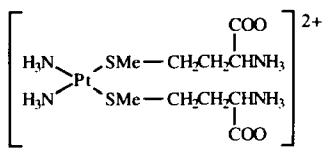


in D_2O (d)

trans to S	*cis* to S
+406.6	+426.4
+406.2	+426.4
+401.2	+421.2
+401.2	+420.9

$n = 1$ (COO *trans* to Me, pH = 5)
(COO *cis* to Me, pH = 7)
$n = 2$ (COO *trans* to Me, major)
(COO *cis* to Me, minor)

Table 32. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	in D_2O	*trans* to S	*cis* to S	(d)
$n = 1$ (COO *trans* to Me)		+406.4	+426.5	
(COO *cis* to Me)		+406.6	+426.7	
$n = 2$		+401.4	+421.3	
	in D_2O	*trans* to S	*cis* to S	(d)
$n = 1$ (isomer not assigned)		+396.6	+441.5	
(isomer not assigned)		+398.7	+443.5	
$n = 2$ (major isomer)		+399.1	+441.5	
(minor isomer)		+402.3	+441.5	
	in D_2O	+401.4 (NH_3Pt)		(d)

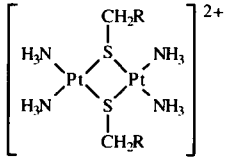
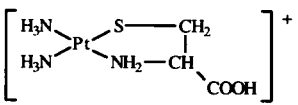
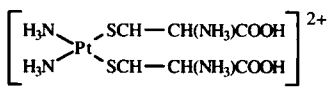
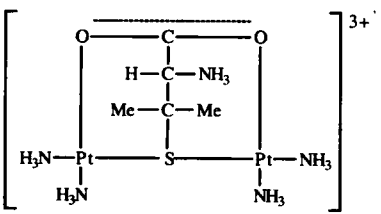
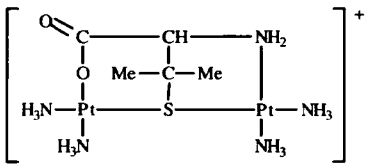
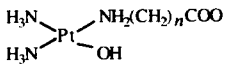
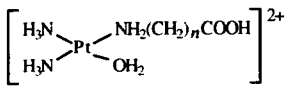
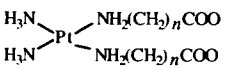
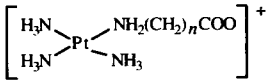
R				
	in D_2O			(e)
MeCONHCHCOOH		+401.1		
$N_3NCHCOO$		+401.8		
$HOOCCH_2NHCOCHNHCOCH_2CH_2CH(COO)NH_3$		+400.7		
$-CH_2CH(COO)NH_3$		+400.8		
		*trans* to S	*cis* to S	(e)
	in D_2O	+405.1	+425.7	
	in D_2O	+402.5		(e)
	in D_2O			(e)
	trans to S	+392.8 +401.0		
	cis to S	+437.7 +440.2		

Table 32. —*cont.*

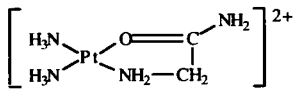
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	in D_2O			(e)
	trans to O	+447.8		
	cis to O	+394.9		
	trans to N	+430.3		
	cis to N	+405.1		
	in D_2O			(a)
		trans to OH	*cis* to OH	
$n = 2$		+437.4	+422.7	
$n = 3$		+437.6	+422.9	
	in D_2O			(a)
		trans to OH_2	*cis* to OH_2	
$n = 3$		+444.6	+422.3	
	in D_2O			(a)
$n = 2$		+423.3		
$n = 3$		+423.5		



in D_2O

(a)

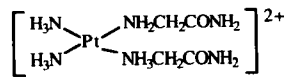
	trans to NH_2	*cis* to NH_2
$n = 1$	+426.3	+424.0
$n = 2$	+425.0	+424.2
$n = 3$	+425.2	+424.3



in D_2O

(f)

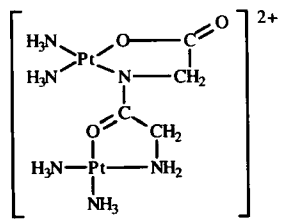
trans to NH_2	*cis* to NH_2
+423.8	+447.3



in D_2O

+424.5

(f)



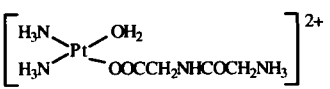
in D_2O

(f)

trans to N	+424.3
cis to N	+443.5
trans to NH_2	+423.3
cis to NH_2	+445.1

trans to OOC	*cis* to OOC
+441.1	+446.3

(f)



in D_2O

+442.9

(f)

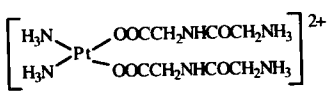
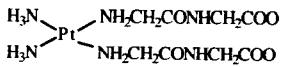
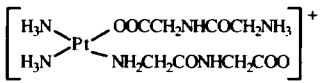
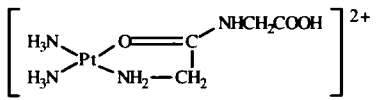
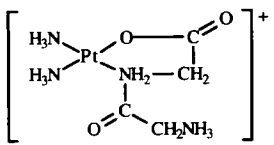
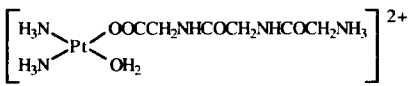
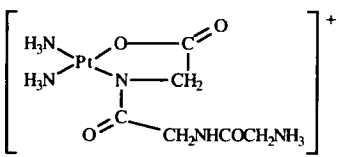
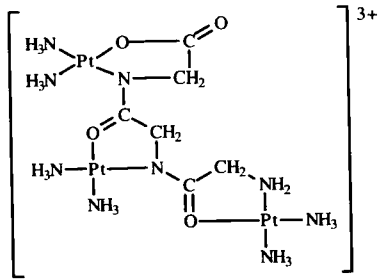


Table 32. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane		Notes
	in D_2O	+424.5		(f)
		trans to OOC	*cis* to OOC	(f)
	in D_2O	+441.6	+425.0	
	in D_2O	*trans* to NH_2	*cis* to NH_2	(f)
		+423.9	+447.6	
	in D_2O	*trans* to N	*cis* to N	(f)
		+423.5	+446.3	
	in D_2O	*trans* to OOC	*cis* to OOC	(f)
		+446.2	+444.1	
	in D_2O	*trans* to N	*cis* to N	(f)
		+423.5	+446.0	

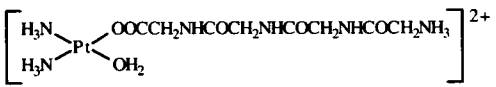


in D_2O

trans to O: +443.5, +443.7, +445.3
cis to O: +423.3, +423.9, +424.3

(f)

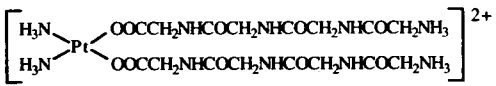
(f)



in D_2O

trans to OOC	*cis* to OOC
+441.1	+446.2

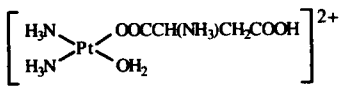
(f)



in D_2O

+441.8

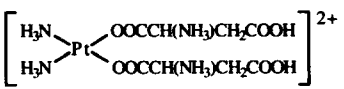
(f)



in H_2O, pH = 1.5

trans to OOC	*cis* to OOC
+441.7	+446.2

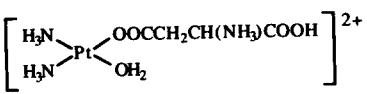
(f)



in H_2O, pH = 1.5

+442.9

(f)

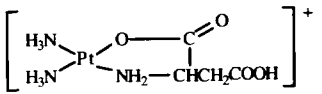
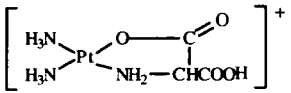
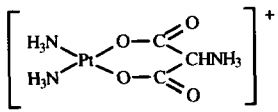
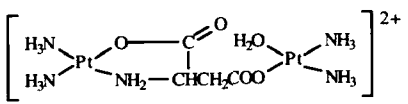
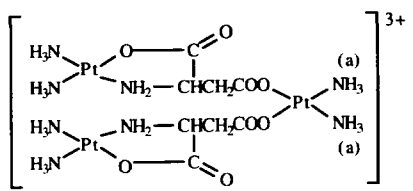


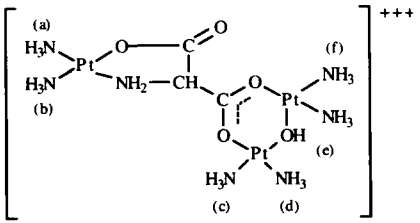
in H_2O, pH = 1.5

trans to OOC	*cis* to OOC
+441.1	+446.2

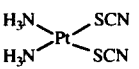
(f)

Table 32. —*cont.*

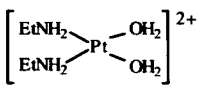
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in H_2O, pH = 1.5	*trans* to N: +423.7; *cis* to N: +443.6	(f)
	in H_2O, pH = 1.5	*trans* to N: +424.3; *cis* to N: +443.8	(f)
	in H_2O, pH = 1.5	+439.7	(f)
	in H_2O, pH = 4.5	+441.1 (*cis* to H_2O) +446.0 (*trans* to H_2O) +443.5 (*cis* to NH_2) +423.5 (*trans* to NH_2)	(f) (f) (f) (f)
	in H_2O, pH = 4.5	+442.4 (a-NH_3)	(f)



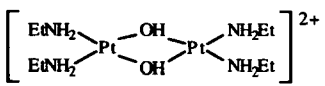
	+424.9 (a-NH_3)		(f)
	+442.0 (b-NH_3)		(f)
in H_2O,	+439.1 (c-NH_3)		(f)
pH = 5	+447.3 (d-NH_3)		(f)
	+447.3 (e-NH_3)		(f)
	+439.1 (f-NH_3)		(f)



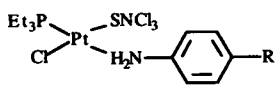
solid state, two non-equivalent positions in crystal cell			(g)
isotropic	+386.0	+399.0	
σ_{xx}	+429.9	+456.3	
σ_{yy}	+379.9	+385.1	
σ_{zz}	+348.3	+355.7	



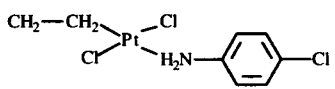
in H_2O	+346.4	(h)



in H_2O	+346.6	(h)

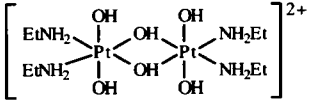
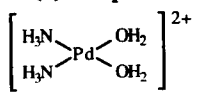
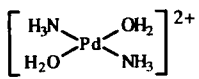
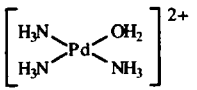
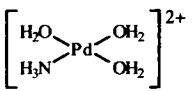
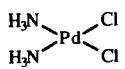
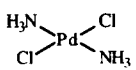


in $CDCl_3$		(i)
R = Me	+344.7	
R = Cl	+344.1	



in $CDCl_3$	+343	(i)

Table 32. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Pt(IV) complexes			
	in H_2O	+373.4	(h)
Pd(II) complexes			
	in D_2O	+431.8	(c)
	in D_2O	+417.2	(c)
	in D_2O,		
	trans to O	+431.3	(c)
	cis to O	+415.6	(c)
	in D_2O	+435.3	(c)
	in D_2O	+416.5	(c)
	in D_2O	+417.4	(c)

Co(III) complexes					
$[Co(NH_3)_6]Cl_3$		in H_2O	+423.4		(j)
$[Co(NH_3)_6](NO_3)_3$		in DMSO	+421.4		(l)
$[Co(NH_3)_5L]X_2$					
L	X		*trans*	*cis*	
CN	$MeSO_3$	in 0.01 M DCl	+401	+437	(k)
	NO_3	in DMSO	+397.8	+423.4	(l)
SCN	Cl	in 0.01 M DCl	?	+428	(k)
NO_2	$MeSO_4$	in 0.012 M $DClO_4$	+413 (unresolved)		(k)
	NO_3	in DMSO	+411	+406	(l)
NCS	$MeSO_3$	in 0.012 M $DClO_4$	+441	+420	(k)
N_3	ClO_4	in 0.012 M $DClO_4$	+449	+424	(k)
I	ClO_4	in 0.01 M DCl	+410	+432	(k)
Cl	ClO_4	in 0.012 M $DClO_4$	+440	+425	(k)
	NO_3	in DMSO	+430.3	+415.5	(l)
Br	ClO_4	in 0.01 M DCl	+435	+428	(k)
	NO_3	in DMSO	+424.5	+418.7	(l)
F	NO_3	in 0.012 M $DClO_4$	+449	+424	(k)
$OOCNH_2$	ClO_4	in 0.01 M DCl	+443	+427	(k)
OOCMe	Cl	in 0.012 M $DClO_4$	+448	?	(k)
$[Co(NH_3)_5(H_2O)](ClO_4)_3$		0.01 M in DCl	+454	+425	(k)
$[Co(NH_3)_5(H_2O)](NO_3)_3$		in DMSO	+442.4	+416.2	(l)
$[Co(H_2NCH_2CH_2NH_2)_3](NO_3)_3$		in aqueous DCl	+395.5		(l)
$[Co(H_2NCH_2CH_2NH_2)_2(H_2O)_2](NO_3)_3$		in DMSO	+404.9	+387.9	(l)
$[Co(H_2NCH_2CH_2NH_2)_2L_2]X_3$					
L	X		*trans*	*cis*	
CN	NO_3	in DMSO	+378.9	+399.5	(l)
NO_2	NO_3	in DMSO	+392.7	+392.7	(l)
$[Co(H_2NCH_2CH_2NH_2)_2(OOCCOO)](NO_3)_3$		in DMSO	+404.9	+386.6	(l)

Table 32. *—cont.*

(a) Data from ref. 920, ^{15}N-labelled ammonia, 10.1 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to NH_4^+ in 5 M NH_4NO_3 in 2 M HNO_3, +359.0 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

(b) Data from ref. 1216, 28.9 MHz ^{14}N spectra, field parallel to sample tube, referenced to neat nitromethane, uncorrected for bulk susceptibility effects.

(c) Data from ref. 1217, details as in footnote (a).

(d) Data from ref. 925, details as in footnote (a).

(e) Data from ref. 927, details as in footnote (a).

(f) Data from refs 926 and 929, details same as in footnote (a).

(g) Data from ref. 349, ^{15}N-labelled NH_3, ^{15}N CPMAS spectra, spectrometer not reported, referenced to 5.6 M aqueous NH_4Cl, +352.9 ppm from neat nitromethane (Table 2), uncorrected for bulk susceptibility effects.

(h) Data from ref. 923, ^{15}N-labelled ethylamine, 25.3 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to formamide, +268.6 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); originally reported vs fictitious ammonia standard taken at +112.6 ppm from the reference employed (the latter value corresponds to experimental conditions where the field is perpendicular to sample tube, Table 2).

(i) Data from ref. 839, ^{15}N spectra, spectrometer not reported, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(j) See ref. 5, p. 400, and reference therein.

(k) Data from ref. 1218, 100 MHz $^1H\{^{14}N\}$ INDOR spectra, field perpendicular to sample tube, referenced originally to aqueous $Co(NH_3)Cl_3$, footnote (j); low-precision measurements, ± 2 to ± 3 ppm.

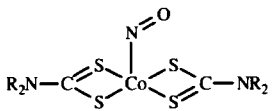
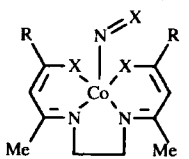
(l) Data from ref. 1219, ^{15}N-labelled NH_3 and ethylenediamine ligands, 6.06 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to aqueous $NaNO_3$, +3.5 ppm from neat nitromethane (Table 2), conversion scheme IIa (Table 1).

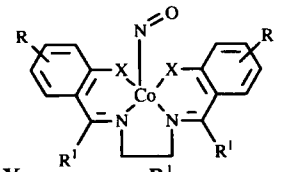
Table 33. Nitrogen shieldings in nitrosyl, thionitrosyl and nitride complexes

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
"Piano-stool" type complexes			
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NO)$	in CH_2Cl_2	−55	(a)
$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$	in CH_2Cl_2	−105	(a)
$(\eta^5\text{-}C_5H_5)Mo(SPh)_2(NO)$	in $CDCl_3$	−36	(a)
$L_3W(CO)_2(X)$	in CH_2Cl_2		(a)
(*L = 3,5-dimethylpyrazolyl*)			
X = NO		+4	
X = NS		−23	
$L_3Mo(R^1)(R^2)(X)$	in CH_2Cl_2		(a)
(*L = 3,5-dimethylpyrazolyl*)			

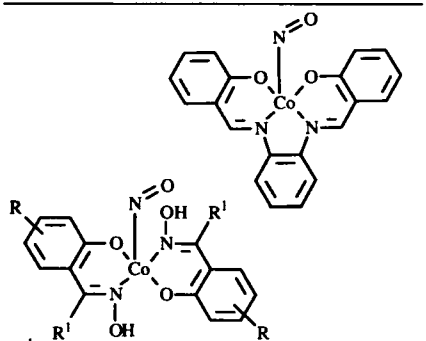
R^1	R^2	X	(NO/NS)
CO	CO	NO	−17
CO	CO	NS	−64
F	F	NO	−14
Cl	Cl	NO	−26
I	I	NO	−46
SPh	SPh	NO	−10
OPh	OPh	NO	−11
OEt	OEt	NO	−9
NHPh	NHPh	NO	−2
Cl	SPh	NO	−17
Cl	OPh	NO	−10
Cl	OEt	NO	−17
Cl	NH-C_6H_4-*p*-Me	NO	−10
Cl	NH-C_6H_4-*p*-Br	NO	−11
Cl	NHEt	NO	−10
I	NH-C_6H_4-*p*-Me	NO	−13
I	NHEt	NO	−11
I	$NHNMe_2$	NO	−7

Table 33. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
"Strongly bent" nitrosyls			
		NO groups	(b)
R = Me	in $CDCl_3$	−501.3	
R = Et	in $CDCl_3$	−500.8	
R = i-Pr	in CD_2Cl_2	−526.9	
	in DMSO	−502.6	
trans-$[Co(NO)(H_2NCH_2CH_2NH_2)_2](ClO_4)_2$			
	in acetone	−717.5; −727.6	(b)
X R		NO or NS	
O Me	in DMSO	−714.3	
	in $CDCl_3$	−521.9	
O Ph	in DMSO	−723.0	
	in CD_2Cl_2	−724.7	
S Me	in DMSO	−672.1	



X	R^1	R		NO groups	(b)
O	H	none	in CD_2Cl_2	−725.4	
			in $CDCl_3$	−726.8	
O	Me	none	in CD_2Cl_2	−710.0	
O	H	5-Bu^t	in CD_2Cl_2	−721.9	
O	H	3,5-$(NO_2)_2$	in DMSO	−820.5	
NH	H	none	in CD_2Cl_2	−734.3; −698.5	

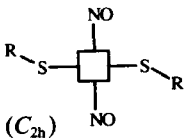


					(b)
			in DMSO	−769.7 (NO)	

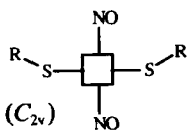
R^1	R		NO groups	(b)
H	none	in DMSO	−824.1	
Me	none	in CD_2Cl_2	−741.1	
		in $CDCl_3$	−740.3	
H	3-OMe	in CD_2Cl_2	−756.6	
		in DMSO	−817.0	
H	5-Cl	in DMSO	−828.7	
H	5-NO_2	in DMSO	−833.1	

Table 33. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Linear and slightly bent nitrosyls			
$Na_2[Fe(CN)_5(NO)]$	in H_2O	+13.5 (NO)	(b)
		+9.9 (NO)	(c)
$[FeRu_3(CO)_{12}(NO)]^-$	in CH_2Cl_2	−8.6	(d)
$Fe_2(SR)_2(NO)_4$	in CD_2Cl_2		(c)



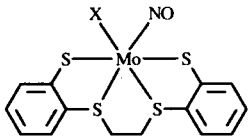
(C_{2h})



(C_{2v})

R	C_{2h}-isomer	C_{2v}-isomer
Me	−30.5	−23.1, −36.2
Et	−31.4	−25.0, −36.1
i-Pr	−30.2	−26.7, −35.7
n-Bu	−31.4	−24.7, −36.0
i-Bu	−31.3	−24.5, −35.6
t-Bu	−38.8	−31.1, −37.1
t-Bu (−53°C)	−36.6	−28.8, −35.6
Ph	−34.2	−25.9, −39.4
CH_2Ph	−32.6	−28.7, −35.4

$(Ph_3PNPPh_3)[Fe_4S_3(NO)_7]$	in CD_2Cl_2	−7.7, −36.0, −76.1 (NO)	(c)
$(Ph_3PNPPh_3)[Fe_4Se_3(NO)_7]$	in CD_2Cl_2	−7.8, −29.5, −74.8 (NO)	(c)
$Fe_4S_4(NO)_4$	in CD_2Cl_2	−12.8	(c)
$Fe_4Se_4(NO)_4$	in CD_2Cl_2	−20.5	(c)
$Mo(NO)(S_2CNR_2)_3$	in CH_2Cl_2		(e)
R = Me		+14 (NO)	
R = Et		+14 (NO)	
$Mo(NS)(S_2CNR_2)_3$	in CH_2Cl_2		(e)
R = Me		−42 (NS)	

R = Et		−39 (NS)	
	in $CDCl_3$		(f)

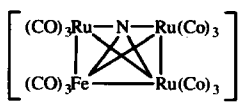
X		NO	Other nitrogen	
$NP(cyclohexyl)_3$		−41	+336	
$NPMePh_2$		−40	+334	
NO		−186	-	
$(NMe_4)_2[Mo(NO)_2(C_6H_4S_2)_2]$	in D_2O	−157 (NO)		(f)
$(PPN)[Ru(CO)_3(NO)]$	in CH_2Cl_2	−22.3 (NO)		(g)
$(PPN)[Cr(CO)_4(NO)]$	in CH_2Cl_2	−23.6 (NO)		(g)
$MeCr(CO)_4(NO)$		−2.5 (NO)		(g)
Nitrido structures				
$[FeRu_3N(CO)_{12}]^-$	in CH_2Cl_2			(d)
 "wing-tip"		−176.4		
 "hinge"		−137.3		
$[W(N)Cl_3(MeCN)]$	in CD_2Cl_2	−211.2 (N)		(h)
$[W(N)Cl_3(MeCN)]_4$	in CD_2Cl_2	−222.7 (N)		(h)
$(PPh_4)[W(N)Cl_4]$	in CH_2Cl_2	−258.8 (N)		(h)

Table 33. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
$(PPh_4)[W_2(N)Cl_{10}]$	in CH_2Cl_2	−251.0 (N)	(h)
α-Si_3N_4	solid state	+309.4 +307.6 +297.0 +284.9	(i) (i) (i) (i)
β-Si_3N_4	solid state	+306.9 +289.7	(i) (i)

(a) Data from refs 948 and 1220, 18.1 MHz ^{14}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects.

(b) Data from refs 947 and 1221, ^{15}N-labelled NO ligands, 40.5 MHz ^{15}N spectra, other details as in footnote (a).

(c) Data from refs 888, 895, 898 and 1222, ^{15}N-labelled nitrosyl ligand, 36.5 MHz ^{15}N spectra, calibration as in footnote (a).

(d) Data from ref. 1223, ^{15}N-labelled samples, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to nitromethane in CH_2Cl_2, +3.2 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); reported originally vs NH_3 standard taken at +379.6 ppm from the actual reference employed; we retrieved the original values and recalculated them as indicated above.

(e) Data from ref. 1224, details as in footnote (a).

(f) Data from ref. 1225, 19.5 ^{14}N spectra, field parallel to sample tube, referenced originally to NO_3^- in aqueous NH_4NO_3, +4.0 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1).

(g) Data from refs. 1226 and 1227, ^{15}N-labelled NO ligands, 30.4 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to nitromethane in $CHCl_3$, +3.8 ppm from neat nitromethane (Table 2), conversion scheme IIb (Table 1); reported originally vs fictitious ammonia standard taken at +379.6 ppm from the reference actually employed; we retrieved the original values and recalculated them as indicated above.

(h) Data from ref. 1228, spectrometer not specified, ^{15}N-labelled nitrido moieties, ^{15}N spectra, calibration as in footnote (a).

(i) Data from ref. 415, ^{15}N-labelled nitrides, 30.4 MHz ^{15}N MAS spectra, referenced originally to NH_4^+ in solid NH_4NO_3, +358.4 ppm from neat nitromethane, uncorrected for bulk susceptibility effects.

Table 34. Nitrogen shieldings in some vitamins, drugs and medicines

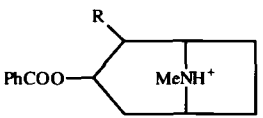
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Vitamins			
Thiamine dihydrochloride	in H_2O/D_2O (4:1)	+135.5 ($S-C=N^+$) +170.1 ($Me-C=N$) +212.5 (NH^+Me) +272.2 (NH_2)	(a)
Riboflavin		see Table 21	
Pyridoxol hydrochloride	in DMSO	+172.7	(a)
Pyridoxal hydrochloride	in DMSO	+166.9	(a)
Pyridoxamine dihydrochloride	in H_2O/D_2O (4:1)	+175.1 (NH^+) +170.1 ($CH_2NH_3^+$)	(a)
Vitamin B_{12}, cyanocobalamin, Cbl(CN)			
	in 70% EtOH		
	CN moiety	+87.2	(a)
	amide moieties	+261.7 +263.0 +264.3 +265.6 +269.9 +271.4 +273.1	(a)
	in DMSO		
	amide	+264.4	(b)
	amide	+266.3	(b)
	f-amide	+267.4	(b)
	amide	+270.0	(b)
	e-amide	+270.4	(b)

Table 34. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	b-amide	+272.8	(b)
	d-amide	+273.5	(b)
	0.01 M in H_2O		
	benzimidazole moiety		
	(ribose-bound N)	+216.0	(b)
	(Co-bound N)	+192.5	(b)
	CN moiety	+91.3	(b)
	0.01 M in 0.52 M H_2SO_4		
	benzimidazole moiety		
	(ribose-bound N)	+207.9	(b)
	(Co-bound N)	+220.8	(b)
	CN moiety	+82.6	(b)
Dicyanocobalamine, $Cbl(CN)_2$			(b)
	0.01 M in 0.1 M NaCN		
	α-CN moiety	+95.8	
	β-CN moiety	+102.6	
	benzimidazole moiety		
	(ribose-bound N)	+218.9	
	(other, pendant N)	+147.9	
	amide	+264.3	
	amide	+266.6	
	f-amide	+267.5	
	amide	+269.0	
	e-amide	+271.6	

	b-amide	+272.3	
	d-amide	+272.4	
Nicotinic acid	in DMSO	+65.4	(a)
Nicotinamide	in DMSO	+65.2 (—N=)	(a)
		+275.1 ($CONH_2$)	(a)
Panthotenic acid	in DMSO	+265.9	(a)
Calcium panthotenate	in DMSO	+262.6	(a)
Dexpanthenol	in DMSO	+264.3	(a)
p-Aminobenzoic acid	in DMSO	+315.6	(a)
Biotin	in DMSO	+290.2 (SCHCHNH)	(a)
		+299.5 (SCH_2CHNH)	(a)

Anaesthetics



in DMSO/H_2O (3:1)

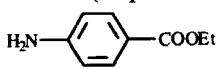
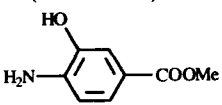
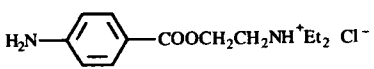
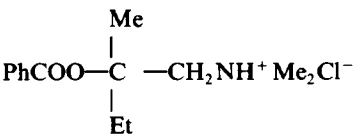
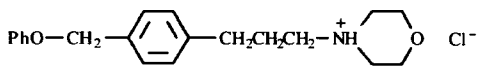
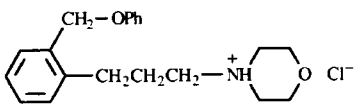
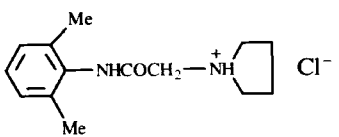
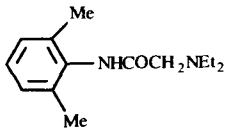
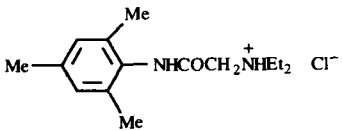
R = COOMe (cocaine hydrochloride)		+314.0	(c)
R = H (tropacocaine hydrochloride)		+309.2	(c)
	in $CDCl_3$	+317.7	(c)
	in DMSO	+310.7	
(benzocaine)			
	in DMSO	+330.4	(c)
(ortoform)			
	in DMSO	+324.3 (NH^+)	(c)
		+306.8 (NH_2)	(c)
(procaine hydrochloride)			

Table 34. *—cont.*

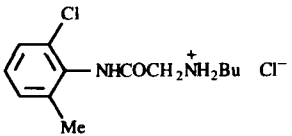
Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
 (tetracaine hydrochloride)	in DMSO	+339.9 (NH^+) +324.0 (BuNH)	(c) (c)
 (stovaine hydrochloride)	in DMSO	+325.3	(c)
 (fomocaine hydrochloride)	in DMSO/H_2O (3 : 1)	+329.0	(c)
 (ortofomocaine hydrochloride)	in DMSO/H_2O (3 : 1)	+329.0	(c)
 (pyrrocaine hydrochloride)	in $CDCl_3$	+249.5 (NHCO) +317.7 (NH)	(c) (c)



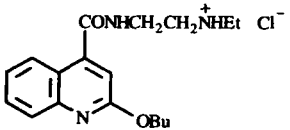
(xylocaine) — in $CDCl_3$ — +259.0 (NHCO) (c); +335.3 (NEt_2) (c)



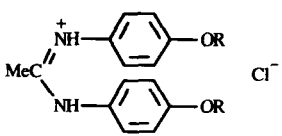
(trimecaine hydrochloride) — in $CDCl_3$ — +248.8 (NHCO) (c); +324.0 (NH) (c)



(butanilicaine hydrochloride) — in DMSO — +254.5 (NHCO) (c); +337.5 (NH_2) (c)



(cinchocaine hydrochloride) — in $CDCl_3$ — +124.6 (—N=) (c); +261.3 (NHCO) (c); +323.3 (NH) (c)

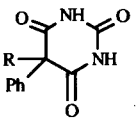
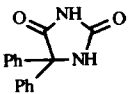
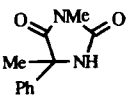
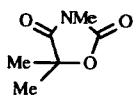
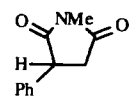
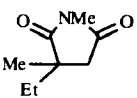


in $CDCl_3$

R = $-CH_2-CH=CH_2$ (diocaine hydrochloride) — +246.7 (c)

R = Et (fenacaine hydrochloride) — +245.3 (c)

Table 34. —*cont.*

Compound		Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
Antiepileptics				
		in DMSO R = Et (phenobarbital R = Me (heptobarbital)	 +226.7 +229.8	 (d) (d)
	(phenytoin)	in DMSO	+233.7 (CONHCO) +271.7 (CONHC)	(d) (d)
	(mephenytoin)	in DMSO	+241.0 (NMe) +281.5 (NH)	(d) (d)
	(trimethadione)	in DMSO	+244.4	(d)
	(phensuximide)	in DMSO	+210.6	(d)
	(ethosuximide)	in DMSO	+205.4	(d)

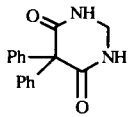
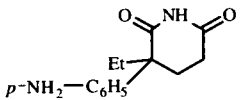
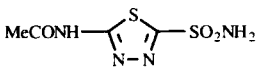
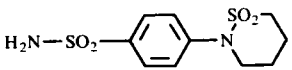
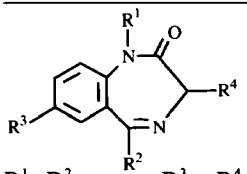
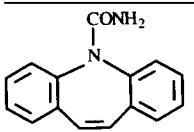
 (primidone)	in DMSO	+264.6	(d)
 (aminoglutethimide)	in DMSO	+206.9 (NH) +320.4 (NH_2)	(d) (d)
$Ph—CH_2—CONHCONH_2$ (phenacemide)	in DMSO	+231.1 (NH) +292.0 (NH_2)	(d) (d)
 (acetazolamide)	in DMSO	+241.2 (NH) +282.4 (NH_2) +15.7 (N=CNH) +58.3 ($N=CSO_2$)	(d) (d) (d) (d)
 (sultiame)	in DMSO	+266.0 (NSO_2) +284.3 (H_2NSO_2)	(d) (d)

Table 34. *—cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
	in DMSO		(d)
R^1 R^2 R^3 R^4			
Me Ph Cl H	diazepam	+52.8 (=N) +253.0 (NMe)	
Me Ph Cl $OOCCH_2CH_2COOH$	oxazepam succinate	+56.7 (=N) +244.4 (NMe)	
H Ph NO_2 H	nitrazepam	+54.4 (=N) +235.0 (NH) +12.2 (NO_2)	
H *o*-Cl-C_6H_5 NO_2 H	clonazepam	+45.5 (=N) +234.1 (NH) +12.5 (NO_2)	
 (carbamazepine)	in DMSO	+266.3 (N—CO) +302.7 ($CONH_2$)	(d) (d)
Carbamates			
Ethyl urethan	in $CDCl_3$	+307.5 (NH_2)	(e)
Meprobamate	in DMSO	+304.5 (NH_2)	(e)
Carlsoprodole	in $CDCl_3$	+308.0 (NH_2) +280.3 (NH)	(e) (e)

Diperodon (Diothane)	in DMSO	+329.0 (N)	(e)
		+274.0 (NH)	(e)
		+272.8 (NH)	(e)
Bendiocarb	in $CDCl_2$	+310.1 (NH)	(e)
Physostygmine salicylate	in DMSO	+316.5 (N)	(e)
		+310.4 (H)	(e)
		+308.3 (NH)	(e)
Carbachole	in DMSO/H_2O, 3:1	+331.1 (N^+)	(e)
		+302.1 (NH_2)	(e)
Neostygmine bromide	in DMSO/H_2O, 3:1	+321.7 (N^+)	(e)
		+308.1 (N)	(e)
Pyridostygmine bromide	in DMSO/H_2O, 3:1	+306.7 (N)	(e)
		+175.3 (ring N^+)	(e)
Pentacaine chloride	in $CDCl_3$	+311.4 (NH^+)	(e)
		+270.3 (NH)	(e)
Heptacaine chloride	in $CDCl_3$	+326.2 (NH^+)	(e)
		+286.2 (NH)	(e)
Carbisocaine chloride	in $CDCl_3$	+324.1 (NH)	(e)
		+284.8 (NH)	(e)
Analgesics and antipyretics			
Salicylamide	in DMSO	+273.8	(f)
Phenacetin	in DMSO	+247.0	(f)
Benorilate	in DMSO	+246.9	(f)
Paracematol	in DMSO	+246.8	(f)
Phenazone	in DMSO	+242.8 (NMe)	(f)
		+196.4 (CO—N)	(f)
Aminophenazone	in DMSO	+365.5 (NMe_2)	(f)
		+255.3 (NMe)	(f)
		+198.8 (CO—N)	(f)
4-Aminophenazone	in DMSO	+352.1 (NH_2)	(f)
		+351.8 (NH_2)	(f)
		+260.1 (NMe)	(f)
		+199.6 (CO—N)	(f)

Table 34. —*cont.*

Compound	Solution or state	Nitrogen shielding (ppm) referred to neat nitromethane	Notes
4-Isopropylaminophenazone hydrochloride	in DMSO	+323.5 (N^+)	(f)
		+242.6 (NMe)	(f)
		+198.6 (CO—N)	(f)
Phenylbutazone	in $CDCl_3$	+216.0	(f)
Ketazone	in $CDCl_3$	+215.7	(f)
	in DMSO	+215.1	(f)
Benzopyrazone	in $CDCl_3$	+215.0	(f)
Tribuzone	in $CDCl_3$	+215.6	(f)
Cinchophen	in DMSO	+67.7	(f)
Indomethacin	in DMSO	+206.9	(f)
Diclofenac sodium	in DMSO	+294.4	(f)
Mefenamic acid	in DMSO	+289.5	(f)
Tolfenamic acid	in DMSO	+289.1	(f)
4-Nitrofenetol	in DMSO	+10.0 (NO_2)	(f)
p-Phenetidine	in DMSO	+325.6	(f)
Salacetamide	in DMSO	+214.8	(f)
HIV and MuLV replication inhibitors			
AZT and AZU	see Table 14		

(a) Data from ref. 808, 10.095 MHz ^{15}N spectra, field perpendicular to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; *ca.* 20% w/w or saturated solutions; vitamin B_{12} spectrum was measured at 40.5 MHz, field parallel to sample tube.

(b) Data from refs. 882, 1229, 1230 and 1231, ^{15}N-labelled samples, 30.4, 40.4 and 50.7 MHz ^{15}N spectra, field parallel to sample tube, referenced originally to neat nitromethane, uncorrected for bulk susceptibility effects; reported originally vs fictitious ammonia standard taken at +380.2 ppm from neat nitromethane; structural formulae and amide group designation are given in ref. 1229.

(c) Data from ref. 778, details as in footnote (a).

(d) Data from ref. 1232, details as in footnote (a).

(e) Data from ref. 1233, details as in footnote (a); also 7.196 MHz ^{14}N spectra.

(f) Data from ref. 1234, details as in footnote (a).

Addendum on ^{14}N NQR and ENDOR

While nuclear quadrupole resonance (NQR) and electron-nuclear double resonance (ENDOR) are not quite within the scope of the present book, we present here, as was done in our earlier accounts of nitrogen NMR,[4,5] a comprehensive list of recent references in the field of ^{14}N NQR and ENDOR: 55–57, 60, 62, 63, 65, 66, 206, 307, 313, 314, 317, 431, 464, 467, 680, 748, 874, 958, 979, 993, 1235–1331.

The references quoted refer to NQR, with the exception of refs 680, 1256, 1275, 1276, 1321, which are relevant to ENDOR.

This Page Intentionally Left Blank

References

1. M. Witanowski and G. A. Webb, *Annu. Rep. NMR Spectrosc.* 1972, **5A,** 395.
2. M. Witanowski and G. A. Webb (eds), *Nitrogen NMR*, Plenum Press, London, 1973.
3. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, 1977, **7,** 117.
4. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, 1981, **11B,** 1.
5. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, 1986, **18,** 1.
6. I. Ando and G. A. Webb, *Theory of NMR Parameters*, Academic Press, London, 1983.
7. M. Schindler, *J. Chem. Phys.*, 1988, **88,** 7638.
8. U. Fleischer and M. Schindler, *Chem. Phys.*, 1988, **120,** 103.
9. M. Schindler, *J. Am. Chem. Soc.*, 1987, **109,** 5950.
10. M. Schindler, *Magn. Reson. Chem.*, 1988, **26,** 394.
11. M. Schindler, *J. Am. Chem. Soc.*, 1988, **110,** 6623.
12. R. Ditchfield, *Mol. Phys.*, 1974, **27,** 789.
13. C. Giessner-Prettre, *J. Biomol. Struct. Dyn.*, 1984, **2,** 233.
14. S. Ferchiou and C. Giessner-Prettre, *J. Magn. Reson.*, 1985, **61,** 262.
15. C. Giessner-Prettre and B. Pullman, *Quart. Rev. Biophys.*, 1987, **20,** 113.
16. D. B. Chesnut and C. K. Foley, *J. Chem. Phys.*, 1966, **84,** 852.
17. J. A. Pople, *Discuss. Faraday Soc.*, 1962, **34,** 7.
18. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski, B. T. Hamdi and G. A. Webb, *Magn. Reson. Chem.*, 1985, **23,** 166.
19. W. Schilf, L. Stefaniak, M. Witanowski and G. A. Webb, *Magn. Reson. Chem.*, 1985, **23,** 181.
20. W. Schilf, L. Stefaniak, M. Witanowski and G. A. Webb, *Magn. Reson. Chem.*, 1985, **23,** 784.
21. L. Kaczmarek, P. Nantka-Namirski, L. Stefaniak, G. A. Webb, R. Davoust and J. J. Basselier, *Magn. Reson. Chem.*, 1985, **23,** 853.
22. W. Schilf, L. Stefaniak, M. Witanowski, G. A. Webb and S. Braun, *Spectrosc. Int. J.*, 1985, **4,** 103.
23. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski and G. A. Webb, *Bull. Pol. Acad. Sci.: Chem.*, 1985, **33,** 375.
24. W. Schilf, L. Stefaniak, M. Witanowski and G. A. Webb, *J. Mol. Struct.*, 1985, **140,** 311.
25. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski and G. A. Webb, *Magn. Reson. Chem.*, 1986, **24,** 911.
26. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski and G. A. Webb, *Bull. Pol. Acad. Sci.: Chem.*, 1986, **34,** 289.
27. L. Stefaniak, M. Witanowski, G. A. Webb and W. B. Smith, *Bull. Pol. Acad. Sci.: Chem.*, 1987, **35,** 301.
28. M. Witanowski, J. Sitkowski, W. Sicińska, S. Biernat and G. A. Webb, *Magn. Reson. Chem.*, 1989, **27,** 88.
29. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski and G. A. Webb, *Bull. Chem. Soc. Jpn*, 1986, **59,** 3263.
30. M. Witanowski, J. Sitkowski, S. Biernat, B. Kamieński, B. T. Hamdi and G. A. Webb, *J. Magn. Reson.*, 1985, **63,** 354.
31. M. Witanowski, J. Sitkowski, S. Biernat, B. Kamieński, B. T. Hamdi and G. A. Webb, *Magn. Reson. Chem.*, 1985, **23,** 748.

32. M. Witanowski, J. Sitkowski, S. Biernat, L. V. Sudha and G. A. Webb, *Magn. Reson. Chem.*, 1987, **25,** 725.
33. M. Witanowski, W. Sicińska and G. A. Webb, *Magn. Reson. Chem.*, 1989, **27,** 380.
34. M. Witanowski, W. Sicińska, S. Biernat and G. A. Webb, *J. Magn. Reson.*, 1989, **83,** 351.
35. T. Asakura, H. Yoshimizu, S. Ando and I. Ando, *J. Mol. Struct.*, 1988, **168,** 135.
36. X. You and W. Wu, *Magn. Reson. Chem.*, 1987, **25,** 860.
37. T. Berstein and H. Pfeifer, *Z. Phys. Chem., Leipzig*, 1985, **266,** 94.
38. M. Comeau, M. T. Beraldin, E. C. Vauthier and S. Fliszar, *Can. J. Chem.*, 1985, **63,** 3226.
39. K. A. Jorgensen, *J. Chem. Soc. Perkin Trans. II*, 1987, 885.
40. S. Li and D. B. Chesnut, *Magn. Reson. Chem.*, 1985, **23,** 625.
41. N. F. Ramsey, *Phys. Rev.*, 1953, **91,** 903.
42. J. Kowalewski, *Annu. Rep. NMR Spectrosc.*, 1982, **12,** 81.
43. J. Geertsen, J. Oddershede and G. E. Scuseria, *J. Chem. Phys.*, 1987, **87,** 2138.
44. V. Galasso, *Chem. Phys. Lett.*, 1988, **145,** 259.
45. Y. Kuroda, Y. Fujiwara, A. Kwae and K. Matsushita, *J. Chem. Soc. Perkin Trans. II* 1986, 675.
46. Y. Kuroda, Y. Fujiwara and K. Matsushita, *J. Chem. Soc. Perkin Trans II*, 1985, 1533.
47. R. Radeglia, R. Wolf, T. Steiger and S. Simova, *Z. Phys. Chem. Leipzig*, 1984, **265,** 1984.
48. T. Steiger and R. Radeglia, *J. Prakt. Chem.*, 1984, **326,** 145.
49. S. M. Susskind, G. E. Scuseria and R. H. Contreras, *Z. Phys. Chem. Leipzig*, 1985, **266,** 395.
50. B. Thomas, A. John, A. Pfützner, G. Grossmann and E. Herrmann, *Z. Anorg. Allg. Chem.*, 1988, **525,** 7.
51. E. Kupče, E. Liepins, O. Pudova and E. Lukevics, *J. Chem. Soc. Chem. Commun.*, 1984, 581.
52. F. B. Mallory and C. W. Mallory, *J. Am. Chem. Soc.*, 1985, **107,** 4816.
53. V. M. S. Gil and W. Von Philipsborn, *Magn. Reson. Chem.*, 1989, **27,** 409.
54. G. E. Scuseria and H. F. Schaefer, *J. Chem. Phys.*, 1987, **87,** 4020.
55. D. Sundholm, P. Pyykkö, L. Laaksonen and A. J. Sadlej, *Chem. Phys.*, 1986, **101,** 219.
56. T. K. Ha, *Chem. Phys. Lett.*, 1984, **107,** 117.
57. T. K. Ha, *Z. Naturforsch.*, 1986, **41a,** 163.
58. P. L. Cummins, G. B. Bocskay, N. S. Hush and R. Ahlrichs, *J. Chem. Phys.*, 1987, **86,** 6908.
59. P. L. Cummins, G. B. Bocskay and N. S. Hush, *Chem. Phys.*, 1987, **115,** 325.
60. J. Murgich and Y. Aray, *J. Chem. Phys.*, 1987, **87,** 3580.
61. Y. Aray, R. Gomperts, J. Saavedra, C. Urdaneta and J. Murgich, *Theor. Chim. Acta*, 1988, **73,** 279.
62. M. H. Palmer, D. Stephenson and J. A. S. Smith, *Chem. Phys.*, 1985, **97,** 103.
63. M. H. Palmer, M. M. I. Haq, D. Stephenson and J. A. S. Smith, *Chem. Phys. Lett.*, 1986, **127,** 615.
64. M. H. Palmer, *Chem. Phys.*, 1988, **127,** 335.
65. R. D. Brown and M. P. Head-Gordon, *Mol. Phys.*, 1987, **61,** 1183.
66. M. Eckert-Maksic and Z. B. Maksic, *J. Mol. Struct.*, 1987, **153,** 133.
67. M. Jaszuński, A. Rizzo and D. L. Yeager, *Chem. Phys.*, 1989, **136,** 385.
68. A. E. Hansen and T. D. Bouman, *J. Chem. Phys.*, 1989, **91,** 3552.
69. D. B. Chesnut and K. D. Moore, *J. Comput. Chem.*, 1989, **10,** 648.
70. T. D. Bouman and A. E. Hansen, *J. Quantum. Chem.*, 1989, **23,** 381.
71. J. Oddershede and J. Geerstsen, *J. Chem. Phys.*, 1990, **92,** 6036.
72. I. Paidarova, J. Komasa and J. Oddershede, *Mol. Phys.*, 1991, **72,** 559.
73. V. Galasso, *J. Magn. Reson.*, 1984, **58,** 311.

74. A. Shoji, T. Ozaki, T. Fujito, K. Deguchi and I. Ando, *Macromolecule*, 1987, **20,** 2441.
75. M. Gruner, D. Pfeifer, H. G. O. Becker, R. Radeglia and J. Epperlein, *J. Prakt. Chem.*, 1985, **327,** 63.
76. R. E. Overill and V. R. Saunders, *Chem. Phys. Lett.*, 1984, **106,** 197.
77. T. Axenrod, X. H. Huang, D. Tufaro, C. Watnick and G. A. Webb, *Magn. Reson. Chem.*, 1988, **26,** 960.
78. M. H. Palmer, *Chem. Phys.*, 1987, **115,** 207.
79. M. H. Palmer, A. J. Blake and R. O. Gould, *Chem. Phys.*, 1987, **115,** 219.
80. Y. Aray, R. Comperts, J. Saavedra, C. Urdaneta and J. Murgich, *Theor. Chim. Acta*, 1988, **73,** 279.
81. M. Witanowski, W. Sicińska and S. Biernat, *Spectrosc. Int. J.*, 1989, **7,** 305.
82. Z. H. Khalil, A. A. Abidel-Hafez, A. A. Geies and A. M. K. El-Dean, *Bull. Chem. Soc. Jpn*, 1991, **64,** 668.
83. B. Wrackmeyer, *Spectrochim. Acta*, 1984, **40A,** 963.
84. J. M. Robert and R. F. Evilia, *J. Am. Chem. Soc.*, 1985, **107,** 3733.
85. L. A. Allen, T. E. Glass and H. C. Dorn, *Anal. Chem.*, 1988, **60,** 390.
86. J. M. Roberts and R. F. Evilia, *Anal. Chem.*, 1988, **60,** 2035.
87. R. F. Evilia, J. M. Robert and S. L. Whittenburg, *J. Phys. Chem.*, 1989, **93,** 6550.
88. M. Witanowski, J. Sitkowski, S. Biernat, L. V. Sudha and G. A. Webb, *Magn. Reson. Chem.*, 1987, **25,** 725.
89. W. Sicińska, L. Sefaniak, M. Witanowski and G. A. Webb, *J. Mol. Struct.*, 1987, **160,** 179.
90. M. Witanowski, J. Sitkowski, W. Sicińska, S. Biernat and G. A. Webb, *Magn. Reson. Chem.*, 1989, **27,** 88.
91. C. M. Adamus and W. Philipsborn, *Magn. Reson. Chem.*, 1985, **23,** 130.
92. D. A. Laude Jr., R. W. K. Lee and C. L. Wilkins, *Anal. Chem.*, 1985, **57,** 1281.
93. A. Péneau, A. H. Fuchs, L. Guibé and H. Szwarc, *C. R. Acad. Sci.*, 1984, **298,** 551.
94. A. W. Bevan, G. C. K. Roberts, J. Feeney and L. Kuyper, *Eur. Biophys. J.*, 1985, **11,** 211.
95. G. B. Fields, C. G. Fields, J. Petefish, H. E. Van Wart and T. A. Cross, *Proc. Natl Acad. Sci. USA*, 1988, **85,** 1384.
96. H. Senn, A. Eugster, G. Otting, F. Suter and K. Wüthrich, *Eur. Biophys. J.*, 1987, **14,** 301.
97. D. H. Live, D. Cowburn and E. Breslow, *Biochemistry*, 1987, **26,** 6415.
98. G. Ortiz-Polo, R. Krishnamoorthi, J. L. Markley, D. H. Live, D. G. Davis and D. Cowburn, *J. Magn. Reson.*, 1986, **68,** 303.
99. P. E. Hansen and H. J. Jakobsen, *Org. Magn. Reson.*, 1984, **22,** 668.
100. H. J. Jakobsen, H. Bildsoe, S. Donstrup and O. W. Sorensen, *J. Magn. Reson.*, 1984, **57,** 324.
101. Y. Hiltunen, J. Jokisaari, J. Lounila and A. Pulkkinen, *J. Am. Chem. Soc.*, 1989, **111,** 3217.
102. E. Sletten, J. Sletten and N. A. Froystein, *Acta Chim. Scand.*, 1988, **A42,** 413.
103. B. J. Stockman, W. M. Westler, E. S. Mooberry and J. L. Markley, *Biochemistry*, 1988, **27,** 136.
104. K. A. Thorn, D. W. Folan, J. B. Arterburn, M. A. Mikita and P. Maccarthy, *The Science of the Total Environment*, 1989, **81/82,** 209.
105. E. Haslinger, M. Schlederer, W. Robien and P. Wolschann, *Monats. Chem.*, 1984, **115,** 1345.
106. F. Seela, H. Rosemeyer, A. Biesewig and T. Jurgens, *Nucleos. Nucleot.*, 1988, **7,** 581.
107. L. Stefaniak, G. A. Webb, C. Brevard, M. Bourdonneau, R. Lejeune, L. Thunus and C. L. Lapiére, *Magn. Reson. Chem.* 1985, **23,** 790.
108. D. Cossette and D. Vocelle, *Can. J. Chem.*, 1987, **65,** 661.
109. G. E. Hawkes, H. Molinari, S. Singh and Lu-Yun Lian, *J. Magn. Reson.*, 1987, **74,** 188.

110. T. Asakura, H. Yoshimizu and F. Yoshizawa, *Macromolecules*, 1988, **21,** 2038.
111. H. R. Kricheldorf, W. E. Hull and D. Müller, *Macromolecules*, 1985, **18,** 2135.
112. H. R. Kricheldorf, D. Müller and W. E. Hull, *Biopolymers*, 1985, **24,** 2113.
113. H. Kricheldorf, D. Müller and W. E. Hull, *Int. J. Biol. Macromol.*, 1986, **8,** 20.
114. G. D. Henry and B. D. Sykes, *Biochem. Cell. Biol.*, 1990, **68,** 318.
115. G. D. Henry and B. D. Sykes, *Biochemistry*, 1990, **29,** 6303.
116. J. Plavec and J. Kobe, *Nucleos. Nucleot.*, 1991, **10,** 249.
117. W. Skawinski, J. Flisak, A. C. Chung, F. Jordan and R. Mendelson, *J. Label. Comp. Radiopharm.*, 1990, **28,** 1179.
118. E. E. Liepins, R. S. El'kinson, J. P. Piskunova and A. V. Erereev, *Khim. Geterosikl. Soedin.*, 1986, 1181.
119. H. Hilpert and R. Hollenstein, *Helv. Chim. Acta*, 1986, **69,** 136.
120. B. Wrackmeyer, *Z. Naturforsch.*, 1986, **41b,** 59.
121. B. Clement and T. Kämpchen, *Arch. Pharm.*, 1987, **320,** 566.
122. G. L'abbe', M. A. Persoons and S. Toppet, *Magn. Reson. Chem.*, 1987, **25,** 362.
123. G. Remaud, J. Kjellberg, H. Bazin, N. G. Johansson and J. Chattopadhyaya, *Tetrahedron*, 1986, **42,** 5073.
124. C. Glemarec, G. Remaud, H. Bazin, X. X. Zhou and J. Chattopadhyaya, *Nucleic Acids Res. (Symp. Ser.)* 1987, 73.
125. W. Holzer and W. von Philipsborn, *Magn. Reson. Chem.*, 1989, **27,** 511.
126. H. Rosemeyer and F. Seela, *Helv. Chim. Acta*, 1988, **71,** 1573.
127. H. Falk and N. Müller, *Magn. Res. Chem.*, 1985, **23,** 353.
128. G. Tóth, A. Szöllösy, I. Hermecz, A. Horváth and Z. Mészáros, *J. Chem. Soc. Perkin Trans. II*, 1985, 1881.
129. B. Wrackmeyer, *Z. Naturforsch.*, 1984, **39b,** 533.
130. B. Wrackmeyer, *J. Magn. Reson.*, 1985, **61,** 536.
131. M. F. Grenier-Loustalot and P. Grenier, *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22,** 4011.
132. E. Kupce, E. Liepins, A. Lapsina, I. Urtāne, G. Zelčāns and E. Lukevics, *J. Organomet. Chem.*, 1985, **279,** 343.
133. I. D. Kalikhman, O. B. Bannikova, L. P. Petukhov, W. A. Pestunovich and M. G. Voronkov, *Dokl. Akad. Nauk CCCP*, 1986, **287,** 870.
134. B. Wrackmeyer, S. Kerschl, C. Stader and K. Horchler, *Spectrochim. Acta*, 1986, **42A,** 1113.
135. W. Maringgele, D. Bromm and A. Meller, *Tetrahedron*, 1988, **44,** 1053.
136. G. C. van Stein, G. van Koten, K. Vrieze, C. Brevard and A. L. Spek, *J. Am. Chem. Soc.*, 1984, **106,** 4486.
137. G. C. van Stein, G. van Koten, K. Vrieze and C. Brevard, *Inorg. Chem.*, 1984, **23,** 4269.
138. G. C. van Stein, G. van Koten, K. Vrieze, A. L. Spek, E. A. Klop and C. Brevard, *Inorg. Chem.*, 1985, **24,** 1367.
139. P. S. Pregosin, R. Rüedi and C. Anklin, *Magn. Reson. Chem.*, 1986, **24,** 255.
140. L. Carlton and M. P. Belciug, *J. Organomet. Chem.*, 1989, **378,** 469.
141. I. D. Kalikhman, O. B. Bannikova, A. V. Kalinin, B. N. Khasanov, S. L. Ioffe, V. A. Tartakovskij and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 463.
142. J. Elguero, R. Faure and J. Llinares, *Spectrosc. Lett.*, 1987, **20,** 149.
143. B. Wrackmeyer, S. M. Frank, M. Herberhold, A. Simon and H. Borrmann, *J. Am. Chem. Soc.*, 1991, 2607.
144. A. Lyčka, J. Jirman, J. Holeček and J. Tká, *J. Organomet. Chem.*, 1989, **372,** 327.
145. T. J. Bastow and S. N. Stuart, *Z. Naturforsch.*, 1990, **45a,** 459.
146. Ad Bax, Chien-Hua Niu and D. Live, *J. Am. Chem. Soc.*, 1984, **106,** 1150.
147. C. Glemarec, G. Remaud and J. Chattopadhyaya, *Magn. Reson. Chem.*, 1988, **26,** 307.

148. C. Glemarec, G. Remaud and J. Chattopadhyaya, *Magn. Reson. Chem.*, 1988, **26,** 435.
149. S. K. Sarkar and Ad Bax, *J. Magn. Reson.*, 1985, **62,** 109.
150. E. Kupče, E. Liepinš, E. Lukevics and B. Astapov, *J. Chem. Soc. Dalton Trans.*, 1987, 1593.
151. C. Stader and B. Wrackmeyer, *J. Magn. Reson.*, 1987, **72,** 544.
152. B. Wrackmeyer, K. Schamel and M. Herberhold. *Z. Naturforsch.*, 1989, **44b,** 55.
153. C. Stader and B. Wrackmeyer, *Z. Naturforsch.*, 1987, **42b,** 1515.
154. J. Elguero, R. Faure and J. Llinares, *Spectrosc. Lett.*, 1987, **20,** 149.
155. S. J. Berners Price, M. J. DiMartino, D. T. Hill, R. Kuroda, M. A. Mazid and P. J. Sadler, *Inorg. Chem.*, 1985, **24,** 3425.
156. A. Costa, M. Tato and R. S. Matthews, *Magn. Reson. Chem.*, 1986, **24,** 547.
157. X. Gao and R. A. Jones, *J. Am. Chem. Soc.*, 1987, **109,** 1275.
158. J. Vervoort, F. Müller, J. LeGall, A. Bacher and H. Sedlmaier, *Flavins Flavoproteins Proc. 8th Int. Symp.* 1984, 269.
159. G. S. Smith, K. D. Berlin, S. A. Zisman, E. M. Holt, V. A. Green and D. von der Helm, *Phosph. Sulph.*, 1988, **39,** 91.
160. R. A. Schiksnis, M. J. Bogusky, P. Tsang and S. J. Opella, *Biochemistry*, 1987, **26,** 1373.
161. M. J. Bogusky, R. A. Schiksnis, G. C. Leo and S. J. Opella, *J. Magn. Reson.*, 1987, **72,** 186.
162. H. A. J. Holterman, A. van Veldhuizen and H. C. van der Plas, *J. Org. Chem.*, 1986, **51,** 1147.
163. J. P. Declercq, *J. Heterocydre Chem.*, 1991, **28,** 477.
164. R. L. Baxter and S. L. Greenwood, *J. Chem. Soc., Chem. Commun.*, 1986, 175.
165. H. J. Jacobsen, U. B. Sorensen, H. Bildsoe and O. W. Sorensen, *J. Magn. Reson.*, 1985, **63,** 601.
166. K. V. Schenker and W. von Philipsborn, *J. Magn. Reson.*, 1985, **61,** 294.
167. M. H. Levitt, *J. Chem. Phys.*, 1991, **94,** 30.
168. B. K. John, D. Plant, S. L. Heald and R. Hurd, *J. Magn. Reson.*, 1991, **94,** 664.
169. Bhim Sen Saraswat and J. Mason, *Polyhedron*, 1986, **5,** 1449.
170. G. E. Hawkes, Lu Yun Lian and E. W. Randall, *J. Magn. Reson.*, 1984, **56,** 539.
171. G. E. Hawkes, Lu-Yun Lian, E. W. Randall, K. D. Sales and E. H. Curzon, *Eur. J. Biochem.*, 1987, **166,** 437.
172. H. Kessler, A. Müller and K. H. Pook, *Liebigs Ann. Chem.*, 1989, 903.
173. X. X. Zhu, F. Sauriol and G. R. Brown, *Can. J. Spectrosc.*, 1988, **33,** 63.
174. H. Kessler, H. R. Loosli and H. Oschkinat, *Helv. Chim. Acta*, 1985, **68,** 661.
175. H. Kessler and M. Bernd, *Liebigs Ann. Chem.*, 1985, 1145.
176. B. Wrackmeyer, E. Kupče and A. Schmidpeter, *Magn. Reson. Chem.*, 1991, **29,** 1045.
177. M. J. Bogusky, P. Leighton, R. A. Schiksnis, A. Khoury, P. Lu and S. J. Opella, *J. Magn. Reson.*, 1990, **86,** 11.
178. S. Roy, M. Z. Papastavros, V. Sanchez and A. G. Redfield, *Biochemistry*, 1984, **23,** 4395.
179. M. Jarema and P. B. Moore, *NATO ASI*, 1986, **110,** 175.
180. M. G. Bogusky, P. Tsang and S. J. Opella, *Biochem. Biophys. Res. Commun.*, 1985, **127,** 540.
181. H. P. Juretschke and A. Lapidot, *Eur. J. Biochem.*, 1985, **147,** 313.
182. H. Kessler, C. Griesinger and K. Wanger, *J. Am. Chem. Soc.*, 1987, **109,** 6927.
183. S. Bulusu, T. Axenrod, B. Liang and L. Yuan, *Magn. Reson. Chem.*, 1991, **29,** 168.
184. S. Bulusu, T. Axenrod, B. Liang, Y. He and L. Yuan, *Magn. Reson. Chem.*, 1991, **29,** 1018.
185. Ad Bax, *Bull. Magn. Reson.*, 1985, **7,** 167.
186. L. Mueller, R. A. Schiksnis and S. J. Opella, *J. Magn. Reson.*, 1986, **66,** 379.

187. G. Otting and K. Wüthrich, *J. Magn. Reson.*, 1988, **76,** 569.
188. H. Molinari and S. Mammi, *J. Magn. Reson.*, 1990, **90,** 355.
189. A. De Marco, L. Zetta and C. Anklin, *Gazz. Chim. Ital.*, 1988, **118,** 295.
190. J. P. Gerothanassis, M. Bourdonneau, T. Karayannis, M. Sakarellos-Daitsiotis and C. Sakarellos, *J. Magn. Reson.*, 1988, **80,** 309.
191. V. Sklenář and Ad Bax, *J. Magn. Reson.*, 1987, **71,** 379.
192. S. K. Sarkar, J. D. Glickson and Ad Bax, *J. Am. Chem. Soc.*, 1987, **109,** 6814.
193. D. H. Live, J. Radhakrishnan, V. Misra and D. J. Patel, *J. Am. Chem. Soc.*, 1991, **113,** 4687.
194. G. B. Henderson, J. Glushka, D. Cowburn and A. Cerami, *J. Chem. Soc. Perkin Trans. I*, 1990, 911.
195. J. Glushka and D. Cowburn, *J. Am. Chem. Soc.*, 1987, **109,** 7879.
196. J. Glushka and D. Cowburn, *J. Am. Chem. Soc.*, 1987, **109,** 7879.
197. J. Glushka, M. Lee, S. Coffin and D. Cowburn, *J. Am. Chem. Soc.*, 1989, **111,** 7716.
198. D. C. Muchmore, L. P. McIntosh, C. B. Russel, D. E. Anderson and F. W. Dahlquist, *Methods in Enzymology*, 1989, **117,** 44.
199. L. P. McIntosch, A. J. Wand, D. F. Lowry, A. G. Redfield and F. W. Dahlquist, *Biochemistry*, 1990, **29,** 6341.
200. A. G. Redfield, L. P. McIntosch and F. W. Dahlquist, *Arch. Biol. Med. Exp.* 1989, **22,** 129.
201. Byung-Ha Oh, E. S. Mooberry and J. L. Markley, *Biochemistry*, 1990, **29,** 4004.
202. Byunh-Ha Oh and J. L. Markley, *Biochemistry*, 1990, **29,** 3993.
203. H. Fritz, H. Kristinsson, M. Mollenkopf and T. Winkler, *Magn. Reson. Chem.*, 1990, **28,** 331.
204. D. M. LeMaster and F. M. Richards, *Biochemistry* , 1985, **24,** 7263.
205. R. H. Griffey, D. R. Davis, Z. Yamaizumi, S. Nishimura, B. L. Hawkins and C. D. Poulter, *J. Biol. Chem.*, 1986, **261,** 12074.
206. R. Ambrosetti, R. Angelone and J. Murgich, *Z. Naturforsch.*, 1986, **41a,** 299.
207. R. H. Griffey, D. Davis, Z. Yamaizumi, S. Nishimura, Ad Bax, B. Hawkins and C. D. Poulter, *J. Biol. Chem.*, 1985, **260,** 9734.
208. D. R. Davis, Z. Yamaizumi, S. Nishimura and C. D. Poulter, *Biochemistry*, 1989, **28,** 4105.
209. A. M. Gronenborn, Ad Bax, P. T. Wingfield and G. M. Clore, *FEBS Lett.*, 1989, **243,** 93.
210. A. G. Redfield and M. Z. Papastavros, *Biochemistry*, 1990, **29,** 3509.
211. K. Shon and S. J. Opella, *J. Magn. Reson.*, 1989, **82,** 193.
212. G. D. Henry and B. D. Sykes, *J. Mol. Biol.*, 1990, **212,** 11.
213. Masahiro Shirakawa, Sang Jong Lee, Misato Takimoto, Hiroshi Matsuo, Hideo Akutsu and Yoshimasa Kyogoku, *J. Mol. Struct.*, 1991, **242,** 355.
214. L. E. Kay and Ad Bax, *J. Magn. Reson.*, 1990, **86,** 110.
215. D. A. Torchia, S. W. Sparks and Ad Bax, *Biochemistry*, 1989, **28,** 5509.
216. L. E. Kay and Ad Bax, *J. Magn. Reson.*, 1989, **84,** 598.
217. J. Glushka, F. Barany and D. Cowburn, *Biochem. Biophys. Res. Commun.*, 1989, **164,** 88.
218. L. Mueller, S. L. Heald, J. C. Hempel and P. W. Jeffs, *J. Am. Chem. Soc.*, 1989, **111,** 495.
219. N. Dekker, A. R. Peters, A. J. Slotboom, R. Boelens, R. Kaptein and G. de Haas, *Biochemistry*, 1991, **30,** 3135.
220. T. Pehk, M. Haga, H. Vija and E. Lippmaa, *Magn. Reson. Chem.*, 1989, **27,** 173.
221. R. A. Venters, T. L. Calderone, L. D. Spicer and C. A. Fierke, *Biochemistry*, 1991, **30,** 4491.
222. G. Kupferschmitt, J. Schmidt, Th. Schmidt, B. Fera, F. Buck and H. Rüterjans, *Nucleic Acids Res.*, 1987, **15,** 6225.

223. Chuan Wang, Hetian Gao, B. L. Gaffney and R. A. Jones, *J. Am. Chem. Soc.*, 1991, **113,** 5486.
224. J. Ashcroft, D. H. Live, D. J. Patel and D. Cowburn, *Biopolymers*, 1991, **31,** 45.
225. D. R. Davis and C. D. Poulter, *Biochemistry*, 1991, **30,** 4223.
226. H. P. Juretschke, *FEBS Letters*, 1984, **178,** 123.
227. B. Wrackmeyer, K. Schamel, K. Guldner and M. Herberhold, *Z. Naturforsch.*, 1987, **42b,** 703.
228. Mitsuhiko Ikura, M. Krinks, D. A. Torchia and Ad Bax, *FEBS Lett.*, 1990, **266,** 155.
229. G. M. Clore, Ad Bax, P. Wingfield and A. M. Gronenborn, *FEBS Lett.*, 1988, **238,** 17.
230. Ad Bax, S. W. Sparks and D. A. Torchia, *J. Am. Chem. Soc.*, 1988, **110,** 7926.
231. B. J. Stockman, M. D. Reily, W.M. Westler, E. L. Ulrich and J. L. Markley, *Biochemistry*, 1989, **28,** 230.
232. W. M. Westler, B. J. Stockman, J. L. Markley, Y. Hosoya, Y. Miyake and M. Kainosho, *J. Am. Chem. Soc.*, 1988, **110,** 6256.
233. E. S. Mooberry, Byung-Ha Oh and J. L. Markley, *J. Magn. Reson.*, 1989, **85,** 147.
234. W. P. Niemczura, G. L. Helms, A. S. Chesnick, R. E. Moore and V. Bornemann, *J. Magn. Reson.*, 1989, **81,** 635.
235. G. T. Montelione and G. Wagner, *J. Am. Chem. Soc.*, 1989, **111,** 5474.
236. G. T. Montelione and G. Wagner, *J. Magn. Reson.*, 1990, **87,** 183.
237. A. G. Palmer III, J. Cavanagh, P. E. Wright and M. Rance, *J. Magn. Reson.*, 1991, **93,** 151.
238. S. Campbell-Burk, P. Domaille and L. Mueller, *J. Magn. Reson.*, 1991, **93,** 171.
239. J. G. Pelton, D. A. Torchia, N. D. Meadow, C. Y. Wong and S. Roseman, *Biochemistry*, 1991, **30,** 10043.
240. H. Matsuo, M. Shirakawa, T. Ohkubo, T. Yamazaki and Y. Kyogoku, *J. Biomol. NMR*, 1991, **1,** 191.
241. Yasushi Oda, Haruki Nakamura, Shigenori Kanaya and Morio Ikehara, *J. Biomol. NMR*, 1991, **1,** 247.
242. G. Wider and K. Wüthrich, *Chem. Biochem. Mol. Biol.*, 1990, **1,** 517.
243. E. R. P. Zuiderweg and S. W. Fesik, *Biochemistry*, 1989, **28,** 2387.
244. L. E. Kay, M. Ikura, R. Tschudin and Ad Bax, *J. Magn. Reson.*, 1990, **89,** 496.
245. M. Ikura, L. E. Kay and Ad Bax, *Biochemistry*, 1990, **29,** 4659.
246. Kuniaki Nagayama, Toshio Yamazaki, Mayumi Yoshida, Shigenori Kanaya and Haruki Nakamura, *J. Biochem.*, 1990, **108,** 149.
247. S. W. Fesik and E. R. P. Zuiderweg, *J. Magn. Reson.*, 1988, **78,** 588.
248. S. W. Fesik, R. T. Gampe Jr, E. R. P. Zuiderweg, W. E. Kohlbrenner and D. Weigl, *Biochem. Biophys. Res. Commun.* 1989, **159,** 842.
249. D. Marion, P. C. Driscoll, L. E. Kay, P. T. Wingfield, Ad Bax, A. M. Gronenborn and G. M. Clore, *Biochemistry*, 1989, **28,** 6150.
250. L. E. Kay, Mitsuhiko Ikura and Ad Bax, *J. Magn. Reson.*, 1991, **91,** 84.
251. G. Wagner, P. Schmieder and V. Thanabal, *J. Magn. Reson.*, 1991, **93,** 436.
252. P. Schmieder, V. Thanabal, L. P. McIntosh, F. W. Dahlquist and G. Wagner, *J. Am. Chem. Soc.*, 1991, **113,** 6323.
253. K. V. R. Chary, G. Otting and K. Wüthrich, *J. Magn. Reson.*, 1991, **93,** 218.
254. B. T. Farmer II, *J. Magn. Reson.*, 1991, **94,** 413.
255. L. E. Kay, M. Ikura, Guang Zhu and Ad Bax, *J. Magn. Reson.*, 1991, **91,** 422.
256. Mitsuhiko Ikura, L. E. Kay, M. Krinks and Ad Bax, *Biochemistry*, 1991, **30,** 5498.
257. P. L. Weber and L. Mueller, *J. Magn. Reson.*, 1989, **81,** 430.
258. D. Marion, L. E. Kay, S. W. Sparks, D. A. Torchia and Ad Bax, *J. Am. Chem. Soc.*, 1989, **111,** 1515.

259. H. Senn, G. Otting and K. Wüthrich, *J. Am. Chem. Soc.*, 1987, **109**, 1090.
260. Toshio Yamazaki, Mayumi Yoshida, Shigenori Kanaya, Haruki Nakamura and Kuniaki Nagayama, *Biochemistry*, 1991, **30**, 6036.
261. K. Chandrasekhar, G. Krause, A. Holmgren and H. J. Dyson, *FEBS Lett.*, 1991, **284**, 178.
262. Yiqing Feng, A. J. Wand and S. G. Sligar, *Biochemistry*, 1991, **30**, 7711.
263. J. M. Schmidt, H. Thûring, A. Werner, H. Rûterjans, R. Quaas and U. Hahn, *Eur. J. Biochem.*, 1991, **197**, 643.
264. M. D. Carr, B. Birdsall, T. A. Frenkiel, C. J. Bauer, J. Jimenez-Barbero, V. I. Polshakov, E. McCormick, G. C. K. Roberts and J. Feeney, *Biochemistry*, 1991, **30**, 6330.
265. R. T. Clubb, V. Thanabal, C. Osborne and G. Wagner, *Biochemistry*, 1991, **30**, 7718.
266. G. M. Clore, Ad Bax, P. C. Driscoll, P. T. Wingfield and A. M. Gronenborn, *Biochemistry*, 1990, **29**, 8172.
267. W. J. Fairbrother, J. Cavanagh, H. J. Dyson, A. G. Palmer, S. L. Sutrina, J. Reizer, M. H. Saier Jr. and P. E. Wright, *Biochemistry* , 1991, **30**, 6896.
268. L. E. Kay, D. A. Torchia and Ad Bax, *Biochemistry*, 1989, **28**, 8972.
269. Ad Bax, L. E. Kay, S. W. Sparks and D. A. Torchia, *J. Am. Chem. Soc.*, 1989, **111**, 408.
270. R. A. Schiksnis, A. L. Rockwell, L. M. Gierasch and S. J. Opella, *J. Magn. Reson.*, 1988, **79**, 318.
271. N. C. Nielsen, H. Bildsoe, H. J. Jakobsen and O. W. Sorensen, *J. Am. Chem. Soc.*, 1987, **109**, 901.
272. R. H. Griffey, M. A. Jarema, S. Kunz, P. R. Rosevear and A. G. Redfield, *J. Am. Chem. Soc.*, 1985, **107**, 711.
273. V. A. Lopyrev, L. I. Larina, T. I. Vakul'skaya, M. F. Larin, E. F. Shibanova, I. A. Titova, M. G. Voronkov and E. E. Liepin'sh, *Magn. Reson. Chem.*, 1985, **23**, 301.
274. V. A. Pestunovich, B. Z. Shterenberg, L. P. Petukhov, V. I. Rakhlin, V. P. Baryshok, R. G. Mirskov and M. G. Voronkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, **8**, 1935.
275. I. Kieper, T. Schmidt, B. Fera and H. Ruterjans, *Nucleos. Nucleot.*, 1988, **7**, 821.
276. J. H. Gilchrist, A. T. Harrison, D. J. Fuller and D. B. Collum, *J. Am. Chem. Soc.*, 1990, **112**, 4069.
277. L. E. Kay, D. A. Torchia and Ad Bax, *Biochemistry*, 1989, **28**, 8972.
278. M. J. Kime, *FEBS Letters*, 1984, **173**, 342.
279. M. J. Kime, *FEBS Letters*, 1984, **175**, 259.
280. W. Massefski Jr, A. Redfield, U. D. Sarma, A. Bannerji and S. Roy, *J. Am. Chem. Soc.*, 1990, **112**, 5350.
281. Yoshihiro Kuroda, Yasuhiro Fujiwara and Kazuhiro Matsushita, *J. Magn. Reson.*, 1985, **61**, 149.
282. Yoshihiro Kuroda and Yasuhiro Fujiwara, *Magn. Reson. Chem.*, 1987, **25**, 335.
283. E. Kupče and B. Wrackmeyer, *J. Magn. Reson.*, 1991, **94**, 170.
284. A. Haase and D. Höpfel, *J. Magn. Reson.*, 1988, **80**, 389.
285. S. Jurga, J. Seliger, R. Blinc and H. W. Spiess, *Phys. Lett. A*, 1986, **116**, 295.
286. K. V. Ramanathan and S. J. Opella, *J. Magn. Reson.*, 1988, **78**, 367.
287. A. N. Garroway and J. B. Miller, *J. Magn. Reson.*, 1989, **82**, 591.
288. R. Tycko, P. L. Stewart and S. J. Opella, *J. Am. Chem. Soc.*, 1986, **108**, 5419.
289. R. Tycko and S. J. Opella, *J. Am. Chem. Soc.*, 1986, **108**, 3531.
290. K. V. Ramanathan and S. J. Opella, *J. Magn. Reson.*, 1990, **86**, 227.
291. P. L. Stewart, R. Tycko and S. J. Opella, *J. Chem. Soc., Faraday Trans. I*, 1988, **84**, 3803.
292. Akira Naito and C. A. McDowell, *J. Chem. Phys.*, 1984, **81**, 4795.
293. C. A. McDowell, A. Naito, D. L. Sastry and K. Takegoshi, *J. Magn. Reson.*, 1986, 283.
294. T. J. Bastow and S. N. Stuart, *Chem. Phys. Lett.*, 1991, **180**, 305.

295. R. A. Santos, Pei Tang, Wei-Jyun Chien, S. Kwan and G. S. Harbison, *J. Phys. Chem.*, 1990, **94,** 2717.
296. T. J. Bastow and S. N. Stuart, *J. Phys.: Condensed Matter* 1989, **1,** 4649.
297. S. Wigand, N. Weiden and A. Weiss, *Ber. Bunsengs. Phys. Chem.*, 1989, **93,** 913.
298. D. Suter and R. R. Ernst, *Phys. Rev. B*, 1985, **32,** 5608.
299. J. Dolinšek, S. Žumer and R. Blinc, *XII Congr. AMPERE Magn. Relat. Phenom. Proc.*, 1984, 64.
300. Akira Naito and C. A. McDowell, *Rev. Sci. Instrum.*, 1989, **60,** 1037.
301. Zhehong Gan and D. M. Grant, *J. Magn. Reson.*, 1990, **90,** 522.
302. R. K. Harris, P. Jonsen and K. J. Packer, *Org. Magn. Reson.*, 1984, **22,** 784.
303. A. Naito, P. B. Barker and C. A. McDowell, *J. Chem. Phys.*, 1984, **81,** 1583.
304. N. J. Heaton, R. R. Vold and R. L. Vold, *J. Chem. Phys.*, 1989, **91,** 56.
305. G. Schnur, R. Kimmich and F. Winter, *J. Magn. Reson.*, 1986, **66,** 295.
306. J. Olliges, A. Lötz, J. Voitländer, H. Barfuss, G. Böhnlein, F. Gubitz, W. Ittner, G. Lanzendorfer, W. Kreische and B. Röseler, *XXII Congr. AMPERE Magn. Reson. Phenom Proc.*, 1984, 436.
307. R. Blinc, J. Seliger, V. Žagar, T. Apih, J. Dolinšek, H. Warhanek and W. Schranz, *Phys. Rev. B*, 1990, **42,** 8125.
308. M. A. Doverspike and M. S. Conradi, *Phys. Rev. B*, 1984, **30,** 4905.
309. L. Mueller, M. H. Frey, A. L. Rockwell, L. M. Gierasch and S. J. Opella, *Biochemistry*, 1986, **25,** 557.
310. R. E. Wasylishen, O. Knop and J. B. Macdonald, *Solid State Commun.*, 1985, **56,** 581.
311. T. K. Pratum and M. P. Klein, *J. Magn. Reson.*, 1989, **81,** 350.
312. T. K. Pratum and M. P. Klein, *J. Magn. Reson.*, 1989, **81,** 350.
313. D. J. Simonovitch, M. F. Brown and K. R. Jeffrey, *Biochemistry*, 1984, **23,** 2412.
314. D. J. Siminovitch, M. Rance, K. R. Jeffrey and M. F. Brown, *J. Magn. Reson.*, 1984, **58,** 62.
315. Y. Kanazawa, R. Takano, I. Nishizono, K. Koga, M. Ishikawa, W. Higuchi and T. Yamada, *Chem. Lett.*, 1985, 717.
316. T. J. Bastow, R. J. C. Brown, A. M. C. Harnden, B. K. Hunter, S. L. Segel and R. D. Weir, *24th AMPERE Congress*, 1988, Poznań, 145.
317. Th. Erge, F. Engelke, D. Michel, W. Windsch and J. Peterssen, *Ferroelectrics*, 1990, **108,** 331.
318. F. Engelke, D. Michel, W. Windsch and J. Petersson, *Phys. Stat. Sol. (b)*, 1986, **134,** 29.
319. T. A. Cross and S. J. Opella, *J. Am. Chem. Soc.*, 1983, **105,** 306.
320. G. S. Harbison, L. W. Jeliński, R. E. Stark, D. A. Torchia, J. Herzfeld and R. G. Griffin, *J. Magn. Reson.*, 1984, **60,** 79.
321. M. A. Doverspike and M. S. Conradi, *Phys. Rev. B*, 1984, **30,** 4905.
322. F. Engelke, D. Michel, W. Windsch and J. Petersson, *Ferroelectrics*, 1988, **80,** 99.
323. A. Shoji, T. Ozaki, T. Fujito, K. Deguchi, S. Ando and I. Ando, *Macromolecules*, 1989, **22,** 2860.
324. T. G. Oas, C. J. Hartzell, F. W. Dahlquist and G. P. Drobny, *J. Am. Chem. Soc.*, 1987, **109,** 5962.
325. K. G. Valentine, A. L. Rockwell, L. M. Gierasch and S. J. Opella, *J. Magn. Reson.*, 1987, **73,** 519.
326. Yukio Hiyama, Chien-Hua Niu, J. V. Silverton, A. Bavoso and D. A. Trochia, *J. Am. Chem. Soc.*, 1988, **110,** 2378.
327. D. G. Powell and L. J. Mathias, *Polym Commun.*, 1990, **31,** 58.
328. M. Munowitz, T. H. Huang and R. G. Griffin, *J. Chem. Phys.*, 1987, **86,** 4362.

329. H. J. M. da Groot, G. S. Harbison, J. Herzfeld and R. G. Griffin, *Biochemistry*, 1989, **28,** 3346.
330. R. E. Wasylishen, G. H. Penner, W. P. Power and R. D. Curtis, *J. Am. Chem. Soc.*, 1989, **111,** 6082.
331. M. Sardashti and G. E. Maciel, *J. Phys. Chem.*, 1988, **92,** 4620.
332. R. E. Wasylishen, W. P. Power, G. H. Penner and R. D. Curtis, *Can. J. Chem.*, 1989, **67,** 1219.
333. M. A. Doverspike, Meng-Chou Wu and M. S. Conradi, *Phys. Rev. Lett.*, 1986, **56,** 2284.
334. K. G. Valentine, D. M. Schneider, G. C. Leo, L. A. Colnago and S. J. Opella, *Biophys. J.*, 1986, **49,** 36.
335. L. A. Colnago, K. G. Valentine and S. J. Opella, *Biochemistry*, 1987, **26,** 847.
336. G. C. Leo, L. A. Colnago, K. G. Valentine and S. J. Opella, *Biochemistry*, 1987, **26,** 854.
337. M. J. Bogusky, G. C. Leo and S. J. Opella, *Proteins: Structure, Function and Genetics*, 1988, **4,** 123.
338. T. A. Cross, *Synt. Appl. Isotop. Label. Comp.*, 1985, 247.
339. L. K. Nicholson, F. Moll, T. E. Mixon, P. V. LoGrasso, J. C. Lay and T. A. Cross, *Biochemistry*, 1987, **26,** 6621.
340. J. A. Killian, L. K. Nicholson and T. A. Cross, *Biochim. Biophys. Acta*, 1988, **943,** 535.
341. P. V. LoGrasso, F. Moll III and T. A. Cross, *Biophys. J.*, 1988, **54,** 259.
342. P. V. LoGrasso, L. K. Nicholson and T. A. Cross, *J. Am. Chem. Soc.*, 1989, **111,** 1910.
343. Q. Teng and T. A. Cross, *J. Magn. Reson.*, 1989, **85,** 439.
344. L. K. Nicholson and T. A. Cross, *Biochemistry*, 1989, **28,** 9379.
345. Bo Ouyang and M. S. Conradi, *Phys. Rev. B*, 1991, **44,** 9295.
346. C. J. Hartzell, T. K. Pratum and G. Drobny, *J. Chem. Phys.*, 1987, **87,** 4324.
347. T. G. Oas, C. J. Hartzell, G. P. Drobny and F. W. Dahlquist, *J. Magn. Reson.*, 1989, **81,** 395.
348. S. O. Smith, G. S. Harbison, D. P. Raleigh, J. E. Roberts, J. A. Pardoen, S. K. Das Gupta, C. Mulliken, R. A. Mathies, J. Lugtenburg, J. Herzfeld and R. G. Griffin, *Biomolecular Stereodynamics III. Proceedings of the Fourth Conversation in the Discipline of Biomolecular Stereodynamics, State Univ. New York* H. S. Ramaswamy and H. S. Mukti, eds), Adenine Press, 1986, p. 159.
349. R. A. Santos, Wei-Jyun Chien and G. S. Harbison, *J. Magn. Reson.*, 1989, **84,** 357.
350. V. Copié, W. S. Faraci, C. T. Walsh and R. G. Griffin, *Biochemistry*, 1988, **27,** 4966.
351. R. M. Dickson, M. S. McKinnon, J. F. Britten and R. E. Wasylishen, *Can. J. Chem.*, 1987, **65,** 941.
352. You Xiaozeng and Wu Weixiong, *Magn. Reson. Chem.*, 1987, **25,** 860.
353. R. E. Wasylishen, *Spectrochim. Acta*, 1984, **40A,** 115.
354. K. Takegoshi and C. A. McDowell, *J. Magn. Reson.*, 1986, **67,** 356.
355. L. Delmotte, M. Soulard and H. Kessler, *Chem. Lett.*, 1990, 1215.
356. E. Grech, L. Stefaniak, I. Ando, M. Yoshimizu, G. A. Webb and L. Sobczyk, *Bull. Chem. Soc. Jpn*, 1990, **63,** 2716.
357. L. Stefaniak, I. Ando, H. Yoshimizu, J. Lipkowski and G. A. Webb, *J. Crystallogr. Spectrosc. Res.*, 1991, **21,** 51.
358. R. Futtero, G. E. Hawkes, E. W. Randall, A. Gasco and C. J. Groombridge, *J. Chem. Soc. Perkin Trans.* II, 1988, 1863.
359. L. J. Mathias, D. G. Powell and A. M. Sikes, *Polym. Commun.*, 1988, **29,** 192.
360. J. Kaválek, V. Macháek, V. Štefba and A. Lyka, *Collect. Czech. Chem. Commun.*, 1988, **53,** 1033.
361. D. G. Powell, A. M. Sikes and L. J. Mathias, *Polymer*, 1991, **32,** 2523.
362. L. J. Mathias and C. G. Johnson, *Macromolecules*, 1991, **24,** 6114.

363. G. A. Duff, J. E. Roberts and N. Foster, *Biochemistry*, 1988, **27,** 7112.
364. H. R. Kricheldorf and D. Müller, *Int. J. Biol. Macromol.*, 1984, **6,** 145.
365. S. Kitagawa, M. Munakata, K. Deguchi and T. Fujito, *Magn. Reson. Chem.*, 1991, **29,** 566.
366. B. Chaloner-Gill, W. B. Euler, P. D. Mumbauer and J. E. Roberts, *J. Am. Chem. Soc.*, 1991, **113,** 6831.
367. B. Chaloner-Gill, W. B. Euler and J. E. Roberts, *Macromolecules*, 1991, **24,** 3074.
368. L. J. Mathias, D. G. Powell, J. P. Autran and R. S. Porter, *Mater. Sci. Eng.*, 1990, **A126,** 253.
369. D. G. Powell, A. M. Sikes and L. M. Mathias, *Polym. Mater. Sci. Eng.*, 1989, **60,** 810.
370. D. G. Powell and L. J. Mathias, *Macromolecules*, 1989, **22,** 3812.
371. D. G. Powell, A. M. Sikes and L. J. Mathias, *Gov. Rep. Annu. Ind.*, 1988, **88,** 559.
372. L. J. Mathias, D. G. Powell, J. P. Autran and R. S. Porter, *Macromolecules*, 1990, **23,** 963.
373. R. L. Willer and D. W. More, *Magn. Reson. Chem.*, 1988, **26,** 95.
374. D. G. Powell, A. M. Sikes and L. J. Mathias, *Macromolecules*, 1988, **21,** 1533.
375. L. J. Mathias and C. G. Johnson, *Polymers*, 1991, **32,** 80.
376. A. F. Richter, A. Ray, K. V. Ramanthan, S. K. Manohar, G. T. Furst, S. J. Opella, A. G. MacDiarmid and A. J. Epstein, *Synth. Metals*, 1989, **29,** E243.
377. Ichiro Tajima, Takao Suda, Minoru Yamamoto, Kozo Satta and Hidetake Morimoto, *Polym. J.*, 1988, **20,** 919.
378. C. N. Matthews, R. Ludicky, J. Schaefer, E. O. Stejskal and R. A. McKay, *Origins of Life*, 1984, **14,** 243.
379. S. Bulusu, *Materials Characterisation for Systems Performance and Reliability* (J. W. McCauley and V. Weiss, eds), 1986, p. 487.
380. S. Bulusu, *Materials Characterisation for Systems Performance and Reliability* (J. W. McCauley and V. Weiss, eds), 1986, p. 479.
381. B. Wehrle, H. H. Limbach and H. Bräuling, *Synth. Metals*, 1991, **39,** 319.
382. B. Wehrle, H. H. Limbach, J. Mortensen and J. Heinze, *Synth. Metals*, 1990, **38,** 293.
383. Yu Chun and Ma Feng-Yun, *Proc. 3rd Beijing Conf. and Exhib. on Instrum. Analysis*, 1989, E35.
384. R. D. Curtis and R. E. Washylishen, *Can. J. Chem.*, 1991, **69,** 834.
385. Shigeki Kuroki, Shinji Ando, Isao Ando, Akira Shoji, Takuo Ozaki and G. A. Webb, *J. Mol. Struct.*, 1990, **240,** 19.
386. A. I. Scott, *J. Mol. Catal.*, 1988, **47,** 139.
387. N. E. Mackenzie, P. E. Fagerness and A. I. Scott, *J. Chem. Soc. Chem. Commun.*, 1985, 635.
388. H. B. R. Cole, S. W. Sparks and D. A. Torchia, *Proc. Natl Acad. Sci. USA*, 1988, **85,** 6362.
389. P. A. Burke, S. O. Smith, W. W. Bachovchin and A. M. Klibanow, *J. Am. Chem. Soc.*, 1989, **111,** 8290.
390. S. O. Smith, S. Farr-Jones, R. G. Griffin and W. W. Bachovchin, *Science*, 1989, **244,** 961.
391. Tai-Huang Huang, W. W. Bachovchin, R. G. Griffin and C. M. Dobson, *Biochemistry*, 1984, **23,** 5933.
392. S. Farr-Jones, S. O. Smith, C. A. Kettner, R. G. Griffin and W. W. Bachovchin, *Proc. Natl. Acad. Sci. USA*, 1989, **86,** 6922.
393. J. E. Garbow, G. S. Jacob, E. O. Stejskal and J. Schaefer, *Biochemistry*, 1989, **28,** 1362.
394. G. E. Wilson Jr., G. S. Jacob and J. Schaefer, *Biochem. Biophys. Res. Commun.*, 1985, **126,** 1006.
395. T. A. Skokut, J. Manchester and J. Schaefer, *Plant. Physiol.*, 1985, **79,** 579.
396. N. Belay, R. Sparling, B.-S. Choi, M. Roberts, J. E. Roberts and L. Daniels, *Biochim. Biophys. Acta*, 1988, **971,** 233.

397. Byong-Seok Choi, J. E. Roberts, J. N. S. Evans and M. F. Roberts, *Biochemistry*, 1986, **25,** 2244.
398. G. S. Jacob, J. Schaefer, J. R. Garbow and E. O. Stejskal, *J. Biol. Chem.*, 1987, **262,** 254.
399. G. S. Jacob, J. Schaefer, E. O. Stejskal and R. McKay, *J. Biol. Chem.*, 1985, **260,** 5899.
400. K. J. Kramer, T. L. Hopkins, J. Schaefer, T. D. Morgan, J. R. Garbow, G. S. Jacob, E. O. Stejskal and R. D. Speirs, *MCLA Symp. Mol. Cel. Biol., Los Angeles, UCLA*, 1987, **49,** 331.
401. J. Schaefer, K. J. Kramer, J. R. Garbow, G. S. Jacob, E. O. Stejskal, T. L. Hopkins and R. D. Speirs, *Science*, 1987, **235,** 1200.
402. L. M. Benzing-Purdie, M. V. Cheshire, B. L. Williams, G. P. Sparling, C. I. Ratcliffe and J. A. Ripmeester, *J. Agric. Food Chem.*, 1986, **34,** 170.
403. L. M. Benzing-Purdie and J. A. Ripmeester, *Chem. Ind.*, 1987, 245.
404. L. M. Benzing-Purdie and J. A. Ripmeester, *J. Carbohydrate Chem.*, 1987, **6,** 87.
405. F. Hayase, S. B. Kim and H. Kato, *Agric. Biol. Chem.*, 1986, **50,** 1951.
406. S. J. Opella and K. M. Morden, *Dynamics Properties of Biomolecular Assemblies*, pp. 196–209.
407. H. J. M. de Groot, S. O. Smith, J. Courtin, E. van den Berg, C. Winkel, J. Lugtenburg, R. G. Griffin and J. Herzfeld, *Biochemistry*, 1990, **29,** 6873.
408. S. O. Smith, G. S. Harbison, D. P. Raleigh, J. E. Roberts, J. A. Pardoen, S. K. Das Gupta, R. A. Mathies, J. Lugtenburg, J. Herzfeld and R. G. Griffin, *Synth. Appl. Isotop. Label. Comp. 1985. Proc. Second Int. Symp., Kansas City, MO, USA, 3–6 Sept. 1985* (R. R. Muccino, ed.), 1986, 239.
409. G. D. Mateescu, E. W. Abrahamson, J. W. Shriver, W. Copan, D. Muccio, M. Iqbal and V. Waterhous, *NATO ASI Ser. C, Spectroscopy of Biological Molecules*, 1984, 257.
410. G. S. Harbison, J. E. Roberts, J. Herzfeld and R. G. Griffin, *J. Am. Chem. Soc.*, 1988, **110,** 7221.
411. R. K. Harris, L. H. Merwin and G. Hägele, *Magn. Reson. Chem.*, 1989, **27,** 470.
412. A. Lyčka, J. Jirman, B. Schneider and J. Straka, *Magn. Reson. Chem.*, 1988, **26,** 507.
413. S. J. Berners-Price, K. Morden, S. J. Opella and P. J. Sadler, *Magn. Reson. Chem.* 1986, **24,** 734.
414. S. Bulusu, R. L. Dudley and J. R. Autera, *Magn. Reson. Chem.*, 1987, **25,** 234.
415. R. K. Harris, M. J. Leach and D. P. Thompson, *Chem. Mater.*, 1990, **2,** 320.
416. D. P. Thompson, M. J. Leach and R. K. Harris, *Proc. C-MRS Int. Symp.*, 1990, **2,** 435.
417. D. Kruppa, R. Dupree and M. H. Lewis, *Mater. Lett.*, 1991, **11,** 195.
418. R. A. Marino and Suryanarayana Bulusu, *J. Energ. Mater.*, 1985, **3,** 57.
419. J. L. White and J. F. Haw, *J. Am. Chem. Soc.*, 1990, **112,** 5896.
420. M. L. H. Gruwel, M. S. McKinnon and R. E. Wasylishen, *Chem. Phys. Lett.*, 1987, **139,** 321.
421. R. D. Curtis, M. J. Schriver and R. E. Wasylishen, *J. Am. Chem. Soc.*, 1991, **113,** 1493.
422. W. L. Earl, P. O. Fritz, A. A. V. Gibson and J. H. Lunsford, *J. Phys. Chem.*, 1987, **91,** 2091.
423. P. D. Majors and P. D. Ellis, *J. Am. Chem. Soc.*, 1987, **109,** 1648.
424. J. A. Rippmester, R. E. Hawkins, J. A. MacPhee and B. N. Nandi, *FUEL*, 1986, **65,** 740.
425. W. Meiler and T. Wutscherk, *Isotopenpraxis*, 1989, **25,** 41.
426. W. Gründer, P. Krumbiegel, K. Buchali and H. J. Blesin, *Phys. Med. Biol.*, 1989, **34,** 457.
427. B. Wehrle and H. H. Limbach, *Chem. Phys.*, 1989, **136,** 223.
428. F. Aguilar-Parrilla, B. Wehrle, H. Bräunling and H. H. Limbach, *J. Magn. Reson.*, 1990, **87,** 592.
429. B. Wehrle, F. Aguilar-Parrilla and H. H. Limbach, *J. Magn. Reson.*, 1990, **87,** 584.
430. H. Rumpel and H. H. Limbach, *J. Am. Chem. Soc.*, 1989, **111,** 5429.

431. J. A. S. Smith, B. Wehrle, F. Aquilar-Parrilla, H. H. Limbach, M. de la Concepcion Foces-Foces, F. H. Cano, J. Elguero, A. Baldy, M. Pierrot, Mian M. T. Khurshid and J. B. Larcombe-McDouall, *J. Am. Chem. Soc.*, 1989, **111,** 7304.
432. B. Wehrle, H. H. Limbach and H. Zimmermann, *Ber. Bunsen. Phys. Chem.*, 1987, **91,** 941.
433. B. Wehrle, H. Zimmermann and H. H. Limbach, *J. Am. Chem. Soc.*, 1988, **110,** 7014.
434. H. H. Limbach, B. Wehrle, M. Schlabach, R. Kendrick and C. S. Yannoni, *J. Magn. Reson.*, 1988, **77,** 84.
435. B. Wehrle, H. H. Limbach, M. Köcher, O. Ermer and E. Vogel, *Angew. Chem.*, 1987, **26,** 934.
436. H. H. Limbach, B. Wehrle, H. Zimmermann, R. D. Kendrick and C. S. Yannoni, *Angew. Chem.*, 1987, **26,** 247.
437. H. H. Limbach, B. Wehrle, H. Zimmermann, R. D. Kendrick and C. S. Yannoni, *J. Am. Chem. Soc.*, 1987, **109,** 929.
438. R. D. Kendrick, S. Friedrich, B. Wehrle, H. H. Limbach and C. S. Yannoni, *J. Magn. Reson.*, 1985, **65,** 159.
439. G. Klebe, K. Hensen and J. von Jouane, *J. Organomet. Chem.*, 1983, **258,** 137.
440. I. S. Chuang, B. L. Hawkins, G. E. Maciel and G. E. Myers, *Macromolecules*, 1985, **18,** 1482.
441. D. W. Duff and G. E. Maciel, *Macromolecules*, 1990, **23,** 4367.
442. G. R. Hatfield and G. E. Maciel, *Macromolecules*, 1987, **20,** 608.
443. W. D. Weber and P. D. Murphy, *Polym. Mater. Sci.*, 1987, **57,** 341.
444. Yong Pan, T. Gullion and J. Schaefer, *J. Magn. Reson.*, 1990, **90,** 330.
445. T. Gullion and J. Schaefer, *J. Magn. Reson.*, 1989, **81,** 196.
446. J. R. Garbow, J. Schaefer, R. Ludicky and C. N. Matthews, *Macromolecules*, 1987, **20,** 305.
447. E. O. Stejskal, J. Schaefer and R. A. McKay, *J. Magn. Reson.*, 1984, **57,** 471.
448. J. Schaefer, E. O. Stejskal, J. R. Grabow and R. A. McKay, *J. Magn. Reson.*, 1984, **59,** 150.
449. G. T. Coker III, J. R. Garbow and J. Schaefer, *Plant Physiol.*, 1987, **83,** 698.
450. G. T. Coker III and J. Schaefer, *Plant Physiol.*, 185, **77,** 129.
451. G. S. Jacob, J. Schaefer and G. E. Wilson Jr, *J. Biol. Chem.*, 1985, **260,** 2777.
452. R. A. McKay, J. Schaefer, E. O. Stejskal, R. Ludicky and C. N. Matthews, *Macromolecules*, 1984, **17,** 1124.
453. C. N. Matthews, R. Ludicky, J. Schaefer, E. O. Stejskal and R. A. McKay, *Origins of Life*, 1984, **14,** 243.
454. Eun Kee Jeong, J. H. Walton, M. A. Doverspike and M. S. Conradi, *J. Magn. Reson.*, 1990, **89,** 381.
455. A. C. Olivieri, *J. Magn. Reson.*, 1989, **81,** 201.
456. B. H. Ruessink and C. Maclean, *Chem. Phys. Lett.*, 1984, **110,** 634.
457. B. H. Ruessink and C. MacLean, *Mol. Phys.*, 1984, **53,** 421.
458. B. H. Ruessink, F. J. J. de Kanter and C. MacLean, *J. Magn. Reson.*, 1985, **62,** 226.
459. Q. Teng, L. K. Nicholson and T. A. Cross, *J. Mol. Biol.*, 1991, **218,** 607.
460. L. K. Nicholson, Q. Teng and T. A. Cross, *J. Mol. Biol.*, 1991, **218,** 621.
461. S. Akoka and C. Tellier, *Biochimie*, 1989, **71,** 137.
462. P. G. Scherer and J. Seelig, *Biochemistry*, 1989, **28,** 7720.
463. Y. Kanazawa, R. Takano, I. Nishizono, K. Koga, M. Ishikawa, W. Higuchi and T. Yamada, *Chem. Lett.*, 1985, 717.
464. H. Gilboa and A. Loewenstein, *Israel J. Chem.*, 1983, **23,** 295.
465. D. Imbardelli, G. Chidichimo and P. Bucci, *Liquid Cryst.*, 1990, **7,** 895.
466. T. M. Barbara, *Mol. Phys.*, 1985, **54,** 651.

467. C. Chachaty, J. Ph. Caniparoli, A. Faure and A. M. Tistchenko, *J. Phys. Chem.*, 1988, **92,** 6330.
468. E. S. Blackmore and G. J. T. Tiddy, *Liquid Cryst.*, 1990, **8,** 131.
469. G. Dombi, P. Diehl, J. Lounila and R. Wasser, *Org. Magn. Reson.*, 1984, **22,** 573.
470. Ch. Tellier, P. Malnoe and S. Poignant, *Org. Magn. Reson.*, 1984, **22,** 727.
471. E. E. Burnell and C. A. de Lange, *Chem. Phys. Lett.*, 1984, **106,** 413.
472. Yoshiteru Seo and Masataka Murakami, *Proc. R. Soc. Lond. B*, 1991, **244,** 191.
473. S. Shapiro, L. C. Vining, M. Laycock, A. G. McInnes and J. A. Walter, *Can. J. Microbiol.* 1985, **31,** 629.
474. P. Krumbiegel, W. Gründer, K. Buchali, K. Hirschberg and H. Faust, *Isotopenpraxis*, 1985, **21,** 316.
475. K. Buchali, W. Gründer, P. Krumbiegel, H. J. Blesin and H. Faust, *Radiobiol. Radiother.*, 1985, **26,** 543.
476. J. Wójcik, L. Stefaniak, M. Witanowski and G. A. Webb, *J. Mol. Struc.*, 1986, **147,** 175.
477. Tetsuo Asakura and Hiroaki Yoshimizu, *Prog. Polym. Phys. Jpn*, 1987, **30,** 741.
478. P. Lundberg, R. G. Weich, P. Jensen and H. J. Vogel, *Plant. Physiol.*, 1989, **89,** 1380.
479. A. B. Venediktov, M. A. Fedotov, S. V. Korenev and A. V. Belyaev, *Koord. Khim.*, 1989, **15,** 556.
480. Keiko Kanamori, R. L. Weiss and J. D. Roberts, *J. Biol. Chem.*, 1987, **262,** 11038.
481. M. F. Roberts, Byong-Seok Choi, D. E. Robertson and S. Lesage, *J. Biol. Chem.*, 1990, **265,** 18207.
482. H. G. O. Becker, D. Pfeifer and R. Radeglia, *Z. Naturforsch.*, 1983, **38b,** 1591.
483. A. H. Clemens, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc. Perkin Trans. II*, 1984, 1667.
484. A. H. Clemens, P. Helsby, J. H. Ridd, F. Al-Omran and J. P. B. Sandall, *J. Chem. Soc. Perkin Trans. II*, 1985, 1217.
485. A. H. Clemens, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc. Perkin Trans. II*, 1984, 1659.
486. A. H. Clemens, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc. Perkin Trans. II*, 1985, 1227.
487. J. F. Johnston, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc. Perkin Trans. II*, 1991, 623.
488. A. M. A. Abu-Namous, J. H. Ridd and J. P. B. Sandall, *Can. J. Chem.*, 1986, **64,** 1124.
489. J. F. Johnston, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc. Chem. Commun.*, 1989, 244.
490. K. M. Morden and S. J. Opella, *J. Magn. Reson.*, 1986, **70,** 476.
491. Nailin Chen, P. J. Witton, C. E. Holloway and I. M. Walker, *Polyhedron*, 1987, **6,** 489.
492. R. E. Wasylishen and J. O. Friedrich, *J. Chem. Phys.*, 1984, **80,** 585.
493. V. P. Tarasov, V. I. Privalov, Yu. A. Buslaev and U. Eichhoff, *Z. Naturforsch.*, 1984, **39b,** 1230.
494. A. Lyčka and P. E. Hansen, *Magn. Reson. Chem.*, 1985, **23,** 973.
495. Yu. A. Strelenko, V. N. Torocheshnikov and N. M. Sergeyev, *J. Magn. Reson.*, 1990, **89,** 123.
496. L. P. Yu and G. M. Smith, *Biochemistry*, 1990, **29,** 2914.
497. R. M. Jarret and M. Saunders, *J. Am. Chem. Soc.*, 1986, **108,** 7549.
498. A. Lyčka and P. E. Hansen, *Org. Magn. Reson.*, 1984, **22,** 569.
499. J. O. Friedrich and R. E. Wasylishen, *J. Chem. Phys.*, 1985, **83,** 3707.
500. K. K. Andersson and A. B. Hooper, *FEBS Letters*, 1983, **164,** 236.
501. J. M. Risley and L. van Etten, *Methods in Enzymology*, 1990, **117,** 376.
502. A. A. DiSpirito and A. B. Hooper, *J. Biol. Chem.*, 1986, **261,** 10534.
503. R. L. van Etten, *Synth. Appl. Isot. Label. Comp.*, 1985, 257.
504. G. Rajendran and R. L. van Etten, *Inorg. Chem.*, 1986, **25,** 876.
505. G. Rajendran, R. E. Santini and R. L. van Etten, *J. Am. Chem. Soc.* 1987, **109,** 4357.
506. J. A. Valley and R. F. Evilia, *Spectrosc. Lett.*, 1990, **23,** 233.
507. M. Audit, D. Davoust, N. Goasdoue and N. Platzer, *Magn. Reson. Chem.*, 1985, **23,** 33.

508. F. Escudero, O. Mó and M. Yáñez, *J. Chem. Soc. Perkin Trans. II*, 1983, 1735.
509. R. T. C. Brownlee and M. Sadek, *Magn. Reson. Chem.*, 1986, **24**, 821.
510. H. Falk, H. Gsaller, E. Hubauer and N. Müller, *Monats. Chem.*, 1985, **116**, 939.
511. Yu. B. Vysotskii, E. A. Zemskaya, B. P. Zemskii and V. I. Dulenko, *Khim. Geterosikl. Soedin.*, 1987, 544.
512. M. Witanowski, L. Stefaniak, P. Dobrowolski, J. Wójcik and G. A. Webb, *Bull. Pol. Acad. Sci.: Chem.*, 1988, **36**, 229.
513. R. Müller, W. von Philipsborn, L. Schleifer, P. Aped and B. Fuchs, *Tetrahedron*, 1991, **47**, 10103.
514. Bo-Long Poh, *Magn. Reson. Chem.*, 1986, **24**, 816.
515. J. Dorie and J. P. Gouesnard, *J. Chem. Phys.* 1985, **82**, 369.
516. M. Witanowski, W. Sicińska and S. Biernat, *Spectrosc. Int. J.*, 1989, **7**, 315.
517. S. Castellino, G. C. Leo, R. D. Sammons and J. A. Sikorski, *Biochemistry*, 1989, **28**, 3856.
518. P. Yu Liping and G. M. Smith, *Biochemistry*, 1988, **27**, 1949.
519. P. Yu Liping and G. M. Smith, *Proc. Natl Acad. Sci. USA*, 1988, **85**, 2894.
520. C. J. Welch, X.-X. Zhou, A. Nyilas, G. Remaud and J. Chattopadhyaya, *Bioactive Molecules*, 1987, **3**, 107.
521. C. Glemarec, J. C. Wu, H. Bazin, G. Remaud, M. Oivanen, H. Lönnberg and J. Chattopadhyaya, *Nucleos. Nucleot.*, 1988, **7**, 801.
522. B. Birdsall, A. W. Bevan, C. Pascual, G. C. K. Roberts, J. Fenney, A. Gronenborn and G. M. Clore, *Biochemistry* , 1984, **23**, 4733.
523. R. Futtero, G. E. Hawkes, E. W. Randall, A. Gasco and C. J. Grombridge, *J. Chem. Soc. Perkin Trans. II*, 1988, 1863.
524. C. T. W. Moonen, W. A. M. van der Berg, M. Boerjan and F. Müller, *Biochemistry*, 1984, **23**, 4873.
525. C. T. W. Moonen, J. Vervoort and F. Müller, *Biochemistry*, 1984, **23**, 4859.
526. S. J. Benkovic, D. Sammons, W. L. F. Armarego, P. Waring and R. Inners, *J. Am. Chem. Soc.*, 1985, **107**, 3706.
527. J. Vervoort, F. Müller, J. LeGall, A. Bacher and H. Sedlmaier, *Eur. J. Biochem.*, 1985, **151**, 49.
528. W. D. Beinert, H. Rüterjans and F. Müller, *Eur. J. Biochem.*, 1985, **152**, 573.
529. P. N. Sanderson, R. D. Farrant, J. C. Lindon and P. Barraclough, *Magn. Reson. Chem.*, 1990, **28**, 874.
530. M. Liu, R. D. Farrant, J. C. Lindon and P. Barraclough, *Spectrosc. Lett.*, 1991, **24**, 665.
531. G. A. Webb and M. Witanowski, *Proc. Indian Acad. Sci.*, 1985, **94**, 241.
532. M. Witanowski, W. Sicińska, S. Biernat and G. A. Webb, *J. Magn. Reson.*, 1991, **91**, 289.
533. M. Witanowski, W. Sicińska, Z. Grabowski and G. A. Webb, *Magn. Reson. Chem.*, 1990, **28**, 988.
534. I. Ando and G. A. Webb, *Org. Magn. Reson.*, 1981, **15**, 111.
535. I. A. Koppel, V. A. Eiber, J. B. Koppel and T. J. Pehk, *Org. Reactivity*, 1988, **25**, 58.
536. B. Tiffon, J. Guillerez and B. Ancian, *Magn. Reson. Chem.* 1985, **23**, 460.
537. Yukio Sasaki, Shin-ichi Watanabe and Yozo Kinoshita, *Acad. Rep. Tokyo Inst. Polytech.*, 1988, **11**, 42.
538. N. S. Rao, M. M. Das, G. B. Rao and D. Ziessow, *Spectrosc. Lett.*, 1985, **18**, 827.
539. S. Toppet, J. De Taeye and Th. Zeegers-Huyskens, *J. Phys. Chem.*, 1988, **92**, 6819.
540. A. M. Avédikian, D. Besserre and R. Spies, *J. Chim. Phys.*, 1988, **85**, 597.
541. A. M. Avédikian, D. Besserre and R. Spies, *J. Chim. Phys.*, 1989, **86**, 625.
542. E. Bojarska-Olejnik, L. Stefaniak, G. A. Webb and I. A. Sadler, *Bull. Pol. Acad. Sci.: Chem.*, 1987, **35**, 81.

543. M. Schlabach, B. Wehrle, H. H. Limbach, E. Bunenberg, A. Knierzinger, A. Y. L. Shu, B. R. Tolf and C. Djerassi, *J. Am. Chem. Soc.*, 1986, **108,** 3856.
544. G. Otting, H. Rumpel, L. Meschede, G. Scherer and H. H. Limbach, *Ber. Bunsenges. Phys. Chem.*, 1986, **90,** 1122.
545. H. H. Limbach and B. Wehrle, *Fresenius Z. Anal. Chem.*, 1987, **327,** 61.
546. G. Scherer and H. H. Limbach, *J. Am. Chem. Soc.*, 1989, **111,** 5946.
547. P. B. Cho, F. F. Kadlubar, S. J. Culp and F. E. Evans, *Chem. Res. Toxicol.*, 1990, **3,** 445.
548. J. A. Connor, R. J. Kennedy, H. M. Dawes, M. B. Hursthouse and N. P. C. Walker, *J. Chem. Soc. Perkin Trans.* II, 1990, 203.
549. B. Clement and T. Kämpchen, *Chem. Ber.*, 1986, **119,** 1101.
550. I. Ya. Mainagashev, O. P. Petrenko, V. V. Lapachev, M. A. Fedotov, I. K. Korobeinicheva and V. P. Mamaev, *Khim. Geterosikl. Soedin.*, 1988, **4,** 514.
551. V. V. Lapachev, A. O. Zagulyaeva, O. P. Petrenko, S. V. Bichkov, V. I. Mamatyuk and V. P. Mamaev, *Tetrahedron*, 1985, **41,** 4897.
552. V. V. Lapachev, S. A. Stekhova, I. Ya. Mainagashev, M. A. Fedotov, V. E. Khall and V. P. Mamaev, *Khim. Geterotsikl. Soedin.*, 1986, 802.
553. V. V. Lapachev, M. A. Fedotov, V. P. Mamaev, L. P. Prikazchikova, V. M. Khutova and V. M. Cherkasov, *Zh. Org. Khim.*, 1986, **22,** 2185.
554. Masahito Niibe and Yoshio Nakamura, *J. Phys. Chem.*, 1984, **88,** 5608.
555. K. Kanamori, B. D. Ross, N. A. Farrow and F. Parivar, *Biochim. Biophys. Acta*, 1991, **1096,** 270.
556. K. Kanamori, B. D. Ross and F. Parivar, *J. Magn. Reson.*, 1991, **93,** 319.
557. N. E. Preece, J. K. Nicholson and J. A. Timbrell, *Biochem. Pharmacol.*, 1991, **41,** 1319.
558. Mao Xian, Xu Guangzhi, Shen Qifeng, Lu Xiaoming and Liu Jun, *Chin. J. Microwave. Radio-freq. Spectrosc.* 1986, **3,** 9.
559. Zhang Xitan and Li Deqian, *Fenxi Huaxue*, 1991, **19,** 353.
560. G. C. K. Roberts and J. Feeney, *Biochemistry* , 1991, **30,** 6330.
561. B. P. Bammel and R. F. Evilia, *Inorg. Chem.*, 1984, **23,** 1574.
562. Mao Xian, Zhao Luji, Xu Guangzhi and Tang Yougi, *Acta Physico-Chim. Sin.*, 1987, **3,** 213.
563. Mamoru Takasuka and Yoshihiro Terui, *J. Chem. Soc. Perkin Trans. II*, 1984, 1545.
564. A. Schanck, R. Brasseur, M. P. Mingeot-Leclercq and P. M. Tulkens, *Magn. Reson. Chem.*, 1992, **30,** 11.
565. S. Akoka, C. Tellier and S. Poignant, *Biochemistry*, 1986, **25,** 6972.
566. O. Lutz, T. Erata, H. Förster and D. Müller, *Naturwissenschschaften*, 1986, **73,** 97.
567. C. F. Poole, B. R. Kersten, S. S. J. Ho, M. E. Coddens and K. G. Furton, *J. Chromatogr.*, 1986, **352,** 407.
568. A. C. Watterson, E. Parkeenvincha, D. N. Chin and J. C. Salamone, *Polymer*, 1991, 87.
569. Yang Li, Liu Peigi, Kong Suling, Dong Ying and Chen Yaozu, *Chem. J. Chin. Univ.*, 1987, **8,** 255.
570. E. Kupče, B. Wrackmeyer and E. Lukevics, *Magn. Reson. Chem.*, 1991, **29,** 444.
571. K. S. Anderson, W. M. Kati, Qi-Zhuang Ye, Jun Liu, C. T. Walsh, A. J. Benesi and K. A. Johnson, *J. Am. Chem. Soc.*, 1991, **113,** 3198.
572. E. Grech, L. Stefaniak, I. Ando, H. Yoshimizu and G. A. Webb, *Bull. Chem. Soc. Jpn*, 1991, **64,** 3761.
573. D. E. Axelson and S. L. Blake, *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23,** 2507.
574. G. G. Furin, M. A. Fedotov, G. G. Yakobson and A. V. Zibarev, *J. Fluorine Chem.*, 1985, **28,** 273.
575. A. Thangaraj, P. R. Rajamohanan, P. M. Suryavanshi and S. Ganapathy, *J. Chem. Soc., Chem. Commun.*, 1991, 493.

576. Chin Yu and G. C. Levy, *Org. Magn. Reson.*, 1984, **22,** 131.
577. S. G. Ward and R. C. Taylor, *Magn. Res. Intr. Adv. Topics and Appl. to Fossil Energy*, 1984, 767.
578. S. J. Berners-Price and P. W. Kuchel, *J. Inorg. Biochem.*, 1990, **38,** 305.
579. S. J. Berners-Price and P. W. Kuchel, *J. Inorg. Biochem.*, 1990, **38,** 327.
580. M. S. Morales-Rios, R. E. del Rio and P. Joseph-Nathan, *Magn. Reson. Chem.*, 1989, **27,** 1039.
581. A. V. Zibarev, M. A. Fedotov and G. G. Furin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 829.
582. S. K. Singh, Y. Singh, A. K. Rai and R. C. Mehrotra, *Polyhedron*, 1989, **8,** 633.
583. E. E. Liepins, M. W. Petrowa, Ya. Ya. Paulinsh, I. Ya. Gubele and E. Yu. Gubriniece, *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 1987, 495.
584. I. J. Chervin, V. S. Nosova, V. F. Rudchenko, W. I. Schevchenko and R. G. Kostyanovskii, *Khim. Geterosikl. Soedin.*, 1988, **3,** 396.
585. H. F. Sleiman, B. A. Arndtsen and L. McElwee-White, *Organometallics*, 1991, **10,** 541.
586. Wang Qi-Wen, Chen Chao-Huan, Zhao En-Yi, Chen Yao-Huan and Sheng Huai-Yu, *Acta Chim. Sinica*, 1986, 332.
587. A. Lyčka, J. Jirman and A. Cee, *Magn. Reson. Chem.*, 1990, **28,** 408.
588. U. Himmelreich, R. Hässner, P. Thomas, F. Tschwatschal and R. Borsdorf, *Monats. Chem.*, 1990, **121,** 923.
589. D. W. Duff and G. E. Maciel, *Macromolecules*, 1991, **24,** 651.
590. M. P. Sibi, *Magn. Reson. Chem.*, 1991, **29,** 401.
591. J. D. Bell, J. A. Lee, H. A. Lee, P. J. Sadler, D. R. Wilkie and R. H. Woodham, *Biochim. Biophys. Acta*, 1991, **1096,** 101.
592. S. M. Zemskova, I. M. Oglezneva, M. A. Fedotov, L. K. Glukhikh and S. V. Larionov, *Izv. Sibir. Otdel. AN SSSR, Ser. Khim.*, 1990, 89.
593. A. Lyčka and K. Palát Jr., *Collect. Czech. Chem. Commun.*, 1991, **56,** 1505.
594. O. Pytela, J. Jirman and A. Lyčka, *Collect. Czech. Chem. Commun.*, 1989, **54,** 2399.
595. A. J. Bennet, V. Somayaji, R. S. Brown and B. D. Santarsiero, *J. Am. Chem. Soc.*, 1991, **113,** 7563.
596. Ichiro Tajima, Takao Suda, Minoru Yamamoto, Kozo Satta and Hidetake Morimoto, *Polym. J.*, 1988, **20,** 919.
597. A. J. Deeming, G. P. Proud, H. M. Dawes and M. B. Hursthouse, *J. Chem. Soc. Dalton Trans.*, 1958, 2475.
598. H. Komber, L. Jakisch, S. Zschoche, H. Möbus, M. Rätzsch and D. Scheller, *Makromol. Chem., Rapid Commun.*, 1991, **12,** 547.
599. Yu. E. Kirsh, S. A. Yakimov, L. A. Sibel'dina and T. M. Karaputadze, *Zh. Fiz. Khim.*, 1988, **62,** 347.
600. I. Hermecz, M. Kajtār, K. Simon, T. Breining, P. R. Surjan, G. Töth and Z. Mêszāros, *J. Org. Chem.*, 1985, **50,** 2918.
601. J. Młochowski, L. Syper, L. Stefaniak, W. Domalewski, W. Schilf and G. A. Webb, *J. Mol. Struct.*, 1992, **268,** 311.
602. R. M. Davidson, G. D. Byrd, E. White, S. A. Margolis and B. Coxon, *Magn. Reson. Chem.*, 1986, **24,** 929.
603. J. Schraml, H. M. Boldhaus, F. Erdt, E. W. Krahe and C. Bliefert, *J. Organomet. Chem.*, 1991, **406,** 299.
604. P. G. De Benedetti, D. Iarossi, M. C. Menziani, C. Frassineti and A. Benedetti, *J. Mol. Struct.*, 1988, **175,** 37.
605. L. B. Dugad and J. T. Gerig, *Biochemistry*, 1988, **27,** 4310.

606. G. Philippossian, D. H. Welti, R. Fumeaux, U. Richli and K. Anantharman, *J. Label. Comp. Radiopharm.*, 1989, **27,** 1267.
607. D. E. Robertson, S. Lesage and M. F. Roberts, *Biochim. Biophys. Acta*, 1989, **992,** 320.
608. G. Uccello-Barretta, C. Rosini, D. Pini and P. Salvadori, *J. Am. Chem. Soc.*, 1990, **112,** 2707.
609. B. P. Pammel and R. F. Evilia, *Inorg. Chim. Acta*, 1984, **81,** L5.
610. Masunobu Maeda, Kohji Okada and Kaname Ito, *J. Inorg. Biochem.*, 1991, **41,** 143.
611. A. J. L. Cooper and A. S. Gelbard, *Biochem. J. Lett.*, 1991, **276,** 271.
612. N. Farrow, K. Kanamori, B. D. Ross and F. Parivar, *Biochem. J. Lett.*, 1991, **276,** 272.
613. S. K. Sarkar, Yukio Hiyama, C. H. Niu, P. E. Young, J. T. Gerig and D. A. Torchia, *Biochemistry*, 1987, **26,** 6793.
614. Yukio Hiyama and D. A. Torchia, *NMR Applications in Biopolymers* (J. W. Finley *et al.*, eds), Plenum Press, New York, 1990, p. 273.
615. P. Krumbiegel, W. Grûnder, K. Buchali and T. Keller, *Isotopenpraxis*, 1990, **26,** 518.
616. M. Neeman, D. Aviv, H. Degani and E. Galun, *Plant. Physiol.*, 1985, **77,** 374.
617. A. Lapidot, *3rd. Eur. Congr. Biotechnol.*, 1984, **2,** 319.
618. L. Inbar and A. Lapidot, *J. Biol. Chem.*, 1988, **263,** 16014.
619. L. Inbar and A. Lapidot, *J. Bacteriol.*, 1988, **170,** 4055.
620. Z. E. Kahana and A. Lapidot, *Anal. Biochem.*, 1985, **149,** 549.
621. B. A. Lewis, S. Cayley, S. Padmanabhan, V. M. Kolb, V. Brushaber, C. F. Anderson and M. T. Record Jr, *J. Magn. Reson.*, 1990, **90,** 612.
622. B. A. Lewis, S. Cayley, S. Padmanabhan, V. M. Kolb, V. Brushaber, C. F. Anderson and M. T. Record Jr, *J. Magn. Reson.*, 1990, **90,** 612.
623. Yiqing Feng, A. J. Wand and S. G. Sligar, *Biochemistry*, 1991, **30,** 7711.
624. J. M. Schmidt, H. Thüring, A. Werner, H. Rüterjans, R. Quaas and U. Hahn, *Eur. J. Biochem.*, 1991, **197,** 643.
625. M. D. Carr, B. Birdsall, T. A. Frenkiel, C. J. Bauer, J. Jimenez-Barbero, V. I. Polshakov, E. McCormick, G. C. K. Roberts and J. Feeney, *Biochemistry*, 1991, **30,** 6330.
626. W. J. Fairbrother, J. Cavanagh, H. J. Dyson, A. G. Palmer, S. L. Sutrina, J. Reizer, M. H. Saier Jr. and P. E. Wright, *Biochemistry*, 1991, **30,** 6896.
627. G. M. Smith, Liping P. Yu and D. J. Domingues, *Biochemistry*, 1987, **26,** 2202.
628. L. P. Yu and G. M. Smith, *Biochemistry*, 1990, **29,** 2920.
629. G. M. Smith and Liping P. Yu, *Biochim. Biophys. Acta*, 1991, **1058,** 75.
630. R. H. Griffey, A. G. Redfield, L. P. McIntosh, T. G. Oas and F. W. Dalquist, *J. Am. Chem. Soc.*, 1986, **108,** 6816.
631. P. Schrader, S. Opella, J. Richards and J. Tomich, *Frontiers of NMR in Molecular Biology*. R. Liss, New York, 1990, p. 109.
632. T. Karayannis, I. P. Gerothanassis, M. Sakarellos-Daitsiotis, C. Sakarellos and M. Marraud, *Biopolymers*, 1990, **29,** 423.
633. F. Martin, *FEBS Letters*, 1985, **182,** 350.
634. F. Martin, G. R. Stewart, I. Genetet and F. Le Tacon, *New Phytol.*, 1986, **102,** 85.
635. D. L. Parry, *Marine Biol.*, 1985, **87,** 219.
636. H. P. Juretschke, *Arch. Int. Physiol. Biochem.*, 1985, **93,** 141.
637. K. Kanamori, R. L. Weiss and J. D. Roberts, *J. Biol. Chem.*, 1988, **263,** 2817.
638. Byong-Seok Choi and M. F. Roberts, *Biochim. Biophys. Acta*, 1987, **928,** 259.
639. N. A. Farrow, K. Kanamori, B. D. Ross and F. Parivar, *Biochem. J.* 1990, **270,** 473.
640. T. Yoneyama, H. Kouchi and O. Ito, *Radioisotopes*, 1988, **37,** 475.
641. J. G. Jones and E. Bellion, *J. Biol. Chem.*, 1991, **266,** 11705.
642. A. Lapidot and L. Inbar, *The Target of Penicillin*, Walter de Gruyter, Berlin, New York, 1983, p. 79.

643. D. G. Reid, D. D. Doddrell, D. H. Williams and K. R. Fox, *Biochim. Biophys. Acta*, 1984, **798**, 111.
644. K. Inouye, T. Hayakawa, Y. Kobayashi, H. Sugeta and Y. Kyogoku, *Peptide Chemistry* (N. Izumiya, ed), 1984, p. 121.
645. V. J. Robinson, P. J. Coles, R. A. Smith and A. Krantz, *J. Am. Chem. Soc.*, 1991, **113**, 7760.
646. D. Neri, G. Otting and K. Wüthrich, *J. Am. Chem. Soc.*, 1990, **112**, 3663.
647. B. E. Schwederski, H. D. Lee and D. W. Margerum, *Inorg. Chem.*, 1990, **29**, 3569.
648. R. Müller, J. D. Wallis and W. von Philipsborn, *Angew. Chem.*, 1985, **24**, 513.
649. P. Crotti, M. Chini, G. Uccello-Barretta and F. Macchia, *J. Org. Chem.*, 1989, **54**, 4525.
650. S. C. V. Au-Yeung, *J. Magn. Reson.*, 1991, **92**, 10.
651. S. Modi, D. V. Behere and S. Mitra, *Biochemistry*, 1989, **28**, 4689.
652. S. Modi, S. S. Deodhar, D. V. Behere and S. Mitra, *Biochemistry*, 1991, **30**, 118.
653. S. Modi, D. V. Behere and S. Mitra, *J. Biol. Chem.*, 1989, **264**, 19677.
654. E. Kupce, E. Upena, M. Trusule and E. Lukevics, *Polyhedron*, 1989, **8**, 2641.
655. E. Kupche, E. Koshkina, M. Trushule and E. Lukevics, *Latv. PSR Zinat. Akad. Vest., Khim. Ser.*, 1989, 751.
656. B. W. Tattershall, *J. Chem. Soc., Chem. Commun.*, 1989, 216.
657. I. A. Grigor'ev, L. B. Volodarsky, A. Z. Gogolev and R. Z. Sagdeev, *Chem. Phys. Lett.*, 1985, **122**, 46.
658. D. W. Aksnes, T. Brekke and K. Maartmann-Moe, *Acta Chem. Scand.*, 1991, **45**, 138.
659. Shyamalava Mazumdar, Okhil K. Medhi and Samaresh Mitra, *J. Chem. Soc. Dalton Trans.*, 1990, 1057.
660. B. J. Gour-Salin, A. C. Storer, A. Castelhano, A. Krantz and V. Robinson, *Enzyme Microbiol. Technol.*, 1991, **13**, 408.
661. E. H. Ellison and D. B. Marshall, *J. Phys. Chem.*, 1991, **95**, 808.
662. M. Ishii, S. Funahashi, K. Ishihara and M. Tanaka, *Bull. Chem. Soc. Jpn*, 1989, **62**, 1852.
663. M. Fourmigue, H. Eggert and K. Bechgaard, *J. Org. Chem.*, 1991, **56**, 4858.
664. L. Stefaniak and M. Witanowski, *Bull. Pol. Acad Sci.: Chem.*, 1987, **35**, 305.
665. L. Stefaniak, M. Witanowski, U. Mahmoud, J. D. Roberts and G. A. Webb, *J. Crystallogr. Spectrosc. Res.*, 1989, **19**, 159.
666. A. Barszczewicz, M. Jaszuński and L. Stefaniak, *Chem. Phys. Lett.*, 1991, **186**, 313.
667. J. Elguero, J. L. G. de Paz, P. Goya, J. A. Páez and I. Rozas, *Heterocycles*, 1990, **31**, 197.
668. J. A. Cano Gorini, J. Farrás, M. Feliz, S. Olivella, A. Solé and J. Vilarrasa, *J. Chem. Soc., Chem. Commun.*, 1986, 959.
669. M. H. Zehfus, M. D. Reily, E. L. Ulrich, W. M. Westler and J. L. Markley, *Arch. Biochem. Biophys.*, 1990, **276**, 369.
670. R. S. Rowlett, T. Klysa and W. W. Shiraki, *J. Label. Comp. Radiopharm.*, 1990, **28**, 1437.
671. W. Schilf, L. Stefaniak, M. Witanowski and G. A. Webb, *Bull. Pol. Ac. Sci. Chem.*, 1985, **33**, 347.
672. L. Stefaniak, B. Kamieński, M. G. Voronkov, L. I. Łarina, V. A. Łopyrev and G. A. Webb, *Bull. Pol. Acad. Sci.: Chem.*, 1991, **39**, 317.
673. V. V. Kozlov, M. E. Niyazymbetov, M. S. Pevzner, B. I. Ugrak and V. A. Petrosyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2814.
674. H. Duddeck, P. Wagner, D. Müller and J. C. Jászbereńyi, *Magn. Reson. Chem.*, 1990, **28**, 549.
675. W. Kożminski, J. Jazwiński, L. Stefaniak and G. A. Webb, *Magn. Reson. Chem.*, 1990, **28**, 1027.
676. W. Kozmiński, J. Jazwiński, L. Stefaniak and G. A. Webb, *J. Mol. Struct.*, 1991, **243**, 369.
677. Seiko Ito and Yoshiko Yano, *Bull. Chem. Soc. Jpn*, 1984, **57**, 2824.

678. D. Jalabert, J. B. Robert, H. Roux-Buisson, J. P. Kintzinger, J. M. Lehn, R. Zinzius, D. Canet and P. Tekely, *Europhys. Lett.*, 1991, **15,** 435.
679. B. Birdsall, J. De Graw, J. Feeney, S. Hammond, M. S. Searle, G. C. K. Roberts, W. T. Colwell and J. Crase, *FEBS Lett.*, 1987, **217,** 106.
680. E. Weilbacher, N. Helle, M. Elsner, H. Kurreck, F. Müller and R. D. Allendoerfer, *Magn. Reson. Chem.*, 1988, **26,** 64.
681. A. W. Afonin, W. K. Woronow, E. I. Enikeewa and M. A. Anbrijankow, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1987, **4,** 769.
682. E. Lukevics, E. Liepins, I. Segal and M. Fleisher, *J. Organomet. Chem.*, 1991, **406,** 283.
683. A. Lyčka, J. Holeček, A. Sebald and I. Tkač, *J. Organomet. Chem.*, 1991, **409,** 331.
684. A. Abbotto, V. Alanzo, S. Bradamante and G. A. Pagani, *J. Chem. Perkin Trans. II*, 1991, 481.
685. C. Sanner, P. Macheroux, H. Rüterjans, F. Müller and A. Bacher, *Eur. J. Biochem.*, 1991, **196,** 663.
686. Fu-Yung Huang, Qing-Xian Yang and Tai-huang Huang, *FEBS Lett.*, 1991, **289,** 231.
687. X. Gao and R. A. Jones, *Nucleos. Nucleot.*, 1988, **6,** 433.
688. L. C. Sowers, D. N. Mahaskar, T. A. Khwaja and M. F. Goodman, *Nucleos. Nucleot.*, 1989, **8,** 23.
689. Chien-Hua Niu, *Anal. Biochem.*, 1984, **139,** 404.
690. B. Fera, B. Singrûn, G. Kupferschmitt, J. Schmidt, F. Buck and H. Rüterjans, *Nucleos. Nucleot.*, 1987, **6,** 477.
691. X. Gao and R. A. Jones, *J. Am. Chem. Soc.*, 1987, **109,** 3169.
692. Chuan Wang, Xiolian Gao and R. A. Jones, *J. Am. Chem. Soc.*, 1991, **113,** 1448.
693. F. E. Evans and R. A. Levine, *J. Biomol. Struct. Dyn.*, 1986, **3,** 923.
694. J. Glushka, O. Bârzu, R. S. Sarfati, V. K. Kansal and D. Cowburn, *Biochem. Biophys. Res. Commun.*, 1990, **172,** 432.
695. G. Barbarella, M. L. Copabianco, L. Tondelli and V. Tugnoli, *Can. J. Chem.*, 1990, **68,** 2033.
696. G. Remaud, X. X. Zhou, C. J. Welch and J. Chattopadhyaya, *Nucleic. Acids Res. Symp. Ser.*, 1987, 169.
697. Chien-Hua Niu, Kyou-hoon Han, H. J. C. Yeh and S. Black, *Biochem. Biophys. Reson. Commun.*, 1987, **148,** 456.
698. T. L. James, P. Bendel, J. W. Keepers and J. E. Taylor, *Bull. Magn. Reson.*, 1983, **5,** 165.
699. Chin Hsiung Lin and L. H. Hurley, *Biochemistry*, 1990, **29,** 9503.
700. B. P. Cho and F. E. Evans, *Nucleic Acid Res.*, 1991, **19,** 1041.
701. A. Nyilas, A. Földesi and J. Chattopadhyaya, *Nucleos. Nucleot.*, 1988, **7,** 787.
702. N. J. Kos, H. Jongejan and H. C. van der Plas, *Gazz. Chim. Ital.*, 1987, **117,** 369.
703. H. Bazin, J. Chattopadhyaya, R. Datema, A. C. Ericson, G. Gilliam, N. G. Jahansson, J. Hansen, R. Koshida, K. Molling, B. Öberg, G. Remaud, G. Steing, L. Vrang, B. Wahren and J. C. Wu, *Biochem. Pharmacol.*, 1989, **38,** 109.
704. C. Giessner-Prettre, *J. Biomol. Struct. Dynam.*, 1984, **2,** 233.
705. B. Thomas and G. Grossmann, *Usp. Khim.*, 1986, **55,** 1124.
706. B. T. Golding, P. K. Slaich and W. P. Watson, *J. Chem. Soc., Chem. Commun.*, 1986, 515.
707. C. W. Allen, P. F. Kelly and J. D. Woollins, *J. Chem. Soc. Dalton Trans*, 1991, 1343.
708. A. Apblett, T. Chivers, A. W. Cordes and R. Vollmerhaus, *Inorg. Chem.*, 1991, **30,** 1392.
709. M. P. Hartshorn, W. T. Robinson, G. W. Wright and Cheng Lin Yong, *Austr. J. Chem.*, 1989, **42,** 1569.
710. L. L. Bondoc and R. Timkovich, *J. Biol. Chem.*, 1989, **264,** 6134.
711. T. Yokoyama, T. Komaki, H. Sato, R. W. Taft and F. Anvia, *J. Org. Chem.*, 1989, **54,** 3983.

712. G. N. Marchenko, V. F. Sopin, V. I. Kovalenko, N. M. Azancheev, E. N. Sergeev and E. M. Belova, *Vysokomol. Soed. Ser. B*, 1988, **30,** 295.
713. I.S. Pronin and A.A. Vashman, *Zh. Neorg. Khim.*, 1987, **32,** 603.
714. G.K. Surya Prakash, L. Heiliger and G. A. Olah, *Inorg. Chem.*, 1990, **29,** 4965.
715. A. Fratiello, V. Kubo-Anderson, S. Azimi, E. Marinez, D. Matejka, R. Perrigan and B. Yao, *J. Soln Chem.*, 1991, **20,** 893.
716. K. H. von Locquenghien, R. Réau and G. Bertrand, *J. Chem. Soc., Chem. Commun.*, 1991, 1192.
717. G. A. Olah, R. Herges, J. D. Felberg and G. K. Surya Prakash, *J. Am. Chem. Soc.*, 1985, **107,** 5282.
718. Wang Qi-Wen, Chen Chao-Huan, Zhao En-Yi, Chen Yao-Huan and Sheng Huai-Yu, *Acta Chim. Sin.*, 1985, **43,** 1101.
719. Wang Qi-Wen, Chen Chao-Huan, Zhao En-Yi, Chen Yao-Huan and Sheng Huai-Yu, *Huaxue Xuebao*, 1985, **43,** 1103.
720. A. Lyčka and V. Machàek, *Dyes and Pigments*, 1986, **7,** 171.
721. J. Jirman and A. Lyčka, *Dyes and Pigments*, 1987, **8,** 55.
722. A. Lyčka, J. Jirman and J. Podstata, *Dyes and Pigments*, 1987, **8,** 465.
723. A. Lyčka and J. Jirman, *Dyes and Pigments*, 1987, **8,** 315.
724. A. Lyčka, T. Liptaj and J. Jirman, *Collect. Czech. Chem. Commun.*, 1987, **52,** 727.
725. Kiyoshi Yamamoto, Kiyoshi Nakai and Toshio Kawaguchi, *Dyes and Pigments*, 1989, **11,** 173.
726. A. Lyčka, M. Nečas, J. Jirman, J. Starka and B. Schneider, *Collect. Czech. Chem. Commun.*, 1990, **55,** 193.
727. A. Lyčka and H. Mustroph, *J. Prakt. Chem.*, 1989, **331,** 11.
728. A. Lyčka, *Dyes and Pigments*, 1990, **12,** 179.
729. S. J. Bell, E. P. Mazzola and B. Coxon, *Dyes and Pigments*, 1989, **11,** 93.
730. S. Simova, R. Radeglia and E. Fanghänel, *J. Prakt. Chem.*, 1983, **5,** 863.
731. D. E. V. Wilman, *Rational Approaches to the Design of Bioactive Compounds* (G. Silipo and A. Vittoria, eds) Elsevier Amsterdam, 1991, p. 159.
732. S. C. F. Au-Yeung, K. W. Kwong and R. J. Buist, *J. Am. Chem. Soc.*, 1990, **112,** 7482.
733. A. R. Butler, A. M. Calsy-Harrison, C. Glidewell and I. L. Johnson, *Inorg. Chim. Acta*, 1988, **146,** 187.
734. M. A. Fedotov and A. V. Belyaev, *Koord. Khim.*, 1990, **16,** 103.
735. S. P. Khranenko, M. A. Fedotov, A. V. Belyaev and A. B. Venediktov, *Koord. Khim.*, 1990, **16,** 991.
736. A. B. Venediktov, S. V. Korenev, M. A. Fedotov and A. V. Belyaev, *Koord. Khim.*, 1990, **16,** 1400.
737. M. A. Fedotov, S. V. Korenev and A. V. Belyaev, *Koord. Khim.*, 1990, **16,** 1272.
738. J. P. Gouesnard, *Bull. Soc. Chim. France*, 1989, 88.
739. J. Oddershede and J. Geersten, *J. Chem. Phys.*, 1990, **92,** 6036.
740. W. Oehme, W. Meiler, J. R. Lochmann and H. Siegel, *Z. Chem.*, 1987, **27,** 431.
741. C. J. Jameson, A. K. Jameson and M. A. ter Horst, *J. Chem. Phys.*, 1991, **95,** 5799.
742. I. S. Pronin and A. A. Washman, *Zh. Neorg. Khim.*, 1983, **28,** 1606.
743. G. V. Lagodzinskaya, N. G. Yunda, E. P. Kirpichev, A. I. Kazakov, Yu. I. Rubcov, V. O. Zavelskii and G. B. Manelic, *Chim. Fiz.*, 1989, **8,** 236.
744. Jun-Jie Yin and J. S. Hyde, *J. Chem. Phys.*, 1989, **91,** 6029.
745. S. Donovan-Mtunzi and R. L. Richards, *J. Chem. Soc. Dalton Trans.*, 1984, 1329.
746. L. Kozerski, K. Kamieńska-Trela, L. Kania and W. von Philipsborn, *Helv. Chim. Acta*, 1983, **66,** 2113.
747. H. D. Franken, H. Rüterjans and F. Müller, *Eur. J. Biochem.*, 1984, **138,** 481.

748. J. D. Halliday, P. E. Bindner and Shahsultan Padamshi, *Can. J. Chem.*, 1984, **62,** 1258.
749. W. Kohl, H. Irschik, H. Reichenbach and G. Höfle, *Liebigs Ann. Chem.*, 1984, 1088.
750. B. N. Hasanow, A. W. Kalinin, A. Ya. Schteyschneyber, A. A. Blumenfeld, S. L. Joffe and W. A. Tartakowskii, *Izv. Akad. Nauk SSSR Ser. Chim.*, 1984, 1296.
751. G. L. Hillhouse and J. E. Bercaw, *J. Am. Chem. Soc.*, 1984, **106,** 5472.
752. H. Sierzputowska-Gracz, M. Wiewiórowski, L. Kozerski and W. von Philipsborn, *Nucleic. Acids Res.*, 1984, **12,** 6247.
753. A. O. K. Nieminen, M. Rautio and E. Rahkamaa, *Magn. Reson. Chem.* 1985, **23,** 419.
754. J. Mistol, N. Grossmann, H. Pietsch and E. Fanghänel, *J. Prakt. Chem.*, 1985, **327,** 371.
755. B. Clement and T. Kämpchen, *Chem. Ber.*, 1985, **118,** 3481.
756. W. W. Bachovchin, *Proc. Natl Acad. Sci. USA*, 1985, **82,** 7948.
757. B. Wrackmeyer, *J. Magn. Reson.*, 1986, **66,** 172.
758. J. Deeming and S. Donovan-Mtunzi, *J. Chem. Soc. Dalton Trans.*, 1985, 1609.
759. I. I. Czerwin, V. F. Rubchenko, S. M. Ignatov and R. G. Kostyanovkii, *Izv. Akad. Nauk Ser. Khim.*, 1986, **3,** 730.
760. Yu Juin and Ye Tingao, *Yuaxue Tongbao*, 1985, **11,** 14.
761. G. M. Blackburn, B. E. Mann, B. F. Taylor and A. F. Worrall, *Eur. J. Biochem.*, 1985, **153,** 553.
762. V. Mlynárik, *Prog. NMR Spectrosc.*, 1986, **18,** 277.
763. Shin-Ichiro Takahashi, Ei-Ichiro Suzuki and Nobuya Nagashima, *Bull. Chem. Soc. Jpn*, 1986, **59,** 1129.
764. J. Vervoort, F. Müller, S. G. Mayhew, W. A. M. van den Berg, C. T. W. Moonen and A. Bacher, *Biochemistry*, 1986, **25,** 6789.
765. G. Otting, H. Rumpel, L. Meschede, G. Scherer and H. H. Limbach, *Ber. Bunsenges Phys. Chem.*, 1986, **90,** 1122.
766. L. Kozerski and A. Krówczyński, *Magn. Reson. Chem.*, 1987, **25,** 46.
767. P. C. Prabhakaran, Nam-Tae Woo, P. Yorgey and S. J. Gould, *Tetrahedron Lett.*, 1986, **27,** 3815.
768. Bhim Sen Saraswat and J. Mason, *Polyhedron*, 1986, **5,** 449.
769. J. Geertsen, J. Oddershede and G. E. Scuseria, *J. Chem. Phys.*, 1987, **87,** 2138.
770. P. Ruostesuo, A. M. Häkkinen and T. Mattila, *Magn. Reson. Chem.*, 1987, **25,** 189.
771. J. Kreutzmann, M. Michalik and B. Thomas, *Z. Chem.*, 1986, **26,** 404.
772. L. N. Kurkovskaya, S. N. Krasnokutskii, V. P. Shabunova, R. N. Akhvlediani and N. N. Suvorov, *Zh. Org. Khim.*, 1986, **22,** 1546.
773. L. N. Kurkovskaya, S. N. Krasnokutskii, L. I. Dmitrevskaya and N. N. Suvorov, *Dokl. Akad. Nauk SSSR*, 1986, **291,** 381.
774. R. E. Reddick and G. L. Kenyon, *J. Am. Chem. Soc.*, 1987, **109,** 4380.
775. Shoichi Ide, Kazuhisa Iwasawa, Akihiro Yoshino, Tadayoshi Yoshida and Kensuke Takahashi, *Magn. Reson. Chem.*, 1987, **25,** 675.
776. H. Haas and M. Willert-Porada, *Z. Anorg. Allg. Chem.*, 1987, **545,** 24.
777. J. Jirman and A. Lyčka, *Collect. Czech. Chem. Commun.*, 1987, **52,** 2474.
778. J. Kizmárik and A. Lyčka, *Pharmazie*, 1987, **42,** 697.
779. F. Boberg, A. Paetz, B. Bruchmann and A. Garming, *Phosph. Sulph.*, 1987, **33,** 99.
780. J. K. M. Sanders, B. K. Hunter, C. J. Jameson and G. Romeo, *Chem. Phys. Lett.*, 1988, **143,** 471.
781. B. Golankiewicz, W. Folkman, H. Rosemeyer and F. Seela, *Nucleic Acids Res.*, 1987, **15,** 9075.
782. G. Albertin, S. Antoniutti, G. Pelizzi, F. Vitali and E. Bordignon, *Inorg. Chem.*, 1988, **27,** 829.

783. A. Lyčka, L. Havlicková, A. Kolonicny and J. Jirman, *Collect. Czech. Chem. Commun.*, 1987, **52,** 736.
784. N. Müller and V. V. Lapachev, *Monats. Chem.*, 1987, **118,** 1201.
785. E. M. M. van der Berg, A. U. Baldew, A. T. J. W. de Goede, J. Raap and J. Lugtenburg, *Recl. Trav. Chim. Pays-Bas*, 1988, **107,** 73.
786. E. T. K. Haupt, H. T. Dieck and P. R. Bontchev, *Z. Naturforsch.*, 1987, **42b,** 1419.
787. D. A. Brown, W. K. Glass, R. Mageswaran and B. Girmay, *Magn. Reson. Chem.*, 1988, **26,** 970.
788. A. Haas and M. Willert-Porada, *Z. Anorg. Allg. Chem.*, 1988, **560,** 169.
789. L. Meschede, D. Gerritzen and H. H. Limbach, *Ber. Bunsenges. Phys. Chem.*, 1988, **92,** 469.
790. V. Mlynárik, *J. Magn. Reson.*, 1988, **79,** 322.
791. V. V. Lapachev, I. Ya. Mainagashev and N. Myuller, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 202.
792. K. M. Larsson and J. Kowalewski, *Spectrochim. Acta*, 1987, **43A,** 545.
793. J. Uzawa and K. Anazi, *Liebiegs Ann. Chem.*, 1988, 1195.
794. I. P. Sekacis, Yu. E. Ancanc, D. A. Biseniece and G. I. Chipens, *Izv. Akad. Nauk Litv. SSR, Ser. Khim.*, 1988, 478.
795. J. Pfeiffer, W. Maringgele, M. Noltemeyer and A. Meller, *Chem. Ber.*, 1989, **122,** 245.
796. V. I. Minkin, A. A. Maksimenko, G. K. Mehrotra, A. G. Maslakov, O. E. Kompan, I. D. Sadekov, Yu. T. Struchkov and D. S. Yufit, *J. Organomet. Chem.*, 1988, **348,** 63.
797. P. Goya, M. L. Jimeno, C. Ochoa, I. Rozas and A. Alemany, *Spectrosc. Int. J.*, 1988, **6,** 33.
798. F. Cristiani, F. A. Devillanova, A. Diaz, F. Isaia and G. Verani, *Spectrosc. Lett.*, 1988, **21,** 767.
799. G. T. Montelione, M. E. Winkler, P. Rauenbuehler and G. Wagner, *J. Magn. Reson.*, 1989, **82,** 198.
800. L. N. Kurkovskaya, V. S. Velezheva, I. K. Sorokina, L. I. Dmitevskaya and V. G. Zhilnikov, *Zh. Org. Khim.*, 1988, **24,** 1541.
801. R. G. Kostyanovski, K. G. Kadorkina, I. I. Chervin and I. K. A. Romiero Mal'donado, *Khim. Geterosikl. Soedin.*, 1988, 757.
802. L. I. Kononov, G. A. Veinberg, E. Liepins and E. Lukevics, *Khim. Geterosikl. Soedin.*, 1988, 1381.
803. A. Kerbal, J. Vebrel, E. Cerutti and B. Laude, *J. Chem. Soc. Chem. Commun.*, 1989, 632.
804. M. von Schlabach, H. Rumpel and H. H. Limbach, *Angew. Chem.*, 1989, **101,** 84.
805. E. Grochowski, J. Winiarski, L. Stefaniak and G. A. Webb, *Bull. Pol. Acad. Sci.: Chem.*, 1991, **39,** 257.
806. D. E. V. Wilman, *Magn. Reson. Chem.*, 1990, **28,** 729.
807. M. de la Concepcion Foces-Foces, F. H. Cano, R. M. Claramunt, D. Sanz, J. Catalán, F. Fabero, A. Furchier and J. Elguero, *J. Chem. Soc. Perkin Trans.* II, 1990, 237.
808. A. Lyčka and J. Cizmárik, *Pharmazie*, 1990, **45,** 371.
809. T. Chivers, D. D. McIntyre, K. J. Schmidt and H. J. Vogel, *J. Chem. Soc., Chem. Commun.*, 1990, 1341.
810. T. Chivers and K. J. Schmidt, *J. Chem. Soc., Chem. Commun.*, 1990, 1342.
811. C. M. Adams and W. von Philipsborn, *Org. Magn. Reson.*, 1985, **23,** 130.
812. A. Fruchier, V. Pellegrin, R. M. Claramunt and J. Elguero, *Org. Magn. Reson.*, 1984, **22,** 473.
813. Yoshihiro Kuroda, Yasuhiro Fujiwara and Kazuhiro Matsushita, *J. Magn. Reson.*, 1985, **62,** 218.

814. A. V. Eremeev, F. D. Polyak, I. A. Vosekalna, I. J. Chervin, Sh. S. Nasibov and R. G. Kostyanovskii, *Khim. Geterosikl. Soedin.*, 1984, 1343.
815. L. Leitis, E. Liepins, D. Jansone and M. Shimanskaya, *Latv. PSR Zinat. Akad. Vestis. Khim. Ser.*, 1984, **6**, 719.
816. K. Michalik, K. Peseke and R. Radeglia, *J. Prakt. Chem.*, 1985, **327**, 103.
817. Ju. Ju. Popelis, E. E. Liepins and E. Ya Lukevics, *Khim. Geterosikl. Soedin.*, 1985, 1172.
818. A. Schmidpeter and B. Wrackmeyer, *Z. Naturforsch*, 1986, **41b**, 553.
819. J. Riand, M. T. Chenon, C. C. Tzeng and R. P. Panzica, *J. Chem. Soc. Perkin Trans. II*, 1986, 931.
820. V. K. Jain, J. Mason and R. C. Mehrotra, *J. Organomet. Chem.*, 1986, **309**, 45.
821. V. K. Jain, J. Mason, B. S. Saraswat and R. C. Mehrotra, *Polyhedron*, 1985, **4**, 2089.
822. J. Jirman and A. Lyčka, *Chemicky Prumysl*, 1987, 482.
823. Jun Uzawa and Kentaro Anzai, *Can. J. Chem.*, 1987, **65**, 2691.
824. G. J. Schrobilgen, *J. Chem. Soc. Chem. Commun.*, 1988, 863.
825. J. R. A. Vogt and P. Renz, *Eur. J. Biochem.*, 1988, **171**, 655.
826. P. G. Jones, H. W. Roesky and J. Schimkowiak, *J. Chem. Soc. Chem. Commun.*, 1988, 730.
827. J. Farrás, E. Fos, R. Ramos and J. Vilarrasa, *J. Org. Chem.*, 1988, **53**, 887.
828. L. Weber and M. Mühlstädt, *Z. Chem.*, 1988, **28**, 26.
829. D. Lenz, *J. Fluorine Chem.*, 1988, **39**, 305.
830. I. Sekacis, J. Ancans, D. Biseniece and G. Cipens, *Latv. PSR Zinat. Akad. Vestis., Khim. Ser.*, 1988, 478.
831. Kioshi Uchida, Akira Toyama, Yukiko Tamura, Michiaki Sugimura, Fumiyuki Mitsumori, Yukiko Furukawa, Hideo Takeuchi and Issei Harada, *Inorg. Chem.*, 1989, **28**, 2067.
832. W. Holzer and W. von Philipsborn, *Magn. Reson. Chem.*, 1989, **27**, 511.
833. B. Wrackmeyer, *Z. Naturforsch.*, 1989, **44b**, 653.
834. L. Stefaniak, M. Witanowski, U. Mahmoud, J. D. Roberts and G. A. Webb, *J. Crystallogr. Spectrosc. Res.*, 1989, **19**, 159.
835. W. A. Dorokhov, A. R. Amamchyan and W. S. Bogdanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 2386.
836. Toshiharu Ohta, Koichi Shudo and Toshihiko Okamoto, *Tetrahedron Lett.*, 1984, **25**, 325.
837. J. W. Lown, S. M. S. Chauhan, R. R. Koganty and A. M. Sapse, *J. Am. Chem. Soc.*, 1984, **106**, 6401.
838. B. P. Mikhova, M. F. Simeonov and S. L. Spassov, *Magn. Reson. Chem.*, 1985, **23**, 474.
839. A. Albinati, H. Moriyama, H. Rüegger, P. S. Pregosin and A. Togni, *Inorg. Chem.*, 1985, **24**, 4430.
840. F. Terrier, J. C. Halle, P. MacCormack and M. J. Pouet, *Can. J. Chem.*, 1989, **67**, 503.
841. Z. E. Kahana, A. Gopher, M. Dorsman and A. Lapidot, *Anal. Biochem.*, 1988, **174**, 374.
842. K. H. Harmon, T. E. Nelson and M. S. Janos, *J. Mol. Struct.*, 1989, **213**, 185.
843. M. Dargatz, C. Preussler, K. Kellner and E. Klienpeter, *Phosp. Sulph. Silic.*, 1990, **47**, 437.
844. A. A. Gakh, B. I. Ugrak and V. V. Kiseleva, *Izv. Akad. Nauk SR, Ser. Khim.*, 1990, 2069.
845. C. Lopez, R. M. Claramunt, D. Sanz, C. Foces Foces, F. H. Cano, R. Faure, E. Cayon and J. Elguero, *Inorg. Chim. Acta*, 1990, **176**, 195.
846. Tetsuo Asakura, Yasuo Watanabe and Takuro Itoh, *Macromolecules*, 1984, **17**, 2421.
847. H. P. Juretschke and A. Lapidot, *Eur. J. Biochem.*, 1984, **143**, 651.
848. W. M. Gołebiewski and J. D. Spenser, *Can. J. Chem.*, 1985, **63**, 2707.
849. J. Rana and D. J. Robins, *J. Chem. Soc., Chem. Commun.*, 1983, 1335.
850. J. Rana and D. J. Robins, *J. Chem. Soc., Chem. Commun.*, 1984, 81.

851. G. Tóth and A. Almásy, *Magyar Kémiai Folyóirat*, 1983, **89**, 555.
852. Yuzo Yoshikawa, Yuichi Masuda and Hideo Yamatera, *J. Magn. Reson.*, 1984, **58**, 473.
853. A. Lyčka and P. Vetešnik, *Collect. Czech. Chem. Commun.*, 1984, **49**, 963.
854. R. M. Elofson, Natsuko Cyr, J. K. Laidler and K. F. Schulz, *Tetrahedron Lett.*, 1984, **25**, 3039.
855. A. Lyčka *Collect. Czech. Chem. Commun.*, 1984, **49**, 2801.
856. R. K. Harris, P. Jonsen and K. J. Packer, *Magn. Reson. Chem.*, 1985, **23**, 565.
857. R. L. Baxter, C. J. McGregor, G. A. Thomson and A. I. Scott, *J. Chem. Soc. Perkin Trans* I, 1985, 369.
858. R. L. Baxter, E. M. Abbot, S. L. Greenwood and I. J. McFarlane, *J. Chem. Soc., Chem. Commun.*, 1985, 564.
859. M. D. Coburn, *J. Label. Comp. Radiopharm.*, 1985, **22**, 183.
860. E. Fanghänel, R. Radeglia, K. H. Bedemann, H. Mohammed, J. Kriwanek and P. Steinmüller, *J. Prakt. Chem.*, 1985, **327**, 627.
861. J. Rana and D. J. Robins, *J. Chem. Res. (S)*, 1985, 196.
862. V. Macháek, A. Lyčka and M. Nádvornik, *Collect. Czech. Chem. Commun.*, 1985, **50**, 2598.
863. S. R. Maple and A. Allerhand, *J. Am. Chem. Soc.*, 1987, **109**, 56.
864. T. Axenrod, X. H. Huang, M. J. Wieder and C. M. Watnick, *Magn. Reson. Chem.*, 1986, **24**, 274.
865. Masatsune Kainosho, Hiromasa Nagao and Takashi Tsuji, *Biochemistry*, 1987, **26**, 1068.
866. H. A. Kelly and D. J. Robins, *J. Chem. Soc. Perkin Trans. I*, 1987, 177.
867. J. Rana and D. J. Robins, *J. Chem. Soc. Perkin Trans. I*, 1986, 1133.
868. Adel A. A. Emara and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1987, 1644.
869. E. Leete, Sung Hoon Kim and Jatinder Rana, *Phytochemistry*, 1988, **27**, 401.
870. P. J. Seaton and S. J. Gould, *J. Am. Chem. Soc.*, 1988, **110**, 5912.
871. M. J. Taylor, D. J. Calvert and C. M. Hobbis, *Magn. Reson. Chem.*, 1988, **26**, 619.
872. Yun-Hwa L. Mau and Wei-Yeh Wang, *Plant Physiol*, 1988, **86**, 793.
873. W. M. Westler, B. J. Stockman, J. L. Markley, Y. Hosoya, Y. Miyake and M. Kainosho, *J. Am. Chem. Soc.*, 1988, **110**, 6256.
874. M. S. Solum, J. C. Facelli, Z. Gan and D. M. Grant, *Mol. Phys.*, 1988, **64**, 1031.
875. E. Leete and Sung Hoon Kim, *J. Am. Chem. Soc.*, 1988, **110**, 2976.
876. C. G. Moreland, E. O. Stejskal, S. C. J. Sumner, J. D. Memory, F. I. Carroll, G. A. Brine and P. S. Portoghese, *J. Magn. Reson.*, 1989, **83**, 173.
877. B. Wrackmeyer, *Z. Naturforsch.*, 1988, **43b**, 923.
878. R. Thiericke, A. Zeeck, J. A. Robinson, J. M. Beale and H. G. Floss, *J. Chem. Soc. Chem. Commun.*, 1989, 402.
879. X. Creary and A. F. Sky, *J. Am. Chem. Soc.*, 1990, **112**, 368.
880. J. Jirman, A. Lyčka and M. Ludwig, *Collect. Czech. Chem. Commun.*, 1990, **55**, 136.
881. L. Weber, R. Szargan, B. Schulze and M. Mühlstädt, *Magn. Reson. Chem.*, 1990, **28**, 419.
882. K. L. Brown and B. D. Gupta, *Inorg. Chem.*, 1990, **29**, 3854.
883. J. Raap, C. M. van der Wielen and J. Lugtenburg, *Rect. Trav. Chim. Pays-Bas*, 1990, **109**, 277.
884. K. Kurumaya and M. Kajiwara, *Chem. Pharm. Bull.*, 1990, **38**, 2589.
885. Whe-Warn Chop, M. Pomerantz and M. K. Witzcak, *J. Org. Chem.*, 1990, **55**, 716.
886. W. N. Chou and M. Pomerantz, *J. Org. Chem.*, 1991, **56**, 2762.
887. R. Radeglia, R. Wolf, Th. Steiger, S. Simowa and E. Fanghänel, *J. Prakt. Chem.*, 1984, **326**, 511.
888. A. R. Butler, C. Glidewell, A. R. Hyde and J. McGinnis, *Inorg. Chem.*, 1985, **24**, 2931.
889. P. Ruostesuo, A. M. Häkkinen and J. Karjalainen, *Spectrochim. Acta*, 1986, **42A**, 1005.

890. Hiroko Suezawa, Tomoaki Yuzuri, Minoru Hirota, Yoshio Ito and Yoshiki Hamada, *Bull. Chem. Soc. Jpn*, 1990, **63**, 328, 891.
891. S. Donovan-Mtunzi, R. L. Richards and J. Mason, *J. Chem. Soc. Dalton Trans.*, 1984, 469.
892. H. von Bandmann, P. Heymanns, C. Siem and P. Rademacher, *Angew. Chem.*, 1984, **96**, 354.
893. R. Radeglia, S. Simowa and E. Fanghänel, *Z. Chem.*, 1984, **24**, 190.
894. S. Donovan-Mtunzi, R. L. Richards and J. Mason, *J. Chem. Soc. Dalton Trans*, 1984, 2729.
895. A. R. Butler, C. Glidewell, A. R. Hyde and J. McGinnis, *Polyhedron*, 1984, **3**, 1165.
896. G. A. Olah, R. Herges, K. Laali and G. A. Segal, *J. Am. Chem. Soc.*, 1986, **108**, 2054.
897. G. G. Furin, O. I. Andreevskaya, A. I. Rezvukhin and G. G. Yakobson, *J. Fluorine Chem.*, 1985, **28**, 1.
898. A. R. Butler, C. Glidewell and I. L. Johnson, *Polyhedron*, 1987, **6**, 1147.
899. Ē. Kupče, E. Lukevics, Y. M. Varezhkin, A. N. Mikhailova and V. D. Sheludyakov, *Organometallics*, 1988, **7**, 1649.
900. B. L. Haymore, M. Hughes, J. Mason and R. L. Richards, *J. Chem. Soc. Dalton Trans*, 1988, 2935.
901. W. B. Jennings, D. Randall, S. D. Worley and J. H. Hargis, *J. Chem. Soc. Perkin Trans. II*, 1981, 1411.
902. A. John, B. Thomas, A. Pfützner and G. Grossmann, *Z. Anorg. Allg. Chem.*, 1984, **511**, 7.
903. W. B. Jennings, M. S. Tolley, J. H. Hargis, S. D. Worley and L. Chang, *J. Chem. Soc. Perkin Trans. II*, 1984, 1207.
904. M. Pomerantz, B. T. Ziemnicka, Z. M. Merchant, Whe-Narn Chou, W. B. Perkins and S. Bittner, *J. Org. Chem.*, 1985, **50**, 1757.
905. B. Thomas, A. John, A. Pfützner, G. Grossmann and E. Herrmann, *Z. Anorg. Allg. Chem.*, 1985, **525**, 7.
906. M. Pomerantz, Whe-Narn Chou, M. K. Witczak and C. G. Smith, *Phosph. Sulph.*, 1987, **30**, 799.
907. J. Szewczyk and L. D. Quin, *J. Org. Chem.*, 1987, **52**, 1190.
908. R. T. Boeré, A. W. Cordes and R. T. Oakley, *J. Am. Chem. Soc.*, 1987, **109**, 7781.
909. P. F. Kelly and J. D. Woollins, *J. Chem. Soc. Dalton Trans.*, 1988, 1053.
910. M. Haddad, J. Barrans, G. Pfister-Guillouxo and J. P. Largox, *J. Chem. Res. (M)*, 1989, 1815.
911. J. Tomasz, S. Bottka and L. Radics, *Nucleos. Nucleot.*, 1989, **8**, 1297.
912. W. Domalewski, W. Schilf, L. Stefaniak and G. A. Webb, *Magn. Reson. Chem.*, 1991, **39**, 295.
913. B. Costisella, J. Schultz, H. Teichmann, C. Donath and M. Meisel, *Phosph. Sulph.*, 1990, **53**, 367.
914. C. W. Allen, P. F. Kelly and J. D. Woolins, *J. Chem. Soc., Dalton Trans*, 1991, 1343.
915. E. Carmona, E. Gutiērrez-Puebla, A. Monge, P. J. Pērez and L. J. Sanchez, *Inorg. Chem.*, 1989, **28**, 2120.
916. A. H. Klahn and D. Sutton, *Organometallics*, 1989, **8**, 198.
917. J. P. Le Ny and J. A. Osborn, *Organometallics*, 1991, **10**, 1546.
918. L. Olgemöller and W. Beck, *Chem. Ber.*, 1984, **117**, 1241.
919. R. Kuroda, I. M. Ismail and P. J. Sadler, *J. Inorg. Biochem.*, 1984, **22**, 103.
920. T. G. Appleton, J. R. Hall and S. F. Ralph, *Austr. J. Chem.*, 1986, **39**, 1347.
921. F. Macdonald and P. J. Sadler, *Biochemical Mechanisms of Platinum Antitumour Drugs* (D. C. H. McBrien and T. F. Slater, eds), p. 361.

922. L. S. Hollis, E. W. Stern, A. R. Amundsen, A. V. Miller and S. L. Doran, *J. Am. Chem. Soc.*, 1987, **109**, 3596.
923. S. Al-Baker and J. C. Dabrowiak, *Inorg. Chem.*, 1987, **26**, 613.
924. S. Al-Baker, J. F. Vollano and J. C. Dabrowiak, *J. Am. Chem. Soc.*, 1986, **108**, 5643.
925. T. G. Appleton, J. W. Connor and J. R. Hall, *Inorg. Chem.*, 1988, **27**, 130.
926. T. G. Appleton, J. R. Hall, T. W. Hambley and P. D. Prenzler, *Inorg. Chem.* 1990, **29**, 3562.
927. T. G. Appleton, J. W. Connor, J. R. Hall and P. D. Prenzler, *Inorg. Chem.*, 1989, **28**, 2030.
928. T. G. Appleton, J. R. Hall, T. W. Hambley and P. D. Prenzler, *Inorg. Chem.*, 1990, **29**, 3562.
929. T. G. Appleton, R. J. Hall, D. W. Neale and C. S. M. Thompson, *Inorg. Chem.*, 1990, **29**, 3985.
930. E. Kupče, E. Liepinš, A. Lapsina, G. Zelcans and E. Lukevics, *J. Organomet. Chem.*, 1987, **333**, 1.
931. B. Wrackmeyer and Hong Zhou, *Magn. Reson. Chem.*, 1990, **28**, 1066.
932. E. Kupče and E. Lukevicš, *J. Organomet. Chem.*, 1988, **358**, 67.
933. E. Kupče, E. Liepinš and E. Lukevicš, *Angew Chem.*, 1985, **24**, 568.
934. V. P. Tarasov, V. J. Privalov, G. A. Kirakosyan and Yu. A. Buslaev, *Z. Naturforsch.*, 1983, **38b**, 1173.
935. C. Stader, B. Wrackmeyer and D. Schlosser, *Z. Naturforsch.*, 1988, **43b**, 707.
936. E. Kupče and E. Lukevicš, *Khim. Geterosikl. Soedin.*, 1989, 701.
937. A. Quassas, J. C. Duplan, B. Fenet and B. Frange, *Magn. Reson. Chem.*, 1990, **28**, 693.
938. K. Seppelt and H. Oberhammer, *Inorg. Chem.*, 1985, **24**, 1227.
939. K. C. Molly, K. Quill, S. J. Blunden and R. Hill, *J. Chem. Soc. Dalton Trans*, 1986, 875.
940. J. Holeček, A. Lyčka and R. Wagener, *Collect. Czech. Chem. Commun.*, 1986, **51**, 2116.
941. C. Stader, B. Wrackmeyer and D. Schlosser, *Z. Naturforsch.*, 1987, **43b**, 707.
942. A. Lyčka, J. Holecek, B. Schneider and J. Straka, *J. Organomet. Chem.*, 1990, **389**, 29.
943. C. Stader and B. Wrackmeyer, *J. Organomet. Chem.*, 1987, **321**, C1.
944. S. J. Blunden, P. A. Cusack and D. G. Gillies, *J. Magn. Reson.*, 1984, **60**, 114.
945. F. Preuss, W. Towae, V. Kruppa and E. Fuchslocher, *Z. Naturforsch.*, 1984, **39b**, 1510.
946. G. C. van Stein, G. van Koten, B. de Bok, L. C. Taylor, K. Vreize and C. Brevard, *Inorg. Chim. Acta*, 1984, **89**, 29.
947. J. Bultitude, L. F. Larkworthy, J. Mason, D. C. Povey and B. Sandell, *Inorg. Chem.*, 1984, **23**, 3629.
948. M. Minelli, J. L. Hubbard, D. L. Lichtenberger and J. H. Enemark, *Inorg. Chem.*, 1984, **23**, 2721.
949. A. S. Galiano-Roth, E. M. Michaelides and D. B. Collum, *J. Am. Chem. Soc.*, 1988, **110**, 2658.
950. F. E. Romesberg, J. H. Gilchrist, A. T. Harrison, D. J. Fuller and D. B. Collum, *J. Am. Chem. Soc.*, 1991, **113**, 5751.
951. F. De Sarlo, A. Brandi, L. Fabrizi, A. Guarna and N. Niccolai, *Org. Magn. Reson.*, 1984, **22**, 372.
952. Adel A. A. Emara and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1988, 257.
953. R. Kimmich, W. Nusser and F. Winter, *Phys. Med. Biol.*, 1983, **29**, 593.
954. S. Donovan-Mtunzi, R. L. Richards and J. Mason, *J. Chem. Soc. Dalton. Trans.*, 1984, 2429.
955. R. Kimmich, W. Nusser and F. Winter, *Phys. Med. Biol.*, 1983, **29**, 593.
956. F. Winter and R. Kimmich, *Biophys. J.*, 1985, **48**, 331.
957. F. Winter, R. Kimmich and W. Nusser, *XXII Congr. AMPERE Magn. Rel. Phenom. Proc.* 1984, 477.

958. S. Koenig, *Biophys. J.*, 1988, **53**, 91.
959. C. F. Beaulieu, R. D. Brown III, J. I. Clark, M. Spiller and S. H. Koenig, *Magn. Reson. Chem.*, 1989, **10**, 362.
960. S. H. Koenig, C. F. Beaulieu, R. D. Brown III and M. Spiller, *Biophys. J.*, 1990, **57**, 461.
961. S. H. Koenig, *Biophys. J.*, 1988, **53**, 91.
962. J. Tritt-Goc, R. Goc, E. Ponnusamy and D. Fiat, *Int. J. Pept. Prot. Res.*, 1987, **29**, 406.
963. J. Tritt-Goc, R. Goc and D. Fiat, *Ferroelectrics*, 1988, **80**, 83.
964. E. D. Gotsis and D. Fiat, *Congr. AMPERE Proc.*, 1984, 502.
965. S. Padmanabhan, B. Richey, C. F. Anderson and M. T. Record Jr, *Biochemistry*, 1988, **27**, 4367.
966. B. M. Braun and M. Holz, *Z. Phys. Chem. Neue Folge*, 1983, **135**, 77.
967. B. M. Braun and M. Holz, *J. Soln. Chem.*, 1983, **12**, 685.
968. M. Holz and A. Sacco, *Z. Phys. Chem.*, 1987, **153**, 129.
969. H. Kovacs, J. Kowalewski, A. Maliniak and P. Stilbs, *J. Phys. Chem.*, 1989, **93**, 962.
970. Tadashi Tokuhiro, *J. Chem. Soc. Faraday Trans. II*, 1988, **84**, 1793.
971. L. Plomp, A. C. Loman and J. Bulthuis, *J. Chem. Phys.*, 1986, **84**, 6591.
972. Huang Yi-Ning, Li Zhi-Fen, Liu Rui-Lin and Yuan Han-Zhen, *Acta Chim. Sin.*, 1989, **47**, 491.
973. B. Ancian and B. Tiffon, *J. Chem. Soc. Faraday Trans. II*, 1984, **80**, 1067.
974. V. F. Galat and E. V. Titov, *J. Mol. Struct.*, 1988, **174**, 303.
975. R. J. Trepanier and M. A. Whitehead, *J. Mol. Struct.*, 1983, **111**, 415.
976. H. M. Ratajczak and J. A. Ladd, *J. Mol. Lig.*, 1984, **29**, 97.
977. T. Eriksen and E. J. Pedersen, *Mol. Phys.*, 1984, **53**, 1411.
978. Seiko Ito and Yoshiko Yano, *Bull. Chem. Soc. Jpn*, 1984, **57**, 2824.
979. Taro Eguchi and Michihiko Kishita, *J. Phys. Soc. Jpn*, 1984, **53**, 3640.
980. O. Söderman, H. Walderhaug, U. Henriksson and P. Stilbs, *J. Phys. Chem.*, 1985, **89**, 3963.
981. Y. Uzu, J. Nakagawa and M. Yokoi, *Bull. Chem. Soc. Jpn*, 1986, **59**, 2891.
982. A. Belmajdoub, J. Brondeau, J. C. Boubel and D. Canet, *Chem. Phys. Lett.*, 1987, **140**, 389.
983. O. Söderman, G. Carlström, M. Monduzzi and U. Olsson, *LANGMUIR*, 1988, **4**, 1039.
984. A. Belamajdoub, K. ElBayed, J. Brondeau, D. Canet, I. Rico and A. Lattes, *J. Phys. Chem.*, 1988, **92**, 3569.
985. A. Belmajdoub, J. C. Boubel and D. Canet, *J. Phys. Chem.*, 1989, **93**, 4844.
986. Tuck, C. Wong, K. Ikeda, K. Meguro, O. Söderman, U. Olsson and B. Lindman, *J. Phys. Chem.*, 1989, **93**, 4861.
987. J. D. Halliday, P. E. Bindner and Shahsultan Padamshi, *Can. J. Chem.*, 1985, **63**, 2975.
988. B. Dietrich, J. P. Kintzinger, J. M. Lehn, B. Metz and A. Zahidi, *J. Phys. Chem.*, 1987, **91**, 6600.
989. Keiko Koga and Yoko Kanazawa, *Chem. Phys. Lipids*, 1984, **36**, 153.
990. Keiko Koga, Yoshitsugu Tanaka and Yoko Kanazawa, *Chem. Phys. Lipids*, 1985, **36**, 285.
991. Yoko Kanazawa, Keiko Koga and Isao Nishizono, *J. Magn. Reson.*, 1985, **62**, 518.
992. D. D. McIntyre, A. W. Apblett, P. Lundberg, K. J. Schmidt and H. J. Vogel, *J. Magn. Reson.*, 1989, **83**, 377.
993. N. S. Golubev, N. D. Orlova and R. Khamitov, *Opt. Spektrosc.*, 1987, **62**, 1005.
994. R. E. Wasylishen and A. M. de P. Nicholas, *Magn. Reson. Chem.*, 1986, **24**, 1031.
995. C. Chang, F. Fish, D. D. Muccio and T. St. Pierre, *Macromolecules*, 1987, **20**, 621.
996. A. Martin de P. Nicholas and R. E. Wasylishen, *J. Phys. Chem.*, 1985, **89**, 5446.

997. A. Martin de P. Nicholas and R. E. Wasylishen, *Can. J. Chem.*, 1987, **65,** 951.
998. R. E. Wasylishen, *Can. J. Chem.*, 1986, **64,** 773.
999. J. Dolinsek and R. Blinc, *J. Phys. C: Solid State Phys.*, 1988, **21,** 705.
1000. A. C. Olivieri, *J. Chem. Soc. Perkin Trans. II*, 1990, 85.
1001. S. D. Kennedy and R. G. Bryant, *J. Magn. Reson.*, 1989, **83,** 565.
1002. J. B. Lambert and D. Stec, *Org. Magn. Reson.*, 1984, **22,** 301.
1003. N. Benetis, J. Kowalewski, L. Nordenskiöld and U. Edlund, *J. Magn. Reson.*, 1984, **58,** 282.
1004. S. Khazaeli and R. E. Viola, *J. Inorg. Biochem.*, 1984, **22,** 33.
1005. H. R. Kricheldorf and W. E. Hull, *Int. J. Biol. Macromol.*, 1984, **6,** 81.
1006. D. G. Powell and L. J. Mathias, *J. Am. Chem. Soc.*, 1990, **112,** 669.
1007. D. W. Urry, T. L. Trapane, R. B. McMichens, M. Jqbal, R. Dean Harris and K. U. Prasad, *Biopolymers*, 1986, **25,** S209.
1008. Byung-Ha Oh and J. L. Markley, *Biochemistry*, 1990, **29,** 4012.
1009. J. Jarvet, A. Olivson, U. Mets, M. Pooga, R. Aguraiuja and E. Lippmaa, *Eur. J. Biochem.*, 1989, **186,** 287.
1010. V. P. Chacko and R. G. Bryant, *J. Magn. Reson.*, 1984, **57,** 79.
1011. C. J. Jameson, A. K. Jameson and N. C. Smith, *J. Chem. Phys.*, 1987, **86,** 6833.
1012. S. Donovan-Mtunzi, C. J. MacDonald, R. L. Richards, G. E. Hawkes and J. Mason, *J. Chem. Soc. Dalton Trans.*, 1985, 2473.
1013. C. L. Perrin and R. K. Gipe, *J. Am. Chem. Soc.*, 1986, **108,** 1088.
1014. C. L. Perrin and R. K. Gipe, *Science*, 1987, **238,** 1393.
1015. A. M. C. Harnden, B. K. Hunter and R. J. C. Brown, *J. Magn. Reson.*, 1990, **88,** 334.
1016. N. Jurani, *XXII Congr. AMPERE Magn. Rel. Phenom Proc.*, 1984, 365.
1017. G. S. Lukat and H. M. Goff, *J. Biol. Chem.*, 1986, **261,** 16528.
1018. S. Modi, D. V. Behere and S. Mitra, *Indian J. Chem.*, 1990, **29A,** 301.
1019. S. Modi, A. K. Saxena, D. V. Behere and S. Mitra, *Biochim. Biophys. Acta*, 1990, **1038,** 164.
1020. A. R. Katritzky, T. I. Yousaf, Ban Chi Chen and Zeng Guang-Zhi, *Tetrahedron*, 1986, **42,** 623.
1021. F. H. Köhler, N. Hertkorn and J. Blümel, *Chem. Ber.*, 1987, **120,** 2081.
1022. G. Anderegg, K. Popov and P. S. Pregosin, *Helv. Chim. Acta*, 1986, **69,** 329.
1023. C. Chang, D. D. Muccio, T. St. Pierre, C. C. Chen and C. G. Overberger, *Macromolecules*, 1986, **19,** 913.
1024. B. Wrackmeyer, C. Stader and Hong Zhou, *Spectrochim. Acta*, 1989, **45A,** 1101.
1025. E. W. Della, B. Kasum and K. P. Kirkbride, *J. Am. Chem. Soc.*, 1987, **109,** 2746.
1026. E. Haslinger, M. Reithmaier, W. Robien and P. Wolschann, *Monats. Chem.*, 1984, **115,** 375.
1027. P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Declerq and M. M. Woolfson, *J. Chem. Res. (H)*, 1987, 1946.
1028. J. P. Picavet and H. Sliwa, *J. Chem. Res. (S)*, 1987, 230.
1029. D. Barbry, B. Hasiak and D. Couturier, *Magn. Reson. Chem.*, 1990, **28,** 560.
1030. L. D. Quin, K. C. Caster, B. G. Marsi and J. A. Miller, *J. Org. Chem.*, 1986, **51,** 3724.
1031. J. W. Davies and J. R. Malpass, *Tetrahedron Lett.*, 1985, **26,** 4537.
1032. E. E. Liepins, P. T. Trapencer and I. Ya. Kalvinsh, *Khim. Geterosikl. Soedin.*, 1988, 1336.
1033. H. Hilpert, L. Hoesch and A. S. Dreiding, *Helv. Chim. Acta*, 1987, **70,** 381.
1034. J. H. Nelson, N. E. Takach, R. A. Henry, D. W. Moore, W. M. Tolles and G. A. Gray, *Magn. Reson. Chem.*, 1986, **24,** 984.
1035. L. N. Kojkow, P. B. Terentev, I. P. Glorizov, W. N. Torocheschnikov and I. G. Bunbel, *Zh. Org. Khim.*, 1984, **20,** 1621.

1036. H. Fritz, *Bull. Soc. Chim. Belg.*, 1984, **93,** 559.
1037. A. R. Katritzky, D. L. Ostercamp and T. I. Yousaf, *Tetrahedron*, 1986, **42,** 5729.
1038. H. Duddeck and M. Kaiser, *Spectrochim. Acta*, 1985, **41,** 913.
1039. B. S. Iyengar, T. Takahashi, W. A. Remers and W. T. Bradner, *J. Med. Chem.*, 1986, **29,** 144.
1040. L. M. Jackmann, L. M. Scarmoutzos, B. D. Smith and P. G. Williard, *J. Am. Chem. Soc.*, 1988, **110,** 6058.
1041. A. V. Afonin, V. K. Voronkov and M. A. Andriyankov, *Zh. Obshch. Khim.*, 1986, **56,** 2806.
1042. I. Ya. Mainagashev, V. V. Lapachev, M. A. Fedotov and V. P. Fedotov, *Khim. Geterosikl. Soedin.*, 1987, 1663.
1043. R. Csuk, N. Müller and H. Sterk, *Z. Naturforsch.* 1985, **40b,** 987.
1044. Zhu Jin-Chang, Sun Xian-Yu, Wu Hua-Ju, Jiang Li-Jin, Chen Bang-Quin and Wu Guan-Li, *Acta Chim. Sin.*, 1985, **43,** 1151.
1045. H. Nöth and H. Prigge, *Chem. Ber.*, 1986, **119,** 338.
1046. C. Habben, A. Meller, M. Noltemeyer and G. M. Sheldrick, *J. Organomet. Chem.*, 1985, **288,** 1.
1047. A. Meller, W. Maringgele, G. Elter, D. Bromm, M. Noltemeyer and G. M. Sheldrick, *Chem. Ber.*, 1987, **120,** 1437.
1048. C. Habben, A. Meller, M. Noltemeyer and G. M. Sheldrick, *Z. Naturforsch.*, 1986, **41b,** 1093.
1049. A. Meller, D. Bromm, W. Maringgele, D. Böhler and G. Elter, *J. Organomet. Chem.*, 1988, **347,** 1..
1050. C. D. Habben, *Chem. Ber.*, 1988, **121,** 1967.
1051. G. Klebe, K. Hensen and J. von Jouane, *J. Organomet. Chem.*, 1983, **258,** 137.
1052. C. Paulmier, P. Lerouge, F. Outurquin, S. Chapelle and P. Granger, *Magn. Reson. Chem.*, 1987, **25,** 955.
1053. J. S. DePue and D. B. Collum, *J. Am. Chem. Soc.*, 1988, **110,** 5518.
1054. Chisako Yamagami, Narao Takao and Yoshito Takeuchi, *Austr. J. Chem.*, 1988, **41,** 1.
1055. T. Yokoyama, I. Hanazome, M. Mishima, M. J. Kamlet and R. W. Taft, *J. Org. Chem.*, 1987, **52,** 163.
1056. Chisako Yamagami, Narao Takao and Yoshito Takeuchi, *Austr. J. Chem.*, 1989, **42,** 463.
1057. D. W. Duff and G. E. Maciel, *Macromolecules*, 1990, **23,** 3069.
1058. A. Garrone, R. Fruttero, C. Tironi and A. Gasco, *J. Chem. Soc. Perkin Trans. II*, 1989. 1941.
1059. Yu Jun and Ye Ting-Gao, *Acta Chim. Sin.*, 1987, 1023.
1060. A. M. Orendt, J. Michl and J. Reiter, *Magn. Reson. Chem.*, 1989, **27,** 1.
1061. P. Goya, A. Herrero, M. L. Jimeno, C. Ochoa, J. A. Páez, F. H. Cano, C. Foces-Foces and M. M. Ripoll, *Heterocycles*, 1988, **27,** 2201.
1062. V. Machaček, V. Štěrba, J. Kolb and A. Lyčka, *Collect. Czech. Chem. Commun.*, 1988, **53,** 1044.
1063. B. J. Clark and R. Grayshan, *J. Chem. Res. (S)*, 1984, 62.
1064. B. J. Clark and R. Grayshan, *J. Chem. Res. (S)*, 1984, 64.
1065. K. Laali, J. Szele and H. Zollinger, *Helv. Chim. Acta*, 1983, **66,** 1737.
1066. J. R. Ebdon, P. E. Heaton, T. N. Huckerby, W. T. S. O'Rourke and J. Parkin, *Polymer*, 1984, **25,** 821.
1067. Yu Jun and Guo Zungru, *Chinese J. Magn. Reson.*, 1989, **6,** 65.
1068. D. R. Doerge, N. M. Cooray, A. B. K. Yee and W. P. Niemczura, *J. Label. Comp. Radiopharm.*, 1990, **28,** 739.
1069. I. Wawer, *Magn. Reson. Chem.*, 1989, **27,** 1031.

1070. H. Köhler, V. I. Nefedov, G. Birkner, M. Jeschke and A. Kolbe, *Z. Anorg. Allg. Chem.*, 1986, **542**, 59.
1071. N. N. Gerasimchuk, W. W. Skopenko and S. I. Tyukhtenko, *Ukr. Chim. J.*, 1985, **51**, 232.
1072. M. S. Samples and C. H. Yoder, *J. Organomet. Chem.*, 1987, **332**, 69.
1073. Rao Lingfen, Chen Yixuan and Li Wenzhao, *Acta Physico-Chim. Sin.*, 1987, **3**, 632.
1074. J. P. Gouesnard, *Bull. Soc. Chim. Fr.*, 1988, 132.
1075. D. G. Powell, A. M. Sikes and L. J. Mathias, *Polym. Preparations*, 1988, **29**, 86.
1076. P. Ruostesuo, A. M. Häkkinen and K. Peltola, *Spectrochim. Acta*, 1985, **41A**, 739.
1077. J. H. Glans and G. R. Hatfield, *J. Label. Comp. Radiopharm.*, 1989, **27**, 1341.
1078. Hiroko Suezawa, Kin-Ya Tsuchiya, Eiji Tahara and Minoru Hirota, *Bull. Chem. Soc. Jpn*, 1988, **61**, 4057.
1079. J. de Abajo and H. R. Kricheldorf, *J. Macromol. Sci. Chem.*, 1984, **A21**, 411.
1080. E. J. Schier, W. Sacher and W. Beck, *Z. Naturforsch.*, 1987, **42b**, 1424.
1081. R. S. Balestrero, D. M. Forkey and J. G. Russell, *Magn. Reson. Chem.*, 1986, **24**, 651.
1082. A. M. Häkkinen and P. Ruostesuo, *Magn. Reson. Chem.*, 1985, **23**, 424.
1083. A. M. Häkkinen, P. Ruostesuo and S. Kurkisuo, *Magn. Reson. Chem.*, 1985, **23**, 311.
1084. P. Rudostesuo, A. M. Häkkinen, R. Liias-Lepistö and U. Salminen, *Spectrochim. Acta*, 1988, **44A**, 1105.
1085. M. I. M. Wazeer and Sk. Asrof Ali, *Magn. Reson. Chem.*, 1990, **28**, 601.
1086. G. Y. Kuo, B.Y-H. Hwang and D. B. Staiger, *Biochem. Pharmacol.*, 1986, **35**, 1613.
1087. A. C. Kuesel, W. Kuhn, J. Sianoudis, L. H. Grimme, D. Leibfritz and A. Mayer, *Arch. Microbiol.*, 1989, **151**, 434.
1088. W. W. Bachovchin, *Biochemistry*, 1986, **25**, 7751.
1089. W. W. Bachovchin, W. Y. L. Wong and S. Farr-Jones, *Bull. Magn. Reson.*, 1986, **8**, 189.
1090. W. W. Bachovchin, W. Y. L. Wong, S. Farr-Jones, A. B. Shenvi and C. A. Kettner, *Biochemistry*, 1988, **27**, 7689.
1091. E. K. Jaffe, G. D. Markham and J. S. Rajagopalan, *Biochemistry*, 1990, **29**, 8345.
1092. J. Glushka, M. Lee, S. Coffin and D. Cowburn, *J. Am. Chem. Soc.*, 1990, **112**, 2843.
1093. P. R. Gooley, M. S. Caffrey, M. A. Cusanovich and N. E. MacKenzie, *Biochemistry*, 1990, **29**, 2278.
1094. P. Leighton and Ponzy Lu, *Biochemistry*, 1987, **26**, 7262.
1095. H. Knoblauch, H. Rüterjans, W. Bloemhoff and K. E. T. Kerling, *Eur. J. Biochem.*, 1988, **172**, 485.
1096. I. P. Gerothanassis, T. Karayannis, M. Sakarellos-Daitsiotis, K. Sakarellos and M. Marraud, *J. Magn. Reson.*, 1987, **75**, 513.
1097. Akira Shoji, Takuo Ozaki, Teruaki Fujito, Kenzo Deguchi, Shinji Ando and Isao Ando, *Macromolecules*, 1989, **22**, 2860.
1098. M. Giffard, J. Cousseau and G. J. Martin, *J. Chem. Soc. Perkin Trans. II*, 1985, 157.
1099. E. Kupčhe, L. Ignatovitch and E. Lukevičš, *Latv. PSR Zinat. Akad. Vestis., Khim. Ser.*, 1988, **5**, 625.
1100. A. V. Mischenko, V. E. Fedotov, B. A. Kolesov and M. A. Fedotov, *Koord. Khim.*, 1989, **15**, 200.
1101. T. Yamaguchi, K. Yamamoto and H. Ohtaki, *Bull. Chem. Soc. Jpn*, 1985, **58**, 3235.
1102. J. B. Lambert, J. A. McConnell and W. J. Schulz Jr, *J. Am. Chem. Soc.*, 1986, **108**, 2482.
1103. Von. V. Bosáček, D. Freude, W. Gründer, W. Meiler and H. Pfeifer, *Z. Phys. Chem.*, 1984, **265**, 241.
1104. E. T. K. Haupt and D. Leibfritz, *Spectrochim. Acta*, 1989, **45A**, 119.
1105. J. Blixt, B. Györi and J. Glaser, *J. Am. Chem. Soc.*, 1989, **111**, 7784.
1106. Kiyoshi Matsumoto, Takane Uchida, Yukio Ikemi, Hideo Fujita, Kinuyo Aoyama and Momoyo Asahi, *Heterocycles*, 1986, **24**, 339.

1107. K. Matsumoto, T. Uchida, K. Aoyama and M. Asahi, *Chem. Express*, 1986, **1**, 423.
1108. M. Minelli and W. J. Maley, *Inorg. Chem.*, 1989, **28**, 2954.
1109. Toshiaki Taura, *Inorganica Chim. Acta*, 1989, **163**, 131.
1110. D. V. Behere, E. Gonzalez-Vergara and H. M. Goff, *Biochim. Biophys. Acta*, 1985, **832**, 319.
1111. G. S. Lukat, K. R. Rodgers, M. N. Jabro and H. M. Goff, *Biochemistry*, 1989, **28**, 3338.
1112. D. V. Behere, D. C. Ales and H. M. Goff, *Biochim. Biophys. Acta*, 1986, **871**, 285.
1113. Yushitsugu Shiro, Tetsutaro Iizuka, Ryu Makino, Yuzuru Ishimura and Isao Morishima, *J. Am. Chem. Soc.*, 1989, **111**, 7707.
1114. H. McNab, *J. Chem. Soc. Perkin Trans.* I, 1987, 657.
1115. P. Dobrowolski, B. Kamieński, J. Sitkowski, L. Stefaniak and Yu Chun, *Bull. Pol. Acad. Sci.: Chem.*, 1988, **36**, 203.
1116. B. Kamieński, W. Schilf, L. Stefaniak and G. A. Webb, *Bull. Pol. Sci. Chem.*, 1989, **37**, 323.
1117. H. P. Köst, E. Benedikt, E. Cmiel and S. Schneider, *Z. Naturforsch.*, 1983, **38c**, 943.
1118. N. Müller, *XXII Congr. AMPERE Magn. Reson. Rel. Phenom. Pres.*, 1984, 337.
1119. H. Falk, N. Müller and S. Wansch, *Monats. Chem.*, 1985, **116**, 1087.
1120. H. Falk and H. Flödl, *Monats. Chem.*, 1985, **116**, 1177.
1121. B. Wrackmeyer, *J. Organomet. Chem.*, 1985, **297**, 265.
1122. N. N. Becker and J. D. Roberts, *Biochemistry*, 1984, **23**, 3336.
1123. W. Schilf, L. Stefaniak and G. A. Webb, *Magn. Reson. Chem.*, 1987, **25**, 721.
1124. F. Compernolle and S. Toppet, *J. Heterocycl. Chem.*, 1986, **23**, 541.
1125. Yasuhiko Yamamoto, Norishige Nanai, Yoshio Inoue and Riichiro Chujo, *J. Chem. Soc., Chem. Commun.*, 1989, 1419.
1126. E. Bojarska-Olejnik, L. Stefaniak, M. Witanowski and G. A. Webb, *Bull. Pol. Acad. Sci.: Chem.*, 1987, **35**, 86.
1127. S. Nagarajan, S. R. Wilson and K. L. Rinehart Jr., *J. Org. Chem.*, 1985, **50**, 2174.
1128. S. Tono-Oka, *Chem. Lett.*, 1987, 2233.
1129. J. Jaźwiński, W. Kożmiński, L. Stefaniak and G. A. Webb, *J. Mol. Struct.*, 1991, **243**, 365.
1130. G. L'abbé, M. Gelinne and S. Toppet, *J. Heterocycl. Chem.*, 1989, **26**, 729.
1131. P. G. Tsoungas and B. F. De Costa, *Magn. Reson. Chem.*, 1988, **26**, 8.
1132. B. Kamieński, W. Schilf, J. Sitkowski, L. Stefaniak and G. A. Webb, *J. Crystallogr. Spectrosc. Res.*, 1989, **19**, 1003.
1133. J. Jaźwiński, L. Stefaniak and G. A. Webb, *Magn. Reson. Chem.*, 1988, **26**, 1012.
1134. J. Jaźwiński and L. Stefaniak, *Bull. Pol. Acad. Sci.: Chem.*, 1991, **39**, 265.
1135. D. B. Adams, M. Hooper, A. G. Morpeth, E. S. Raper, W. Clegg and B. Stoddart, *J. Chem. Soc. Perkin Trans.* 2, 1990, 1269.
1136. J. Jaźwiński, L. Stefaniak, M. Witanowski and G. A. Webb, *Bull. Pol. Acad. Sci.: Chem.*, 1989, **37**, 313.
1137. J. C. Lindon, J. M. Williams and P. Barraclough, *Magn. Reson. Chem.*, 1986, **24**, 55.
1138. D. Freude, H. Pfeifer, H. Schmidt and B. Staudte, *Z. Phys. Chem.*, 1984, **265**, 250.
1139. Z. Dega-Szafran, M. Szafran, L. Stefaniak, C. Brevard and M. Bourdonneau, *Magn. Reson. Chem.*, 1986, **24**, 424.
1140. R. M. Claramunt, J. Elguero, R. Faure and E. Elguero, *J. de Chim. Phys.*, 1984, **81**, 413.
1141. Yu. A. Strelenko, O. A. Rakitin, V. A. Ogurtsov, T. I. Godovikova and L. I. Khmel'nitskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 2848.
1142. G. Toth, A. Szllsy, C. Szantay, A. Almasy, I. Hermecz, A. Horvath, L. Vasvari-Debreczy and Z. Meszaros, *Magy. Kem. Foly*, 1988, **94**, 132.
1143. M. V. Jovanovic, *Spectrochim. Acta*, 1984, **40A**, 637.

1144. J. Schripsema, R. Verpoorte, A. B. Svendsen and C. Erkelens, *Spectrosc. Lett.*, 1987, **20,** 777.
1145. A. Lyčka, J. Holeček, M. Nádvornik and K. Handlíř, *J. Organomet. Chem.*, 1985, **280,** 323.
1146. J. Jirman, A. Lyčka, J. Holeček, K. Hadlíř, M. Nádvornik and S. T. M. Teleb, *Sb. Věd. Praci. Vys. Škola Chem. Technol. Pardubice*, 1987, **50,** 57.
1147. H. McNab and G. S. Smith, *J. Chem. Soc. Perkin Trans. I*, 1984, 381.
1148. B. J. Clark, R. Grayshan and K. J. McCullough, *J. Chem. Res. (S)*, 1985, 50.
1149. L. Kaczmarek, L. Stefaniak and G. A. Webb, *J. Crystallogr. Spectrosc. Res.*, 1987, **17,** 411.
1150. A. F. Janzen, T. Q. Nguyen, Fangi Qu and K. Marat, *J. Chem. Soc., Chem. Commun.*, 1988, 1274.
1151. G. Klebe, K. Hensen and J. von Jouanne, *J. Organomet. Chem.*, 1983, **258,** 137.
1152. P. Goya, C. Ochoa, I. Rozas, A. Alemany and M. Luisa Jimeno, *Magn. Reson. Chem.*, 1986, **24,** 444.
1153. J. Elguero, M. J. Jimeno, R. Nieves, C. Ochoa and A. Alemany, *J. Chem. Soc. Perkin Trans. II*, 1988, 859.
1154. W. D. Beinert, H. Rüterjans and F. Müller, *Flavins and Flavoproteins Proc. Int. Symp.*, 1984, 211.
1155. W. D. Beinert, H. Rüterjans, F. Müller and A. Bacher, *Eur. J. Biochem.*, 1985, **152,** 581.
1156. J. Vervoort, F. Muller, D. J. O'Kane, J. Lee and A. Bacher, *Biochemistry*, 1986, **25,** 8067.
1157. S. Pust, J. Vervoot, K. Decker, A. Bacher and F. Müller, *Biochemistry*, 1989, **28,** 516.
1158. J. Vervoort, D. J. O'Kane, F. Müller, A. Bacher, G. Strobl and J. Lee, *Biochemistry*, 1990, **29,** 1823.
1159. F. Seela, H. Rosemeyer, A. Biesewig and T. Jurgens, *Nucleos. Nucleot.*, 1988, **7,** 581.
1160. G. Remaud, C. J. Welch, X-X. Zhou and J. Chattopadhyaya, *Nucleos. Nucleot.*, 1988, **7,** 167.
1161. G. Remaud, X-X. Zhou, J. Chattopadhyaya, M. Oivanen and H. Lönnberg, *Tetrahedron*, 1987, **43,** 4453.
1162. P. B. Cho, F. F. Kadlubar, S. J. Culp and F. E. Evans, *Chem. Res. Toxicol.*, 1990, **3,** 445.
1163. G. Barbarella, A. Bertoluzza and V. Tugnoli, *Magn. Reson. Chem.*, 1987, **25,** 864.
1164. G. Barbarella, A. Bertoluzza and V. Tugnoli, *Nucleic Acids Res.*, 1988, **16,** 7202.
1165. G. W. Buchanan and M. J. Bell, *Magn. Reson. Chem.*, 1986, **24,** 493.
1166. G. Barbarella, A. Bertoluzza, M. A. Morelli, M. R. Tosi and V. Tugnoli, *Gazz. Chim. Ital.*, 1988, **118,** 637.
1167. R. H. Griffey, D. Davis, Z. Yamaizumi, S. Nishimura, Ad Bax, B. Hawkins and C. D. Poulter, *J. Biol. Chem.*, 1985, **260,** 9734.
1168. L. Kozerski, H. Sierzputowska-Gracz, W. Krzyżosiak, M. Bartek-Wiewiórowska, M. Jaskólski and M. Wiewiórowski, *Nucleic Acids Res.*, 1984, **12,** 2205.
1169. U. Hahn, R. Desai-Hahn and H. Rüterjans, *Eur. J. Biochem.*, 1985, **146,** 705.
1170. G. Barbarella, M. L. Copabianco, A. Carcuro, F. P. Colonna, A. Garbesi and V. Tugnoli, *Can. J. Chem.*, 1988, **66,** 2492.
1171. G. Remaud, J. Kjellberg, N. G. Johansson and J. Chattopadhyaya, *Tetrahedron*, 1987, **43,** 365.
1172. D. R. Davis, R. H. Griffey, Z. Yamaizumi, S. Nishimura and C. D. Poulter, *J. Biol. Chem.*, 1986, **261,** 3584.
1173. M. Pomerantz, Whe-Narn Chou, M. K. Witczak and C. S. Smith, *J. Org. Chem.*, 1987, **52,** 159.
1174. Von B. Thomas, G. Grossman, W. Bieger and A. Porzel, *Z. Anorg. Allg. Chem.*, 1983, **504,** 138.

1175. G. S. Harbison, S. O. Smith, J. E. Roberts, J. A. Pardoen, P. P. J. Mulder, C. Winkel, J. M. L. Courtin, R. A. Mathies, J. Lugtenburg, J. Herzfeld and R. G. Griffin, *MNR in Biology and Medicine*, 1986, 33.
1176. J. P. Gouesnard and J. Dorie, *Bull. Soc. Chim. France*, 1985, **II**, 132.
1177. P. S. Belton and J. D. Woollins, *Magn. Reson. Chem.*, 1986, **24**, 1080.
1178. A. W. Zibarev, G. G. Furin, I. K. Korobeinicheva, M. A. Fedotov and G. G. Jacobson, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1983, 2259.
1179. W. Sicińska, L. Stefaniak, M. Witanowski and G. A. Webb, *J. Mol. Spectrosc.*, 1987, **158**, 57.
1180. K. T. Bestari, R. T. Boeré and R. T. Oakley, *J. Am. Chem. Soc.*, 1989, **111**, 1579.
1181. J. Passmore and M. J. Schriver, *Inorg. Chem.*, 1988, **27**, 2749.
1182. A. Apblett and T. Chivers, *Inorg. Chem.*, 1989, **28**, 4544.
1183. A. Haas and M. Rieland, *Chimia*, 1988, **42**, 67.
1184. M. D. Coburn, C. B. Storm, D. W. Moore and T. G. Archibald, *Magn. Reson. Chem.*, 1990, **28**, 16.
1185. M. D. Coburn, C. B. Storm, D. W, Moore and T. G. Archibald, *Magn. Reson. Chem.*, 1990, **28**, 16.
1186. A. Lyčka, V. Machaček and J. Jiřman, *Collect. Czech. Chem. Commun.*, 1987, **52**, 2946.
1187. G. A. Olah, G. K. Surya-Prakash, Massoud Arvanaghi, V. V. Krishnamurthy and Subhash C. Narang, *J. Am. Chem. Soc.*, 1984, **106**, 2378.
1188. M. R. Amin, L. Dekker, D. B. Hibbert, J. H. Ridd and J. P. B. Sandall, *J. Chem. Soc., Chem. Commun.*, 1986, 658.
1189. T. Axenrod, B. Liang and S. Bulusu, *Magn. Reson. Chem.*, 1989, **27**, 925.
1190. V. A. Lagutenkov, D. I. Skorovarov, V. S. Ulyanov, A. A. Vashman and I. S. Pronin, *Zh. Fiz. Khim.*, 1986, **60**, 1299.
1191. A. E. Lemire, A. F. Janzen and K. Marat, *Inorg. Chim. Acta*, 1985, **110**, 237.
1192. A. E. Lemire, A. F. Janzen and K. Marat, *Inorg. Chim. Acta*, 1986, **114**, 211.
1193. I. S. Pronin and A. A. Washman, *Zh. Neorg. Khim.*, 1987, **32**, 728.
1194. A. Fratiello, V. Kubo-Anderson, S. Azimi, T. Flores, E. Marinez, D. Matejka, R. Perrigan and M. Vigil, *J. Soln Chem.*, 1990, **19**, 811.
1195. M. I. Khalil, *Inorg. Chem.*, 1990, **29**, 5131.
1196. L. M. Anderson, A. R. Butler and A. S. McIntosch, *J. Chem. Soc. Perkin Trans. II*, 1987, 1239.
1197. H. Hilpert, L. Hoesch and A. S. Dreiding, *Helv. Chim. Acta*, 1985, **68**, 325.
1198. M. Sawada, Y. Takai, T. Tanaka, T. Hanafusa, M. Okubo and Y. Tsuno, *Bull. Chem. Soc. Jpn*, 1990, **63**, 702.
1199. R. J. Buist, S. C. F. Au-Yeung and D. R. Eaton, *Can. J. Chem.*, 1985, **63**, 3558.
1200. Y. Odaka, A. Yamasaki and M. Watabe, *Bull. Chem. Soc. Jpn*, 1985, **58**, 3407.
1201. A. W. Belyaev, A. B. Benediktov, M. A. Fedotov and S. C. Khranenko, *Koord. Chim.*, 1986, **12**, 690.
1202. M. M. Gerasimchuk, W. W. Skopenko and S. I. Tiuchtenko, *Dokl. Akad. Ukr. PCP, Ser. B: Geol. Chim.*, 1984, 33.
1203. V. V. Skopenko, N. N. Gerasimchuk, S. I. Tjuchtenko and H. Köhler, *Z. Anorg. Allg. Chem.*, 1986, **542**, 65.
1204. O. A. Domaschevskaya, W. D. Khavruchenko and N. N. Gerashimchuk, *Ukr. Chim. Zh.*, 1988, **54**, 235.
1205. J. D. Roberts, L. Stefaniak, G. A. Webb and M. Witanowski, *Bull. Pol. Acad. Sci.: Chem.*, 1986, **34**, 81.
1206. R. Kupper, B. D. Hilton, M. B. Kroeger-Koepke, S. R. Koepke and C. J. Michejda, *J. Org. Chem.*, 1984, **49**, 3781.

1207. R. L. Willer, C. K. Lowe-Ma, D. W. Moore and LeRoy F. Johnson, *J. Org. Chem.*, 1984, **49,** 1481.
1208. J. Dorie, J. P. Gouesnard, B. Mechin and P. Mellet, *J. Mol. Struct.*, 1986, **144,** 185.
1209. S. Affolter and P. S. Pregosin, *J. Organomet. Chem.*, 1990, **398,** 197.
1210. V. M. Mastikhin, I. L. Mudrakovsky and S. V. Filimonova, *Chem. Phys. Lett.*, 1988, **149,** 175.
1211. V. M. Mastikhin, I. L. Mudrakovsky and S. V. Filimonova, *Zeolites*, 1990, **10,** 593.
1212. G. I. Bordokin, I. R. Elanov, M. M. Shakirov and V. G. Shubin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 206.
1213. M. Witanowski, W. Sicińska and G. A. Webb, *Spectrosc. Int. J.*, 1991, **9,** 55.
1214. S. N. Anderson, R. L. Richards and D. L. Hughes, *J. Chem. Soc. Dalton Trans.*, 1986, 245.
1215. N. J. Lazarowych, R. H. Morris and J. M. Ressner, *Inorg. Chem.*, 1986, **25,** 3926.
1216. R. E. Norman and P. J. Sadler, *Inorg. Chem.*, 1988, **27,** 3583.
1217. T. G. Appleton, J. R. Hall, S. F. Ralph and C. S. M. Thompson, *Austr. J. Chem.*, 1988, **41,** 1425.
1218. R. Bramley, M. Brorson, A. M. Sargeson and C. E. Schaffer, *Inorg. Chem.*, 1987, **26,** 314.
1219. Yoshiaki Nakashima, Masayuki Muto, Keiichi Kawano, Yoshimasa Kyogoku and Yuzo Yoshikawa, *Bull. Chem. Soc. Jpn*, 1989, **62,** 2455.
1220. C. G. Young, M. Minelli, J. H. Enemark, W. Hussain, C. J. Jones and J. A. McCleverty, *J. Chem. Soc. Dalton Trans.*, 1987, 619.
1221. P. D. Duffin, L. F. Larkworthy, J. Mason, A. N. Stephens and R. M. Thompson, *Inorg. Chem.*, 1987, **26,** 2034.
1222. C. Glidewell and I. L. Johnson, *Chim. Scripta*, 1987, **27,** 441.
1223. D. E. Fjare and W. L. Gladfelter, *J. Am. Chem. Soc.*, 1984, **106,** 4799.
1224. M. Minelli, C. G. Young and J. H. Enemark, *Inorg. Chem.*, 1985, **24,** 1111.
1225. D. Sellmann, J. Keller, M. Moll, C. Campana and M. Haase, *Inorg. Chim. Acta*, 1988, **141,** 243.
1226. R. E. Stevens, D. E. Fjare and W. L. Gladfelter, *J. Organomet. Chem.*, 1988, **347,** 373.
1227. D. R. Mantell and W. L. Gladfelter, *J. Organomet. Chem.*, 1988, **347,** 333.
1228. T. Godemeyer, K. Dehnicke and E. Fluck, *Z. Anorg. Allg. Chem.*, 1988, **565,** 41.
1229. T. J. DiFeo, R. A. Schiksnis, R. K. Kohli, S. J. Opella and A. Nath, *Magn. Reson. Chem.*, 1989, **27,** 127.
1230. K. Kurumaya, T. Okazaki and M. Kajiwara, *Chem. Pharm. Bull.*, 1990, **38,** 1058.
1231. K. L. Brown, H. B. Brooks, Xiang Zou, M. Victor, A. Ray and R. Tomkovich, *Inorg. Chem.*, 1990, **29,** 4841.
1232. A. Lyčka and J. Čižmárik, *Pharmazie*, 1988, **43,** 133.
1233. A. Lyčka and J. Čižmárik, *Pharmazie*, 1987, **42,** 271.
1234. J. Čižmárik and A. Lyčka, *Pharmazie*, 1988, **43,** 794.
1235. R. Cervellati, D. G. Lister, A. Degli Espostiand F. Ortolani, *Il Nuovo Cimento*, 1984, **3,** 475.
1236. C. Stutz and D. Early, *J. Mol. Struct.*, 1983, **111,** 31.
1237. M. Gourdji, L. Guibé, A. Kaplan and A. Péneau, *J. Mol. Struct.*, 1983, **111,** 371.
1238. A. Péneau, M. Gourdji and L. Guibé, *J. Mol. Struct.*, 1983, **111,** 227.
1239. R. Ambrosetti, R. Angelone, A. Colligiani and J. Murgich, *J. Mol. Struct.*, 1983, **111,** 255.
1240. A. Lötz and J. Voitländer *J. Magn. Reson.*, 1984, **58,** 235.
1241. M. L. Buess and P. J. Bray, *Org. Magn. Reson.*, 1984, **22,** 233.
1242. E. A. Keiter, Y. Hiyama and T. L. Brown, *J. Mol. Struct.*, 1983, **111,** 1.
1243. B. Ancian and B. Tiffon, *J. Chem. Soc. Faraday Trans.*, 1980, **80,** 1076.
1244. J. Murgich, Magaly Santana R. and J. Abanero, *Magn. Reson. Chem.*, 1985, **23,** 145.

1245. R. Blinc, M. Vilfan and J. Seliger, *Bull. Magn. Reson.*, 1983, **5,** 51.
1246. A. Péneau, A. H. Fuchs, L. Guibé and H. Szwarc, *C. R. Acad. Sci.*, 1984, **298,** 551.
1247. Hisao Negita, Toshinori Suzuki, Tsuneo Kubo, Michio Maekawa, Shinei Gima and Tsutomu Okuda, *Bull. Chem. Soc. Jpn*, 1984, **57,** 3378.
1248. V. L. Ermakov and D. Ya. Osokin, *Mol. Phys.*, 1984, **53,** 1335.
1249. S. V. Anferova, V. S. Grechishkin and N. Ya. Sinyavskii, *Izv. Vyssh. Uchebn. Zaved. Fiz.*, 1985, **28,** 110.
1250. G. A. Gartman, W. D. Pak and N. S. Kozłov, *Wessh. Akad. Nauk Belorus. CCP, Ser. Chim. Nauk*, 1984, 71.
1251. G. S. Beloglazov and V. S. Grechishkin, *J. Strukt. Chim.*, 1984, **25,** 61.
1252. P. M. Woyciesjes, N. Jones, S. Ganapathy, Y. Hiyama, T. L. Brown and E. Oldfield, *Magn. Reson. Chem.*, 1985, **23,** 315.
1253. P. J. Bray, R. V. Mulkern and S. G. Greenbaum, *Magn. Reson. Chem.*, 1985, **23,** 801.
1254. E. Hadjoudis, I. Moustakali-Mavridis, F. Milia, J. Seliger, R. Blinc and V. Zegar, *Bull. Magn. Reson.*, 1984, **6,** 116.
1255. S. W. Anferova, W. S. Grechishkin and W. P. Anferov, *Teor. Elektr. Chim.*, 1985, 237.
1256. B. Kirste, M. Bock, H. Kurreck and R. Alder, *XXII Congr. AMPERE Magn. Relat. Phenom Proc.*, 1984, 430.
1257. W. S. Grekhishkin, *Fiz. Tverd. Tela*, 1985, **27,** 3425.
1258. K. V. Ermolaev, V. P. Tarasov and L. N. Erofeev, *Prib. Tekh. Exp.*, 1985, **6,** 112.
1259. J. Olliges, A. Lötz, J. Voitländer, H. Barfuss, G. Böhnlein, F. Gubitz, W. Ittner, G. Lanzendorfer, W. Kreische and B. Röseler, *Z. Naturforsch.*, 1986, **41a,** 203.
1260. T. L. Haslett, R. J. C. Brown, Y. S. Park and H. F. Shurvell, *Z. Naturfosch.*, 1986, **41a,** 335.
1261. B. Manallach, *Z. Naturforsch.*, 1986, **41a,** 396.
1262. A. Péneau, L. Guibé and C. Stutz, *Nouv. J. Chim.*, 1985, **9,** 427.
1263. R. J. Trepanier and M. A. Whitehead, *Z. Naturforsch.*, 1986, **41a,** 392.
1264. C. Bessada, A. H. Fuchs, A. Péneau and H. Szwarc, *Z. Naturforsch.*, 1986, **41a,** 348.
1265. A. Lötz, J. Voitländer and J. A. S. Smith, *Z. Naturforsch.*, 1986, **41a,** 206.
1266. A. Lötz, J. Voitländer, J. A. S. Smith, V. Hyna and H. Nöth, *Chem. Phys.*, 1986, **103,** 317.
1267. Shin-ichi Fukada, Keizo Horiuchi, Tetsuo Asaji and Daiyu Nakamura, *Ber. Bunsenges. Chem. Phys.*, 1986, **90,** 22.
1268. Y. Hiyama, E. A. Keiter and T. L. Brown, *J. Magn. Reson.*, 1986, **67,** 202.
1269. M. H. Frey and S. J. Opella, *J. Magn. Reson.*, 1986, **66,** 144.
1270. A. Lötz and J. Voitländer, *Z. Naturforsch.*, 1986, **41a,** 200.
1271. A. P. Cox, J. Randell and A. C. Legon, *Chem. Phys. Lett.*, 1986, **126,** 481.
1272. R. J. Trepanier and M. A. Whitehead, *Z. Naturforsch.*, 1986, **41a,** 386.
1273. G. E. Scuseria, T. J. Lee, R. J. Saykally and H. F. Schaefer III, *J. Chem. Phys.*, 1986, **84,** 5711.
1274. S. H. Choh, Y. J. Park and H. K. Kim, *Jpn J. Appl. Phys.*, 1985, **24,** Suppl. 242, 634.
1275. Masamoto Iwaizumi, Takanori Kudo and Shouichi Kita, *Inorg. Chem.*, 1986, **25,** 1546.
1276. E. J. Reijerse, N. A. J. M. van Aerle, C. P. Keijzers, R. Böttcher, R. Kirmse and J. Stach, *J. Magn. Reson.*, 1986, **67,** 114.
1277. C. J. Winscom, A. L. Maniero and K. Möbius, *Chem. Phys. Lett.*, 1986, **128,** 244.
1278. S. V. Anferova, V. S. Grechishkin and G. V. Mozzhukhin, *Zh. Strukt. Khim.*, 1986, **27,** 55.
1279. M. A. Whitehead and R. J. Trepanier, *A. Mickiewicz Univer. Ser. Fiz. (Radio and Microwave Spectrosc.)*, 1985, 181.
1280. J. Olliges, A. Lötz, J. Voitländer, H. Barfuss, G. Böhnlein, F. Gubitz, W. Ittner, G. Lanzendorfer, W. Kreische and B. Röseler, *J. Magn. Reson.*, 1986, **69,** 302.

1281. R. Stryczek, *J. Mol. Struct.*, 1986, **143,** 297.
1282. C. Stutz, K. Garcia and S. Cochran, *Z. Naturforsch.*, 1986, **41a,** 399.
1283. A. Péneau, B. Manallah and L. Guibé, *Z. Naturforsch.*, 1986, **41a,** 192.
1284. J. Murgich and J. A. Abanero, *J. Phys. Chem.*, 1986, **90,** 6102.
1285. P. M. G. Bavin, D. Stephenson and J. A. S. Smith, *Z. Naturforsch.*, 1986, **41a,** 195.
1286. J. Murgich, J. A. Abanero, M. Santana R. and M. V. Capparelli, *J. Chem. Phys.*, 1986, **85,** 6047.
1287. T. Tsang, R. M. Fronko and H. A. Resing, *J. Magn. Reson.*, 1987, **72,** 315.
1288. S. R. Rabbani, D. T. Edmonds, P. Gosling and M. H. Palmer, *J. Magn. Reson.*, 1987, **72,** 230.
1289. Kaoru Yamanouchi, Shigeki Kato, Keiji Morokuma, Masaaki Sugie, Harutoshi Takeo, Chi Matsumura and Kozo Kuchitsu, *J. Phys. Chem.*, 1987, **91,** 828.
1290. J. Murgich, M. Santana and J. A. Abanero, *Magn. Reson., Chem.*, 1987, **25,** 115.
1291. Tae Ho Yeom and Sung Ho Choh, *J. Korean. Phys. Soc.*, 1986, **19,** 300.
1292. J. Murgich, *Phys. Rev. B*, 1987, **35,** 3563.
1293. S. R. Rabbani, D. T. Edmonds and P. Gosling, *J. Magn. Reson.*, 1987, **72,** 422.
1294. S. V. Rodin, J. Seliger, R. Blinc and V. Sagar, *Fiz. Tverd. Tela*, 1987, **29,** 1871.
1295. J. Murgich and T. Oja, *J. Chem. Soc. Dalton Trans.*, 1987, 1637.
1296. J. Murgich and R. Ambrosetti, *J. Magn. Reson.*, 1987, **74,** 344.
1297. D. Stephenson and J. A. S. Smith, *J. Chem. Soc. Faraday Trans. II*, 1987, **83,** 2123.
1298. M. H. Palmer, R. O. Gould, A. J. Blake, J. A. Smith, D. Stephenson and D. E. Ames, *Chem. Phys.*, 1987, **112,** 213.
1299. Bvrrk Murty, Gkrishna Kishore, D. Krishna Rao and G. Satynandam, *Pramana – J. Phys.*, 1987, **28,** 45.
1300. T. Minamisono, *Hyperfine Interactions*, 1987, **35,** 979.
1301. H. Kubota, K. Matsuta, Y. Nojiri, T. Minamisono, N. Itoh, T. Kawabata and S. Koike, *Hyperfine Interactions* 1987, **35,** 605.
1302. T. Okuda, K. Yamada, H. Ishihara and S. Ichiba, *Z. Naturforsch.*, 1987, **42b,** 835.
1303. R. A. Marino, J. Murgich, M. Gourdji, A. Péneau and L. Guibé, *Nouv. J. Chem.*, 1987, **11,** 495.
1304. J. Seliger, V. Žagar, R. Blinc, R. Kind, H. Arend, G. Chapuis, K. J. Schenk and F. Milia, *Z. Phys. B – Condensed Matter*, 1987, **69,** 379.
1305. D. Stephenson and J. A. S. Smith, *Proc. R. Soc. Lond. A*, 1988, **416,** 149.
1306. S. V. Anferova, V. P. Anferov, N. Ya. Sinyavski and V. S. Grechishkin, *Izv. Vyssh. Uchebn. Zaved., Fiz.*, 1987, **30,** 61.
1307. J. Seliger and R. Blinc, *Ferroelectrics*, 1988, **78,** 223.
1308. R. Janssen and V. S. Veeman, *J. Chem. Soc. Faraday Trans. I*, 1988, **84,** 3747.
1309. F. Millia, *Ferroelectrics*, 1988, **78,** 283.
1310. R. Blinc, J. Dolinšek, M. Luzar and J. Seliger, *Liquid Cryst.*, 1988, **3,** 663.
1311. V. P. Anferov and O. V. Starovoitova, *Zh. Fiz. Khim.*, 1988, **62,** 1663.
1312. V. S. Grechishkin, G. V. Mozzhukhin, N.Ya. Sinavskii and E. V. Yurepina, *Izv. Vyssh. Uchebn. Zaved. Fiz.*, 1988, 48.
1313. Jae-Ryun Suhr, Chang-Ju Yoon, Seong-Gu Ro and Young-Sang Choi, *Bull. Korean Chem. Soc.*, 1987, **8,** 230.
1314. G. V. Boyd, M. M. P. Khurshid, G. A. Nicolaou and J. A. S. Smith, *J. Chem. Soc. Perkin Trans. II*, 1988, 933.
1315. Taro Eguchi, Michihiko Kishita, Nobuo Nakamura and Hideaki Chihara, *J. Phys. Soc. Jpn*, 1988, **57,** 4375.
1316. Taro Eguchi, Koichi Mano and Nobuo Nakamura, *Z. Naturforsch.*, 1989, **44a,** 15.
1317. F. Milia, E. Hadjoudis and J. Seliger, *J. Mol. Struct.*, 1988, **177,** 191.

1318. N. Ya. Sinyavskii and V. S. Grechishkin, *Izv. Vyssh. Uchebn. Zaved. Fiz.*, 1989, **32,** 61.
1319. A. Colligiani, J. Murgich, R. Angelone and R. Ambrosetti, *Phys. Rev. B*, 1989, **39,** 6765.
1320. J. Murgich, *24th Ampere Congress Proc.*, 1988, Poznan, p. 547.
1321. J. M. Baker, J. H. N. Loubser and M. E. Newton, *24th Ampere Congress. Proc.*, 1988, Poznań, p. 904.
1322. A. Péneau, M. Gourdji, L. Guibé and J. Murgich, *Europhys. Lett.*, 1989, **9,** 289.
1323. J. G. Yoon, S. I. Kwun and I. Yu, *J. Korean Phys. Soc.*, 1988, **21,** 304.
1324. S. Sharma, N. Weiden and A. Weiss, *J. Chem. Phys.*, 1989, **90,** 483.
1325. J. Seliger, V. Žager and R. Blinc, *Z. Phys. B - Condensed Matter*, 1989, **77,** 439.
1326. J. Seliger, V. Zagar, R. Blinc, E. Hadjoudis and F. Milia, *Chem. Phys.*, 1990, **142,** 237.
1327. J. Murgich, I. Bonalde and J. A. Abanero, *Z. Naturforsch.*, 1990, **45a,** 353.
1328. J. Murgich and I. Bonalde, *Solid State Commun.*, 1990, **75,** 309.
1329. Kee Tae Han, Tae Ho Yeom and Sung Ho Choh, *Ferroelectrics*, 1990, **107,** 349.
1330. J. Murgich and I. Bonalde, *Solid State Commun.*, 1990, **75,** 309.
1331. V. S. Grekhishkin, R. V. Grekhishkina and O. V. Starovoitova, *Zh. Strukt. Khim.*, 1989, **30,** 149.

Index