

**ANNUAL REPORTS ON
NMR SPECTROSCOPY**

Volume 16

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ANNUAL REPORTS ON NMR SPECTROSCOPY

Edited by

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PREFACE

The current extent of applications of NMR spectroscopy to molecular problems is indicated by the diversity of the reviews presented in this volume. Dr. H. W. E. Rattle reports on NMR of amino acids, peptides, and proteins, which brings his account in Volume 11A up to date.

It is a pleasure to welcome Dr. B. Wrackmeyer as a contributor to Annual Reports on NMR Spectroscopy. He has reviewed the field of ^{119}Sn -NMR parameters, a subject which was previously covered, *inter alia*, in Volume 8 of this series. Rotational processes involving N–X bonds are dealt with by Professors G. J. and M. L. Martin and Dr. X. Y. Sun, who are also newcomers to this series. The present account serves to extend that by Dr. I. O. Sutherland in Volume 4.

Finally, Professor W. McFarlane and Dr. D. S. Rycroft report on multiple magnetic resonance, which follows on from their previous reviews, the most recent of which appeared in Volume 9.

It is a great pleasure for me to be able to express my thanks to all of the contributors for the careful preparation of their manuscripts. Their efforts contribute significantly to the continuing success of Annual Reports on NMR Spectroscopy.

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G. A. WEBB
May 1984

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NMR Studies of Amino Acids, Peptides, and Proteins: A Brief Review, 1980–1982

H. W. E. RATTLE

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I. INTRODUCTION

The three years 1980–1982 were marked by a steady advance in NMR methods, improving the effectiveness of the technique particularly for the study of proteins. The improvements were principally in magnets, with 500- and even 600-MHz instruments now available for ^1H -NMR, probes, where signal-to-noise ratio has been slowly but steadily improved, and to a very great extent in the computation facility dedicated to each machine. Large core memories and fully interactive use of disk storage have not only made instruments more efficient in the use of time (accumulation of data and processing carried out simultaneously) but have also permitted the development of two-dimensional methods as outlined in Section II. The result of all these advances is that we are getting closer to the day when full secondary and tertiary structure analyses of small protein molecules in solution will become possible using NMR methods, with gradual extension of the method to larger molecules. Superconducting magnet technology may have reached a plateau at a corresponding ^1H frequency of about 600 MHz, but it will take some years to fully exploit that field and to explore the possibilities of the many new sample preparation and data analysis techniques being reported. The “eternally rosy future” of NMR is really here already.

II. ADVANCES IN NMR METHODS

The long-standing problem of peak assignment in NMR spectra takes a step toward solution, at least for smaller proteins, in the development of two-dimensional NMR spectroscopy originally proposed by Jeener. A sequence of four papers¹ presents the first examples of the full assignment of a protein ^1H -NMR spectrum using these methods, together with an experimental strategy which may ultimately lead to full three-dimensional structures of smaller proteins in solution. A multipulse experiment is performed, in which the sample is subjected to a pulse sequence of the general form (90° pulse) (evolution time t_1) (90° pulse) (data acquisition time t_2). Data are collected as a function of t_2 , but do of course depend on the value of t_1 , and if a number (several hundreds) of experiments are performed, each for a different value of t_1 , a matrix of data points is obtained, each point being a function of both t_1 and t_2 . This matrix is Fourier transformed twice, along first the t_2 and then the t_1 direction, to yield a new matrix which may be presented as a square “contour map” in which the normal spectrum appears along the diagonal. Any intensity away from this diagonal reveals a “connectivity” between two of the resonances on the diagonal. Such a connectivity might, for example, be

the spin coupling between adjacent NH and CH protons along the peptide backbone. Starting from one known resonance, peaks may thus be assigned one by one along the entire backbone. Side-chain peaks may be assigned in the same way, ultimately leading to a full assignment of the spectrum. Spectra of this type are known by the acronym COSY (for correlated spectroscopy). An extension of this method, in which a third 90° pulse is inserted midway between the others, leads to NOESY, in which the connectivities revealed are due to the across-space nuclear Overhauser effect (NOE) between nuclei that are in close spatial proximity to one another. The majority of protons which satisfy this condition are on the same or contiguous residues; since the effect is distance sensitive, estimates may be obtained of the distances between the α -CH proton of the i th residue and the backbone NH of the $(i + 1)$ th, between backbone NH protons of adjacent residues, and between the α -CH or β -CH of residue i and the NH of residue $(i + 1)$. These distances, in sets of three, are entirely equivalent to the Ramachandran angles ϕ , χ , and ψ , thus opening the possibility of an entirely NMR-based structural study of protein molecules in solution, at least for molecules of up to 60 or 70 residues which maintain a stable conformation. Examples are given^{2,3} of the application of these methods to the basic pancreatic trypsin inhibitor (58 residues) in free solution and to the 29-residue peptide hormone glucagon in its membrane-bound form (Fig. 1). Further information about the methods employed and preliminary experiments is available.^{4–9}

A discussion has been presented of the correlation between the stability and internal mobility of a protein, viewed as being (in solution) a dynamic ensemble of rapidly interconverting structures,⁹ backed by a study of the rotational motion of buried ring structures in proteins measured as a function of applied hydrostatic pressure. Large activation volumes are observed, implying that ring flipping occurs in the unoccupied volume provided by fluctuations of the overall protein conformation.¹⁰ Further information on internal motion in proteins may be obtained using the fact that peak intensities are affected by the application of off-resonance radio frequency (rf) fields, and that the effect is related to an induced relaxation rate which complements the usual $1/T_1$, line width, and NOE data in internal motion determination.¹¹ If the system under investigation is an enzyme activated by both monovalent and divalent cations, a new method for interior distance determination using relaxation effects has been described.¹² The divalent cation is replaced by a paramagnetic ion, and the resultant paramagnetic effect on the longitudinal relaxation of the monovalent ion is measured separately for two isotopes of the monovalent ion. Suitable monovalent ion pairs are $^6\text{Li}^+$ and $^7\text{Li}^+$, $^{14}\text{NH}^+$ and $^{15}\text{NH}^+$, and $^{85}\text{Rb}^+$ and $^{87}\text{Rb}^+$. Application of the Solomon–Bloembergen equation leads to unambiguous distance data.

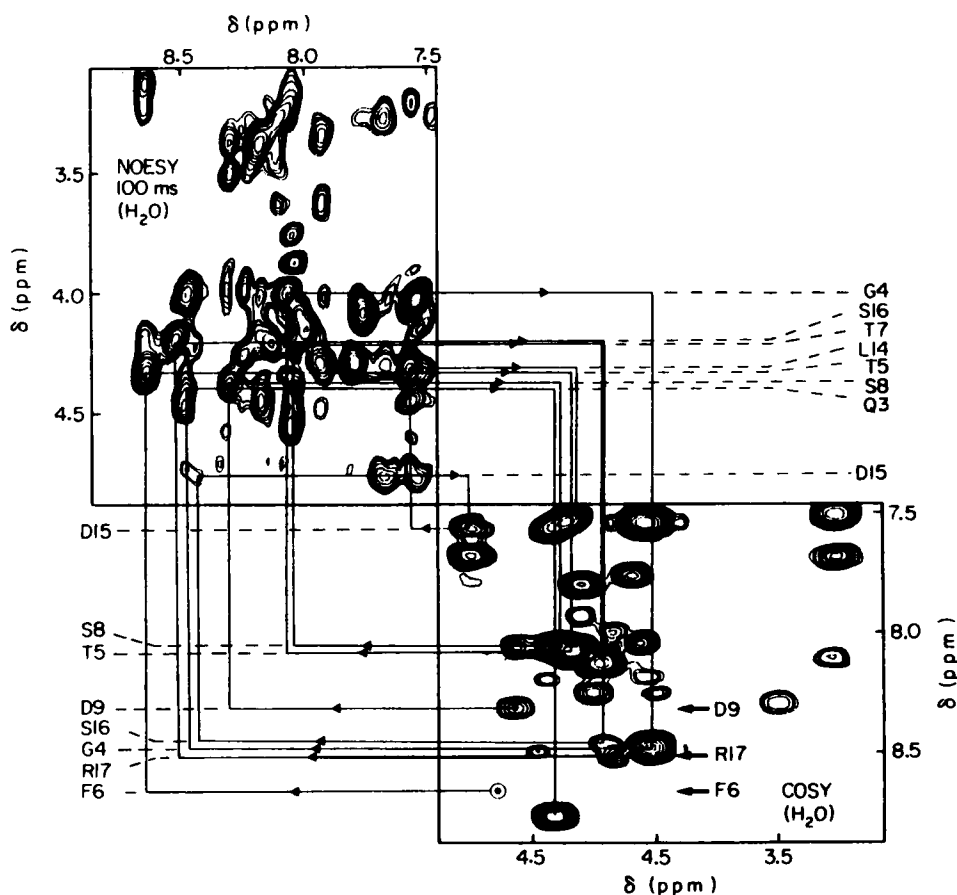


FIG. 1. Part of a two-dimensional spectrum of glucagon bound to perdeuterated dodecylphosphocholine micelles, produced by combining results from both COSY and NOESY experiments. The "normal" spectrum, not shown, would lie along the diagonal from bottom left to top right. Off-diagonal peaks above the diagonal arise from NOE effects between NH_{i+1} and $\alpha\text{-CH}_i$; peaks below the diagonal arise from normal spin-coupling effects. The straight lines and arrows indicate the sequential resonance assignments obtained for residues 3-6, 7-9, and 14-17. From reference 3.

Theoretical calculations have always played an important role in the interpretation of NMR spectra, and are steadily becoming more sophisticated and more valuable. The application of ring-current calculations,¹³ theories and techniques for studying the internal dynamics of proteins,¹⁴ and the theory and applications of the transferred NOE for the study of small ligands bound to proteins¹⁵ have been reviewed. The development of two-

dimensional NMR spectroscopy has brought the term "connectivity" into our vocabulary; connectivities between amide and α -protons in peptides and proteins may be established by selective population transfer in combination with the Redfield (2-1-4-1-2) pulse sequence.¹⁶ Two-dimensional correlated NMR spectroscopy may be used for the unequivocal assignment of histidine residues.¹⁷ The "normal" protein ^1H spectrum may be simplified by a related technique, in which the summation of spectra obtained with different spin-echo delay times eliminates signals from all even multiplets and collapses odd multiplets such as triplets into single lines.¹⁸ Of course, when J values are accessible, they are very valuable in the analysis of protein spectra. Recent papers investigate the limiting couplings for side-chain rotamers,¹⁹ the conformational dependence of the vicinal proton coupling for the $\alpha\text{-C}-\beta\text{-C}$ bond in peptides,²⁰ and the importance of solvent interactions on the values of the five-bond $[\text{H } \alpha\text{-C}(\text{O}) \text{N } \alpha\text{-CH}]$ coupling in the peptide moiety.²¹

Another new technique is used for the assignment of NMR signals in an 18-residue neurotoxin according to the position of the amino acids in the sequence.²² Heteronuclear decoupling of the natural-abundance carbonyl ^{13}C and the α -proton of adjacent residues is employed, with additional irradiation to suppress interactions of the carbonyl ^{13}C with protons of the same residue. The rather difficult task of assigning backbone amide proton resonances of small proteins has been approached²³ by decoupling them from $\alpha\text{-CH}$ resonances while exchange for deuterons is taking place; the authors term this "on-the-fly" decoupling (Fig. 2). The well-known reluctance of hydrogen-bonded peptide NH hydrogen to exchange for deuterium in D_2O solution may be of additional use here, but makes it all the more surprising that²⁴ hydrogen-bonded NH exchanges much more readily with chlorine than do solvent-exposed NH groups.²⁵

Methods continue to advance in other areas of protein NMR as well, of course. The synthetic introduction of ^{17}O into various sites in oxytocin²⁶ and of deuterium into the egg white proteins of Japanese quail²⁷ is described: > 80% incorporation of selected deuterated amino acids into lysozyme is achieved using a synthetic diet. A $^{13}\text{C}/^{15}\text{N}$ double-label method has been used to estimate a protein half-life of some 30 days in soybean leaves,²⁸ while a simple multinuclear multipulse technique²⁹ is described which enables the collection of the spectrum of only those protons which are directly bonded to ^{13}C atoms in ^{13}C -enriched samples. A review has been given of high-resolution solid-state ^{13}C NMR in biopolymers (including proteins and whole viruses) using magic-angle spinning.³⁰ The transfer-of-saturation method is of increasing importance; theoretical calculations of the effects to be expected in a three-site exchange situation are presented.³¹

Among other new techniques reported we may note a method for the quantitative determination of the total protein content of natural products

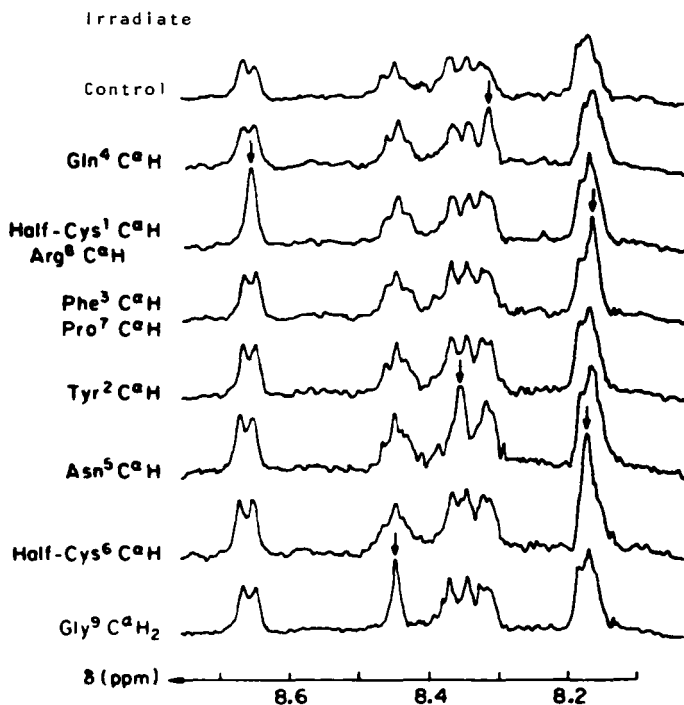


FIG. 2. Assignment of the NH protons in the 360-MHz spectrum of arginine vasopressin by spin decoupling, with irradiation at the resonances indicated on the left. Arrows denote multiplet collapse. As all the protons are exchangeable, the entire data set for the spectra was collected within 3 minutes, using a concentrated solution. From reference 23.

using a copper relaxation reagent³² and (rather the opposite) the suppression of the total haemoglobin spectrum in ^1H -NMR spectroscopy of intact erythrocytes by using selective transfer of saturation by spin diffusion, in order to reveal the spectra of other components of the system.³³ A new possibility for the study of enzyme mechanisms involving phosphorus is opened by confirmation that for most phosphate derivatives of biochemical interest, a broadening effect due to the presence of a neighbouring ^{17}O nucleus is detectable. This effect can be combined with direct ^{17}O -NMR measurements to study the interaction of diamagnetic enzyme-bound metal ions with nucleotides.³⁴

Workers engaged in labeling studies may also be interested in a strategy for uniform ^{15}N labeling of both nucleic acids and proteins for subsequent solid-state NMR,³⁵ and in a paper on the use of special strains of *Escherichia coli* to produce specifically ^{13}C -labeled amino acids for subsequent biosynthetic

incorporation into proteins.³⁶ The characteristics of ^{13}C -labeled peptides have been discussed³⁷ with particular reference to the relation between information content and labeling pattern.

III. AMINO ACIDS AND SYNTHETIC PEPTIDES

A. Amino acids

As always, the mainstream of amino acid studies concentrates on their use as simple systems for the testing of new techniques or theories. Cross-relaxation effects in the photochemically induced dynamic nuclear polarisation (photo-CIDNP) spectra of *N*-acetyltyrosine and *N*-acetyltryptophan have been used, for example,³⁸ to assess the possibilities for observing population transfer between amino acids in proteins. Trials of the methods and the effects of isotopic labeling have been reported using deuterium in phenylalanine³⁹ and ^{17}O in glycine, alanine, glutamic acid, and aspartic acid⁴⁰ while the more familiar ^{13}C labeling, this time biosynthetically accomplished in *Spirulina maxima* and *Synechococcus cedrorum*, is shown to be neither random nor statistical.⁴¹ Carbon-carbon couplings are reported for labeled tryptophan⁴² and ^{13}C - ^{15}N vicinal couplings for a number of other amino acids.⁴³ The further development of ^{15}N labeling as a usable technique is also exemplified in studies of the stereospecificity of the polymerisation of DL-leucine and α -OMe-DL-glutamic acid anhydrides⁴⁴ and of the acid-base and tautomeric equilibria in solid histidine.⁴⁵ Even closer to our ultimate biological goals is the use of ^{15}N relaxation times and NOE data to probe the intracellular environment in intact *Neurospora crassa*, yielding microviscosity data unobtainable by any other technique.⁴⁶ More conventional conformational studies have been reported for 5-adenosyl-L-homocysteine⁴⁷ and for the 5-cis and 5-trans isomerism in a number of acylproline analogues.⁴⁸ The use of relaxation times of ^{13}C nuclei as a probe of proline ring conformations has been discussed.⁴⁹ High salt solvent conditions can induce conformational changes in aspartate, stabilising the conformers with gauche carboxylates at the expense of trans conformers.⁵⁰

The use of a UV excimer laser will enable a number of new photoreagents to be used in chemically induced dynamic nuclear polarisation (CIDNP) experiments, and has been tested using solutions of histidine, tyrosine, and tryptophan,⁵¹ while more normally excited CIDNP measurements on tryptophan⁵² reveal details of the unpaired spin-density distribution in the Trp radical cation. Analysis of coupling data, NOE data, and lanthanide perturbations reveals no less than six conformers in solutions of DL-tryptophan,⁵³ while the solvent dependence of tyrosine and tryptophan side

chain conformations has been discussed.⁵⁴ Detailed studies of the interactions of aqueous lanthanide ions with various amino acids are discussed,^{55,56} while the modes of binding of Ca^{2+} and Mg^{2+} to aspartic acid and asparagine are also covered⁵⁷; both cations interact with the carboxyl groups of the amino acids, but only Mg^{2+} binds to the amino group.

B. Synthetic polypeptides

Polypeptides are no longer the vital protein models they once were; however, they can still prove useful in the study of some aspects of protein origin and behaviour. A comparison of poly(aspartic acid), prepared by common methods⁵⁸ and by thermal polycondensation,⁵⁹ reveals that the latter has β -peptide bonds in a mole fraction of about 0.8, which may have some significance in the study of protein evolution. The relaxation behaviour of poly(γ -benzyl-L-glutamate) shows some interesting features which can only be explained in terms of internal rotations about $\alpha\text{-C-H}$ and $\alpha\text{-C-}\beta\text{-C}$ bonds.^{60,61} The relative stabilities of the poly(proline II) helix formed by poly[Gly-(Pro)_n], with $n = 3$ or 4, have been determined; the polypeptide is a model for a proline-rich human salivary protein.⁶² Solid-state NMR techniques are used to determine conformation-dependent ^{13}C shifts in polyvaline, polyisoleucine, and polyleucine in the α -helical and β -sheet forms.⁶³ Analysis of the ^{13}C spectra of poly(aspartic acid) samples, prepared by hydrolysis of polysuccinimide under various conditions, reveals a random distribution of α - and β -bonds in all samples.⁶⁴ However, the stereoselectivity of polymerisation of DL-valine and DL-leucine monomers, also investigated by ^{13}C NMR, reveals the expected preference for isotactic sequences but with no isotactic block longer than six units.⁶⁵ Experiments with ^{15}N NMR⁶⁶ show that separate signals are detected from the central residue in each of the four possible triads L-L-L, L-D-L, L-L-D, and D-L-L. An interesting amphiphilic block copolypeptide, with hydrophilic termini and hydrophobic central block, alters the liquid crystal-gel phase transition in a deuterium-labeled dipalmitoylphosphatidylcholine membrane.⁶⁷

C. Synthetic linear peptides

A review of structural studies of peptides, including many using NMR, may be found in the Proceedings of the 6th American Peptide Symposium.⁶⁸ The development of ^{15}N -NMR spectroscopy for peptide and protein studies continues, and some of the advantages of this relatively new probe into the peptide backbone are now becoming apparent. In proline-containing peptides, the ^{15}N nucleus is very sensitive to conformational changes induced by cis/trans isomerism of the proline. These effects are long range and depend on both the amino acid side chains and the solvent.⁶⁹ Strong neighbouring residue effects have been seen in random copolymers of Gly, Leu, and Val; the

spectra resemble a superposition of the corresponding binary copolymers.⁷⁰ In a series of tripeptides of the form Gly–Gly–L–X a combination of double resonance and difference NMR spectroscopy gives values for $^1J(^{15}\text{N}–^1\text{H})$ and ^{15}N chemical shifts, though not yet sufficient for a systematic analysis of their behaviour.⁷¹ Attempts to improve structure analysis using shift reagents on ^{15}N samples have not yet been entirely successful.⁷² Solvent effects have proved to be more useful. An attack on the sensitivity problem for ^{15}N using NOE⁷³ and the INEPT (insensitive nuclei enhanced by polarisation transfer) pulse sequence, to transfer spin polarisation from amide protons to ^{15}N , produces an improvement over unenhanced spectra by factors of 8 for ^1H decoupled and 15 for ^1H coupled spectra, a very worthwhile improvement.^{74–76}

Other studies involving small synthetic peptides include a series^{77–79} on the binding of various divalent cations to the tripeptide Asp–Ala–His–N–methylamide, the N terminus of the human serum albumin molecule, with clear evidence for metal coordination in each case. Another study⁸⁰ involves a combination of transfer of saturation and selective saturation recovery methods to estimate amine H exchange rates, and hence to some extent conformational mobility, in a pentapeptide that represents the active fragment of thymopoietin. The pentapeptide is found to be in a very mobile conformational equilibrium between several conformations.

The stereoselectivity of oligopeptide syntheses can be slightly affected by the solvent and activating agents. This effect is shown in the formation of di- and tripeptides.⁸¹ Conformational and dynamic studies of Ala–Trp and Gly–His show that their internal motions are slow compared to overall tumbling⁸² while a type II β -turn is detected in Me₃CCO–Pro–Aib–NHMe (Aib = aminoisobutyric acid) in solution⁸³ in line with X-ray studies of the crystalline form. Comparison has also been made between the crystal and solution conformations of (Ac–Asp– α -Abu) (Abu = aminobutyric acid).⁸⁴ The N-terminal tripeptide of human serum albumin (HSA), Asp–Ala–His, shows a marked preference for binding to Zn(II) rather than to Pr(III).⁸⁵ This may or may not account for the ability of HSA to bind transition metal ions in the presence of Ca²⁺.

A number of one-bond α - ^{13}C –H couplings for amino acids and small peptides, with variations of substituents and pH, are presented for use in spectrum prediction and assignment.⁸⁶ Conformational studies are also reported for histidine-containing peptides,⁸⁷ Ac–Ala–Ala–NHMe,⁸⁸ and the methylamides of the four lysine and/or tyrosine dipeptides.⁸⁹ An NMR investigation has been presented of the racemisation of benzoyl dipeptide methyl esters.⁹⁰

An interesting example of a β -turn locked by a salt bridge has been presented.⁹¹ The peptide is Boc–Arg–Ala–Gly–Glu–NH₂ (Boc = butoxy-carbonyl) and the Arg–Glu hydrogen bonds forming the β -turn are considerably reinforced by the Arg⁺–Glu[–] interaction (Fig. 3).

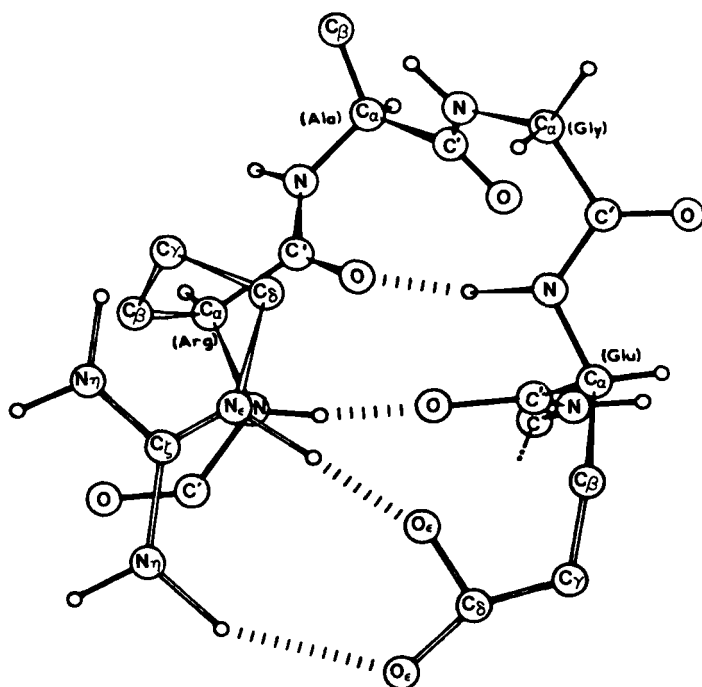


FIG. 3. Proposed conformation of the tetrapeptide Arg-Ala-Gly-Glu, a β -bend locked by a salt bridge. From reference 91.

The effect of solvent and pH on ^{13}C chemical shifts in derivatised amino acids and tripeptides has been reported.⁹² The ^{13}C -NMR spectra of solid carnosine, a dipeptide (Ala-His) found in muscle, are greatly enhanced in intensity without serious loss of resolution by the introduction of cobalt chloride into the powdered sample. It appears that this provides a general way of improving spectra obtained, using cross polarisation and magic-angle spinning, from solid peptide samples.⁹³

A number of proline-containing peptides have been investigated by NMR methods. The model peptide pivaloyl-Pro-Pro-Ala-NHMe exhibits a trans/trans isomeric structure in solution, with successive $4 \rightarrow 1$ intramolecular hydrogen bonds (β -turns) leading to an incipient 3_{10} helix.⁹⁴ β -Turns are also found in a series of tetrapeptides with proline as residue 2,⁹⁵ while $3 \rightarrow 1$ intramolecular hydrogen bonds (γ -turns) characterise the structure of both the cyclic tetrapeptides (Ala⁴)-desdimethylchlamydocin and cyclo(D-Phe-Pro-D-Phe-Pro) in deuterated chloroform-dimethyl sulphoxide solvent mixtures.⁹⁶ The rapid conformational flexibility of γ -C of proline residues is largely inhibited in hydroxyproline, leading to a much more rigid

structure with much more puckered rings. Hydroxyproline residues could thus play a key role in the stability of the triple-helical peptides of collagen.⁹⁷ In experiments⁹⁸ on two cyclic (Tyr-Ile-Pro-Leu) diastereoisomers, which are simplified analogues of a phytotoxic peptide produced by *Cylindrocladium*, a unique trans-trans-cis-trans conformation is deduced, the Ile-Pro bond being cis.

An interesting NMR study of some dipeptides at high pressure reveals differences in the activation volume for amide rotation if proline is one of the residues.⁹⁹ This will clearly add to the influence that proline has on any conformational rearrangement within proteins. The steric effects of proline on an antecedent alanine residue are reported¹⁰⁰ to result in the predominant conformation always being the one in which the β -methyl of alanine eclipses its carbonyl group. β -Turn stability in the tripeptide Ac-Pro-Gly-X-OH varies as X = Leu > Ala > Ile, Gly > Phe.¹⁰¹ Rates of proline cis/trans isomerisation in oligopeptides have also been determined.¹⁰²

360-MHz proton NMR has been used to study the basis for the high cis/trans ratio observed in Gly-Pro-Phe tripeptides.¹⁰³ An electrostatic interaction involving the π -electrons of the Phe side chain and the Gly-Pro peptide bond appears to destabilise the trans conformer. A series of peptides with α -aminoisobutyric acid residues adjacent to proline reveals the propensity of this combination to form β -bends,^{104,105} and also provides an NMR parameter to help determine whether the β -bend at the amino-terminal end of alamethicin is retained.¹⁰⁶

D. Synthetic cyclic peptides

Turning now to cyclic peptides, we find more papers dealing with proline-containing molecules, including ¹³C- and ¹⁵N-NMR studies of cyclo(Pro-Phe-Gly-Phe-Gly),¹⁰⁷ solid-state ¹³C-NMR¹⁰⁸ and solution ¹H-NMR investigations¹⁰⁹ of cyclotriproline, and two-dimensional spectroscopy¹¹⁰ of the conformational equilibrium of cyclo(Pro-NBGly), where NBGly is *O*-nitrobenzylglycine. A cyclic analogue of the proline-containing repeat pentapeptide of tropoelastin, cyclo(Val-Pro-Gly-Val-Gly) shows temperature-dependent conformational behaviour at low temperature, combining a β -turn with a 10-membered H-bonded ring similar to a 3_{10} helix. At higher temperatures it assumes an antiparallel β -pleated sheet similar to that of gramicidin S.¹¹¹ The modeling of β -bends has occupied other workers: cyclo(Gly-Cys-Gly) triply bridged by 1,3,5-tris(thiomethyl)benzene forms a structure consisting of three β -bends,¹¹² while a comparison¹¹³ between cyclo(L-Ala-L-Ala- ϵ -aminocaproyl) and cyclo(L-Ala-D-Ala- ϵ -aminocaproyl) reveals that the first exists as types I and III, and the second as type II β -bends. Other studies of cyclic peptides include the synthesis,

conformation, and interaction with small molecules of some bis(cyclic dipeptides),¹¹⁴ the isomerisation of azobenzene-containing cyclic oligosarcosine,¹¹⁵ and a conformational analysis of the Cys-Pro-Val-Cys loop closed by a disulphide bridge as a model for small disulphide loops in proteins.¹¹⁶ The possibility of suitably designed cyclic peptides acting as metal-binding agents has been investigated using peptides with acidic side chains,¹¹⁷ such as cyclo(Glu-Glu), cyclo(Glu-Pro), and cyclo(LysZ-Pro). In other investigations,^{118,119} specifically directed at the binding of Ca^{2+} by cyclic octapeptides, the metal ion is found to be coordinated in a central binding cavity to four carbonyl oxygen atoms in a coplanar arrangement. Binding of calcium stabilises the octapeptide to a single conformation. A model for the zinc-binding site of carbonic anhydrase has been produced in the form of cyclo(Gly-His-Gly-His-Gly-His-Gly); Zn^{2+} binds all three imidazole side chains.¹²⁰

One of the best-studied synthetic peptides is the repeat pentapeptide of elastin mentioned earlier (Val-Pro-Gly-Val-Gly). Cyclic mono- and oligomers of this have been prepared^{121,122} in order to determine which cyclooligopeptide has a structure matching the β -spiral of the linear polypentapeptide. Cyclic oligopentapeptides with $n = 3$ and $n = 6$ meet this requirement very well. Energy calculations¹²³ for the former of these, together with the threefold symmetry revealed by NMR, allow the construction of probable models of the structure in solution. Cyclic peptides provide a useful vehicle for the investigation of localised conformation. A series of cyclic hexapeptides having the sequence (X-L-Pro-Y) produces a set of rules for determining whether a type I, type II, or type II' β -turn would be formed according to the sequence around the proline residue. The rules derived are in accordance with data from known protein structures.¹²⁴ Solid-state NMR of crystals of two cyclic peptides containing proline show that sufficient conformationally dependent spectral data are obtained to effectively compare crystal with solution structures.¹²⁵ A cyclic octapeptide which mimics the zinc-binding site of carboxypeptidase A has been synthesised.¹²⁶ The octapeptide forms a 1:1 complex with zinc, with the imidazoles of both histidines and the carboxyl side chain of the single glutamic acid residue complexed to the metal ion. Other NMR studies of cyclic peptides which may be of interest are to be found elsewhere.¹²⁷⁻¹³²

IV. SMALL NATURAL PEPTIDES

A. Enkephalins and endorphins

The pentapeptide neurotransmitters methionine and leucine enkephalin have aroused a great deal of interest of late. A review including earlier work on enkephalins has been presented.¹³³ Interest is now centred on studying the

roots of the enkephalin conformation by using modified and analogue molecules. The adduct formed by Met-5-enkephalin and acetaldehyde does not¹³⁴ take up the folded conformation characteristic of native enkephalins in DMSO-*d*₆, while enkephalins dansylated at the C terminus remain very flexible in a variety of solvents.¹³⁵ The conformational equilibrium of the molecules in question is greatly shifted by complexation with zinc.¹³⁶ Elimination of the C-terminal leucine¹³⁷ yields a tetrapeptide which has a more rigid structure than Leu-enkephalin, while the analogues (D-Met-2, Pro-5)-enkephalin and enkephalinamide,¹³⁸ which show high specificity for the μ -receptor site (guinea pig ileum), appear to derive their conformational stability from their high content of hydrophobic side chain rather than from the more usual β -turn. A strong correlation is shown to exist¹³⁹ between the specificity of enkephalin derivatives for μ - or δ - (mouse vas deferens) receptor sites and the acid or amide of the C-terminal carboxyl group. Selective deuteration of the N-terminal tyrosine residue¹⁴⁰ permits analysis of rotamer populations of its side chain, and substitution of D-alanine for glycine-2 in the sequence produces a relatively rigid backbone.¹⁴¹ The native molecule exists in its dipolar form in water in the region of neutral pH values.¹⁴²

Photo-CIDNP experiments on human β -endorphin¹⁴³ show that both the mobility and accessibility to solvent of tyrosines 1 and 27 are severely restricted on binding to lipid micelles, while the local conformation of the Tyr-Gly-Gly-Phe segment of 5-Met-enkephalin is shown¹⁴⁴ to be maintained in β -endorphin. A conformational transition in Met-enkephalin from an equilibrium between unfolded conformations in aqueous solution to a folded structure in nonpolar solvents has been found.¹⁴⁵ A theoretical analysis reinforces the picture of a number of alternative conformations in water.¹⁴⁶ Enkephalin has been cyclised¹⁴⁷ and its complexes with Cu²⁺¹⁴⁸ and Al³⁺ have been studied by NMR.¹⁴⁹

B. Other hormones

The hypothalamic hormone somatostatin is a 14-residue cyclic peptide with a single intramolecular disulphide bridge. The molecule can inhibit the release of insulin and glucagon as well as growth hormone. Its ¹³C¹⁵⁰ and ¹H-NMR^{151,152} spectra have been assigned and seem to lead to the conclusion that the molecule has a number of preferred conformations and exchanges rapidly between them, with possibly a region of somewhat higher stability in the part of the molecule furthest from the disulphide bridge. Energy calculations have been used¹⁵³ to predict a number of low-energy conformations from which those compatible with NMR data can be selected—an interesting approach, which finds an echo in a paper on melanostatin.¹⁵⁴ Experiments on somatostatin analogues¹⁵⁵ appear to show stacking between phenylalanine-6 and phenylalanine-11 as a stabilising factor in the structure.

Once the ring structure is opened, the resulting acyclic precursor appears to settle into a stable β -turn/ β -sheet conformation¹⁵⁶; the conformations of side chains in the native peptide, with some reassignments, have been determined by 500- and 600-MHz ^1H -NMR studies.¹⁵⁷

The pancreatic hormone insulin has been the subject of a number of studies; its histidine residues have been assigned¹⁵⁸ and a Ca^{2+} binding site, specific for calcium and separate from the two Zn^{2+} sites of the hexamer, has been demonstrated using ^{113}Cd NMR.¹⁵⁹ Removal of the C-terminal octapeptide of the B chain appears to destroy the three-dimensional structure of the head end of the A chain¹⁶⁰ and also removes the biological activity of the hormone. Other hormone fragments studied include nine model peptides of the insulin A chain (by ^{15}N NMR in natural abundance).¹⁶¹

Two molecules related to each other and very widely distributed, thymopoietin and ubiquitin, are going to be of great interest. The pentapeptides which may apparently be associated with the active sites of these molecules (Arg-Lys-Asp-Val-Tyr) and (Tyr-Asn-Ile-Glu-Lys), respectively, have been subjected to considerable NMR experimentation, particularly in their associations with lanthanides¹⁶²⁻¹⁶⁴

A low-molecular-weight analogue of human growth hormone, in which residues 32-46 of the normal hormone are missing, has been shown¹⁶⁵ to fold in a similar, but not identical, manner to the normal (22,000 Da) protein, and to occur most frequently as a heterologous dimer with it. The linear octapeptide hormone angiotensin is a potent hypertensive agent which stimulates the smooth muscles of blood vessels. It also mediates the transport of manganese ions across phosphatidylcholine bilayers, which, studied by NMR, may lead to a clear understanding of the role of metal ions in its physiological activity.¹⁶⁶ Angiotensin has been assigned various solution conformations in the literature. These are discussed in the light of lanthanide ion perturbations of the molecule.¹⁶⁷ Some peptide exchange rates in analogues and agonists have been compared.¹⁶⁸ Analogues involving replacement of isoleucine-5 exhibit a strict requirement for a β -branched residue¹⁶⁹ and other analogue studies¹⁷⁰ indicate that it may be possible to produce potent angiotensin II analogues which are more resistant to enzymatic degradation than is the native molecule. The conformational mobility of the hormone, and some of its analogues, has been discussed.¹⁷¹ L-His-L-Pro interconverts between the s-cis and s-trans rotational isomers of the amide bond with an average rate constant of about 2000 sec^{-1} ; the same residues, at positions 6 and 7 in angiotensin II, interconvert at least 70 times faster.¹⁷² Conformation-activity relationships in a substituted angiotensin are reported,¹⁷³ as are the effects of lanthanide shift reagents on the spectra of angiotensin and (Gln-4) oxytocin.¹⁷⁴

The contribution of intramolecular hydrogen bonding to the solution structure of oxytocin has been evaluated via amide deuteration rates.¹⁷⁵ Evidence is found for some hydrogen bonding involving the cystyl residues, especially Cys-6. Slow exchange at Asn-5 is attributed to steric hindrance preventing solvent access, although in another paper¹⁷⁶ the slowness is considered to be the result of hydrogen bond formation in (Gln-4) oxytocin. A conformationally restricted analogue of oxytocin, 1-penicillamine (2-leucine-oxytocin), is a more potent hormone antagonist than the equivalent analogue without the leucine modification. This is assumed to be due to a greater similarity to native oxytocin at residues 2 and 3. The orientation of the asparagine side chain in the oxytocin analogue 2-alanineoxytocin has been deduced from ¹H spin–spin coupling data.¹⁷⁷ Another analogue, D-glutamine-4 oxytocin, seems from ¹³C-NMR measurements to have a very similar conformation to the native molecule, but exhibits a greatly reduced activity.¹⁷⁸ A selenium derivative of oxytocin has been used to investigate the disulphide bridge region of the molecule.¹⁷⁹ A series of specifically designed and synthesised isotopic isomers containing ¹³C and ¹⁵N nuclei at selected sites in the two half-cystyl residues has been used to show that the torsion angle *X* has the eclipsed value of -120° for half-cystyl-1 and approximately $+120^\circ$ for half-cystyl-6.¹⁸⁰ Labeling with ¹³C at the meta positions of tyrosine-2 of oxytocin reveals that the tyrosine undergoes hindered rotation when oxytocin is bound to neurophysin.¹⁸¹ Further light on the binding of peptides to neurophysin will be cast by the application of newly described spin labels capable of binding to its hormone-binding sites.¹⁸² First results obtained by means of these labels suggest that residue 3 of the hormone is $> 14 \text{ \AA}$ from tyrosine-49 in the neurophysin. Other reports of structural studies of oxytocin antagonists such as 1-penicillamine-oxytocin have appeared,^{183,184} in addition to studies of the rather similar hormone vasopressin.^{185,186}

C. Peptide antibiotics

The membrane channels formed by gramicidin A have been investigated by a series of specific ¹³C-labeling experiments.¹⁸⁷ Two symmetrically related binding sites for Na⁺ and Tl⁺ are detected, centred at the tryptophan carbonyls and separated by 23 Å, with all three tryptophan residues (9, 11, and 13) combining in the ion coordination. Studies using ²⁰⁵Tl NMR¹⁸⁸ reveal two binding sites for gramicidin in trifluoroethanol, but¹⁸⁹ only one site when the gramicidin is incorporated in micelles.

Another relatively little-used NMR nucleus, ²³Na, has been used to study the dynamics of the transport of sodium ions through membranes via the malonyl gramicidin channel.¹⁹⁰ ¹⁵N-NMR spectroscopy has been applied to

solutions of gramicidin S in organic solvents in order to distinguish between solvent-exposed and solvent-shielded peptide groups. Three methods are described¹⁹¹, employing the solvent dependence and temperature dependence of ^{15}N chemical shifts and the liability of the N proton in the presence of added base. Intramolecular hydrogen bonding in gramicidin S has been studied by NMR/IR following selective deuteration¹⁹² and by ^1H and ^{15}N NMR of the ornithine side chain,¹⁹³ indicating the presence of intramolecular hydrogen bonds between ornithine NH_3^+ and D-phenylalanine carbonyl groups. Hydrogen bonds are also delineated in gramicidin S in spin-label relaxation enhancement experiments using 1-oxy-2,2,6,6-tetramethylpiperidine in dimethylsulphoxide solvent.¹⁹⁴ Gramicidin S analogues Pro-4,4'-Ala-5,5' and Pro-4,4'-Asn-5,5' in the same solvent show less propensity to form normal hydrogen bond patterns than they do in aqueous solution. Since the action of the native molecule is initiated by interaction with phospholipid membranes, this may explain the antibiotic inactivity of the analogues.¹⁹⁵ Successful application to the librational motions of gramicidin S of a theory of ^{13}C relaxation behaviour has been reported¹⁹⁶ as has the binding of Li^+ to gramicidin S and valinomycin.¹⁹⁷

The cyclic depsipeptide valinomycin, incorporated into small phospholipid vesicle bilayers, exhibits a conformation similar to that in nonpolar organic solvents, suggesting a location in the interior of the bilayer.¹⁹⁸ Several analogous molecules have been studied in terms of their ability to transport alkali metal ions into the organic phase of a two-phase system.¹⁹⁹ Valinomycin in acetonitrile forms two types of complex with Ca^{2+} , a 2:1 (peptide/ion/peptide) sandwich and an equimolar complex; the significance of these has been discussed.²⁰⁰ Only a few years ago, gramicidin and valinomycin would have been the only peptide antibiotics discussed in NMR studies, but now the range has broadened considerably. Two-dimensional NMR spectroscopy of siomycin²⁰¹ has permitted the assignment of the ^{13}C spectrum directly from the known ^1H shieldings. The complete structure of the antibiotic glycopeptide ristomycin A is reported²⁰² as are the structures of cirriatomycin A and B²⁰³ and the conformation of triostin A.²⁰⁴ The microdynamics of molecular motion in the cyclic hexadepsipeptide pristina-mycin I have been determined by ^{13}C relaxation measurements,²⁰⁵ and the parts of cephalosporin molecules engaged in interactions with human serum albumin have been identified by high-resolution NMR.²⁰⁶ A general ^1H -NMR study of the cyclic hexadepsipeptide antibiotic beauvericin²⁰⁷ reveals it to have different conformations in polar and nonpolar solvents. However, complexation with ions in aqueous solution makes it adopt the conformation found in nonpolar solvents. Nonpolar solvents are also used in studies^{208,209} of synthetic fragments of suzukacillin, a membrane channel-forming polypeptide, showing them to adopt 3_{10} helical structures. Suzukacillin is very rich

in α -aminoisobutyric acid, and model peptide studies on fragments of bradykinin suggest that substitution of Aib for proline might lead to a 3_{10} structure in this molecule, too. However, ^1H -NMR measurements²¹⁰ of the whole substituted molecule, while indicating several conformations involving β -turns, have failed to reveal any 3_{10} helix. β -Turns are detected in des-Arg bradykinin in DMSO and water,²¹¹ although other NMR studies at 600 MHz²¹² indicate that the molecule is in rapid equilibrium among many conformers with no persistent structural features at all in aqueous solution. On the basis of a number of 270-MHz ^1H -NMR studies of synthetic fragments of alamethicin,²¹³ a largely 3_{10} helical folding pattern is postulated for the hydrophobic segment (residues 1–17) with a polar flexible C-terminal tripeptide. A helical or, possibly, a β -sheet conformation is supported in a study of natural alamethicin.²¹⁴

D. Peptide toxins

The long neurotoxins (72 residues) of snake venom provide a fascinating set of variant active peptides with some invariant features, such as tryptophan-29. Small but important differences between the crystal and solution structures of α -cobrotoxin have been reported²¹⁵; differences between the long and short neurotoxins, in terms of the rigidity of the three-strand β -sheet which contains the active residues, are revealed by hydrogen–deuterium exchange studies.²¹⁶ The results correlate well with the different kinetic properties of the long and short neurotoxins. The unfolding of a cobra neurotoxin is discussed.²¹⁷

The structure of the crystalline form of the erabutoxins A, B, and C from the sea snake *Laticauda semifasciata* have been determined by X-ray methods. The data thus available have been used²¹⁸ to assist in the assignment of a large number of signals in the 270-MHz ^1H -NMR spectrum, including the lysine ϵ -CH₂ resonances and all of those due to the valine, leucine, and isoleucine methyl groups. These assignments will undoubtedly be of value in NMR studies of other snake venom toxins, with their closely related sequences and, presumably, structures. Hydrogen–deuterium exchange rates for erabutoxins show²¹⁹ that some 17 backbone and 9 side chain NH atoms exchange slowly, indicating that the erabutoxin B molecule in solution does in fact have the number of hydrogen bonds indicated by the crystal data. NMR does reveal, however,²²⁰ some structural differences between the crystal and solution conformations of erabutoxins rather similar to those mentioned earlier for cobrotoxin. ^1H -NMR data at various frequencies show structural similarities and differences between toxins from several other species.^{221,222} As might be expected, the functionally invariant part of the molecule is more rigid than the tail, forming the three-strand antiparallel β -sheet as shown by X rays for

related molecules. These results are borne out by work on neurotoxin III from *Naja mossambica mossambica* from two other laboratories.^{223,224} The dynamics of erabutoxin have been measured via the relaxation times of methyl groups using both ^1H -²²⁵ and ^{13}C -²²⁶ NMR data. The results agree well for the regions of the molecule which show restricted motion, while still being consistent with the idea of flexible and dynamic structures for the proteins. Slow interconversion (2.5 sec^{-1}) between two conformations of toxin B from *Naja naja* is found at the midpoint of a pH-induced conformational transition; the rate rises to some 600 sec^{-1} at 60°C .²²⁷ ^{19}F labeling of neurotoxin II also from *N. naja* has been used to determine a number of intramolecular distances, and stands up well to comparison with the X-ray structure.²²⁸ It has subsequently been possible²²⁹ to bind spin-labeled derivatives of the molecule to purified acetylcholine receptor protein, and²³⁰ to demonstrate the presence in solution of a β -structure in the central loop of the molecule, with a β -turn at residues 31–34. Other toxins investigated using NMR include six from Latin American scorpions, which like the snake toxins include extensive β -structure.²³¹ The collection of NMR quantities of apamin, a toxin from bee venom, would seem to present even greater difficulties, but it has nevertheless been subjected to extensive NMR and model-building studies, the result of which is an α -helix from residues 6–13 coupled with three β -turns, giving a very plausible tertiary structure for this 18-residue peptide.^{232,233} Other toxins studied include toxin 401 from bee venom,²³⁴ cholera toxin,²³⁵ toxin II from *Anemonia sulcata* which, like the related polypeptide anthopleurin A, has cardiac stimulating activity,²³⁶ and the cytotoxic depsipeptides known as the didemnins.²³⁷

E. Inhibitors

Like neurotoxins and enkephalins, the peptide inhibitors of enzymes offer particular interest in conformational studies because of their very explicit dependence on shape for activity. Many of them also have the advantages of being very stable in solution and of being an appropriate size for NMR studies. The basic pancreatic trypsin inhibitor (BPTI; 6500 Da) continues to provide a useful model system for proteins of intermediate size and to be of intrinsic interest. A number of papers on this molecule are mentioned in Section II. Two recent studies have probed its internal motions; both find that there is a small contribution to relaxation from low-frequency distortional motion of the protein backbone.^{238,239} The following figures are quoted: for overall rotational motions, $T_{\text{R}} = 4 \times 10^{-9}$ seconds; for librational wobbling of backbone α atoms, $T_{\text{W}} = 1 \times 10^{-9}$ seconds; for librational motions of side chains, $T_{\text{W}} = 4 \times 10^{-10}$ to 3×10^{-9} seconds; for methyl rotation, $T_{\text{F}} < 1 \times 10^{-11}$ seconds.²³⁹ An interesting study of the internal dynamics of the

protein has been presented.²⁴⁰ Theoretical calculations of the internal mobility predict results in striking agreement with NMR data on the conformational stability of backbone residues. Internal solvent water is included in the calculations, and it will be interesting to compare the results with those from deuterium exchange studies of internal amide protons.²⁴¹ In the latter a reduction of the S–S bond between residues 14 and 38 increases some NH exchange rates between 100- and 1000-fold. Two-dimensional studies of BPTI amide proton exchange rates²⁴² reveal rates for 38 of the 53 backbone amides. The data include exchange rates for a number of amide protons near the protein surface which cannot be correlated readily with the apparently accessible surface areas indicated by the crystal structure. Further amide exchange rates are reported,²⁴³ and the dynamics of the molecule are investigated in terms of their effect on ^1H -²⁴⁴ and ^{13}C -²⁴⁵NMR measurements. The stability of BPTI, as related to electrostatic interactions, has been discussed²⁴⁶ following employment of the Tanford–Kirkwood electrostatic theory in the evaluation of pK values obtained via ^{13}C -NMR spectroscopy. The total electrostatic free energy of the molecule is a stabilising influence at neutral pH despite the substantial net positive charge borne by the molecule. CIDNP studies of the tyrosines of BTPI indicate a major loss of solvent accessibility on binding to trypsin and chymotrypsin and their zymogens.²⁴⁷ Spin–spin splittings, revealed by two-dimensional J -resolved spectroscopy,²⁴⁸ show that internal residues have their side chains locked into unique orientations identical to those found for the crystal, with differences between crystal and solution side-chain orientations being common for surface residues (Fig. 4). Rapid fluctuations are found even for the locked internal side chains. Another theoretical paper²⁴⁹ points out that such picosecond fluctuations must be accounted for when interpreting T_1 longitudinal relaxation measurements in terms of overall molecular motion. Specific labeling of the carbonyl carbon of lysine-15 of the inhibitor with ^{13}C permits studies of the reactive site peptide bond (Lys-15–Ala-16) in complexes with trypsin. The results show that no formation of a covalent bond to this carbonyl carbon takes place during formation of the complex.²⁵⁰ A similar conclusion is drawn from a related study, this time involving ^{13}C labeling near the (Arg-63–Ile-64) reactive site peptide bond of soybean trypsin inhibitor.²⁵¹ Formation of a nonnative, but stable, conformer of BPTI on refolding the protein with its normal disulphide bridges²⁵² may cast some light on the sources of the conformational stability of the protein. Assignments of the ^1H -NMR spectrum of trypsin inhibitor E from *Dendroaspis polylepsis* are reported following two-dimensional NMR spectroscopy at 500 MHz.²⁵³ The protons of virtually all 59 residues are assigned, using only the known sequence and the NMR data. Assignment of the three methionyl carbonyl carbon resonances in the *Streptomyces* subtilisin inhibitor has required double

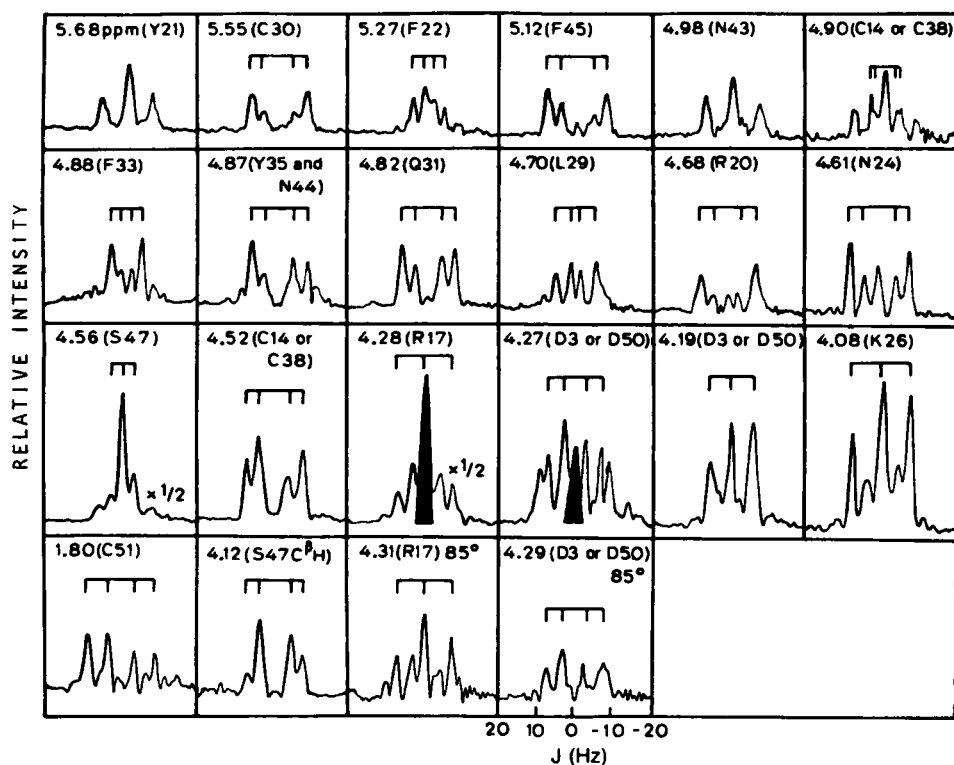


FIG. 4. Measurement of spin-spin couplings between protons on the α - and β -carbon atoms of the residues of the basic pancreatic trypsin inhibitor by two-dimensional J -resolved spectroscopy. Cross-sections of the two-dimensional spectrum are taken parallel to the J axis at the chemical shift values indicated, and assignments are indicated in parentheses. From the J values obtained, partial side-chain orientations can be calculated for comparison with X-ray data. From reference 248.

labeling using both ^{13}C and ^{15}N .²⁵⁴ Since being assigned, their dynamics have been investigated over a wide range of temperatures.²⁵⁵ Deuterium labeling has been used in measurements on tryptophan-86 of the same protein.²⁵⁶ The local conformation around the residue is stable up to pH 11.5, and up to 85°C at pH 7. Some photo-CIDNP²⁵⁷ and titration²⁵⁸ studies of the aromatic residues of *Streptomyces* subtilisin inhibitor show that tyrosine-7 is always well exposed, tyrosine-93 buried, and tyrosine-75 in a variable microenvironment, more restricted in solution than it apparently is in the solid crystalline form. Finally, in a study of pepstatin²⁵⁹, clear evidence has been adduced for a tetrahedral intermediate in the binding of pepstatin to pepsin. Difference NMR spectroscopy, utilising protonated and partly deuterated pepstatin

bound to pepsin, points the way to a potentially useful method for simplifying the spectra of high-molecular-weight complexes.²⁶⁰

NMR studies on a number of other biologically important small peptides, including the cyclic pentapeptides malformin A²⁶¹ and viscumamide,²⁶² the antineoplastic agent dolastatin 3,²⁶³ and some biotin-containing peptides,²⁶⁴ have been reported. It has also been established²⁶⁵ that the agent responsible for binding methylmercury in human erythrocytes is glutathione, and in a further use of ¹H and ¹³C NMR for identification it has been established that ferribactin, a siderochrome (iron-chelating peptide) from *Pseudomonas fluorescens*, is a nonapeptide that contains two residues each of lysine and N⁶-formyl-N⁶-hydroxyornithine.²⁶⁶

V. ENZYMES

A. Oxidoreductases

Metal substitution at the catalytic site of liver alcohol dehydrogenase (LADH) has formed the basis of several studies. Manganese ions²⁶⁷ do not bind at the active site but at two other types of site, from which they are displaced, respectively, by Zn²⁺ or Cd²⁺, the zinc binding possibly being an intermediate for the return of zinc to its normal binding site. Cu²⁺ and Co²⁺ substitution²⁶⁸ shows that because of a strong spin-orbit interaction of the electronic spin of Co²⁺ no true paramagnetic effects of Co²⁺ on solvent relaxation are detectable. Thus earlier studies may need to be reinterpreted. ESR results²⁶⁹ reveal Co²⁺ to be tetracoordinated in the free enzyme but pentacoordinated in binary enzyme–NAD and higher complexes. Coordination of Cd²⁺ in LADH is also reported.²⁷⁰ Two models for the active site of LADH have been proposed. X-Ray data imply a direct coordination between substrate and the active site zinc atoms, while NMR studies on the Co²⁺ derivative deny such direct binding. Careful new NMR work²⁷¹ supports the latter conclusion, being consistent with a model in which a metal water ligand forms a bridge between substrate and metal. Various attempts to explain the discrepancy between NMR and X-ray results have been presented.^{272–274} The ability of a number of dehydrogenase and other enzymes to bind modified NADH as coenzyme, when the modification causes the nucleotide to be in the syn, rather than the anti, conformation, has been discussed.²⁷⁵

A novel method involving ¹H–¹H transferred NOE has been used to investigate the conformation of NAD bound to alcohol dehydrogenases.²⁷⁶ The conformation of the adenosine and nicotinamide ribose is found to be 3' endo of the N type. A tentative design for the hydrophobic pocket of the substrate binding site of aldehyde reductase I, containing two anion binding

sites, has been proposed following binding of NAD-P-2-oxodiacid adducts as NMR probes.²⁷⁷ The possibilities of ^{19}F as a probe for dehydrogenase mechanisms are explored in a series of papers in which fluorinated substrates and inhibitors are employed.²⁷⁸⁻²⁸⁰ Dehydrogenase activity in an intact cell system has been monitored by ^1H -NMR measurements of bulk isotope exchange in the cells,²⁸¹ and the role of the essential histidine in the activity of lipoamide dehydrogenase elucidated through monitoring its signal following photoinactivation of the enzyme in the presence of Rose Bengal.²⁸²

In lactate dehydrogenase, the ^1H signals of tyrosine-237 have been assigned. The residue is reported to be on the enzyme surface and has considerable freedom of motion.²⁸³ Phosphorus NMR studies of the glycoprotein glucose oxidase show it to contain a disubstituted phosphorus residue, with the phosphorus moieties bound to be the protein at a point remote from the flavin coenzyme and possibly involved in a phospho bridge linking two amino acid residues.²⁸⁴ Substrate binding to galactose oxidase, studied by competition between fluoride and cyanide ions and by ^{19}F relaxation as a function of substrate concentration,²⁸⁵⁻²⁸⁷ gives a dissociation constant for the anaerobic binding of dihydroxyacetone substrate of 0.059 M. Remarkably mobile regions of the polypeptide chains of the large multienzyme complex pyruvate dehydrogenase have been reported,²⁸⁸ as well as for the similarly large 2-oxoglutarate dehydrogenase.²⁸⁹ The regions involved may be those encompassing the lipoylysine residues. Highly mobile peptide chains in the multienzyme pyruvate dehydrogenase complex from *Bacillus stearothermophilus* appear likely following monitoring of chain mobility through partial proteolysis of the complex.²⁹⁰

Dihydrofolate reductase (DHFR) continues to arouse considerable interest. Complexes of the enzyme with an inhibitor, trimethoprim, have been shown by ^1H ²⁹¹ and ^{31}P ²⁹² NMR to exist in two slowly interconverting forms. The trimethoprim itself, like methotrexate, another inhibitor, is protonated when bound to the enzyme.²⁹³ Few of the histidine resonances of DHFR are affected by coenzyme binding; the ligand-induced conformational changes appear to be different for NADP and NADPH.²⁹⁴ Only one of the diastereoisomers of folinic acid binds to the enzyme in its biologically active form²⁹⁵; the 6*S*, α *S* isomer has a binding constant of $1.3 \times 10^{-8} \text{ M}^{-1}$,²⁹⁶ some 10^4 times larger than that of the 6*R*, α *S* isomer. Binding of coenzymes is the subject of a number of interesting papers on DHFR from *Lactobacillus casei*²⁹⁷⁻³⁰⁰ and *E. coli*.³⁰¹ These show differences between the two enzymes; rates of interaction and some steric details are presented. Various aspects of DHFR ligand binding are reported by the same investigators. Photo-CIDNP measurements reveal ligand-induced conformational changes in the enzyme.³⁰² Other techniques applied include selective deuteration,³⁰³ saturation transfer,³⁰⁴ modification with *N*-bromosuccinimide,³⁰⁵ and titrat-

ion³⁰⁶ of a histidine resonance required by the sequence of the protein but not previously observed. Other studies on DHFR cover specific labeling with (γ -¹³C) tryptophan³⁰⁷ and the effect of chloride ion on the reduction of dihydrofolate to tetrahydrofolate catalysed by the enzyme.³⁰⁸ Labeling with γ -¹³C tryptophan permits a number of partial assignments, and subsequent measurements suggest different modes of binding for different ligands.³⁰⁹ The dihydrofolate–folate–NADP complex has been shown by ¹H, ³¹P, and ¹³C NMR³¹⁰ to exist in three interconverting conformational states which occur in different proportions at different pH values. The ionisable group is reported to be responsible for the change rather than one of the seven histidine residues (Fig. 5). Strong isotope effects on the methylene/methyl interconversion, catalysed by methylenetetrahydrofolate reductase from pig liver, are reported.³¹¹

Contact shifts due to the high-spin nonhaem iron atom in catechol dioxygenases have been used³¹² to show a monodentate catecholate configuration in catechol 1,2-dioxygenase from *Pseudomonas orvilla* and a chelated catecholate structure in protocatechuate 3,4-dioxygenase from *Pseudomonas aeruginosa*. In lipoyxygenase I³¹³ it has been shown that the Fe is definitely in a high-spin state. ¹H-NMR measurements of the molybdoferredoxin of nitrogenase from *Klebsiella pneumoniae* show³¹⁴ that metal-binding sites, detected through relaxation enhancement by Mn²⁺, are essential for the enzymatic function of the nitrogenase. The spin states of a similar MoFe



FIG. 5. ¹³C-NMR spectra at 50.3 MHz of the nicotinamide carboxamide carbon in the dihydrofolate reductase–folate–NADP⁺ complex at various pH values, showing the three coexisting states I, IIA, and IIB. From reference 310.

protein from *Azotobacter vinelandii* are reported to be two M centres ($S = \frac{3}{2}$) and 4 P centres ($S = 0$) in the native states, and diamagnetic M centres with $S = \frac{5}{2}$ P centres in the oxidised form.³¹⁵

Relaxation measurements in soybean lipoxygenase inhibitors and substrates that have been selectively deuterated indicate considerable internal motions.³¹⁶ The binding of water³¹⁷ and several different anions³¹⁸ to superoxide dismutase (a copper–zinc protein also known as erythrocuprein) has been reported. All anions bind at the Cu site, though a high pH value is needed for OH^- to bind. Similar results are reported elsewhere.³¹⁹ Addition of anions causes a deshielding of the histidines bonded to the Cu ion, but has no effect on Zn ligands in the same molecule, an exception being the case of enzyme extracted from yeast³²⁰ which seems to have a slightly different Zn site from enzymes found in vertebrates. With superoxide dismutase in steady-state turnover, it appears from ^{19}F relaxation measurements that Cu^+ and Cu^{2+} are present at the active site in equal proportions.³²¹ Other results on superoxide dismutase, which is known specifically to inhibit adrenaline autooxidation, come from several groups; results include the assignment of a number of histidine resonances,³²² exchange studies on histidine NH protons which show that only one of the four histidines is not bonded to the Zn atom,³²³ the binding of adrenalin,^{324,325} and the binding of anions to the copper atom.³²⁶

An interesting structural inference may be drawn from the relaxation rates of the ^1H and ^{17}O nuclei of water in the presence of the copper protein laccase from *Rhus vernicifera*.³²⁷ The relative inertness of the water ^{17}O nuclei to paramagnetic relaxation enhancement contrasts with the much stronger effect on the ^1H nuclei. This implies that the type 2 and 3 copper sites are buried in such a way as to be accessible only to protons.³²⁸

Other enzymes of class 1 which have been studied include the cuproprotein diamine oxidase: the ^1H magnetic relaxation dispersion shows two values for $1/T_1$, at 16 and 75 MHz, whereas $1/T_2$ shows a minimum at 20 MHz. The implication is that the two Cu^{2+} ions of the protein are in quite different chemical environments.³²⁹

B. Transferases

The surface exposure of a number of residues in α -lactalbumin (one of the two proteins forming lactose synthase) from several sources has been studied by CIDNP methods.³³⁰ Several differences are noted; however, all species have a common buried tyrosine. A ^{19}F probe, 5-fluoro-2'-deoxyuridylate, has been used³³¹ to study binding to thymidylate synthase. ^{19}F chemical shift changes on binding vary with protein preparation methods, and are greatly enhanced by the formation of a ternary complex with methylenetetrahydro-

folate. ^{13}C labeling work on thymidylate synthetase from *L. casei*³³² suggests that the active site arginyl residue has a ^{13}C resonance at 156.9 ppm. The acid-base catalysis of α -glucan phosphorylases has been discussed.³³³ ^{31}P NMR has been used to monitor the production of ribose 1-phosphate from orthophosphate by nucleoside phosphorylase,³³⁴ to study the activation of glycogen phosphorylase,³³⁵ and, via ^{15}O - ^{14}O isotope shifts of the ^{31}P signal, the scissile bond of purine nucleoside phosphorylases.³³⁶ Apparently there is no phosphoryl enzyme intermediate in the reaction. The enzyme-catalysed formation of *S*-adenosylmethionine has been shown³³⁷ to occur with inversion of the configuration at the 5'-C of ATP. Proton NMR³³⁸ shows a strong interaction between succinate and native cytosolic aspartate aminotransferase, but not such a specific interaction with enzyme modified at a single arginine residue. A detailed ^{31}P -NMR study of a similar enzyme from mitochondria has been described.³³⁹

In a careful selective ^{13}C -labeling experiment on the binding of ATP (effector) and CTP (inhibitor) to aspartate transcarbamylase³⁴⁰ it is shown that while three histidine residues react identically to ATP and to CTP binding, two phenylalanines are affected only by CTP. The bovine galactosyltransferase/manganese/UDP-galactose ternary complex apparently exists in two forms, an initially formed, rapidly exchanging conformer, effective in enhancing the relaxation of solvent water protons, which slowly converts to a second form in which the metal centre is much less accessible to solvent.³⁴¹ Isotope shifts using specifically labeled adenosine 5' [γ (*S*)- ^{16}O , ^{17}O , ^{18}O]-triphosphate have been used to determine the stereochemical course of phosphoryl transfer catalysed by yeast hexokinase³⁴² and glucokinase from rat liver.³⁴³ In both cases the results suggest an in-line mechanism. Glucose and glucose 6-phosphate appear to bind to brain hexokinase quite differently, with the former apparently close to a site which will bind Mn^{2+} .³⁴⁴ The histidines³⁴⁵ and monovalent cation sites³⁴⁶ of pyruvate kinase have also been discussed. The roles played by histidine residues in the catalytic activity of pyruvate kinase (237,000 Da) have been studied at 250 MHz. Substrate binding alters the pK of only one histidine, due either to a stronger interaction of the cation activators with the histidine or to some substrate-induced conformational change in its vicinity.³⁴⁷ The effect of an Mn^{2+} centre on the T_1 values of a large number of monovalent cations³⁴⁸ in pyruvate kinase has permitted accurate distance measurements from less than 4 to 20 Å between the paramagnetic ion and the bound cation. The method may find application in many other proteins. The ternary complex ^{31}P -NMR spectrum of halibut muscle 3-phosphoglycerate kinase can be accounted for entirely on the basis of the various binary complex spectra, there being no evidence therefore for any substantial involvement of phosphoenzyme intermediates.³⁴⁹

Magnesium NMR has been used to investigate the binding of Mg^{2+} -ADP and Mg^{2+} -ATP to creatine kinase.³⁵⁰ The spectra suggest that the cation in the ternary complex is not in the fast-exchange state, while the paramagnetic effects of Cr-ADP have been used³⁵¹ to deduce that metal ion coordination of the transferable phosphoryl group precedes phosphoryl transfer and is a requirement of the creatine kinase reaction. Similar experiments are reported for adenylate kinase.³⁵² Another study³⁵³ of the creatine kinase molecule shows three histidine resonances affected by substrate binding, a conclusion reinforced by the results of experiments using the paramagnetic substrate analogue Cr^{3+} -ATP. ^{31}P -NMR studies allow equilibrium constants and interconversion rates to be measured for creatine kinase-catalysed reactions.³⁵⁴

The effect of different isotopes of oxygen on the shielding of phosphorus aids in the characterisation of the course of the reactions. Adenosine 5' [$\gamma(\text{S})$ - ^{16}O , ^{17}O , ^{18}O]-triphosphate is used as a substrate, and the phosphorylation reaction is defined as an associative in-line transfer of the phosphoryl group.³⁵⁵ Saturation-transfer ^{31}P NMR in intact frog muscle³⁵⁶ reveals that the enzyme is active even with the muscle in the resting state. In bovine heart protein kinase, the mechanism of regulation has been investigated by NMR. It appears that the regulatory subunit acts by physically blocking the substrate binding site.³⁵⁷ Hill plots of histidine titrations have been used to show that the NMR signals of two histidines in arginine kinase are affected by the same three titratable groups. Histidine titrations and the lack of pH-dependent structural isomerisation of human muscle adenylate kinase have been discussed.³⁵⁸ Interactions of RNA polymerase with substrate have been studied via ^{31}P NMR³⁵⁹ and paramagnetic substitution.³⁶⁰ In the latter study, with CO^{2+} substituted for one of the two Zn^{2+} ions of the enzyme, direct metal-ATP coordination is demonstrated. The stereochemical course of nucleotidyl transfer catalysed by T7-induced DNA polymerase is outlined³⁶¹ as well as the 3',5' exonuclease activity of T4 polymerase.³⁶²

In the phosphoenolpyruvate-dependent phosphotransferase system of *Staphylococcus aureus*, ^1H -NMR data show that factor III forms a complex with phosphocarrier protein HPr, the interaction not surprisingly being abolished when both proteins are phosphorylated.³⁶³ The protein kinase from bovine heart binds specific heptapeptides; if there is any absolute requirement for the conformation of these peptides, it is not³⁶⁴ any of the normal (α -, β -, β -turn) secondary structures. The interaction of ATP with RNA polymerase has been reported.³⁶⁵

C. Hydrolases

All known phospholipase A_2 molecules have Glu-4 and Phe-5 in their sequences. A series³⁶⁶ of modified proteins is used to show that both Tyr-5- and norleucine-4-substituted enzymes are inactivated by the substitution, but

for different reasons, the first due to a distortion of the catalytic site, the second due to loss of a binding site for micelles. Evidence from ^{31}P NMR seems to show that cobra venom phospholipase A has an activator site separate from its catalytic site.³⁶⁷ Values of the parameters of calcium binding to porcine pancreatic prothrombinase A, as measured by ^{43}Ca NMR, have been reported.³⁶⁸

Inhibitors bound to acetylcholinesterase from *Electrophorus electricus* show considerable conformational flexibility which is reduced when the active site serine is modified.³⁶⁹ The reduction in mobility is proportional to the size of the inhibitor, indicating that it binds in a large anionic pocket near the serine residue. A comparison of inhibitor and fluorescent probe binding to acetylcholinesterases with that to cholinesterase from horse serum has been discussed.³⁷⁰

When the 10 histidine residues of alkaline phosphatase are labeled at the γ -carbon with ^{13}C , the resultant ^{13}C -NMR spectrum has nine signals spread over 14 ppm.³⁷¹ Only four of the signals appear to depend on pH; the other six appear to be deeply buried, three bonded to the active site metal ion(s) and two at or near the active site. Unambiguous identification of the three metal-bonded histidines is possible using $^{113}\text{Cd}/^{13}\text{C}$ spin-spin couplings.³⁷² ^{113}Cd NMR^{373,374} is also employed in a most interesting study of the dimeric alkaline phosphatase, showing that in the absence of sufficient metal ions, ions may migrate from one monomer to the other in order to permit binding of phosphate, thus giving a half of the sites reactivity (Fig. 6). Binding of Mn^{2+} at a structural site and a nitroxide spin label at an $-\text{SH}$ site allow some active site mapping in fructose bisphosphatase.³⁷⁵ Acid phosphatase from sweet potato tubers already contains manganese(III), which has permitted ^{17}O - and ^{31}P -NMR experiments to reveal direct metal-phosphate interactions and the course of $\text{P}-\text{O}$ cleavage.³⁷⁶ ^{18}O Isotope shifts demonstrate³⁷⁷ that acid hydrolysis of α -D-ribofuranose 1-(^{18}O)phosphate cleaves the $\text{C}-\text{O}$ bond, while both acid and alkaline phosphatases cleave the $\text{O}-\text{P}$ bond.

The ready availability, reasonable size, and extensive earlier literature of lysozyme make it a continuing subject for a number of researchers. It has been used as a "typical globular protein" for studies of relaxation dispersion in the crystalline³⁷⁸ and lyophilised powder³⁷⁹ forms. Relaxation studies in solid lysozyme show³⁸⁰⁻³⁸² that the main source of relaxation is methyl group rotation, but with other contributions from slow motions and groups with exchangeable protons. Relaxation³⁸³ and denaturation³⁸⁴ of lysozyme in solution have also been discussed. The indole NH ^1H signals in the tryptophan residues of lysozyme seem to suggest an exchange for solvent deuterium by two different mechanisms with different activation energies.³⁸⁵ Assignments of a number of protons from residues in the β -sheet region of lysozyme have been made,³⁸⁶ and assignments of the N-methyl resonances in ^{13}C reductively

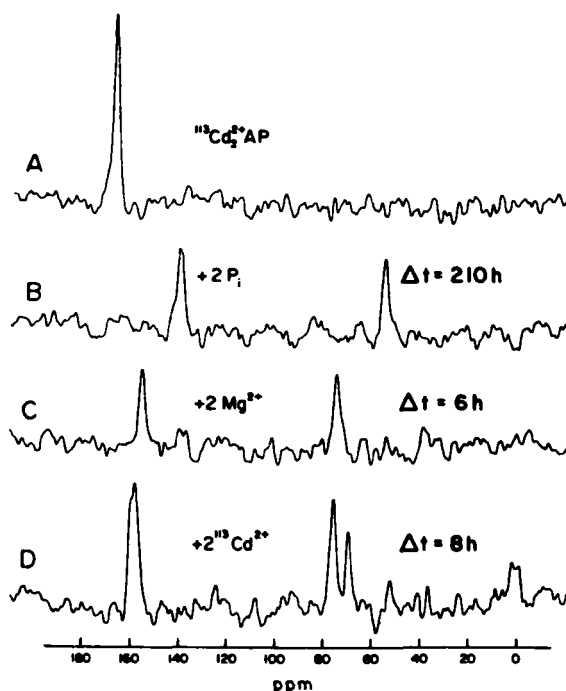


FIG. 6. ^{113}Cd -NMR spectra at 19.96 MHz of phosphoryl ^{113}Cd alkaline phosphatase at pH 6.3. With only two equivalents of cadmium per dimeric apophosphatase (AP) molecule, a single resonance (A) indicates that the metal atoms occupy equivalent sites on the two subunits. With this amount of metal (there are six metal sites on the dimer) only one phosphate will bind per dimer; addition of phosphate produces spectrum (B), indicating that the cadmium has migrated to occupy two different sites on one subunit, permitting phosphate binding. Addition of magnesium (C) permits phosphorylation of the other subunit, and of further cadmium (D) occupation of all possible metal sites. From reference 373.

methylyated lysozyme are also reported.³⁸⁷ Assignment of the ^1H -NMR spectrum of lysozyme now extends to some 70 resonances from 25 residues.³⁸⁸

Simultaneous binding of lanthanide shift reagents and *N*-acetylglucosamine inhibitors to hen egg white lysozyme reveals one of two or more sugar binding sites to be subsite E of the enzyme³⁸⁹ and another to be subsite C.³⁹⁰ The indole rings of tryptophan-62 and -63 rotate toward subsite C on binding. *N*-Bromosuccinimide modification of tryptophan-62³⁹¹ inactivates the enzyme, although the pK values of catalytically important carboxyl groups glutamic acid-355 and aspartic acid-52 are unchanged by the modification. The modification appears to obstruct subsite B. The hydration of lysozyme has been studied by two groups^{392,393}; in the latter case ^1H -NMR measure-

ments show that every gram of lysozyme is associated with 0.3 g of "unfreezable" water, which accords with the amount which can be directly linked with polar sites on the surface of the molecule.

Another "golden oldie" for the NMR spectroscopist, RNase A, appears these days to be popular largely for the light it can cast on the folding and unfolding mechanisms of proteins. Current reports include ^1H relaxation measurements taken during unfolding,³⁹⁴ the equilibrium between cis and trans proline conformers in fragments of RNase A,³⁹⁵ observation of methanol-stabilised intermediates in the unfolding process,^{396,397} salt-bridge stabilisation of the helix formed by the isolated C-peptide (residues 1-13) of RNase A,³⁹⁸ and the existence of a purine ligand-induced conformational change in the active site of the enzyme, revealed through perturbations in the titration behaviour of histidine-12, -48, and -119.³⁹⁹ Thermal denaturation of RNase A is reported by two groups^{400,401} to leave considerable structured regions even at elevated temperatures, hydrophobic effects being responsible for the retention of structure. The interaction of ribonuclease A with nucleotides is reported by a number of workers.⁴⁰²⁻⁴⁰⁵

Evidence is presented for an interaction between lysine-41 and a histidyl residue.⁴⁰⁵ In ribonuclease T_1 , on the other hand, it appears that each histidyl group interacts with the carboxyl group of an aspartate or glutamate residue,⁴⁰⁶ and the same appears to be true of histidine-60 of ribonuclease S, in which histidine-91 also appears to be coupled to a COO^- group, although its pK value, which is not abnormal, argues for the presence of a positively charged group in the vicinity as well.⁴⁰⁷ Similar studies are reported for the guanyl-specific ribonuclease from the fungus *Penicillium brevicompactum*.⁴⁰⁸

Investigation of the ribonuclease S-protein S-peptide complex has become more sophisticated. The enthalpy of binding of residues 1-15 to the S-protein is 1.7 kcal/mol less than that of the full (1-20) S-peptide⁴⁰⁹ with a five times greater dissociation constant. The hybrid between rat S-peptide and bovine S-protein confirms earlier findings that the catalytic properties of the native enzyme are modulated by the S-protein region of the molecule.⁴¹⁰ The tautomeric states of the histidines of RNase are reported⁴¹¹ along with a probable hydrogen-bonding scheme. It is claimed that the intermediate states of regeneration of RNase A, from its reduced form, are more disordered than the reduced form itself.⁴¹²

AMP nucleosidase catalyses the hydrolysis of the N-glycosidic bond of AMP, and requires a metal- ATP^{2-} complex as an allosteric activator. A combination of NMR and ESR methods reveals that the catalytic and allosteric sites are at least 25 Å apart.⁴¹³

Replacement of the Zn^{2+} at the activation site of bovine lens leucine aminopeptidase by Mn^{2+} has permitted elucidation of some aspects of the action of the inhibitor *N*-(leucyl)-*O*-aminobenzenesulphonate.⁴¹⁴ Similar

substitutions, this time with Co^{2+} , in carboxypeptidase A permit both inhibition by β -phenylpropionate⁴¹⁵ and the catalytic role of the metal ion⁴¹⁶ to be investigated. In both cases one metal-bound water molecule is affected. ^{15}N -NMR measurements of carboxypeptidase A, selectively enriched with ^{15}N , have enabled experimenters⁴¹⁷ to establish that β -phenylpropionate can successfully compete with an azo nitrogen as the hydrogen bond acceptor of the phenolic proton of tyrosine-248, which is complexed in its azo form to the catalytically essential Zn^{2+} ion.

NMR studies of the active sites of serine proteinases are reviewed⁴¹⁸ and comparison between the results of X-ray and NMR studies made.⁴¹⁹ Peptide models for the active site have been prepared for serine proteases in general⁴²⁰ and for α -chymotrypsin in particular.⁴²¹ Both ^1H - and ^{19}F -NMR data⁴²² show the formation of a hemiacetal between the free aldehyde of *N*-acetyl-DL-*p*-fluorophenylalaninal and the active site serine residue of chymotrypsin. Binding of 4-(trifluoromethyl)- α -bromoacetanilide to the enzyme, involving alkylation of methionine-192, is also reported.⁴²³

Tosylchymotrypsin, labeled with ^2H or ^{13}C in the tosyl group, has been used to demonstrate⁴²⁴ that the local structure of the active site is rather loose, in that the tosyl group moves freely and is in a solvent-rich environment.

The active site methionine-192 of chymotrypsin provides an open invitation to labeling experiments. It has been *S*- ^{13}C methylated,⁴²⁵ giving two resonances, one of which does not appear in the phenylmethylsulphonyl derivative of the enzyme. A method for preparing ($[\epsilon\text{-}^{13}\text{C}]$ methionine-192)chymotrypsin is described⁴²⁶ while ^{19}F -NMR experiments on monofluorocinnamoyl chymotrypsins⁴²⁷ reveal that the presence of the fluorocinnamoyl group stabilises the protein toward urea denaturation. The conformational transition from trypsinogen to trypsin has been carefully investigated using a series of signals whose shieldings are increased by ring currents, and calibrated with Johnson-Bovey calculations. It seems clear that activation involves subtle changes of conformation and flexibility in certain regions of the molecule not detectable within the precision of X-ray crystallographic studies.⁴²⁸ Fragments 1 and 2 of bovine prothrombin appear, from their 270-MHz ^1H -NMR spectra, to be random coils containing a small amount of tertiary structure, probably in the structurally homologous Kringle regions.⁴²⁹ A number of binding sites for Eu^{3+} , falling into at least two types, exist on prothrombin fragment 1.⁴³⁰ Temperature and pH effects on human prothrombin fragment 1 are reported.⁴³¹

A very deshielded ^1H signal is found in the spectra of aqueous solutions of serine proteases and their zymogens. This appears to be characteristic of the hydrogen bond between imidazolium and aspartate groups of the catalytic triad Ser-His-Asp. It is not visible in the spectra of native subtilisins but appears in the spectra of their thiol derivatives. The stable hydrogen bond

should be more important during catalysis than in the substrate-free enzyme.^{432,435} Evidence from fluorimetric and ^1H -NMR titration studies of papain and some methylthio derivatives lends support to the involvement of histidine-159 in the deacylation step in papain catalysis.⁴³³ Strong evidence for the existence of an ion-pair interaction between the active site cysteine-25 and histidine-159 in papain is discussed. The pK of the histidine is 8.6 in the active enzyme (succinylated to improve solubility at high pH).⁴³⁴ The results of some molecular orbital calculations on the histidine-57/aspartic acid-102 couple in β -trypsin agree with those of NMR experiments in not supporting an earlier charge-relay mechanism proposed for the enzyme.⁴³⁶ The active site histidine⁴³⁷ and catalytic mechanism⁴³⁸ of α -lytic protease have also been discussed. Other hydrolase enzymes reported recently include thermolysin,⁴³⁹ *Mucor* rennin,⁴⁴⁰ papain at low temperatures,⁴⁴¹ and the conformations and conformational changes of pepsin on binding the potent peptide inhibitor pepstatin.^{442,443} The inactivation of β -lactamase I (penicillinase) by 6-bromopenicillanic acid has been shown by NMR and other studies to be associated with acylation of serine-70 and with rearrangement and cyclisation of the inhibitor.⁴⁴⁴ The binding of CO_2 to the enzyme has also been discussed.⁴⁴⁵

In a sheep kidney medulla sodium–potassium ATPase, with lithium substituted for potassium, titration with Cr^{3+} -ATP gives a Cr^{3+} – Li^+ distance of 4.8 Å.⁴⁴⁶ A K^+ -sensitive phosphorylated intermediate of Na^+ , K^+ -ATPase from the salt gland of the duck is reported, following ^{31}P -NMR studies in which a signal at +17 ppm, from phosphoric acid, is attributed to the formation of an acyl phosphate at an aspartyl residue of the catalytic site.⁴⁴⁷

D. Lyases

A structural model has been proposed⁴⁴⁸ for the active site of chicken liver mitochondrial phosphoenolpyruvate, which has been shown to have one binding site for Mn^+ . The kinetics of threonine aldolase reactions have been followed using a model system.⁴⁴⁹ The C-2 ^1H signals of 6 of the 10 histidyl residues in yeast aldolase have been detected at 360 MHz. Their behaviour⁴⁵⁰ is consistent with coordination of the enzyme-bound metal (Zn^{2+}) by three imidazole ligands which, with a previously reported rapidly exchanging water ligand, provide all four necessary ligands. The inhibition of yeast enolase– Mn^{2+} by fluoride ions⁴⁵¹ and inorganic phosphate appears to be due to the formation of a quaternary enzyme– Mn^{2+} – F^- – P_i complex which isolates the catalytic site, thus preventing the dehydration of 2-phosphoglycerate and inhibiting glycolysis. Rates of carbon dioxide/carbonate exchange catalysed by human carbonic anhydrase I are reported following

^{13}C -NMR studies.⁴⁵² The interaction of sulphate with the enzyme has also been investigated.⁴⁵³ A CO_2 hydration activity for Mn^{2+} -substituted carbonic anhydrase B of some 7% of that of the native Zn^{2+} enzyme has been found. This series of experiments also demonstrated a direct binding of HCO_3^- to the metal ion, while CO_2 is much more weakly attached to the enzyme.⁴⁵⁴

A number of earlier studies of carbonic anhydrase have used metal substitutions. It is pointed out⁴⁵⁵ that coordination of carboxymethylated histidine-200 takes place only to the native active site Zn^{2+} and possibly to Co^{2+} , but not to Cd^{2+} or Hg^{2+} . Caution is advised in using metal replacement techniques for this protein. The effects of pH and bicarbonate on ^{113}Cd -carbonic anhydrase cadmium-NMR spectra show that there is a rapid equilibrium between hydroxide, water, and bicarbonate occupancy of the open coordination site of the metal ion.⁴⁵⁶ According to other workers,⁴⁵⁷ the Cd^{2+} enzyme is inactive in the reversible hydration of acetaldehyde. Photo-CIDNP studies of the binding of sulphanilimide inhibitor to carbonic anhydrase^{458,459} enable the direct observation of bound and free ligand. Inhibition of carbonic anhydrase has been studied by using ^1H NMR with the Co^{2+} -substituted enzyme⁴⁶⁰ and by ^{17}O NMR with Cu^{2+} substitution.⁴⁶¹

Manganese substitution has been used in studies of the binding of glutathione to glyoxalase I.⁴⁶² Two water molecules are bound in the coordination sphere of the metal, and one of them is displaced on attachment of the glutathione; the remaining water is implicated⁴⁶³ in the catalytic step.

^{31}P -NMR spectra, taken following the binding of an analogue of the cofactor pyridoxal phosphate to D-serine dehydratase, show shifts in pK which may be useful in studying the binding of cofactors generally.⁴⁶⁴ The mechanism of action of 5-aminolevulinic acid dehydratase has been elucidated by ^{13}C NMR.⁴⁶⁵

E. Isomerases and ligases

Some studies of steroid isomerase, including histidine titration and the detection of some unusually mobile residues in the chain, form one of only two protein studies reported here for isomerases.⁴⁶⁶ In the other the stereochemistry of lysine 2,3-amino mutase has been established using ^2H -NMR data of its products.⁴⁶⁷ Slightly better represented are the ligases: the active site phosphohistidine of succinyl-CoA synthetase from *E. coli* has been observed through its ^{31}P -NMR signal, showing that the phosphorus atom is rigidly held and that the phosphoryl group is in the monoanionic form at pH 7.25.⁴⁶⁸ The same workers have detected the existence of two phosphorylated intermediates in catalysis by the enzyme, leading to a detailed model for the catalysis.⁴⁶⁹ Rates of synthesis of various dinucleotide tri- or tetraphosphates by *E. coli* lysyl-tRNA synthetase have been monitored by ^{31}P - and

^1H -NMR spectroscopy. Considerable enhancement of the rate occurs on addition of $150\ \mu\text{M}$ ZnCl_2 to the reaction mixture.⁴⁷⁰ ^{31}P NMR has been used⁴⁷¹ to investigate the catalysis of the enzyme-bound methionine- $\text{MgATP} \rightleftharpoons$ methionine-AMP-Mg pyrophosphate reaction by methionyl-tRNA synthetase. An upper rate of $360\ \text{sec}^{-1}$ is found for the left-to-right reaction. Similar techniques are used⁴⁷² on the action of carbamoyl-phosphate synthetase, supporting the formation of two intermediates, carboxy phosphate and carbamate, in the overall reaction catalysed. The role of enzyme-bound Mn^{2+} , an essential activator bound at the active site of phosphoribosyl pyrophosphate synthetase, has been probed by ^{31}P and ^1H relaxation studies. The conformation of the bound nucleotide has a torsional angle at the glycosidic bond which differs by at least 20° from that found in solution. The arrangement of the substrates at the active site has been determined.⁴⁷³

The activity of mitochondrial carbamoyl-phosphate synthetase has been investigated by following the fate of phosphate metabolites identified via oxygen-isotope shift effects on ^{31}P -NMR signals.⁴⁷⁴ In the enzyme- ATP_A - HCO_3 - ATP_B complex there is reversible transfer of the γ - PO_3 group of ATP_A to HCO_3 without dissociation of products.

VI. HAEM PROTEINS

A. Myoglobins

A new technique for the investigation of haem protein crystals has been presented.⁴⁷⁵ Microcrystals of the protein, suspended in nearly saturated ammonium sulphate solution, are perfectly aligned in strong magnetic fields (Fig. 7). The orientation of specifically labeled residues in the crystal may then be determined directly by combining NMR with powder X-ray results.⁴⁷⁶ The dynamic behaviour of exchangeable protons in the haem pocket of myoglobins has been discussed,^{477,478} as well as that of a number of histidine titrations in myoglobins and derivatives.⁴⁷⁹

Selective deuteration of protohaemins and deuterohaemins has enabled workers to resolve 17, and unambiguously assign 12, of the 22 possible haem resonances in native sperm whale myoglobin.^{480,481} Different hyperfine shift patterns for the low-spin and high-spin states are concluded to arise from differential sensitivities of the dominant spin transfer mechanisms to the same rhombic perturbation.⁴⁸² Among other recent work involving myoglobins, we may note ^{129}Xe -NMR measurements of xenon binding,⁴⁸³ high-pressure studies,⁴⁸⁴ a review of the motions of aliphatic residues,⁴⁸⁵ and model studies of the electronic state of the haem group.⁴⁸⁶

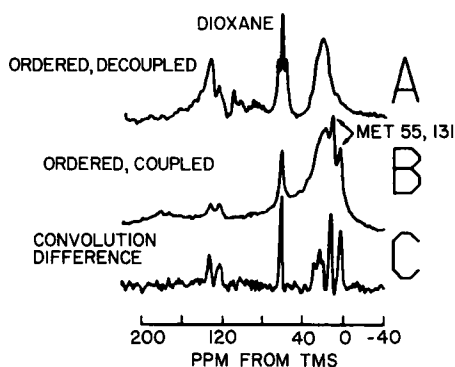


FIG. 7. ^{13}C -NMR spectra taken at 37.7 MHz of $[^{13}\text{C}]$ methylmethionine-labeled sperm whale aquoferrimyoglobin microcrystals. The crystals were ordered in a field of 3.5 T, and the information is equivalent to single-crystal NMR, permitting direct determination of the spatial orientation of the labeled residues. From reference 475.

B. Haemoglobins

A series of cross-linked, mixed-valency hybrid haemoglobins has been prepared from derivatives of Hb C and human normal adult Hb. The spectral changes of these are not concerted on ligation, implying that a simple two-state model is inadequate and that intermediate structures may exist during the cooperative oxygenation of Hb.⁴⁸⁷ In another study of highly deshielded signals from valency hybrids, resonances at 58.5 and 71.0 ppm to high frequency of the water signal are assigned to proximal histidine exchangeable NH resonances from α - and β -chains, respectively.^{488,489} The surface histidines of Hb have been titrated,⁴⁸⁹ with a number of assignments being made using modified Hb molecules, and their relaxation behaviour followed.⁴⁹⁰ A number of the corresponding surface histidines in haemoglobin S (sickle haemoglobin) have pK values that differ from those in the normal molecule, in particular indicating that the N- and C-terminal regions of the sickle molecule are altered.⁴⁹¹ Methods for identifying Hb S have been described.⁴⁹²

Interest continues in the mechanism of aggregation of haemoglobin S. Evidence⁴⁹³ from relaxation measurements points to the formation of small molecular aggregates as precursors to the fully gelled form, thus providing the possibility of investigating the intermolecular contacts responsible for the aggregation. An NMR method for measuring the amount of Hb S polymer within sickle erythrocytes as a function of oxygen saturation has been presented.^{494,495} The proximal histidines of haemoglobin form an effective probe of the haem pocket, and have been used in a comparison between variant Hb molecules.⁴⁹⁶ The influence of quaternary structure on

iron–histidine binding is reflected in the hyperfine-shifted resonances of exchangeable imidazole NH protons, though a detailed analysis of the contributing factors is not yet possible.^{497,498} Histidine- β 146 of human adult haemoglobin has been the subject of an investigation of the alkaline Bohr effect⁴⁹⁹ with the following conclusions: in 0.2 *M* phosphate, 0.2 *M* NaCl, a salt bridge between histidine- β 146 and aspartic acid- β 94 is broken during the quaternary structural transition, and the β 146 is partly responsible for the Bohr effect, while in 0.1 *M* Tris neither of these statements is true. Thus the alkaline Bohr effect varies in its detailed mechanism according to the experimental conditions. Complexes between imidazole derivatives and methaemoglobin and metmyoglobin have been reported⁵⁰⁰ as well as binding of inositol hexaphosphate (IHP) to human haemoglobin.^{501,502} Apparently human low-spin metHb can be switched from the R to T quaternary structure by the binding of IHP. A similar conclusion is drawn regarding a conformational change in carboxyhaemoglobin on binding of myoinositol hexakisphosphate.⁵⁰³ Comparison of IR and ¹³C-NMR measurements of ¹³CO bound to haemoglobin shows rapid interconversion between conformers, too rapid to be detected by NMR.⁵⁰⁴ The role of internal water as a spin carrier in spin relaxation in paramagnetic Hb molecules has been considered.⁵⁰⁵

Small chemical shift differences are found between haem resonances from different components of soybean leghaemoglobin, possibly indicating substitutions among the haem contact residues.⁵⁰⁶ Solvent-exchange dynamics in soybean ferric leghaemoglobin show the haem to be more accessible in this molecule than in vertebrate ferric myoglobin or haemoglobins.⁵⁰⁷ This result may be borne out by others⁵⁰⁸ in which the absence of a hyperfine-shifted exchangeable NH peak for the distal histidine suggests either a very different orientation for this ligand or a faster exchange rate with bulk solvent than is found in metmyoglobin. Further studies of the monomeric insect haemoglobin from *Chironomus thummi thummi* confirm earlier reports that there are two haem orientations possible in the molecule; ligation on-rates may depend on both pH and haem orientation.⁵⁰⁹

Other recent studies involving haemoglobin include methylmercury binding,⁵¹⁰ diffusion coefficients measured by pulsed-field gradient NMR,^{511,512} and the interactions between haemoglobin and 2,3-diphosphoglycerate,⁵¹³ inositol hexaphosphate,⁵¹⁴ and model membranes.⁵¹⁵ The first report of subunit specificity in monooxygenase-like activity in tetrameric haemoglobin has appeared.⁵¹⁶

C. Cytochromes

A review of NMR studies on low-spin cytochromes has been published.⁵¹⁷ In the cytochromes *b*, unlike the *c* group, the haem is not bound covalently to

the protein. A major discrepancy between the results of an NMR study⁵¹⁸ of the haem crevice in cytochrome *b*₅, a cytochrome present mainly in animal microsomes, and previous X-ray studies has now been resolved. The NMR results reveal that the orientation of the haem group previously reported is 180° in error. Subsequent X-ray reanalysis at 2 Å resolution has confirmed this.⁵¹⁹ There is no evidence of any difference in peptide conformation near the haem between crystal and solution structures. Reconstitution of cytochrome *b*₅ apoprotein with specifically deuterated haemin⁵²⁰ shows the two haem orientations, related by a 180° rotation about the α - γ -meso axis (Fig. 8). The tendency for a haem to exhibit multiple orientations appears to be attributable to the 4-vinyl group: pemptohaemin yields two components, isopemptohaemin only one. Models of the cytochromes *b* have been proposed following unsymmetrical phenyl substitution⁵²¹ and temperature dependence of ¹H isotopic shifts.⁵²² Cytochrome P-450 is technically a cytochrome *b*, although relaxation studies⁵²³ indicate that acetanilide binds to it in a specific complex not found with cytochrome *b*₅. Proton NMR studies of high-spin ferrous P-450 models have been reported.⁵²⁴ Water relaxation time measurements are used to compare the solvation spheres of cytochromes P-450 and *b*₅ in the presence of acetanilide and imidazole.⁵²⁵ Water ¹H relaxation enhancement, found in the presence of P-450 but not of *b*₅, is removed by imidazole. While acetanilide has no effect on water *T*₁, its own phenyl or

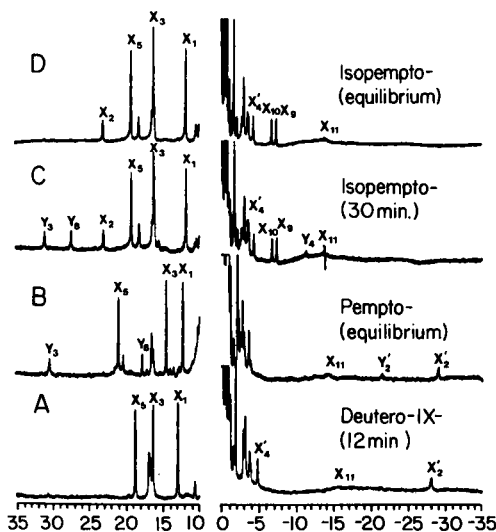


FIG. 8. The hyperfine shifted portions of the 360-MHz ¹H-NMR spectrum of cytochrome *b*₅''' reconstituted with (A) deuterohaemin, (B) pemptohaemin, (C, D) isopemptohaemin. The small peaks labeled Y characterise a component of the reconstituted protein in which the haem group is rotated through 180°. From reference 520.

methyl protons experience a selective relaxation enhancement in the presence of various cytochrome P-450's, indicating at least a close approach of these groups to the metal centre.⁵²⁶ A close approach to the metal of P-450 has been observed by ³H NMR of the labeled region of 6-³H-benzo[a]pyrene.⁵²⁷ Model compounds for cytochrome P-450 are also discussed.^{528,529}

The dihaem cytochrome *cd*₂ from *P. aeruginosa*, which acts as a nitrite reductase, appears from ¹⁵N-NMR data to have a weak interaction with NO₂⁻.⁵³⁰ Its ¹H spectrum indicates a structural transition with a p*K* value of 5.8, although not many resonances are resolvable since the molecular weight is 120,000.⁵³¹

Cytochromes of the *c* class, in which haem side chains are covalently linked to the protein, are reported to induce nonbilayer structures in cardiolipin-containing model membranes.⁵³² Substitution of various diamagnetic and paramagnetic metal ions for the Fe atom in horse cytochrome *c* reveals a small conformational change on oxidation.⁵³³ Other papers on the NMR of cytochrome *c* include the assignment of aromatic⁵³⁴ and aliphatic⁵³⁵ residues, the pH and temperature dependence of ferro-⁵³⁶ and ferri-⁵³⁷ cytochrome *c*, and comparison between horse, tuna, and various eukaryotic cytochromes.^{538,539} Given suitable X-ray data, it will be interesting to compare these spectra with those predicted, using various ring-current models for the haem ring.⁵⁴⁰ The chirality of the axial methionine coordinated to the iron atom has been shown to differ⁵⁴¹ between cytochrome *c* and cytochrome *c*-551, apparently explaining previous reports of different electronic haem structures between the two proteins. Anion binding to cytochrome *c* has been discussed^{542,543} as well as electron spin relaxation.⁵⁴⁴ The low-potential, low-spin cytochrome *c* from *Desulfovibrio gigas* has been studied through reoxidation⁵⁴⁵ and in its interaction with rubredoxin and flavodoxin.⁵⁴⁶ Some doubt has been cast, however, on the state of the NMR studies of this protein, since an earlier outline structure based on sequence and NMR data of cytochrome *c* from *Desulfovibrio desulfuricans* has been shown not to fit the recently acquired X-ray data.⁵⁴⁷

Electron-transfer mechanisms in the cytochrome *c* from *Desulfovibrio vulgaris* have been analysed by a series of saturation transfer experiments taking into account all 16 redox states of the protein.⁵⁴⁸ The binding of iron hexacyanide^{549,550} and platinum complexes⁵⁵¹ to cytochrome *c* assists in X-ray structure determination and ¹H-NMR assignments. Comparison of the structures of several variant cytochromes *c* in which tyrosine residues are substituted variously by leucine or phenylalanine indicates⁵⁵² that the effects on the structure are minimal. Acetylation experiments^{553,554} show widely differing reactivities of the tyrosines, with acetylation at tyrosine-74 leading to conformational change in the molecule. Comparative studies of the haem environment in a number of cytochromes *c*-553 have been reported,⁵⁵⁵ as has

the electron-transfer reactivity, monitored by NMR and photochemical methods, of cytochrome *c*⁵⁵⁶ and the magnetic susceptibility of ferri-cytochrome *c*.⁵⁵⁷ The resonances of phenylalanine-82 and -10 of horse cytochrome *c* have been reassigned⁵⁵⁸ and modification of methionine-65 is shown to produce an extremely small structural perturbation in one part of the molecule.⁵⁵⁹ The source of the asymmetric electron spin density distribution in cytochrome *c* has been investigated using the active site haem octapeptide as a model system showing that the orientation of the axial methionine is an important determinant of the electronic structure of the haem.⁵⁶⁰ The octapeptide has also been used in experiments leading to a model for anion binding to the active site,⁵⁶¹ and an outline structure is presented for the haem undecapeptide.⁵⁶² Comparison of a number of cytochrome *c* samples from different sources reveals that those which have a phenylalanine at position 46 exhibit temperature-dependent line widths of a hyperfine shifted haem methyl resonance, while those with tyrosine in this position do not.⁵⁶³ Ligation states in cytochrome *c'* from *Rhodospirillum rubrum* have been reported.⁵⁶⁴ The pH and temperature dependence of chemical shifts in the 270-MHz ¹H-NMR spectrum of the same protein show haem methyl resonances with p*K* values of 5.8 and 8.7 and NMR spectral changes which correlate with changes in the visible spectrum.^{565,566} Labeling of the methionyl groups of cytochrome *c* with either ¹³C or ²H(567) have enabled the acid and alkaline unfoldings of cytochrome *c* to be followed in some detail. Labeling by conversion of lysine residues to ¹³C-labeled homoarginine in cytochromes from a number of sources, with full retention of electron-transport reactivity with cytochrome oxidases, may also provide a useful structural probe in the future.⁵⁶⁸ Another lysine modification experiment, in which lysine-13 or lysine-72 is altered to 4-carboxy-2,6-dinitrophenyllysine, reveals two rapidly exchanging conformers in which the conformation of methionine-80 (ligand 6) and phenylalanine-82 depends on the "on" or "off" position of lysine-13 in its salt bridge with glutamic acid-90.⁵⁶⁹ Other studies of cytochrome *c* include a partial delineation of homologies of polypeptide conformation near the haem group between horse ferrocytochrome *c* and cytochrome *c*-552 from *Euglena gracilis*,⁵⁷⁰ kinetic studies of the oxidation of horse heart ferrocytochrome *c* by (pentaammine) pyridine Ru³⁺,⁵⁷¹ and the binding of copper, probably at histidine-33, to cytochrome *c*.⁵⁷²

D. Other haem proteins

Another haem protein susceptible to NMR study is horseradish peroxidase. Water ¹H relaxation studies of the haem environment of this protein have been reported.⁵⁷³ Deuteration⁵⁷⁴ of selected positions of haemin and deuterohaemin yield hyperfine shift patterns consistent with an Fe³⁺ porphy-

rin exhibiting appreciable $S = \frac{3}{2}$ character. Horseradish peroxidase reconstituted with deuterohaemin reveals a 180° rotation of the porphyrin relative to the native protein similar to that discussed above for cytochromes *b*.⁵⁷⁵

The haem-containing enzymes cytochrome peroxidase and horseradish peroxidase have been compared.⁵⁷⁶ Formation of the initial oxidised intermediate, compound I, with H_2O_2 causes drastic changes in the hyperfine shifted ^1H -NMR spectrum of the former, but not the latter. More detailed studies of the electronic structure of horseradish peroxidase compound I are presented⁵⁷⁷, as well as of compound II of horseradish peroxidase and catalase.⁵⁷⁸ The geometry of the complexes between horseradish peroxidase and aromatic substrates has been elucidated with a modified NMR spectrometer,⁵⁷⁹ and the axial imidazole in the reduced enzyme shown, in contrast to the interpretation of other spectroscopic data, not to be deprotonated.⁵⁸⁰

Cytochrome *c* oxidase is difficult to place in this review, being classified as both an enzyme and a cytochrome, and also containing copper. Specific trifluoroacetylation at single lysine side chains of cytochrome *c* shows that only those lysines near the haem crevice affect reaction rates on modification. Their ^{19}F relaxation is unaffected on binding of the oxidase, indicating that no detectable conformational changes occur.⁵⁸¹ ^1H -NMR studies of cytochrome *c* oxidase at 360 MHz reveal signals spread over a range of 96 ppm, with dramatically pH-dependent behaviour.⁵⁸²⁻⁵⁸⁹ A number of features of solvent relaxation found in cytochrome oxidase are reported⁵⁹⁰ to be similar to those found for both microbial and microsomal cytochrome P-450.

Another case of haem asymmetry in a reconstituted haem protein, this time cytochrome peroxidase, has been discovered.⁵⁹¹ Twice the expected number of ^1H signals is seen in the spectrum.

Some sophisticated new double resonance and spin-echo techniques have been applied to ferredoxin from *Anabaena variabilis*, resulting in the assignment of a number of ^1H and ^{13}C resonances.^{592,593} Ferredoxins are also the subjects of electronic structure calculations,⁵⁹⁴ pH dependence studies,⁵⁹⁵ and electronic spin-lattice relaxation measurements.⁵⁹⁶ A $g' = 1.74$ ESR signal, severely reduced by phosphate binding, in the iron-containing bovine spleen purple acid phosphatase, has been reported.⁵⁹⁷

VII. PROTEINS ASSOCIATED WITH NUCLEIC ACIDS

A. Histones

Studies of chromosomal proteins have been extended to H1 from the sperm of *Sphaerechinus granularis*⁵⁹⁸ in which a lack of conservation of secondary and tertiary structures in the evolution of H1 histones is demonstrated. The

recently discovered H1° histone associated with the absence of mitotic activity in mammalian cells appears to share a number of structural features with the H5 of avian erythrocytes, and possibly to bind at the point of exit of DNA from the nucleosome in a more stable way than does H1.⁵⁹⁹ NMR data, showing the single tyrosine in histone H1 to be buried, have been challenged following the attachment of a spin label to it for ESR studies.⁶⁰⁰ However, even small substituents at this residue disrupt the folded structure, so this conclusion is unlikely to be correct. Earlier NMR reports on the existence of unique globular domains in histones H1 and H5 have been supported by experiments on the related ϕ 1 from the sperm of the sea urchin *Arbacia lixula*⁶⁰¹ and by recent microcalorimetric data⁶⁰² and (for H1) by ¹³C-NMR in both aqueous and 2-chloroethanol solution.⁶⁰³ A method for the precise elimination of the N-terminal domain of H1 prior to NMR experiments has been reported,⁶⁰⁴ as have methods for deuteration of histones of *Physarum polycephalum*, monitored by ²H NMR.⁶⁰⁵ N-Trimethylalanine has been identified as the blocked N-terminal residue of histone H2B from *Tetrahymena pyriformis*.⁶⁰⁶ A study⁶⁰⁷ of the binding of acetylated peptides of histone H4 to DNA supports the view that acetylation *in vivo* lifts the N-terminal region of this histone off the DNA and thereby permits, or initiates, structural changes in chromatin. Progress toward characterisation of the phosphorylation of histone H4 *in vivo* is presented⁶⁰⁸ following ³¹P-NMR studies of enzymatically and chemically phosphorylated H4, with the phosphorylated residues appearing to be histidines-18 and -75. Trout testes contain two nonhistone chromosomal proteins of the high-mobility group. One of these, termed H6, has been shown⁶⁰⁹ to behave structurally like the homologous calf high-mobility group (HMG) proteins 14 and 17, but another, HMG-T, shows major structural differences from homologous proteins from calf. Proton NMR studies of an active pentapeptide fragment of ubiquitin, which is found in the unusual covalently branched A24 complex with histone H2A, have been reported.⁶¹⁰ Unlike histones, the basic clupeine proteins of salmon sperm do not appear to fold in solution.⁶¹¹ Relaxation studies of clupeine extracted from herring sperm reveal the molecules as being essentially extended in aqueous solution, with side-chain flexibility whose phosphate dependence differs from fraction to fraction.⁶¹²

A comparison, using ³¹P NMR, of protein-RNA interactions in a variety of systems, including ribosomes, polysomal mRNA, and RNA viruses, reveals⁶¹³ a wide range of relaxation and NOE effects. Clearly the protein-RNA complexation differs widely between the complexes. A series of studies of ribosomal proteins indicates⁶¹⁴ considerable independent mobility of protein in L7/L12 *in situ* on the ribosome, and compact globular structures for proteins L11,⁶¹⁵ L29, and L30^{616,617} and S4, S7, S8, S15, and S16.⁶¹⁸ Spectra of whole ribosomes have been presented.⁶¹⁹ The L11 study confirms

earlier reports that the conformation of isolated ribosomal proteins depends critically on their previous treatment.

A detailed analysis of the 500-MHz ^1H -NMR spectrum of the helix-destabilising gene-V protein encoded by coliphage M13 indicates that the phenylalanyl and two tyrosyl residues are involved in its interaction with DNA. This is a conclusion which is reinforced by NOE evidence for the proximity of these aromatic rings to DNA bases⁶²⁰ and by deuteration work on gene-V protein, which shows it⁶²¹ to interact with oligo[d(CG)] by a mechanism involving a tyrosine and more than one phenylalanine residues via stacking with base pairs. ^{31}P -NMR measurements on the binding of oligonucleotides to the gene-V protein of phage fd reflect a specific binding site for the 5-phosphate dianions.⁶²² Binding of oligonucleotides is found⁶²³ to affect two tyrosine and one phenylalanine residue in the protein. For the coat protein of fd phage, solid-state NMR reveals a rigid backbone⁶²⁴ with some flipping of aromatic side-chain rings.⁶²⁵ The main part of the isolated coat protein of alfalfa mosaic virus⁶²⁶ is also rather rigid, but with a flexible N terminus of about 36 residues. No such flexible region has been detected in ^{13}C resonances of southern bean mosaic virus, whose only sharp peaks seem to come from the side chains of surface residues on the coat protein.⁶²⁷

NMR and model-building experiments⁶²⁸ indicate that direct interactions between the backbone atoms of peptide molecules and the base pairs in single- and double-stranded polynucleotides may play a role in protein-nucleic acid recognition. Addition of kirromycin, an inhibitor of protein synthesis, to the complex between elongation factor Tu and GDP alters its conformation, as monitored by ^1H NMR, to one similar to the elongation factor-GTP complex,⁶²⁹ which probably explains the inhibitory effect. Preliminary NMR results on the *E. coli* translational initiation factors IF1, IF2, and IF3 have been presented.⁶³⁰ Photooxidation of *E. coli* initiation factor 3 inactivates the protein, and is shown by a number of methods including NMR to be due to the selective loss of histidine-139,⁶³¹ which participates in the binding of the initiation factor to the 30 S ribosomal subunit. The stereochemical course of GTPase activity⁶³² and the structure of the GDP-Me²⁺ complex⁶³³ of the elongation factor of *E. coli* have also been investigated by NMR methods; both studies use oxygen isotopic substitution.

A considerable number of papers are now appearing on studies of lac repressor protein. The DNA-binding site of the protein appears to lie in the first 51 residues, termed the headpiece, which can be removed from the rest of the protein with little apparent alteration in its secondary and tertiary structure. Assignments have been made of the four tyrosine residues⁶³⁴ and of several methyl resonances⁶³⁵ in the headpiece, permitting the following of its thermal unfolding by NMR⁶³⁶ and comparison with calorimetric results.⁶³⁷ A general unfolding of the headpiece appears to occur above pH

10,⁶³⁸ and selective NOE and other effects indicate that the molecule has a structure which folds back on itself, with residues in the N- and C-terminal portions near to each other.⁶³⁹ Exchange studies are reported,⁶⁴⁰ and the interaction of headpiece with synthetic poly[d(AT)], leading to a significant shift of many resonances in the headpiece spectrum, has also been considered.⁶⁴¹ Another group working on lac repressor reports on a method of genetically introducing specific modifications and labels into the molecule⁶⁴²: ¹⁹F-NMR signals are introduced at position 44 by substituting 3-fluoro tyrosine for the normal glutamic acid (Fig. 9). The two sections of the molecule (N-terminal headpiece, which is flexible, and the more rigid C-terminal region, which is $\frac{5}{6}$ of the molecule) are discussed,⁶⁴³ as are a set of headpieces, in each of which one of the four tyrosines is missing, thus permitting accurate assignment of the aromatic resonances of the molecule.⁶⁴⁴ The specific assignments resulting from the application of this method to lac repressor⁶⁴⁵ permit comparison between the interaction of the repressor with lac operon and other DNA, showing that the N-terminal region is capable of recognising the operon sequence.⁶⁴⁶ The interaction of the N-terminal DNA-binding domain of the lac repressor with oligo[d(AT)], investigated by photo-CIDNP, shows that two of four tyrosines, and the only histidine residue in the region, are involved in the binding.⁶⁴⁷ The relation between conformational changes and DNA binding activity of λ tof repressor protein has also been investigated.⁶⁴⁸

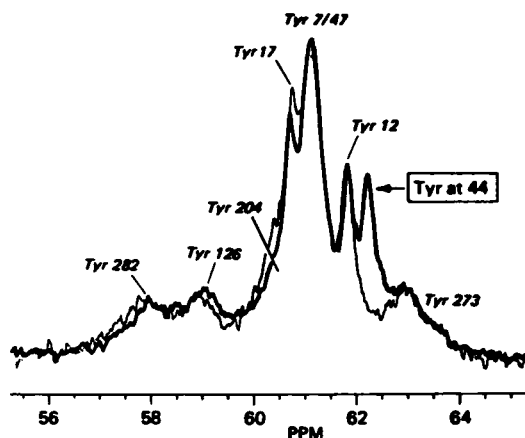


FIG. 9. ¹⁹F-NMR spectrum of lac repressor from *E. coli* containing biosynthetically introduced 3-fluorotyrosine. The thin line represents the spectrum of the wild-type repressor, and the heavy line that of a repressor in which 3-fluorotyrosine has been introduced at residue 44 (normally a glutamic acid) by suppression of the *amber* nonsense codon UAG. From reference 642.

B. Muscle proteins

Comparison of the 400-MHz ^1H -NMR spectra of native and denatured rabbit skeletal muscle G-actin shows that a large proportion of the aromatic residues are motionally constrained. This is consistent with the known existence of a compact, globular proteinase-resistant core in the protein containing some 80% of the residues.⁶⁴⁹ The high-affinity metal-binding site on G-actin appears to be less than 1 nm from the ATP-binding site.⁶⁵⁰ A ^{31}P -NMR study of rabbit skeletal muscle myosin shows that phosphoserine-14 or -15 probably acts, analogously to the phosphoserine in troponin-T, to prevent interactions with other parts of the molecule.⁶⁵¹ NMR evidence for a short hinge region in the myosin rod takes the form of the observation that less than 4% of the fragment gives resonances consonant with random-coil structures.⁶⁵² Similar conclusions are drawn by other workers⁶⁵³ who find sharp resonances corresponding to <25 residues per chain in rabbit long S2 myosin fragments (Fig. 10). The S2 “head” subfragment appears to exist in

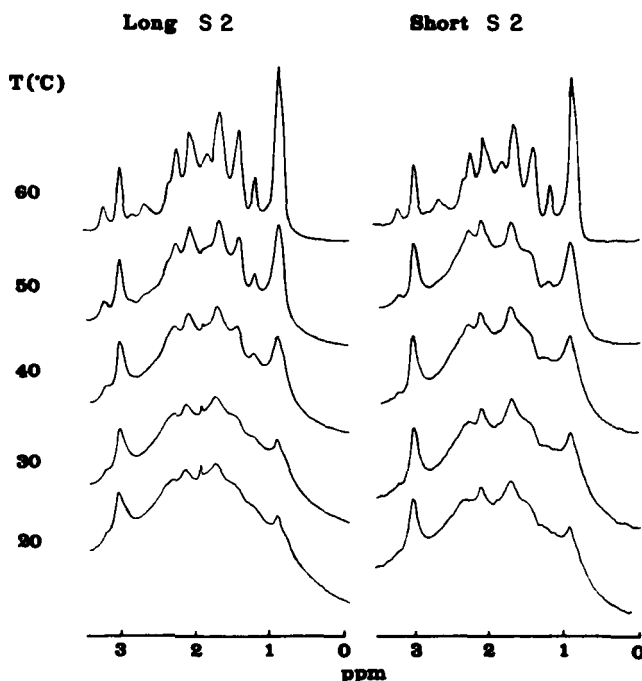


FIG. 10. ^1H -NMR spectra taken at 270 MHz of long and short myosin S2 fragments at temperatures from 20 to 60°C. The small excess of sharp peaks visible for long S2 at 40–50°C indicates the presence of a small flexible “hinge” region in long S2, rather than an extensive flexible region able to provide contractile forces. From reference 653.

equilibrium between two conformational states, with the one which predominates at low temperatures being identified with the state obtained by binding MgADP.^{654,655} A sharp resonance in the spectrum of fast twitch muscle S1 has been assigned to α -N-trimethylalanine at the N-terminal blocking group of the myosin light chain A1. The signal broadens on binding actin, indicating immobilisation.⁶⁵⁶ Further studies⁶⁵⁷ using shift and broadening probes help to identify labile regions in different parts of the head group which are differentially constrained on actin binding, and an ¹H-NMR study⁶⁵⁸ establishes that the mobile regions are internal to myosin and reside mainly inside the subfragment 1 moiety. Presumably the quenching of the motion by actin results from a structural change in the myosin. A theory for the evaluation of rate constants for ATP-hydrolysing enzymes, using ¹⁵O labeling of ³¹P resonances, is presented⁶⁵⁹ and agrees very well with previous measurements of ¹⁵O exchange catalysed by myosin S1. Further experimental measurements of S1 kinetics may be found elsewhere.⁶⁶⁰ *In vivo*, the interaction between actin and myosin is modulated by tropomyosin; the cooperativity visible in the titration of histidine-153 and -276 of this protein in its polymerised form disappears when monomeric tropomyosin is prepared, arguing for some allosteric mechanism between tropomyosin monomers.⁶⁶¹

C. Calcium-binding proteins

The trimeric protein troponin is essential to the action of tropomyosin; the tyrosine assignments and calcium-induced structural changes of the calcium-binding troponin-C component of bovine cardiac troponin have been compared⁶⁶² to those of two homologous proteins, rabbit skeletal troponin C and bovine brain calmodulin. There are many structural similarities, as might be expected from the high degree of primary sequence homology. Laser CIDNP comparisons of these three proteins⁶⁶³ reveal which tyrosine residues are exposed in solution. Tyrosine-5, -11, and -150 are exposed in cardiac troponin apoprotein, becoming buried as Ca²⁺ is bound; a similar behaviour is seen for tyrosine-10 and -109 of skeletal troponin and tyrosine-99 of calmodulin. Binding constants for Ca²⁺ and Mg²⁺ on skeletal troponin C have been determined by ⁴³Ca- and ²⁵Mg-NMR measurements⁶⁶⁴ and the binding of the drug trifluoroperazine to calmodulin has been reported.⁶⁶⁵ The binding site appears to be close to a methionine-rich region of the protein. Also published recently are reports of interactions between troponin C and CnBr-cleaved fragments of troponin I.⁶⁶⁶

⁴³Ca-NMR has been used to delineate the calcium-binding sites of calmodulin^{667,668} and of calmodulin, parvalbumin, and troponin C.⁶⁶⁹ Proton-NMR data show a number of conformational changes induced in calmodulin by Ca²⁺ binding.⁶⁷⁰ Detailed studies on synthetic analogues of

the high-affinity site III of rabbit skeletal troponin C⁶⁷¹ and on cleavage fragments of troponin C containing single Ca²⁺-binding sites⁶⁷² have been performed and comparisons between rabbit and pike troponin C published.⁶⁷³ The phylogenetic division of parvalbumins into two classes, α and β , is supported by comparative ¹¹³Cd and ¹H measurements.⁶⁷⁴ In other studies of parvalbumin, the principal axis of the magnetic susceptibility tensor of bound ytterbium is determined as a necessary precursor to detailed lanthanide-shift measurements.⁶⁷⁵ Yb³⁺ sequentially replaces the two bound calcium ions of the molecule, and causes very large shielding changes, with ¹H signals appearing between -32 and +19 ppm.⁶⁷⁶⁻⁶⁷⁸ The binding of calcium in the human salivary acid proline-rich phosphoproteins A and C appears to be in the N-terminal tryptic peptide, and to involve an aspartic acid and a phosphoserine residue, as shown by ⁴³Ca, ³¹P, and ¹H NMR.⁶⁷⁹

D. Copper proteins

The molecular motion of methionine-121, one of the copper ligands of azurin, increases with pH and temperature, indicating a lengthening and perhaps breaking of the Cu-S bond. This correlates with redox inactivation of the molecule and with deprotonation of the histidine-35 copper ligand. The coupling between methionine motion and histidine deprotonation has also been discussed.⁶⁸⁰ No major structural changes are observed when the Cu of azurin is replaced by nickel⁶⁸¹; these studies are said to strengthen the case for the central role of histidine-35. ²³Na- and ⁴³Ca-NMR data have been used to investigate sodium- and calcium-binding sites on haemocyanin.⁶⁸² The electron-transfer reaction between ferrocyanide ion and the blue copper protein stellacyanin has an activation energy of 17 kJ mol⁻¹ as indicated by ¹³C line broadening of the oxidant.⁶⁸³

E. Metallothioneins

A metallothionein, which binds up to six Zn ions per molecule, has been shown by ¹H NMR to exist in a well-defined folded form with metal ions bound, but as a random-coil structure in its apoprotein form.⁶⁸⁴ A series of cadmium-NMR studies on the structure of these sulphur-rich proteins has been reviewed.⁶⁸⁵ Recent additions to the series provide unambiguous evidence⁶⁸⁶ for a two-domain structure in rat liver metallothionein containing separate three-metal and four-metal clusters. In the mud crab *S. serrata* the two clusters are each identical to the mammalian three-metal site.⁶⁸⁷ Four- and three-metal sites are also found for human metallothionein,⁶⁸⁸ and selectivity for copper⁶⁸⁹ at the three-metal "B" site in the calf protein (see also reference 690). ESR and NMR studies⁶⁹¹ indicate that rat-liver Cu-metallothionein is very susceptible to oxidation, with 18 titratable

cysteines in anaerobically prepared protein decreasing to 1–12 in metallothionein prepared in the presence of air.

F. Glycoproteins

Space precludes discussion of a number of studies concerned with the structure and conformation of the polysaccharide components of glycoproteins. However, it has been shown by energy calculations⁶⁹² that the conformation of glycosylated β -turns consistently found by NMR, with the amide proton of the glycoside amide bond nearly trans to the anomeric proton of the sugar, in fact lies very close in energy to the cis form. The carbohydrate–protein linkage has been studied for glycoserines,⁶⁹³ for *N*-acetylmuramyl-L-alanyl-D-isoglutamine,⁶⁹⁴ and for phenylalanylglycopyranoside enantiomers.⁶⁹⁵

Proton-NMR data (360 MHz) indicate that the heterogeneity of chick ovalbumin glycopeptides AC-C and AC-D is greater than has previously been reported⁶⁹⁶; the structures of four glycopeptides have been confirmed.⁶⁹⁷ Labeling with ¹³C in a chondrocyte culture system for chick limb bud cells produced a proteoglycan core protein whose ¹³C relaxation behaviour suggests considerable flexibility.⁶⁹⁸ Cation binding to multichain and single-chain glycosaminoglycan peptides has also been investigated,⁶⁹⁹ as has the microheterogeneity in a glycopeptide fraction derived from human plasma α_1 acid glycoprotein; previously unreported variation in the position of attachment of fucose is found.⁷⁰⁰ Glycophorin is one of the intrinsic proteins of erythrocyte membranes, a glycoprotein whose structure falls into three domains. Proton-NMR studies reveal very different mobilities in the three regions, particularly in the central intramembranous hydrophobic region, which is extremely resistant to normal denaturing conditions, eventually submitting to the gentle ministrations of trifluoroacetic acid.⁷⁰¹ Methionine-8 and -81 of glycophorin have been used as probes into the structure of the protein, revealing possible metastable states.^{702–704} Lateral diffusion of glycophorin and other proteins in bilayers has been discussed,⁷⁰⁵ as has the effect of glycophorin on lipid order.^{706–708} Other glycoproteins studied by NMR include fibrinogen,⁷⁰⁹ human plasma α_1 acid glycoprotein,⁷¹⁰ and antifreeze glycoproteins from the Antarctic cod.⁷¹¹

VIII. PROTEINS ASSOCIATED WITH MEMBRANES

In the field of protein–lipid interactions, a combined NMR and ESR spin-label experiment on the orientation of glucagon in mixed micelles with dodecylphosphocholine shows the glucagon backbone to lie parallel with the

micelle surface, with apolar and polar side chains pointing, respectively, into and out of the lipid.⁷¹² Melittin appears to assume the same conformation in a self-aggregated tetramer as in its monomeric form bound to micelles.⁷¹³ It has been shown⁷¹⁴ that monomeric melittin is predominantly in an extended flexible form, with fragments 5–9 and 14–20 more highly structured. The structure of melittin has been determined by X-ray diffraction and related to the NMR studies, particularly with regard to folding of the monomer into the tetrameric form⁷¹⁵; two-dimensional NMR has been used to determine the conformation and orientation of melittin at the lipid–water interface,⁷¹⁶ and the interaction between melittin and lipids has also been discussed.^{717–719} ¹H-NMR studies at 400 MHz of peptidolipin⁷²⁰ indicate the heptameric peptide moiety to form a β -turn around the central proline residue. The conformations of a number of hydrophobic peptides have been investigated in membrane-mimetic environments,⁷²¹ as have a series of synthetic fragments of bacteriorhodopsin.⁷²² The lipid-binding site on porcine colipase is proposed⁷²³ to be a surface domain formed from regions 49–57 and 77–86, with β -sheet fragments brought into proximity by the protein folding. Specific deuteration of lipids has been used⁷²⁴ to show that protein has little effect on order in an *Acholeplasma laidlawii* B membrane system, but large effects in *E. coli* membranes; above the gel–liquid crystal transition temperature in model membrane systems, protein has far greater effect on lipid mobility than does cholesterol, although the situation reverses below the transition, probably due to a phase separation.⁷²⁵ Results of a study of the interaction between deuterated model membrane and cytochrome oxidase⁷²⁶ are consistent with weak, short-lived protein–lipid interactions, with 0.18 mg phospholipid/mg protein being necessary to cover the surface of the enzyme.

Specific labeling with deuterium of the protein bacteriorhodopsin, which is active in the photosynthetic purple membrane of *Halobacterium halobium*, permits observation of individual amino acid side chains of the proteins in the intact membranes.^{727,728} The side chains are rather rigid, with the principal motions being methyl group rotation and discontinuous benzene ring flipping. Refolding of denatured bacteriorhodopsin is possible if phospholipids, cholate, and retinal are added to the protein in the presence of SDS, which is subsequently dialysed out, leaving vesicles fully active in light-driven proton translocation.⁷²⁹

Lipids are transported in blood by lipoproteins. Comparative studies of human high-density lipoprotein (HDL) fractions HDL₂ and HDL₃ suggest that the motions of phospholipids with correlation times in excess of 10^{-6} sec are more restricted in the latter.⁷³⁰ Lipoprotein-X, one of the low-density lipoproteins (LDL), yields ¹H-, ³¹P-,⁷³¹ and ¹³C-⁷³² NMR spectra which are quite different from spectra of other low-density lipoproteins. Relaxation measurements suggest that the motions of cholesterol rings and fatty acid side

chains are more restricted in LP-X than in either HDL₃ or LDL. The involvement of the sequence around methionine-38 in phospholipid binding by apolipoprotein C-1 has been probed by both nitroxide labeling for ESR and ¹³C labeling for NMR. Significant structural change in the region of this residue is observed both on the binding of phospholipid and on denaturing the protein.⁷³³ Two different types of complex are found in the binding of apolipoprotein A-1 with sonicated vesicles of dimyristoylphosphatidylcholine.⁷³⁴ Application of NMR to the study of high-density lipoproteins has been reviewed.⁷³⁵ Truncated-driven NOE difference spectroscopy is suggested as a powerful method of investigating lipid-bound proteins.⁷³⁶ The ¹³C relaxation times of phosphatidylcholine vesicles are unaffected by cytochrome *c* but are reduced, for ¹³C nuclei near the bilayer centre, by myelin basic protein, indicating a penetration of the bilayer by this protein.⁷³⁷ Membrane-bound ATPase has been investigated by ²H NMR⁷³⁸ and also by ESR and NMR using paramagnetic probes.⁷³⁹ In the latter case the Mn²⁺/Cr²⁺ distance in the ATPase-Mn-Cr-ATP complex is 8.1 Å. Evidence for multiple-ion occupancy in malonylgramicidin trans-membrane channels has been presented.⁷⁴⁰ Another channel-forming peptide, suzukacilin, appears to contain a large amount of ₃₁₀ helix, at least if the whole protein behaves like its peptide fragments.⁷⁴¹⁻⁷⁴³ Proton-NMR evidence for secondary and tertiary structure in myelin basic protein has been reported,⁷⁴⁴ as have the effects of lipid interactions on the spectrum of the protein.⁷⁴⁵ Differential broadening of the resonance from methionine-20, relative to lines from near the protein termini, is attributed to motional restriction on binding to the micelle. Also discussed are the crystalline lipovitellin/phosvitin complex,⁷⁴⁶ phospholipid binding to cytochrome oxidase,⁷⁴⁷ and the environment and mobility of hydrophobic and hydrophilic regions in ¹⁹F-labeled coat protein from phage M13 in micelles and vesicles.⁷⁴⁸

IX. STRUCTURAL PROTEINS

Under the broad heading of structural proteins we may include viral coat proteins. The aggregation of tobacco mosaic virus coat protein has been compared with that of mutant versions,⁷⁴⁹ and the major coat protein of the filamentous bacteriophage fd characterised by ¹H and ¹³C NMR.^{750,751} A method of improving the selection of nonprotonated ¹³C resonances in such spectra has been described.⁷⁵² The coat protein of virus fd shows evidence of folding, but with significant internal mobility for the two tyrosine rings and two of the three phenylalanines.⁷⁵³ Qualitative comparisons may be made with the intact virus, whose DNA is shown by solid-state ³¹P NMR to be immobilised by the coat protein.⁷⁵⁴ Evidence is presented⁷⁵⁵ for considerable internal mobility in the coat protein of intact alfalfa mosaic virus, the mobile

residues apparently being in the N-terminal region of the molecule. A series of studies of collagen fibrils which have been specifically biosynthetically labeled with deuterium and ^{13}C has been presented.^{756–758} Among the main conclusions is that the contact regions between the helices in collagen fibrils are fluid and that there is no fixed unique set of interactions between side chains. The temperature dependence of the ^1H spectrum of hydrated collagen is reported,⁷⁵⁹ as are molecular motion in collagen fibrils measured by solid-state NMR⁷⁶⁰ and the molecular mechanism of mineralisation of collagen monitored by ^{13}C NMR of the model polypeptide (Pro–Pro–Gly).⁷⁶¹ Earlier NMR studies, indicating a mobile contact region between collagen molecules, are also supported by measurements on collagen fibrils labeled with deuterated leucine.⁷⁶² Both conformations, determined by X-ray diffraction for the leucine side chain, are found. They appear to interconvert at rates which are proportional to temperature. Gelatin gel formation⁷⁶³ and the temperature dependence of molecular mobility in gelatin solutions⁷⁶⁴ have been investigated, as have molecular motions in cellulose, pectin, and bean cell walls.⁷⁶⁵ It has proved possible⁷⁶⁶ to monitor directly by ^{13}C NMR the synthesis of silk fibroin in the silk glands of the silkworm *Bombyx mori*. NMR data on elastin⁷⁶⁷ show that the protein is a network of mobile chains whose motions are strongly influenced by protein–solvent interactions.

X. IMMUNOGLOBULINS

A detailed study of the binding of tetra-L-alanine haptens, each enriched with ^{13}C in a single methyl group, to F(ab') fragments of purified sheep anti[poly(L-alanine)] has been reported. Deshielding by 2.8 ppm is observed on antibody–hapten binding, presumably due to van der Waals interactions. While the methyl groups are rotating freely, the backbone of the peptide appears to be firmly bound.⁷⁶⁸ Data from NMR work on a number of λ -type Bence–Jones proteins are compared with the X-ray structure of the Fab fragment of human immunoglobulin, and show the probability of close similarities between solution and crystal structures of the constant domain of the λ -chain.⁷⁶⁹ Strategies for spectral assignments in antibody fragment F_v of the murine antibody M31 have been described.⁷⁷⁰ These involve feeding mice on a diet which incorporates deuterated tryptophan. Binding of dinitrophenyl compounds to the V_L dimer of protein 315 causes spectral perturbations in about 10 resonances. Comparison of these with shifts caused by DNP binding to the F_v fragment is interpreted to mean that the binding is specific rather than fortuitous,⁷⁷¹ being determined by the size and shape of a largely nonpolar combining site. Conformation of the hinge region of the IgG1 immunoglobulin is discussed,⁷⁷² as is the correspondence between structure and function in the various IgG subclasses.⁷⁷³

XI. OTHER PROTEINS

Molecular motion in solid proteins has been measured for polycrystalline insulin,⁷⁷⁴ in which most of the relaxation is found to be attributable to methyl rotation, and for crystalline enkephalin, in which the tyrosyl ring is flipping at some $5 \times 10^4 \text{ sec}^{-1}$ at room temperature.⁷⁷⁵ Internal motions in seven different enzymes are shown to be more intense than in four nonenzymatic proteins studied at the same time.⁷⁷⁶ Water effects may produce fluctuations important in catalytic activity. Cross-relaxation effects between water and protein protons are considered.⁷⁷⁷ Proton-NMR studies of thionins of known sequence from barley and wheat⁷⁷⁸ have revealed features of their secondary and tertiary structures similar to those of crambin, a related hydrophobic protein from *Crambe abyssinica*; the methyl spectrum of crambin has been analysed.⁷⁷⁹ The highly thermostable crambin has been studied with variations in temperature and solvent composition⁷⁸⁰; it retains most of its structure at 105°C in dimethylformamide. The structure and mobilities of wheat gliadins, components of gluten, are also reported,^{781,782} the gliadins apparently being much more tightly folded than the glutenin components. Moving finally to proteins that specifically bind and/or transport other ions or molecules, an interesting stoichiometry of two molecules of uteroglobin, a progesterone-binding protein, to one molecule of progesterone has been confirmed by NMR.⁷⁸³ The mechanism of interaction critically involves histidine-8 of the protein, which is not at the active site but influences the protein conformation through the charge carried on its imidazole ring. The iron-transferring proteins ovotransferrin and serum transferrin lose their Fe-binding activity on periodate treatment, and NMR shows that oxidation of four tyrosine side chains is apparently responsible.⁷⁸⁴ It appears that histidyl residues are also involved in metal ion binding in ovotransferrin.⁷⁸⁵ Anion binding to transferrin has been studied with ¹³C NMR. Considerable details of the anion sites have been revealed, leading, in particular, to the conclusion that the anion-binding ligand at the B site is probably the guanidino group of arginine, whereas that at the A site may instead be the ε-amino group of lysine.⁷⁸⁶ In ovotransferrin, by contrast, three histidines are reported to be involved in each binding site, one being involved in binding to anions and two to metal ions.⁷⁸⁷

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^{119}Sn -NMR Parameters

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I. INTRODUCTION

In the past three decades the chemistry of tin compounds has gained considerable importance both in basic research and in industrial applications. There are so many interesting aspects of inorganic and organic tin chemistry that the need for a convenient analytical tool is clearly indicated. This can be filled by tin NMR spectroscopy since there are three magnetically active ($I = \frac{1}{2}$) tin isotopes (^{115}Sn , ^{117}Sn , ^{119}Sn) (Table 1). Most tin NMR parameters refer to the ^{119}Sn nucleus owing to its properties (Table 1) (although there is no problem in observing ^{117}Sn resonances); the low natural abundance makes the measurement of ^{115}Sn resonances unfavourable.

Multinuclear facilities, which became available with pulse Fourier transform (PFT) NMR spectrometers in the last 5–6 years, have stimulated much work in the area of ^{119}Sn NMR. Therefore, the present review is intended to

TABLE 1

NMR properties of tin isotopes

Isotope	Natural abundance (%)	Magnetic moment (μ/μ_N)	Magnetogyric ratio γ ($10^7 \text{ rad T}^{-1} \text{ sec}^{-1}$)	NMR frequency ^a (Ξ , Hz)	Relative receptivity ^b (D^p, D^c)
^{115}Sn	0.35	-1.582	-8.7475	—	1.22×10^{-4} , 0.7
^{117}Sn	7.61	-1.723	-9.530	35632295	3.44×10^{-3} , 19.5
^{119}Sn	8.58	-1.803	-9.971	37290665	4.44×10^{-3} , 25.2

^a Neat $(\text{CH}_3)_4\text{Sn}$, for various solvents.¹⁰^b Relative to $^1\text{H}(D^p)$, relative to $^{13}\text{C}(D^c)$. See R. K. Harris in *NMR and the Periodic Table* (R. K. Harris and B. E. Mann, eds), Academic Press, London, 1978, p. 4.

serve several purposes: (1) the compilation of ^{119}Sn chemical shifts ($\delta^{119}\text{Sn}$) from previous reviews on organotin compounds¹⁻⁴ and inorganic tin compounds^{2,4,5} is updated (literature covered up to the end of 1983); (2) indirect nuclear spin-spin couplings, $^nJ(^{119}\text{SnX})$ ($n \geq 1$), are reviewed although no complete survey can be given since there are too many data available [e.g., $J(^{119}\text{Sn}^1\text{H})$ or $J(^{119}\text{Sn}^{13}\text{C})$]; (3) relaxation mechanisms concerning the ^{119}Sn nucleus are discussed briefly; and (4) experimental details for ^{119}Sn -NMR measurements are given.

Most of the references can be found in the tables for ^{119}Sn chemical shifts. For organotin compounds many references that contain the $\delta^{119}\text{Sn}$ data very often list ^1H - and ^{13}C -NMR parameters too, including the couplings $^nJ(^{119}\text{Sn}^1\text{H})$ or $^nJ(^{119}\text{Sn}^{13}\text{C})$. The discussion in the text does not aim for completeness but is necessarily restricted to those aspects that the author believes to be of particular significance. There are, however, so many exciting developments in the field of tin chemistry that have been explored using ^{119}Sn -NMR parameters that an unbiased selection is difficult to achieve.

II. EXPERIMENTAL

The observation of ^{119}Sn resonances can be achieved either by heteronuclear double resonance, e.g., $^1\text{H}\{^{119}\text{Sn}\}$,^{6,7} or by direct observation. Although the latter approach, in principle, presents no difficulty with modern PFT NMR spectrometers there are still a number of useful applications for heteronuclear double resonance experiments. Continuous wave (CW) methods for the direct observation of ^{119}Sn resonances are of limited value owing to the relatively low receptivity D^p (relative to ^1H NMR) of 4.44×10^{-3} for the ^{119}Sn nucleus (Table 1).

A. Referencing

In view of the difficulties encountered for heavy nuclei by using a particular compound as an internal (chemical reactions, solvent effects) or external reference (bulk susceptibility corrections), it appears preferable to use a known absolute frequency $\Xi(^{119}\text{Sn})^{8-10}$ as reference (Table 1). This is a straightforward procedure for PFT NMR spectrometers. In heteronuclear double resonance experiments (e.g., $^1\text{H}\{^{119}\text{Sn}\}$) this is the method of choice in most cases anyhow. For most purposes it seems that corrections for different bulk susceptibilities are unnecessary. All $\delta^{119}\text{Sn}$ data in the tables given here, and in general in the literature too, are referred to $(\text{CH}_3)_4\text{Sn}$, a positive sign denoting lower shielding or a shift to higher frequencies (lower field). Depending on the referencing procedure, differences for the reported ^{119}Sn chemical shifts of up to several ppm may be found even for identical compounds studied under comparable conditions.

B. $^1\text{H}\{^{119}\text{Sn}\}$ Heteronuclear double resonance

The techniques for $^1\text{H}\{^{119}\text{Sn}\}$ heteronuclear double-resonance experiments have been reviewed.^{6,7} In CW ^1H -NMR spectra, a ^{119}Sn satellite, arising from ^{119}Sn - ^1H spin-spin coupling, is monitored while the irradiation frequency field B_2 for the ^{119}Sn nucleus is swept through the range expected for the ^{119}Sn resonance in question. Provided that the power adjustment of B_2 is correct, the maximum effect on the ^{119}Sn satellite corresponds accurately to the centre of the related ^{119}Sn resonance.

In PFT mode several ^1H -NMR spectra are recorded, each with a different ^{119}Sn irradiation frequency and otherwise unchanged parameters. By comparison of the absolute intensity of the ^{119}Sn satellites, or by subtraction of the undistorted from the distorted spectra, the relevant information can be obtained. It is obvious that a series of these experiments may be particularly helpful in studying reaction mixtures by correlating the ^1H -NMR signals with the various ^{119}Sn resonances. The latter are in general very useful for structural assignments. As shown later, this type of experiment is the one-dimensional equivalent of the two-dimensional (2D) heteronuclear shift correlated spectra¹¹ that can be obtained with modern spectrometers, *vide infra*. Experiments with $^1\text{H}\{^{119}\text{Sn}\}$ are always very useful when it is difficult to measure the ^{119}Sn resonance directly, even with modern equipment. This applies when the ^{119}Sn resonance is very broad (e.g., in the case of partially relaxed scalar coupling between ^{119}Sn and a quadrupolar nucleus—such as ^{11}B —or in cases of chemical exchange) while the ^1H resonances are not significantly affected.¹²⁻¹⁵ However, the accurate measurement of the line width of the ^{119}Sn resonances in the internuclear double resonance (INDOR) mode requires a careful setting of the power of the ^{119}Sn irradiating field, B_2

so as to observe the condition $[(\gamma_{119\text{Sn}} B_2)/2\pi] \geq \Delta \nu$ ($\Delta \nu$ is the breadth of the perturbed line). Frequently, this is difficult to achieve, in particular when the ^{119}Sn nucleus is coupled to several different protons with differing $^nJ(^{119}\text{Sn}^1\text{H})$ couplings.

In addition to the determination of the ^{119}Sn chemical shifts ($\delta^{119}\text{Sn}$) the $^1\text{H}\{^{119}\text{Sn}\}$ experiments can be used in either mode, continuous wave or pulse Fourier transform, to determine relative signs of indirect nuclear spin-spin couplings.^{6,7} The absolute signs of a great number of $^nJ(^{119}\text{Sn}^1\text{H})$ values are known, which allows the absolute sign of other $J(^{119}\text{SnX})$ couplings to be determined using the appropriate $^1\text{H}\{^{119}\text{Sn}\}$ double resonance experiment.

Of course, one can think of other heteronuclear double resonance experiments, e.g., $^{19}\text{F}\{^{119}\text{Sn}\}$ or $^{31}\text{P}\{^{119}\text{Sn}\}$, which will be useful in dealing with special problems.

C. Direct observation of ^{119}Sn resonances by pulse Fourier transform (PFT) NMR

For most applications, ^{119}Sn PFT NMR is the preferred alternative to heteronuclear double resonance $^1\text{H}\{^{119}\text{Sn}\}$, particularly, when modern NMR spectrometers with multinuclear equipment are available. This is readily seen by looking at the values for the receptivity $D^c(^{119}\text{Sn})$ in Table 1. The only drawback in the nuclear magnetic properties (always in comparison with ^{13}C NMR) is the negative sign of the magnetogyric ratio $\gamma_{119\text{Sn}}$. Therefore, a significant contribution from Sn-H dipole-dipole interactions in organotin compounds to the relaxation of the ^{119}Sn nucleus causes a negative nuclear Overhauser effect (NOE) which may lead to a serious loss of signal intensity in normal ^1H broadband decoupled ^{119}Sn -NMR spectra ($^{119}\text{Sn}\{^1\text{H}\}$) (Fig. 1). Therefore, it is important (1) to consider the relative importance of the various relaxation mechanisms (Section III) and (2) to select suitable techniques for recording $^{119}\text{Sn}\{^1\text{H}\}$ spectra (e.g., gated decoupling of ^1H in order to suppress the NOE as shown in Fig. 1, spin-polarization transfer techniques, *vide infra*).

It appears that in most organotin and inorganic tin compounds, under normal conditions, the longitudinal relaxation times T_1 are of the order of a few seconds. This enables one either to use fairly large pulse angles [the optimum pulse angle α corresponds to the relationship $\cos \alpha = \exp[-(AT + PD)]/T_1$, where AT is the acquisition time, PD is the pulse delay or relaxation delay time]¹⁶ in normal $^{119}\text{Sn}\{^1\text{H}\}$ spectra without pulse delay times or to use fairly short delay times (ca. $\geq 5 \times T_1$) and 90° pulses in NOE-suppressed $^{119}\text{Sn}\{^1\text{H}\}$ spectra.

In addition to circumventing the negative NOE the various polarization transfer (PT) techniques, e.g., insensitive nuclei enhanced by polari-

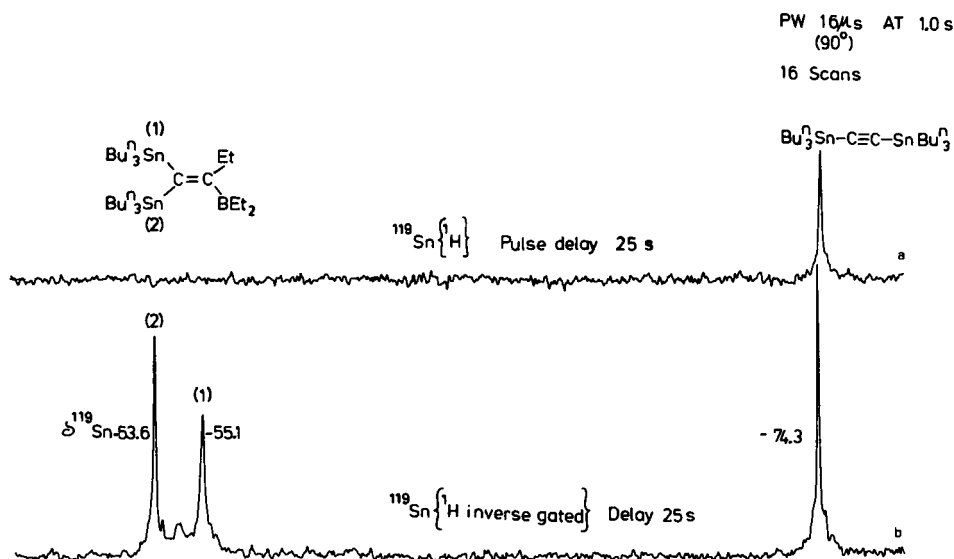


FIG. 1. ^{119}Sn -NMR spectra at 74.63 MHz of the reaction mixture $\text{Bu}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnBu}_3$ and Et_3B in CDCl_3 (20% v/v) at 28°C . (a) $^{119}\text{Sn}\{^1\text{H}\}$ -NMR spectrum, parameters as shown. (b) NOE suppressed, parameters same as in (a). The broader ^{119}Sn resonance of $\text{Bu}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnBu}_3$ in (a) as compared to (b) is the result of a temperature gradient $\delta^{119}\text{Sn}/\text{K}$ caused by the ^1H decoupler.

zation transfer and distortionless enhancement by polarization transfer (INEPT, DEPT),¹⁷⁻²⁰ offer additional advantages for the measurement of ^{119}Sn resonances of organotin compounds. The optimum enhancement factor, E_{opt} ,²¹ of the intensity of the ^1H decoupled ^{119}Sn resonance signal depends upon the number of protons coupled to ^{119}Sn with identical $^nJ(^{119}\text{Sn}^1\text{H})$ couplings (e.g., for six protons, $E_{\text{opt}} = |\gamma_{1\text{H}}/\gamma_{119\text{Sn}}| \cdot 1.55 = 4.16$). It is important to note that the repetition time of the pulse sequence is now governed by the relaxation time, T_1 , of the protons, which may be shorter than $T_1(^{119}\text{Sn})$. There are numerous $^nJ(^{119}\text{Sn}^1\text{H})$ ($n \geq 1$) data known²² and many of these values can be predicted with reasonable accuracy. Therefore, the corresponding ^{119}Sn -NMR spectra (either ^1H coupled, DEPT,²³ or INEPT⁺²⁰ pulse sequence preferred, or ^1H decoupled) are readily obtained. It should be noted that the relaxation behaviours of the ^1H and the ^{119}Sn nuclei must be considered. In some cases the transverse relaxation times $T_2(^{119}\text{Sn})$ are relatively short for various reasons (*vide infra*). Therefore, it is important to select the PT techniques with respect to the behaviour of the transverse magnetization $M_{x,y}$ of the ^{119}Sn nucleus. If T_2 is relatively short, which is true for many organotin halides, the INEPT pulse sequence (refocused INEPT for

^1H decoupled spectra) gives a better S/N ratio than the DEPT pulse sequence since the evolution time for $M_{x,y}$ in the refocused INEPT experiment is shorter. Similarly, if $T_1(^{119}\text{Sn})$ is shorter than $T_1(^1\text{H})$ the PT technique fails to give results. This situation may arise in very high field ^{119}Sn NMR ($B_0 > 4.7$ T) if chemical shielding anisotropy (CSA) relaxation becomes dominant.

Although there are no examples in the literature so far, it is expected that two-dimensional NMR techniques,¹¹ like hetero correlated 2D ^1H – ^{119}Sn NMR, will be extremely helpful in studying complex reaction mixtures of organotin compounds. This type of experiment yields a 2D spectrum in which the coupled nuclei (e.g., ^{119}Sn and ^1H) share a signal with the coordinates of $\delta^{119}\text{Sn}$ and $\delta^1\text{H}$.

The ^{119}Sn -NMR spectra in Figs. 2–4 give some idea of the wealth of information to be gained from direct ^{119}Sn -NMR spectra. Thus, values for the couplings $^1J(^{119}\text{Sn}^{13}\text{C})$, $^1J(^{119}\text{Sn}^{77}\text{Se})$, and $^2J(^{119}\text{Sn}^{117}\text{Sn})$ are readily obtained (Fig. 2). In particular, $^2J(^{119}\text{Sn}^{117}\text{Sn})$ data [or $^2J(^{119}\text{Sn}^{119}\text{Sn})$] are of great value for structural assignments (Fig. 3) and, therefore, in the analysis

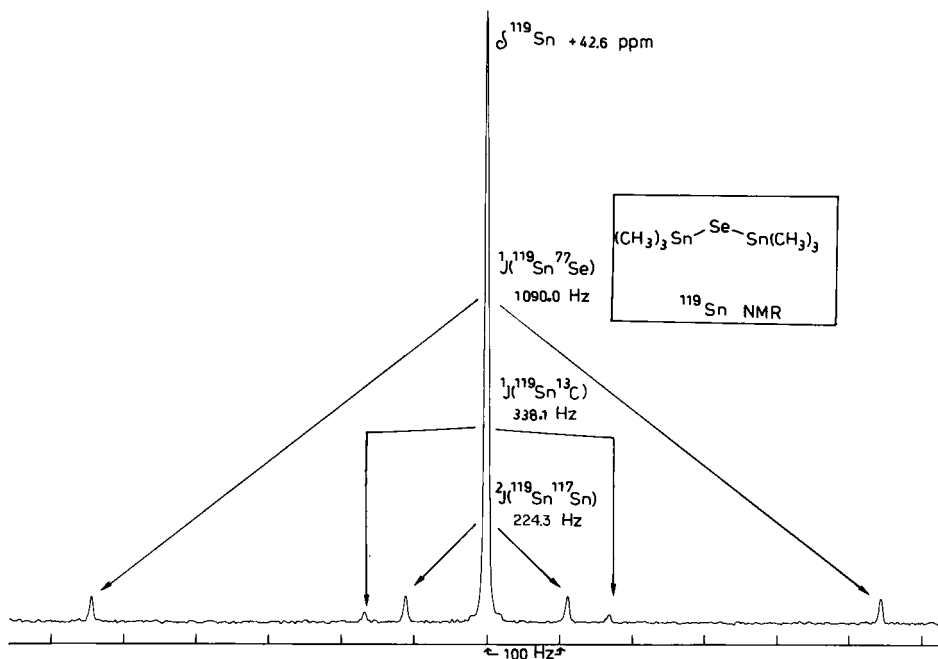
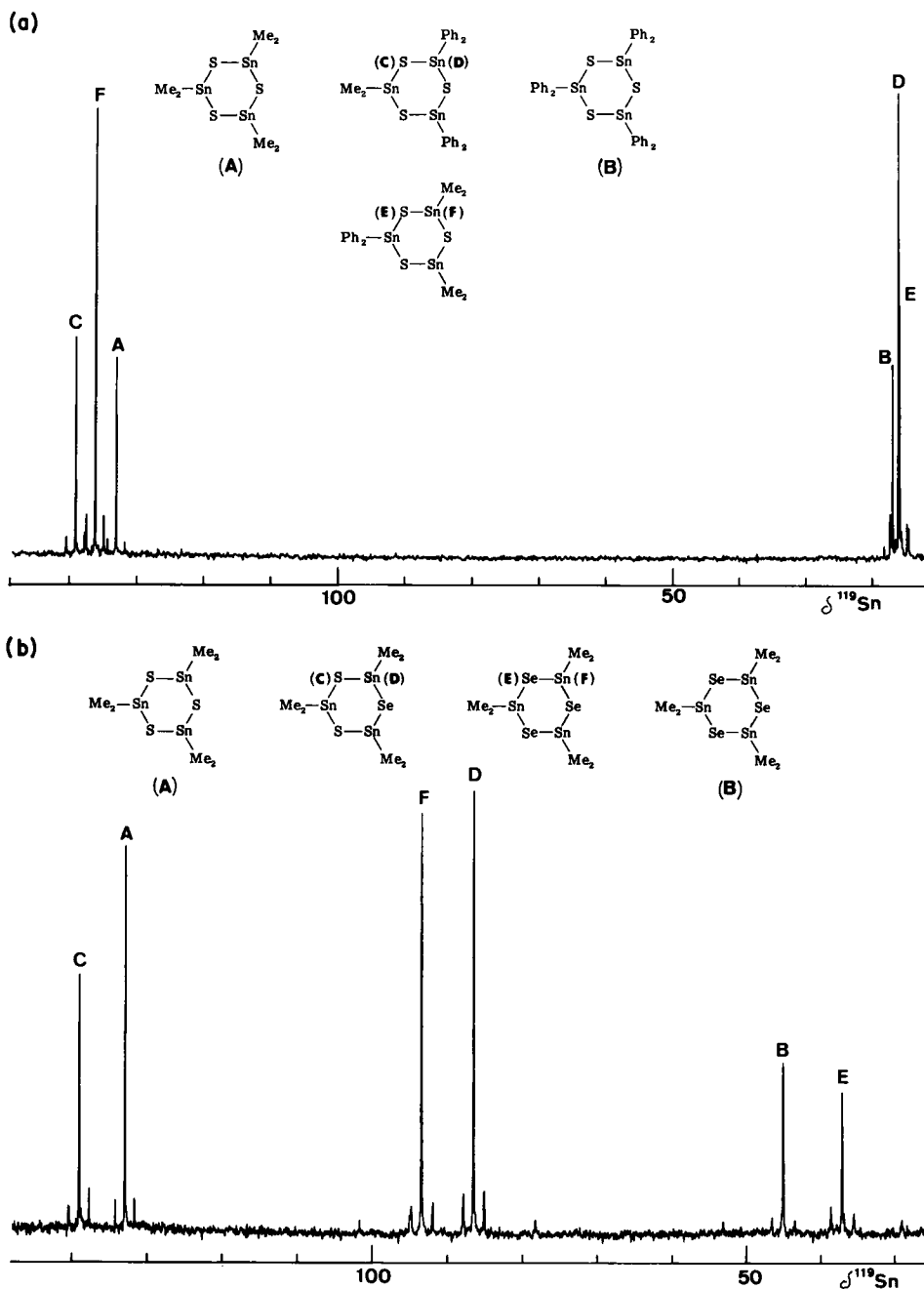


FIG. 2. ^{119}Sn -NMR spectrum at 74.63 MHz (^1H broadband decoupled) of bis-(trimethylstannyl)selenide (10% C_6D_6 in 10-mm o.d. tube); time required: ~ 15 minutes.



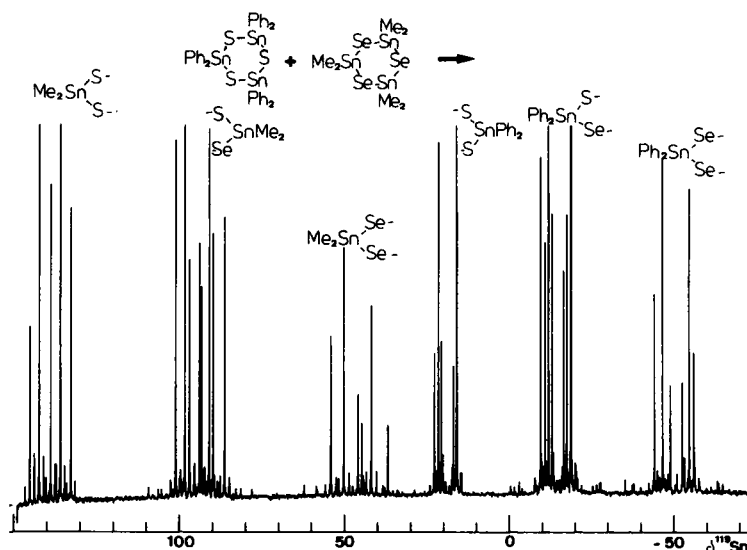


FIG. 4. ^{119}Sn -NMR spectrum at 74.63 MHz of a mixture $(\text{Me}_2\text{SnSe})_3 + (\text{Ph}_2\text{SnS})_3$ (1:1) in CDCl_3 in a 10-mm o.d. tube; ^1H inverse gated decoupling for NOE suppression; time required: 6 hours. Most ^{117}Sn , ^{119}Sn , and ^{77}Se satellite signals can be detected and have been used for assignment purposes.

of mixtures. In general, chemical shifts, $\delta^{119}\text{Sn}$, and couplings are excellent tools in tin chemistry. This is evidenced by Fig. 4, which shows that the reaction of only two compounds leads to a mixture consisting of 20 different compounds. This mixture is readily analysed using ^{119}Sn -NMR spectroscopy.

III. NUCLEAR SPIN RELAXATION

A. General

In general, numerous intra- and intermolecular interactions contribute to the values of T_1 and T_2 . For the purposes of this article, it is appropriate to consider mainly the influence of relaxation phenomena on experimental conditions. There are many excellent accounts on nuclear spin relaxation in the literature.²⁴⁻²⁸ Furthermore, we assume conditions which are referred to as those of the motional narrowing limit:

$$\omega_0^2 \tau_0^2 \ll 1 \quad (1)$$

where ω_0 is the resonance angular frequency and τ_0 is the correlation time to characterize molecular motions which produce local fluctuating magnetic

fields necessary for nuclear spin relaxation. Since T_1 becomes frequency independent under these conditions (relatively nonviscous samples), $T_1 = T_2$ can be assumed in the absence of CSA relaxation or scalar relaxation of the second kind (*vide infra*). We may distinguish between three types of correlation time: (1) the rotational correlation time, τ_c , (Brownian molecular motion) increases with molecular size (molecular association) and viscosity (decreasing temperature); (2) the translational correlation time, which is similar to τ_c as far as its dependence on molecular size and temperature is concerned; (3) the spin-rotation correlation time, τ_{SR} , which characterizes the interaction between the nuclear magnetic moment and the rotational magnetic moment (spin-rotation interaction). For the following it is important to note the inverse temperature dependence of τ_c and τ_{SR} since the latter increases with increasing temperature (or decreasing viscosity):

$$\tau_c \tau_{\text{SR}} = (I/6kT) \quad (2)$$

where I is the moment of inertia (Hubbard's relation²⁹).

B. Relaxation mechanisms

Contributions to nuclear spin relaxation can arise from intramolecular magnetic dipole interactions (T_1^{DD} , T_2^{DD}) (for the present discussion intermolecular magnetic dipole interactions will be neglected), from spin-rotation interactions (T_1^{SR} , T_2^{SR}), from scalar coupling (T_1^{SC} , T_2^{SC}), and from chemical shielding anisotropy (T_1^{CSA} , T_2^{CSA}). Among these, magnetic dipole and spin-rotation relaxation are of particular importance, at least for many organic and inorganic tin compounds. Scalar coupling must be considered for the ^{119}Sn nucleus linked to quadrupolar nuclei (e.g., Cl, Br, I, N, B), whereas CSA can be of importance at high magnetic field strengths (> 4.7 T). According to Eq. (3), T_1^{DD} and, of course, T_2^{DD} depend upon the inverse sixth power of the internuclear separation (in general the ^{119}Sn -H distance, r_{SnH}). Therefore, the magnetic dipole interaction in many organotin compounds will become increasingly important at low temperature or for molecules or molecular associates of fairly large size. In any case, one has also to consider the intramolecular mobility of the organotin molecule which discourages the use of an effective correlation time τ_c for the whole molecule (Fig. 5).

$$[T_2^{\text{DD}}(^{119}\text{Sn})]^{-1} = [T_1^{\text{DD}}(^{119}\text{Sn})]^{-1} = \sum_{\text{H}} \frac{\hbar^2 \gamma_{\text{H}} \gamma_{^{119}\text{Sn}}}{(r_{\text{SnH}})^6} \tau_c \quad (3)$$

The amount of cross-relaxation by intramolecular dipole-dipole coupling in liquids is determined by the NOE.³⁰ The changes in signal intensity are readily observed by comparison of the ^{119}Sn -NMR spectra which have been obtained by normal broadband ^1H decoupling with those obtained by gated

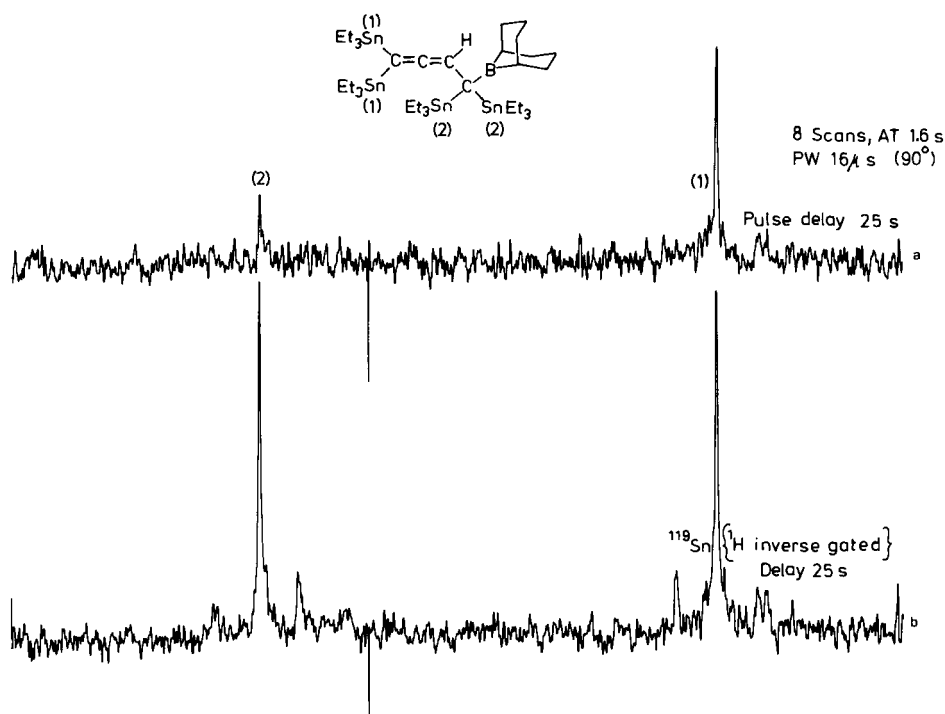


FIG. 5. ^{119}Sn -NMR spectrum at 74.63 MHz of an allene derivative containing two different types of triethylstannyl groups. NOE values: $\eta_{\text{max}} = -1.34$; $\eta_{\text{obs}} = -0.33$ (1) and -0.82 (2). The different NOEs observed for the ^{119}Sn (1) and ^{119}Sn (2) nuclei are attributed to their different mobilities. For steric reasons a greater mobility of the Et_3Sn (1) group is expected, leading to a shorter effective correlation time τ_c and, consequently, to longer values of $T_1^{\text{DD}}(^{119}\text{Sn})$. Therefore, spin-rotation relaxation is believed to be the more effective mechanism for ^{119}Sn (1), with respect to ^{119}Sn (2). (a) Normal ^1H broadband decoupled ^{119}Sn -NMR spectrum. (b) NOE-suppressed ^1H broadband decoupled ^{119}Sn -NMR spectrum.

^1H decoupling leading to suppression of the NOE (Figs. 1, 5). The maximum NOE, in the extreme narrowing limit, corresponds to

$$\eta_{\text{max}}(^{119}\text{Sn}) = 0.5(\gamma_{1\text{H}}/\gamma_{119\text{Sn}}) \quad (4)$$

which gives $\eta_{\text{max}}(^{119}\text{Sn}) = -1.34$, leading to an inverted ^{119}Sn resonance signal with 34% of the intensity of the ^{119}Sn resonance recorded with NOE suppression. Therefore, owing to the negative sign of $\gamma_{119\text{Sn}}$ the intensity of the ^{119}Sn resonance in $^{119}\text{Sn}\{^1\text{H}\}$ experiments varies between $+1$ and -0.34 , depending upon the relative contribution of Sn-H magnetic dipole relaxation in comparison with the other relaxation mechanisms.

Experimental $T_1(^{119}\text{Sn})$ data available³¹⁻³⁷ (Table 2) clearly support the proposal of competition between magnetic dipole and spin-rotation inter-

TABLE 2

Longitudinal relaxation times $T_1(^{119}\text{Sn})^a$

Compound	$T_1(^{119}\text{Sn})^b$ (seconds)	T_1^{DD} (seconds)	NOE ^c	T_1^{SR} (seconds)	Solvent	Molecular weight	T (K)	Field strength (T)
Pr^n_4Sn	4.76	17.24	-0.37	6.67	Neat	291	307	2.11
Bu^n_4Sn	6.29	9.80	-0.86	17.54	Neat	347	307	2.11
Pr^n_3SnCl	4.78	22.73	-0.28	6.06	Neat	283	307	2.11
Bu^n_3SnCl	5.81	11.49	-0.68	11.76	Neat	326	307	2.11
Bu^n_3SnH	4.65	14.49	-0.43	6.85	Neat	291	307	2.11
$(\text{Bu}^n_3\text{Sn})_2\text{O}$	6.55	13.33	-0.66	12.82	Toluene/50%	596	298	2.35
Ph_3SnH	1.51	1.67	-1.21	15.63	Toluene/50%	351	303	2.11

^a From reference 37.^b $1/T_1(^{119}\text{Sn}) = (1/T_1^{\text{DD}}) + (1/T_1^{\text{SR}})$.^c Observed NOE; $\eta_{\text{max}} = -1.34$ for $^{119}\text{Sn}\{^1\text{H}\}$.

actions. Considering the inverse relationship of the correlation times, which describe the time dependence of the fluctuating magnetic field created by the tumbling of the molecule in solution (τ_c) and the energy exchange between the nuclear spin and the rotational magnetic moment of the molecule (τ_{SR}), the dominance of one or the other mechanism is readily evident from the following measurements: (1) determination of the NOE (Figs. 1, 5); and (2) temperature dependence of $T_1(^{119}\text{Sn})$, which also indicates whether another mechanism (T_1^{SC} , T_1^{CSA}) may be operating.

It has been shown that scalar interactions and CSA (^{119}Sn NMR at 2.07 and 2.3 T) are insignificant mechanisms for the longitudinal relaxation of the ^{119}Sn nucleus. However, CSA might be expected to become important at higher field strengths (> 4.7 T) for the ^{119}Sn nucleus in molecules with lower than cubic symmetry, as has been found for the ^{207}Pb nucleus.³⁸ Since CSA relaxation appears to be of minor importance³⁷ for $B_0 < 4.7$ T and $T_1^{\text{CSA}} = 1.17T_2^{\text{CSA}}$ (in the motional narrowing limit), significant contributions to the line width of ^{119}Sn resonances can be expected only from scalar coupling contributions due to scalar relaxation of the second kind.²⁴ From (5) and (6) it follows that significant broadening of ^{119}Sn resonances may be expected when the ^{119}Sn nucleus is coupled to a quadrupolar nucleus X (see Fig. 9, Section V,B,3,c).

$$W_{1/2}(^{119}\text{Sn}) = [\pi T_2(^{119}\text{Sn})]^{-1} \quad (5)$$

(for Lorentzian line shape and negligible inhomogeneity the full width at half height is given by $W_{1/2}$)

$$[T_2^{\text{SC}}(^{119}\text{Sn})]^{-1} = \frac{4}{3}\pi^2[J(\text{SnX})]^2 S_X(S_X + 1)T_1(\text{X}) \quad (6)$$

$[T_1^{\text{SC}}(^{119}\text{Sn})]$ has been neglected, S_X refers to the nuclear spin of X].

The linewidth in Eq. (5) results from the ^{119}Sn -NMR spectrum, and the value of $T_1(\text{X})$ for the quadrupolar nucleus X can readily be obtained from the X-NMR spectra. Thus, the value of $J(\text{SnX})$ can be estimated from Eqs. (5) and (6) if other contributions to $T_2(^{119}\text{Sn})$ are small.

IV. CHEMICAL SHIFTS, $\delta^{119}\text{Sn}$

A. General

Following Ramsey's terminology³⁹ the nuclear screening σ , results from diamagnetic (σ_d) and paramagnetic (σ_p) components:

$$\sigma = \sigma_d + \sigma_p \quad (7)$$

In agreement with Ramsey's theory, σ_d and σ_p are large and of opposite sign, even for molecules of small or moderate size. Therefore, the calculation of

reliable values for the nuclear screening of the heavier nuclei has not yet been realized. Serious errors can be introduced from the choice of the atomic basis set, since the value of σ depends upon the origin chosen.⁴⁰ Among the various semiempirical approaches,⁴¹ Pople's MO treatment of nuclear screening (independent electron model) circumvents some of these problems and the screening is given mainly as the sum of diamagnetic and paramagnetic local and nonlocal contributions.⁴²⁻⁴⁴ These terms, σ_d^{loc} , σ_p^{loc} , etc., must not be confused with the terms in Ramsey's equation. The independent electron model shows that σ is controlled by σ_d^{loc} and σ_p^{loc} . While σ_d^{loc} is expected to remain fairly constant for a given nucleus in different

$$\sigma = (\sigma_d^{\text{loc}} + \sigma_p^{\text{loc}}) + (\sigma_d^{\text{non-loc}} + \sigma_p^{\text{non-loc}}) \quad (8)$$

surroundings, large changes in the magnitude of σ_p^{loc} may result. This approach is further simplified by using an average excitation energy (AEE = ΔE)⁴⁵ instead of summing over all excitation energies for the excited singlet states which are mixed with the ground state as the result of the application of an external magnetic field B_0 .

This has led to the widely used expression for σ_p^{loc} considering np and nd electrons only⁴⁶:

$$\sigma_p^{\text{loc}}(\text{A}) = -\frac{2\mu_0\mu_B^2}{3\pi\Delta E}[\langle r^{-3} \rangle_{np} P_u + \langle r^{-3} \rangle_{nd} D_u] \quad (9)$$

where μ_0 is the permeability of free space, μ_B the Bohr magneton, r the radius of the np and of the nd orbitals, and P_u and D_u correspond, respectively, to the imbalance of the valence np and nd electrons on the atom A.

This model may be applied with some success to screening data for nuclei in series of closely related compounds and it aids in the qualitative understanding of the physical principles of nuclear shielding. However, it should be made clear that the discussion of variations in the local paramagnetic term $\sigma_p^{\text{loc}}(\text{A})$ is of limited value owing to the simplifications assumed. Indeed, it appears that the influence of nearest neighbours (point dipole approximation) is not properly reflected by $\sigma_p^{\text{loc}}(\text{A})$, in particular for heavy atom substituents.⁴⁷⁻⁴⁹

B. Patterns of ¹¹⁹Sn chemical shifts

1. Coordination number

Assuming the relevant excitation energies to be fairly constant, the local paramagnetic term may be said to represent the imbalance of charge. Therefore, we expect some correlation between σ_p^{loc} and local symmetry. This is evident from the increase in ¹¹⁹Sn nuclear shielding for compounds in which the coordination number increases from 2 to ≥ 6 .^{5,50-73,365} The significant

TABLE 3

Organotrimethyltin compounds,^a tin coordination number = 4

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
Me_4Sn	0	—	<i>b</i>	—
Me_3SnEt	+3.0	CCl_4	<i>c</i>	8
	+4.2	25% CH_2Cl_2	<i>c</i>	254
	+5.3	C_6D_6	<i>c</i>	255
Me_3SnPr^a	-2.3	25% CH_2Cl_2	<i>c</i>	254
Me_3SnPr^i	+8.6	25% CH_2Cl_2		254
	+9.8	C_6D_6	<i>d</i>	102
Me_3SnBu^a	-1.0	25% CH_2Cl_2	<i>c</i>	254
	-0.56	C_6D_6	<i>e</i>	102
Me_3SnBu^b	+5.3	C_6D_6	<i>f</i>	102
	+3.3	C_6D_6		86
Me_3SnBu^f	+19.5	CDCl_3	<i>c</i>	170
$\text{Me}_3\text{Sn-CH}_2\text{Bu}^f$	-14.2	25% CH_2Cl_2		254
	-14.4	CDCl_3		170
$\text{Me}_3\text{Sn-cyclo-Pr}$	+14.0	25% CH_2Cl_2		254
$\text{Me}_3\text{Sn-chex}$	-4.7	25% CH_2Cl_2	<i>c</i>	254
1- $\text{Me}_3\text{Sn-2-Ph-chex}$	-9.1	C_6D_6	<i>g,h</i>	101
1- $\text{Me}_3\text{Sn-norbornane (exo)}$	+4.4	25% CH_2Cl_2		254
	+3.3	C_6D_6	<i>g,i</i>	101
1- $\text{Me}_3\text{Sn-norbornane (endo)}$	-0.5	C_6D_6	<i>g,j</i>	101
7- $\text{Me}_3\text{Sn-norbornane}$	-9.2	25% CH_2Cl_2		254
1,3-(Me_3Sn) ₂ -bicyclo[2.2.1]heptane	+2.5	CDCl_3	<i>k</i>	256
1- $\text{Me}_3\text{Sn-4-Me-bicyclo[2.2.2]octane}$	+3.4	CDCl_3	<i>l</i>	256
1- $\text{Me}_3\text{Sn-adamantane}$	-6.9	25% CH_2Cl_2		254
2- $\text{Me}_3\text{Sn-adamantane}$	-13.7	25% CH_2Cl_2		254
$\text{Me}_3\text{Sn-CH}_2\text{CH=CH}_2$	+5.4	CH_2Cl_2		4
(<i>cis</i>)-1- $\text{Me}_3\text{Sn-5-Me-2-cyclohexenyl}$	-0.29	C_6D_6	<i>m</i>	102, 257

(<i>trans</i>)-1-Me ₃ Sn-5-Me-2-cyclohexenyl	-2.72	C ₆ D ₆	<i>m</i>	102, 257
1-Me ₃ Sn-3,4-Me ₂ -6-Ph-3-cyclohexenyl	-5.2	C ₆ D ₆	<i>n</i>	101
7-Me ₃ Sn-norbornene (<i>syn</i>)	-11.3	25% CH ₂ Cl ₂		254
	-13.2	C ₆ H ₆		258
7-Me ₃ Sn-norbornene (<i>anti</i>)	-25.6	25% CH ₂ Cl ₂		254
5-Me ₃ Sn-2-norbornene (<i>exo</i>)	+7.8	C ₆ H ₆		258
5-Me ₃ Sn-2-norbornene (<i>endo</i>)	-1.2	C ₆ H ₆		258
3-Me ₃ Sn-nortricyclene	-11.4	C ₆ H ₆		258
Me ₃ Sn—CH ₂ Ph	+4	50% H ₂ Cl ₂		9
	+3.57	0.25 <i>M</i> CDCl ₃	<i>a</i>	164
1,2-(Me ₃ SnCH ₂) ₂ C ₆ H ₄	+3.76	C ₆ D ₆ /CD ₂ Cl ₂		259
1,3-(Me ₃ SnCH ₂) ₂ C ₆ H ₄	+2.20	C ₆ D ₆ /CD ₂ Cl ₂		259
1,4-(Me ₃ SnCH ₂) ₂ C ₆ H ₄	+0.98	C ₆ D ₆ /CD ₂ Cl ₂		259
Me ₃ Sn—CH ₂ (C ₆ H ₄ - <i>o</i> -OMe)	+2.94	C ₆ D ₆ /CD ₂ Cl ₂		259
Me ₃ Sn—CH ₂ (C ₆ H ₄ - <i>o</i> -NMe ₂)	-0.78	C ₆ D ₆ /CD ₂ Cl ₂		259
Me ₃ Sn—CH ₂ (C ₆ H ₄ - <i>o</i> -PPh ₂)	+3.35	C ₆ D ₆ /CD ₂ Cl ₂		259
Me ₃ Sn—CH ₂ —CHEtC≡CH	-4.7	CDCl ₃		245
Me ₃ SnCH ₂ -1-naphthyl	+9.97	CDCl ₃		164
Me ₃ SnCH ₂ -2-naphthyl	+4.88	CDCl ₃	<i>p</i>	164
1-Me ₃ Sn-4-Me-1,4-ethano-1,2,3,4-tetrahydronaphthalene	-3.89	CDCl ₃	<i>q</i>	164
Me ₃ Sn—CH ₂ Cl	+4	C ₆ H ₆	<i>c</i>	8
Me ₃ Sn—CH ₂ Br	+6	C ₆ H ₆		8
Me ₃ Sn—CHCl ₂	+33	C ₆ H ₆		8
Me ₃ Sn—CHBr ₂	+42	C ₆ H ₆		8
Me ₃ Sn—CCl ₃	+85	90% C ₆ H ₆		8
Me ₃ Sn—CBr ₃	+101	90% C ₆ H ₆		8
Me ₃ Sn—CH ₂ SiMe ₃	+7.6	CDCl ₃		170
Me ₃ Sn—CH ₂ GeMe ₃	+11.6	CDCl ₃		170
(Me ₃ Sn) ₂ CH ₂	+23.3	C ₆ D ₆		243
(Me ₃ SnCH ₂) ₂ SnMe ₂	+22.2 (Me ₃ Sn)	CDCl ₃		170
	+45.5 (Me ₂ Sn)			

TABLE 3 (cont.)

	Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
	$(\text{Me}_3\text{SnCH}_2)_3\text{SnMe}$	+22.5 (Me_3Sn)	CDCl_3		170
		+67.7 (MeSn)			
	$(\text{Me}_3\text{SnCH}_2)_4\text{Sn}$	+20.9 (Me_3Sn)	CDCl_3		170
		+87.4 (Sn)			
	$\text{Me}_3\text{Sn}-\text{CH}_2\text{SnMe}_2-\text{NEt}_2$	+20.6 (Me_3Sn)	Toluene- d_8		100
		+75.0 (Me_2Sn)			
	$(\text{Me}_3\text{Sn})_2\text{CHMe}$	+27.5	C_6D_6		243
	$(\text{Me}_3\text{Sn})_2\text{CHEt}$	+19.5	CDCl_3		243
	$(\text{Me}_3\text{Sn})_2\text{CHPh}$	+17.8	CDCl_3		243
	$(\text{Me}_3\text{Sn})_2\text{CH}(\text{C}_6\text{H}_4\text{-}p\text{-Me})$	+17.4	CDCl_3		243
	$(\text{Me}_3\text{Sn})_2\text{CH}(\text{C}_6\text{H}_4\text{-}p\text{-OMe})$	+17.0	CDCl_3		243
88	$(\text{Me}_3\text{Sn})_2\text{CMe}_2$	+30.9	CDCl_3		170
	7,7- $(\text{Me}_3\text{Sn})_2$ -norcarane	+36.8, -2.0	C_6D_6		243
	$(\text{Me}_3\text{Sn})_3\text{CH}$	+41.0	C_6D_6		243, 212
	$(\text{Me}_3\text{Sn})_3\text{CEt}$	+34.1	CDCl_3		170
	$(\text{Me}_3\text{Sn})_3\text{CC}_5\text{H}_{11}$	+35.0	CDCl_3		170
	$(\text{Me}_3\text{Sn})_3\text{CCH}_2\text{Ph}$	+34.7	CDCl_3		170
	$(\text{Me}_3\text{Sn})_3\text{CCH}_2\text{OPh}$	+30.9	CDCl_3		170
	$(\text{Me}_3\text{Sn})_3\text{C}(\text{CH}_2)_2\text{OPh}$	+37.8	CDCl_3		170
	$(\text{Me}_3\text{Sn})_4\text{C}$	+49.8	C_6D_6		243, 212
	$\text{Me}_3\text{Sn}-\text{CH}_2\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}$	+14	C_6H_6		260
	$\text{Me}_3\text{Sn}-\text{CH}_2\text{Ti}(\text{C}_5\text{H}_5)_2\text{CH}_2\text{SiMe}_3$	+4	C_6H_6		260
	$\text{Me}_3\text{Sn}-\text{CH}_2\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}$	+15	C_6H_6		260
	$\text{Me}_3\text{Sn}-\text{CH}_2\text{Hf}(\text{C}_5\text{H}_5)_2\text{Cl}$	+16.5	C_6H_6		260
	$[(\text{Me}_3\text{Sn})_2\text{C}_2\{\text{Co}_2(\text{CO})_6\}]$	+15.0	CDCl_3		252
	$[\text{Me}_3\text{Sn}(\text{Ph})\text{C}_2\{\text{Co}_2(\text{CO})_6\}]$	+20.7	CDCl_3		252
	$\text{Me}_3\text{Sn}-\text{C}_5\text{H}_5$	+26.0	CCl_4	c	261
		+32.3	THF- d_8		76

$(\text{Me}_3\text{Sn})_2\text{C}_3\text{H}_4$
1- Me_3Sn -indene

+ 10.6

 CCl_4

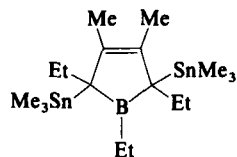
c

261

+ 31.3

—

261, 262



+ 34.0

 CDCl_3

r

263

$\text{Me}_3\text{Sn}-\text{Ph}$

- 28.6

20% CH_2Cl_2

c, s

254

1- Me_3Sn -naphthalene

- 31.8

25% CH_2Cl_2

254

2- Me_3Sn -pyridine

- 56.7

95% C_6D_6

264

3- Me_3Sn -pyridine

- 27.4

95% C_6D_6

264

4- Me_3Sn -pyridine

- 27.8

95% C_6D_6

264

3- Me_3Sn -furan

- 40.4

 CDCl_3

265

2- Me_3Sn -thiophene

- 27.5

 CDCl_3

240, 266

3- Me_3Sn -thiophene

- 38.3

 CDCl_3

240

$\text{Me}_3\text{SnCH}=\text{CH}_2$

- 39

10% CCl_4

c

2

$\text{Me}_3\text{SnC}(\text{Me})=\text{CH}_2$

- 34

 CDCl_3

90

$\text{Me}_3\text{SnCH}=\text{CHMe}$ (cis)

- 58

 CDCl_3

90

$\text{Me}_3\text{SnCH}=\text{CHMe}$ (trans)

- 42

 CDCl_3

90

$\text{Me}_3\text{SnCH}=\text{CHPh}$ (cis)

- 50.8

 C_6D_6

102

$\text{Me}_3\text{SnCH}=\text{CHPh}$ (trans)

- 32.2

 C_6D_6

102

$\text{Me}_3\text{SnC}(\text{CO}_2\text{Me})=\text{CH}_2$

- 27.8

 C_6D_6

102, 257

$\text{Me}_3\text{SnCH}=\text{CHCO}_2\text{Me}$ (cis)

- 51.2

 C_6D_6

102, 257

$\text{Me}_3\text{SnCH}=\text{CHCO}_2\text{Me}$ (trans)

- 32.5

 C_6D_6

102, 257

6- Me_3Sn -bicyclo[3.2.1]-octa-2,6-diene

- 47.7

?

267

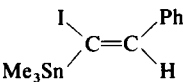
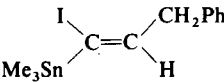
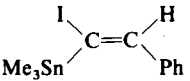
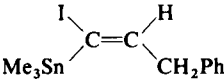
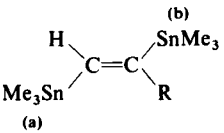
7- Me_3Sn -bicyclo[3.2.1]-octa-2,6-diene

- 46.3

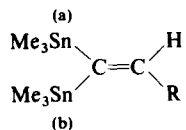
?

267

TABLE 3 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
	+ 12.5	?		268
	+ 4.4	?		268
	- 1.7	?		268
	- 10.7	?		268
				
R				
H	- 52.3 (a)(b)	CDCl_3		251
Me	- 69.7 (a)	CDCl_3		241
	- 45.5 (a)			
Bu^n	- 70.7 (a)	CDCl_3		241
	- 47.6 (b)			
Bu^t	- 69.2 (a)	CDCl_3		241
	- 47.0 (b)			

Ph	−68.4 (a) −43.3 (b)	CDCl ₃	241
CH ₂ Ph	−68.4 (a) −43.3 (b)	CDCl ₃	241
CH ₂ OMe	−68.8 (a) −46.1 (b)	CDCl ₃	241
CH ₂ OPh	−65.4 (a) −43.4 (b)	CDCl ₃	241
Me ₃ SnCH=CHSnMe ₃ (<i>cis</i>)	−60.5	CDCl ₃	251



R

H	−19.3 (a)(b)	CDCl ₃	170, 241
CH ₃	−15.7 (a) −45.0 (b)	CDCl ₃	170, 241
Bu ^{''}	−158 (a) −45.6 (b)	CDCl ₃	170, 241
Bu [']	−1.1 (a) −46.8 (b)	CDCl ₃	170, 241
Ph	−9.6 (a) −38.0 (b)	CDCl ₃	170, 241
CH ₂ OMe	−9.9 (a) −43.9 (b)	CDCl ₃	170, 241
CH ₂ OPh	−9.4 (a) −40.5 (b)	CDCl ₃	170, 241
OPh	−7.2 (a) −28.3 (b)	CDCl ₃	170, 241

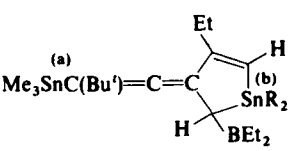
$\text{Me}_3\text{SnC}(\text{Me})=\text{C}=\text{CHMe}$	-13.8	25% CH_2Cl_2	254
$(\text{Me}_3\text{Sn})_2\text{C}=\text{C}=\text{CHSnMe}_3$	-4.0 ($\text{Sn}_2\text{C}=\text{)$ -9.3 ($\text{SnCH}=\text{)$	C_6D_6	248
$(\text{Me}_3\text{Sn})_2\text{C}=\text{C}=\text{C}(\text{SnMe}_3)_2$	+3.1	C_6D_6	248
$(\text{Me}_3\text{Sn})_2\text{C}=\text{C}=\text{CH}-\text{C}\equiv\text{C}-\text{SnMe}_3$	+1.7 ($\text{Sn}_2\text{C}=\text{)$ -69.8 (SnC)	CDCl_3	273
$\text{Me}_3\text{SnC}(\text{Bu}^i)=\text{C}=\text{C}(\text{Et})\text{CH}_2\text{SnMe}_3$	-24.0 ($\text{SnC}=\text{)$ -0.3 (SnCH_2)	CDCl_3	245
$\text{Me}_3\text{SnC}(\text{SiMe}_3)=\text{C}=\text{C}(\text{Et})\text{CH}_2\text{SnMe}_3$	14.1 ($\text{SnC}=\text{)$ -2.8 (SnCH_2)	CDCl_3	245
$(\text{Me}_3\text{Sn})_2\text{C}=\text{C}=\text{C}(\text{Et})\text{CH}_2\text{SnMe}_3$	-12.2 ($\text{Sn}_2\text{C}=\text{)$ -1.1 (SnCH_2)	CDCl_3	245
$\text{Me}_3\text{SnC}(\text{Bu}^i)=\text{C}=\text{C}(\text{Et})\text{CH}(\text{BEt}_2)\text{SnMe}_3$	-20.6 ($\text{SnC}=\text{)$ +0.2 (SnCH)	CDCl_3	245
$\text{Me}_3\text{SnC}(\text{Bu}^i)=\text{C}=\text{C}(\text{Et})\text{C}(\text{Me})(\text{BEt}_2)\text{SnMe}_3$	-24.1 ($\text{SnC}=\text{)$ -2.8 (SnC)	CDCl_3	245
33 $(\text{Me}_3\text{Sn})_2\text{C}=\text{C}=\text{C}(\text{Et})\text{CH}(\text{BEt}_2)\text{SnMe}_3$	-10.9, -14.7 ($\text{Sn}_2\text{C}=\text{)$ -4.9 (SnCH)	CDCl_3	245
$(\text{Me}_3\text{Sn})_2\text{C}=\text{C}=\text{C}(\text{Et})\text{C}(\text{BEt}_2)(\text{SnMe}_3)_2$	-9.9 ($\text{Sn}_2\text{C}=\text{)$ -3.2 (Sn_2C)	CDCl_3	245, 274
$(\text{Me}_3\text{Sn})\text{C}(\text{SiMe}_3)=\text{C}=\text{CHC}(\text{SiMe}_3)(\text{BC}_8\text{H}_{14})\text{SnMe}_3$	-12.6, -12.8 ($\text{SnC}=\text{)$ +1.7, +2.6 (SnC)	CDCl_3 u	23, 271
$(\text{Me}_3\text{Sn})_2\text{C}=\text{C}=\text{CHC}(\text{BC}_8\text{H}_{14})(\text{SnMe}_3)_2$	-9.6 ($\text{Sn}_2\text{C}=\text{)$ +9.0 (Sn_2C)	CDCl_3 u	23, 271
			
R = Me	-27.1 (a) +69.8 (b)	CDCl_3	245
R = Et	-27.0 (a) +77.8 (b)	CDCl_3	245

TABLE 3 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{H}$	-68.1	CH_2Cl_2		91
	-70.1	$\text{THF}/\text{C}_6\text{D}_6$		76
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Me}$	-73.8	C_6D_6		157, 159
	-73.2	CDCl_3		
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Bu}^a$	-73.0	?		156
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Bu}^i$	-72.7	C_6D_6		159
	-72.5	CDCl_3		159
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{C}_5\text{H}_{11}$	-73.1	?		156
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Ph}$	-66.3	?		156
	-69.0	CDCl_3		157
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{C}(\text{Me})=\text{CH}_2$	-67.0	C_6D_6		159
	-66.7	CDCl_3		159
94 $\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{CH}=\text{C}(\text{Me})\text{NEt}_2$	-72.5	CDCl_3		273
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{C}(\text{SnMe}_3)=\text{C}(\text{Pr}^i)\text{BPr}^i_2$	-68.6 ($\text{SnC}\equiv$)	CDCl_3		269
	-42.0 ($\text{SnC}\equiv$)			
$\text{Me}_3\text{Sn}-\text{C}=\text{C}-\text{CH}=\text{C}=\text{C}(\text{SnMe}_3)_3$	-69.8 ($\text{SnC}\equiv$)	CDCl_3		273
	+ 1.7 ($\text{Sn}_2\text{C}=\text{C}$)			
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{SiMe}_3$	-59.9	C_6D_6		158
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{SnMe}_3$	-61.5	C_6D_6		158
	-59.0	CDCl_3		
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{OEt}$	-61.5	C_6D_6		157
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SiMe}_3$	-75.9	$\text{C}_6\text{D}_6/\text{CDCl}_3$		157
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{GeMe}_3$	-75.2	CDCl_3		157
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnMe}_3$	-80.9	C_6D_6		159
	78.0	CDCl_3		159
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{PbMe}_3$	-84.0	C_6D_6		159
	-81.0	CDCl_3		159
<i>trans</i> -[Pt($\text{C}\equiv\text{C}-\text{SnMe}_3$) ₂ (PEt ₃) ₂]	-93.7	C_6D_6		253
$\text{Me}_3\text{SnC}(\text{SiMe}_3)\text{N}_2$	+ 35.8			275

(Me ₃ Sn) ₂ CN ₂	+ 37.8			275
[(Me ₃ SnC ₅ H ₄) ₂ V]	+ 755	Toluene	x	276

^a For more $\delta^{119}\text{Sn}$ data of organotrimethyltin compounds see review 3 and references 371–377.

^b Reference compound, $\delta^{119}\text{Sn}$ is little affected by different solvents and concentration; see, e.g., reference 10.

^c For other conditions see review 3.

^d Deuterated in 1-position.

^e Deuteration in positions 4, 3, 2, and 1 gives the $\delta^{119}\text{Sn}$ values -0.56 , -0.54 , -0.50 , -0.74 , respectively.¹⁰²

^f Deuteration in positions 1 and 4 gives the $\delta^{119}\text{Sn}$ values $+5.31$, $+5.30$, respectively.¹⁰²

^g Deuterated in 2-position.

^h The Me₃Sn and the Ph groups are in axial and equatorial positions, respectively.

ⁱ $\delta^{119}\text{Sn}$ for the 2-Ph (*endo*)-derivative: $+4.9$ (C₆D₆).¹⁰¹

^j $\delta^{119}\text{Sn}$ for the 2-Ph (*endo*)-derivative: -16.5 (C₆D₆).¹⁰¹

^k $\delta^{119}\text{Sn}$ values for other 3-substituted (X) 1-Me₃Sn-bicyclo[2.2.1]heptanes in CDCl₃. X = OMe (-3.1), F (-1.83).²⁵⁶

^l $\delta^{119}\text{Sn}$ values for other 4-substituted (X) 1-Me₃Sn-bicyclo[2.2.2]octanes in CDCl₃. X = CN (10.0, 9.19), F (11.67, 10.83), Cl (10.35, 9.66), Br (11.67, 10.95), I (14.08, 13.37), NMe₂ (6.17, 5.11), OMe (8.76, 7.65), Ph (4.9, 4.46), C₆H₄-*p*-F (5.32, 5.05), Bu^t (2.04, 1.89), Me₃Sn (-5.53 , -5.90).

^m Deuterated in 3-position.

ⁿ Ph in equatorial and Me₃Sn group in axial position, deuterated in 6-position; $\delta^{119}\text{Sn}$ for Ph and Me₃Sn both in equatorial positions in C₆D₆: -3.4 .¹⁰¹

^o $\delta^{119}\text{Sn}$ values for other substituted (X) benzyltrimethylstannanes in CDCl₃. X = *p*-OMe (1.51), *p*-Me (1.77), *p*-F (3.47), *m*-OMe (3.99), *p*-Ph (4.04), *p*-Cl (4.81), *m*-F (6.00), *m*-Cl (6.49), *m*-CF₃ (7.44), *o*-OMe (3.80).¹⁶⁴

^p $\delta^{119}\text{Sn}$ for Me₃SnCH₂-1-(6-Me)naphthyl in CDCl₃: 4.3.¹⁶⁴

^q $\delta^{119}\text{Sn}$ for 6- or 7-substituted (X) 1-Me₃Sn-4-Me-1,4-ethano-1,2,3,4-tetrahydronaphthalenes in CDCl₃: X = 6-F (-2.84), 7-F (-2.74), 6-NMe₂ (-4.09), 7-NMe₂ (-5.22), 6-NO₂ (-1.64), 7-NO₂ (-0.77).¹⁶⁴

^r The Me₃Sn groups migrate about the BC₄ ring.

^s See review 3 for an extensive collection of substituted phenyltrimethylstannanes.

^t The value obtained by ¹H{¹¹⁹Sn} NMR²⁴⁶ is less accurate, see also Fig. 9.

^u BC₈H₁₄ = 9-borabicyclo[3.3.1]nonane.

^v $\delta^{119}\text{Sn}$ of the isomer 9-ethyl-10[2-trimethylstannyl-(*E*)-ethylidene]-9-borabicyclo[3.3.2^{1.5}]decane, -60.4 ; of the (*Z*) isomer, -65.6 .

^w $\delta^{119}\text{Sn}$ of the isomer 9-ethyl-10[2-trimethylstannyl-(*Z*)-propylidene]-9-borabicyclo[3.3.2^{1.5}]decane, -45.9 .

^x To low-field relative to diamagnetic [(Me₃SnC₅H₄)₂Fe] ($\delta^{119}\text{Sn}$, -4.2); $\delta^{119}\text{Sn}$ value is temperature dependent: 307.9 K, $+755$; 318.5 K, $+731$; 329 K, $+709$; 344.9 K, $+689$; 360.7 K, $+670$.

TABLE 4

Organotriethyltin compounds, tin coordination number = 4^a

Compound	$\delta^{119}\text{Sn}$	Solvent	Notes	Reference
Et_3SnMe	+9.0	20% CCl_4		277
Et_4Sn	+1.4	20% CCl_4	<i>b,c</i>	262, 277
Et_3SnBu^t	-0.5	—		163
$(\text{Et}_3\text{SnCH}_2\text{CH}_2)_2$	-1.1	95% C_6D_6		99
$\text{Et}_3\text{Sn}-\text{CH}_2\text{Ph}$	-6	saturated CCl_4		277
$[\text{Et}_3\text{SnC}_2\text{HCo}_2(\text{CO})_6]$	+10.6	CDCl_3		277
$[(\text{Et}_3\text{Sn})_2\text{C}_2\text{Co}_2(\text{CO})_6]$	+2.3	CDCl_3		252
$\text{Et}_3\text{Sn}-\text{Ph}$	-34	25% CCl_4		277
$\text{Et}_3\text{SnCH}=\text{CH}_2$	-42	50% CCl_4		277
$\text{Et}_3\text{SnCH}=\text{CHSnEt}_3$ (<i>trans</i>)	-59.4	CDCl_3		251
$\begin{array}{c} \text{R}^2 \qquad \text{R}^3 \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{Et}_3\text{Sn} \qquad \text{BR}_2^1 \end{array}$				
R^1	R^2	R^3		
Et	H	Et	CDCl_3	272
Et	Me	Et	CDCl_3	272
Et	SnEt_3	Et	CDCl_3	272
			-42.2 (R^2)	
$(\text{Et}_3\text{Sn})_2\text{C}=\text{C}=\text{C}(\text{Et})\text{C}(\text{BEt}_2)(\text{SnEt}_3)_2$	-19.4 ($\text{SnC}=\text{C}$)	CDCl_3		272
	-7.8 (Sn_2C)			
$(\text{Et}_3\text{Sn})_2\text{C}=\text{C}=\text{CHC}(\text{BC}_8\text{H}_{14})(\text{SnEt}_3)_2$	-19.9 ($\text{Sn}_2\text{C}=\text{C}$)	CDCl_3	<i>d</i>	272
	-4.8 (Sn_2C)			
$\text{Et}_3\text{Sn}-\text{C}\equiv\text{CH}$	-52	30% CCl_4		277
	-56.5	C_6D_6		159
	-56.3	CDCl_3		159
$\text{Et}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Me}$	-56.7	C_6D_6		159
	-56.4	CDCl_3		159
$\text{Et}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnEt}_3$	-60.2	C_6D_6		159
	-60.0	CDCl_3		159

^a For more $\delta^{119}\text{Sn}$ values of organotriethylstannanes see review 3.^b For other conditions see review 3.^c This appears to be the correct value, in agreement with recent direct PFT ^{119}Sn -NMR measurements.⁷⁶^d BC_8H_{14} = 9-Borabicyclo[3.3.1]nonane.

shift of the ^{119}Sn resonances to lower frequencies in going from tetrahedral to trigonal-pyramidal or octahedral symmetry is particularly convenient for studying even weak donor-acceptor interactions in solution. This includes covalent solute/solvent interaction, autoassociation, and/or intramolecular coordination.

There are, of course, other factors to be considered besides the coordination number. These are mainly related to the presence of low-lying excited states

TABLE 5

Organotrialkyl(C₃H₇, C₄H₉, C₈H₁₇) tin compounds, coordination number = 4^a

Compound	$\delta^{119}\text{Sn}$	Solvent	Notes	Reference
Pr ⁿ ₄ Sn	-16.8	—		278
Pr ⁿ ₃ SnBu ⁱ	-11.8	—		99
Pr ⁿ ₃ SnCH=CHOBu ⁿ	-50.6	CCl ₄		279
Pr ⁱ ₄ Sn	-43.9	—		278
	-42.6	?		280
Pr ⁱ ₃ SnBu ⁱ	-42.6	C ₆ D ₆		86
Pr ⁱ ₃ SnBu ⁱ	-48.7	—		99
Pr ⁱ ₃ Sn-chex	-55.4	?		280
Bu ⁿ ₄ Sn	-12.0	—		281
	-6.6	CCl ₄		262, 279
	-11.5	CDCl ₃		161
Bu ⁿ ₃ SnBu ⁿ	-14.1	C ₆ D ₆		86
Bu ⁿ ₃ SnBu ⁱ	-7.9	—		99
1-Bu ⁿ ₃ Sn-norbornane (<i>exo</i>)	-13.5	C ₆ D ₆	<i>b,c</i>	101
1-Bu ⁿ ₃ Sn-norbornane (<i>endo</i>)	-12.4	C ₆ D ₆	<i>b,d</i>	101
1-Bu ⁿ ₃ Sn-2-Ph-chex	-21.8	C ₆ D ₆	<i>b,e</i>	101
(<i>cis</i>)-1-Bu ⁿ ₃ Sn-5-Me-2-cyclohexenyl	-18.7	C ₆ D ₆		102, 282
(<i>trans</i>)-1-Bu ⁿ ₃ Sn-5-Me-2-cyclohexenyl	-19.6	C ₆ D ₆		102, 282
Bu ⁿ ₃ SnCH ₂ OEt	-37.4	C ₆ D ₆		364
1-Bu ⁿ ₃ Sn-3,4-Me ₂ -6-CO ₂ Me-3-cyclohexenyl	-13.0	C ₆ D ₆	<i>f,g</i>	101
Bu ⁿ ₃ SnCH(Cl)OEt	-28.2	C ₆ D ₆		364
Bu ⁿ ₃ SnCH(OEt) ₂	-57.8	—		283
Bu ⁿ ₃ Sn—Ph	-41.7	—	<i>h</i>	284
Bu ⁿ ₃ SnCH=CHPh (<i>cis</i>)	-56.0	C ₆ D ₆		102
Bu ⁿ ₃ SnCH=CHPh (<i>trans</i>)	-43.2	C ₆ D ₆		102
Bu ⁿ ₃ SnCH=CHBu ⁿ (<i>cis</i>)	-60.8	C ₆ D ₆		102
Bu ⁿ ₃ SnCH=CHBu ⁿ (<i>trans</i>)	-50.3	C ₆ D ₆		102
Bu ⁿ ₃ SnC(Pr ⁿ)=CHPr ⁿ (<i>cis</i>)	-53.5	C ₆ D ₆		102
Bu ⁿ ₃ SnC(CO ₂ Me)=CH(CO ₂ Me) (<i>cis</i>)	-37.8	C ₆ D ₆		102
Bu ⁿ ₃ SnC(CO ₂ Me)=CH(CO ₂ Me) (<i>trans</i>)	-20.5	C ₆ D ₆		102
Bu ⁿ ₃ SnCH=CH(CO ₂ Me) (<i>cis</i>)	-57.6	C ₆ D ₆		102
Bu ⁿ ₃ SnCH=CH(CO ₂ Me) (<i>trans</i>)	-46.0	C ₆ D ₆		102
Bu ⁿ ₃ SnC(CO ₂ Me)=CH ₂	-40.0	C ₆ D ₆		102
Bu ⁿ ₃ SnC(Me)=CH(CO ₂ Et) (<i>cis</i>)	-52.7	C ₆ D ₆		102
Bu ⁿ ₃ SnC(CO ₂ Et)=CHMe (<i>cis</i>)	-48.6	C ₆ D ₆		102
Bu ⁿ ₃ SnC(CO ₂ Et)=CHMe (<i>trans</i>)	-32.9	C ₆ D ₆		102
Bu ⁿ ₃ SnCH=C(Et)BEt ₂ (<i>cis</i>)	-62.2	CDCl ₃		272
(Bu ⁿ ₃ Sn) ₂ C=C(Et)BEt ₂	-53.7 (<i>cis</i>)	CDCl ₃	<i>i</i>	272
	-55.2 (<i>trans</i>)			
(Bu ⁿ ₃ Sn) ₂ C=C=C(Et)C(BEt ₂)(SnBu ⁿ ₃) ₂	-28.3 (Sn ₂ C=)	CDCl ₃		272
	-18.9 (Sn ₂ C)			
(Bu ₃ Sn) ₂ C=C=CHC(BC ₈ H ₁₄)(SnBu ⁿ ₃) ₂	-27.5 (Sn ₂ C=)	CDCl ₃	<i>j</i>	272
	-14.0 (Sn ₂ C)			
Bu ⁿ ₃ Sn—C≡C—H	-69.0	CDCl ₃		161
Bu ⁿ ₃ Sn—C≡C—SnBu ⁿ ₃	-74.3	CDCl ₃		
Bu ⁱ ₃ SnBu ⁱ	-27.4	C ₆ D ₆		86

TABLE 5 (*cont.*)

Compound	$\delta^{119}\text{Sn}$	Solvent	Notes	Reference
Bu^t_4Sn	-45.2 -45.34 -45.76	C_6D_6		86
Bu^t_3SnMe	-25.4	—		4
$(\text{Bu}^t\text{CH}_2)_3\text{SnBu}^s$	-40.6	C_6D_6		86

^a For more $\delta^{119}\text{Sn}$ data of organotrialkyltin compounds see review 3.

^b Deuterated in the 2 position.

^c $\delta^{119}\text{Sn}$ of the 2-Ph(*exo*) derivative: -11.1.¹⁰¹

^d $\delta^{119}\text{Sn}$ of the 2-Ph(*exo*) derivative: -26.4.¹⁰¹

^e The Bu^n_3Sn and Ph groups are in axial and equatorial positions, respectively.

^f Deuterated in 6 position.

^g The Bu^n_3Sn — and CO_2Me — groups are in axial and equatorial positions, respectively; $\delta^{119}\text{Sn}$ of the isomer with both groups in equatorial positions: -15.5.

^h For other conditions see review 3.

ⁱ See Fig. 1.

^j BC_8H_{14} , 9-Borabicyclo[3.3.1]nonane.

and to the effective nuclear charge of the tin atom. Frequently, these influences mask each other and their separation is difficult. A proper example for a consideration of the effects of paramagnetic circulation of charge is found in the monomeric bis[*N,N*-bis(trimethylsilyl)amino]tin(II), which has a bent structure (N-Sn-N angle = 96°) in the vapour phase.⁷⁴ It can be assumed that circulation of charge from the trigonal plane into the underoccupied tin $p\pi$ orbital deshields the tin atom as evidenced by the extreme high-frequency shift of the ^{119}Sn resonance.^{75,366} This corresponds

TABLE 6

Various tetraalkyltin compounds, tin coordination number = 4

Compound	$\delta^{119}\text{Sn}$	Solvent	Reference
Me_2SnEt_2	+7	20% CCl_4	277
$\text{Me}_2\text{SnPr}^n\text{Et}$	-2	80% C_6H_6	8
$\text{Me}_2\text{SnPr}^n_2$	-4.5	—	89
$\text{Me}_2\text{SnBu}^n_2$	-3.0	CDCl_3	76
$\text{Me}_2\text{SnBu}^t_2$	+11.5	—	4
$\text{Me}_2\text{Sn}(\text{CH}_2)_4$	+53.5	—	89
$\text{Me}_2\text{Sn}(\text{CH}_2)_5$	-42.5	—	89
$(\text{CH}_2)_4\text{Sn}(\text{CH}_2)_4$	+121	—	4
$(\text{CH}_2)_5\text{Sn}(\text{CH}_2)_5$	-80	—	4

TABLE 7

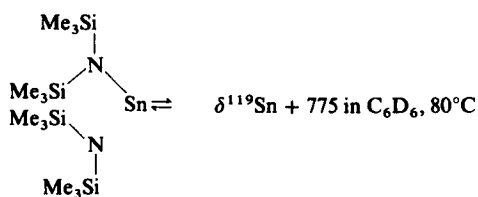
Organotriphenyltin compounds, tin coordination number = 4^a

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
Ph_3SnMe	-98	30% CCl_4		277
	-93	CH_2Cl_2		8
Ph_3SnEt	-98.6	C_6D_6		285
Ph_3SnPr^i	-106.7	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{cPr}$	-105.2	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{Bu}^n$	-101.5	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{Bu}^s$	-105.5	CDCl_3		86
$\text{Ph}_3\text{Sn}-\text{cBu}$	-101.5	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{chex}$	-113.7	CHCl_3		278
$\text{Ph}_3\text{Sn}-\text{CH}_2\text{chex}$	-103.1	C_6D_6		285
$\text{Ph}_3\text{Sn}^a(\text{CH}_2)_3\text{CH}(\text{Me})\text{SnPh}_3^b$	-95.5	C_6D_6		286
	-90.2			
$\text{Ph}_3\text{Sn}-\text{CH}_2\text{CH}(\text{Me})\text{Ph}$	-107.3	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{CH}_2\text{CH}=\text{CH}_2$	-123.2	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	-100.9	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{CH}_2\text{Ph}$	-118.0	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{CH}_2$ -1-naphthyl	-118.6	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{CH}_2\text{SPh}$	-118	CH_2Cl_2	<i>b</i>	133
Ph_4Sn	-128.1	CDCl_3	<i>c</i>	66
$\text{Ph}_3\text{SnCH}=\text{CHPh}$	-132.4	C_6D_6		285
$\text{Ph}_3\text{Sn}-\text{C}\equiv\text{C}-\text{H}$	-171.0	CDCl_3		76
$\text{Ph}_3\text{Sn}-\text{C}\equiv\text{C}-\text{SnPh}_3$	-176.1	CDCl_3		76
$\text{Ph}_3\text{Sn}-\text{C}(\text{S})\text{SMe}$	-192	CH_2Cl_2		287
$\text{Ph}_3\text{Sn}-\text{C}(\text{S})\text{SCH}_2\text{Ph}$	-191	CH_2Cl_2		287
$\text{Ph}_3\text{Sn}-\text{C}(\text{S})\text{SC}_3\text{H}_5$	-192	CH_2Cl_2		287
$\text{Ph}_3\text{Sn}-\text{C}(\text{S})\text{NHMe}$	-49	CH_2Cl_2		287
$\text{Ph}_3\text{Sn}-\text{C}(\text{S})\text{N}(\text{CH}_2)_4$	-55	CH_2Cl_2	<i>d</i>	287

$ \begin{array}{c} \text{Ph}_3\text{Sn} \quad \text{S} \quad \text{PPh}_3 \\ \quad \diagdown \quad \diagup \\ \quad \text{C} \quad \text{Pt} \\ \quad \diagup \quad \diagdown \\ \text{R} \quad \quad \text{PPh}_3 \\ \text{R} \end{array} $				
SMe	-185	CH_2Cl_2	<i>e</i>	287
SCH_2Ph	-182	CH_2Cl_2	<i>e</i>	287
SC_3H_5	-184	CH_2Cl_2	<i>e</i>	287
NHMe	-54	CH_2Cl_2	<i>e</i>	287
$\text{N}(\text{CH}_2)_4$	-56	CH_2^2Cl_2	<i>d,e</i>	287

^a For other organotriphenyltin compounds see review 3 and references 370 and 371.^b The sign in review 3 for this $\delta^{119}\text{Sn}$ value and for the $\delta^{119}\text{Sn}$ values of the analogous compounds $\text{Ph}_3\text{SnCH}_2-\text{S}(\text{C}_6\text{H}_4-\text{X})$ should be negative, as given in review 288.^c For other conditions see review 3; this value is believed to be correct.^d In the paper the amino group is given as *pyrr*, with *N*-pyrrolyl in the text but $\text{N}(\text{CH}_2)_4$ in the scheme.^e $^2J(^{195}\text{Pt}^{119}\text{Sn})$: 237–250 Hz.

to a high-frequency shift of ~ 700 ppm with respect to the trimethylstannyl-amides (see Table 19).



In contrast to the monomeric stannylenes the ^{119}Sn resonances of bis(cyclopentadienyl) derivatives of Sn(II) are found at exceptionally low frequency^{4,77} (Table 8). Molecular orbital calculations⁷⁸ assign the highest occupied molecular orbital (HOMO), $3a_1$, of the bent $(\text{C}_5\text{H}_5)_2\text{Sn}$ molecule⁷⁹ to the nonbonding electron pair on the tin atom. However, the antibonding MO, $2b_2$, in the stannocene, corresponding to the lowest unoccupied molecular orbital (LUMO) with almost pure p character in the stannylenes, is expected to lie at rather high energy. This prevents efficient paramagnetic charge circulation as shown by the highly shielded tin atoms in stannocenes. Similar arguments, based on MO calculations for $[(\text{C}_5\text{H}_5)\text{Sn}]^+$,⁷⁸ predict a highly shielded tin atom in the pentamethylcyclopentadienyl tin cation in spite of the positive charge. Accepting the π complex (η^5) structure of the $(\text{C}_5\text{H}_5)\text{Sn}(\text{II})$ compounds we find again that a high coordination number of the tin atom is related to high shielding [see, for comparison, $\delta^{119}\text{Sn}$ of η^1 -cyclopentadienyltin(IV) compounds, Table 8].

On the other hand, both the effective charge of the tin atom *and* high coordination number may be invoked to account for the highly shielded tin atoms in the naked nonrigid polyhedral anions like $[\text{Sn}_9]^{4-}$ ($\delta^{119}\text{Sn}$ -1230^{80,81}) or $[\text{Sn}_4]^{2-}$ ($\delta^{119}\text{Sn}$ - 1895)⁸² (see Table 21). MO calculations⁸³ of these clusters corroborate this with respect to the charge of the tin atoms (e.g., in the series $[\text{Sn}_8\text{Ge}]^{4-}$, $[\text{Sn}_9]^{4-}$, $[\text{Sn}_8\text{Pb}]^{4-}$).

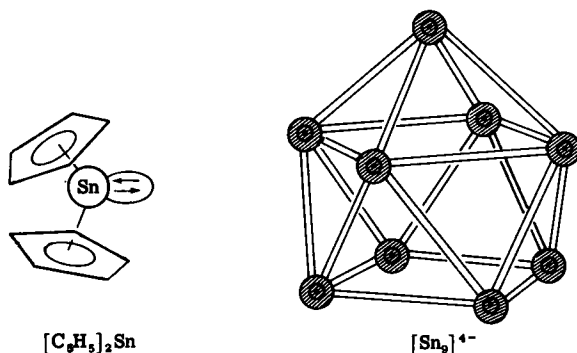


TABLE 8

Tetraorganyltin compounds, tin coordination number $\geq 4^a$

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$(\text{CH}_2=\text{CH}-\text{CH}_2)_3\text{SnBu}^a$	-34.3	—		279
$(\text{CH}_2=\text{CH}-\text{CH}_2)_4\text{Sn}$	-47.9	—	<i>b</i>	279
$(\text{PhCH}_2)_2\text{SnEt}_2$	-13	40% CH_2Cl_2		277
$(\text{PhCH}_2)_3\text{SnEt}$	-23	40% CH_2Cl_2		277
$(\text{PhCH}_2)_4\text{Sn}$	-36	CH_2Cl_1		289
$(\text{C}_5\text{H}_5)_2\text{SnMe}_2$	+23	CCl_4		261
$(\text{C}_5\text{H}_5)_3\text{SnMe}$	-7.0	CCl_4		261
$(\text{C}_5\text{H}_5)_4\text{Sn}$	-24.4	CCl_4	<i>d</i>	261
	-27.2	?		77
$(\text{C}_5\text{H}_5)_2\text{Sn}$	-2199	C_6H_{12}		4
$(\text{C}_5\text{H}_4\text{Me})_2\text{Sn}$	-2171.1	CDCl_3		77
Ph_2SnMe_2	-60	—		278
$(p\text{-CH}_2=\text{CH}-\text{C}_6\text{H}_4)_2\text{SnMe}_2$	-56.2	C_6D_6		286
Ph_2SnEt_2	-66	50% CH_2Cl_2		277
$\text{Ph}_2\text{SnBu}^a_2$	-65.9	—		278
$(p\text{-CH}_2=\text{CH}-\text{C}_6\text{H}_4)_2\text{SnBu}^a_2$	-69.4	CDCl_3		286
$\text{Ph}_2\text{Sn}(\text{CH}_2)_4$	0	CH_2Cl_2		(96, 290)
$\text{Ph}_2\text{Sn}(\text{CH}_2)_5$	-66	CH_2Cl_2		(96, 290)
	-107.7	C_6D_6		286
$(p\text{-CH}_2=\text{CH}-\text{C}_6\text{H}_4)_2\text{Sn}(\text{CH}_2)_5$	-106.2	C_6D_6		286
$\text{Ph}_2\text{Sn}(\text{CH}_2)_6$	-57.4	40% CH_2Cl_2		4
$\text{Ph}_2\text{Sn}(\text{CH}_2)_8\text{SnPh}_2$	-74	CH_2Cl_2		(96, 290)
$\text{Ph}_2\text{Sn}(\text{C}_8\text{H}_4\text{-}p\text{-CH}=\text{CH}_2)_2$	-126.2	C_6D_6		286
$(p\text{-Me-C}_6\text{H}_4)_2\text{Sn}(\text{C}_6\text{H}_4\text{-}p\text{-CH}=\text{CH}_2)_2$	-122.3	C_6D_6		286
$(p\text{-CH}_2=\text{CH}-\text{C}_6\text{H}_4)_4\text{Sn}$	-123.9	C_6D_6		286
$(3\text{-furyl})_2\text{SnMe}_2$	-80.1	CDCl_3		265
$(3\text{-furyl})_3\text{SnMe}$	-118.9	CDCl_3		265
$(3\text{-furyl})_4\text{Sn}$	-157.4	CDCl_3		265
$(2\text{-thienyl})_2\text{SnMe}_2$	-69.3	CDCl_3		266
$(2\text{-thienyl})_3\text{SnMe}$	-104.5	CDCl_3		266
$(2\text{-thienyl})_4\text{Sn}$	-143.6	CDCl_3		240
	-148.6	CDCl_3		266
$(\text{CH}_2=\text{CH})_2\text{SnMe}_2$	-79.4	—		278
	-84.0	—		3
$[\text{CH}_2=\text{C}(\text{Me})]_2\text{SnMe}_2$	-69	CDCl_3		90
$[\text{CH}(\text{Me})=\text{CH}]_2\text{SnMe}_2$ (<i>cis,cis</i>)	-116	CDCl_3		90
$[\text{CHMe}=\text{CH}]_2\text{SnMe}_2$ (<i>trans,trans</i>)	-84	CDCl_3		90
$[\text{CHMe}=\text{CH}]_2\text{SnMe}$ (<i>cis,trans</i>)	-100	CDCl_3		90
$[\text{CH}_2=\text{C}(\text{Me})][\text{CHMe}=\text{CH}]\text{SnMe}_2$ (<i>cis</i>)	-92	CDCl_3		90
$[\text{CH}_2=\text{C}(\text{Me})][\text{CHMe}=\text{CH}]\text{SnMe}_2$ (<i>trans</i>)	-76	CDCl_3		90
$(\text{CH}_2=\text{CH})_2\text{SnEt}_2$	-81	20% CCl_4		277
$(\text{CH}_2=\text{CH})_2\text{SnBu}^a_2$	-86.4	—		278
$(\text{CH}_2=\text{CH})_3\text{SnMe}$	-124	—		3
$(\text{CH}_2=\text{CMe})_3\text{SnMe}$	-106	CDCl_3	<i>c</i>	90

TABLE 8 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$[\text{CH}(\text{Me})=\text{CH}]_3\text{SnMe}$ (<i>cis</i>)	-175	CDCl_3	<i>c</i>	90
$[\text{CH}(\text{Me})=\text{CH}]_3\text{SnMe}$ (<i>trans</i>)	-123	CDCl_3	<i>c</i>	90
$(\text{CH}_2=\text{CH})_4\text{Sn}$	-157.4	CCl_4	<i>d</i>	279
$(\text{CH}_2=\text{CMe})_4\text{Sn}$	-143	CDCl_3	<i>e</i>	90
$[\text{CH}(\text{Me})=\text{CH}]_4\text{Sn}$ (<i>cis</i>)	-234	CDCl_3	<i>e</i>	90
$[\text{CH}(\text{Me})=\text{CH}]_4\text{Sn}$ (<i>trans</i>)	-162	CDCl_3	<i>e</i>	90
$(\text{HC}\equiv\text{C})_2\text{SnMe}_2$	-153.8	CH_2Cl_2	<i>f</i>	91
	-154.5	C_6D_6		159
$(\text{MeC}\equiv\text{C})_2\text{SnMe}_2$	-156.0	CH_2Cl_2		91
	-157.6	C_6D_6		159
$(\text{Bu}^*\text{C}\equiv\text{C})_2\text{SnMe}_2$	-156.7	?		156
$(\text{Bu}^*\text{C}\equiv\text{C})_2\text{SnMe}_2$	-157.6	CH_2Cl_2		91
$(\text{PhC}\equiv\text{C})_2\text{SnMe}_2$	-147.6	CDCl_3		
$(\text{HC}\equiv\text{C})_2\text{SnEt}_2$	-141.0	CCl_4		277
	-141.3	C_6D_6		159
	-141.0	CDCl_3		159
$(\text{MeC}\equiv\text{C})_2\text{SnEt}_2$	-142.9	C_6D_6		159
	-141.0	CDCl_3		159
$(\text{HC}\equiv\text{C})_2\text{SnPr}^i$	-141.7	CH_2Cl_2		91
$(\text{HC}\equiv\text{C})_2\text{SnPh}_2$	-227.5	CDCl_3	<i>g</i>	252
$(\text{Me}_3\text{SiC}\equiv\text{C})_2\text{SnMe}_2$	-167.4	CDCl_3		157
$(\text{MeC}\equiv\text{C})_2\text{SnPh}_2$	-225.3	CDCl_3		
$(\text{PhC}\equiv\text{C})_2\text{SnPh}_2$	-219.5	CDCl_3		
$(\text{HC}\equiv\text{C})\text{Sn}(\text{Ph}_2)\text{C}\equiv\text{CSn}(\text{Ph}_2)\text{C}\equiv\text{C}-\text{H}$	-234.6	CDCl_3	<i>h</i>	252
$(\text{Bu}^*\text{C}\equiv\text{C})_3\text{SnMe}$	-248.6	?		156
$(\text{HC}\equiv\text{C})_3\text{SnPr}^i$	-244.9	CH_2Cl_2		274
$(\text{HC}\equiv\text{C})_4\text{Sn}$	-356.3	CDCl_3	<i>i</i>	161
$(\text{MeC}\equiv\text{C})_4\text{Sn}$	-348.0	CDCl_3	<i>j</i>	159
$(\text{Bu}^*\text{C}\equiv\text{C})_4\text{Sn}$	-345.9	?		156

^a Alkyl, benzyl, cyclopentadienyl, aryl, heteroaryl, vinyl, and alkynyl derivatives. For other tetra-organyltin compounds see reviews 3 and 4 and references 369 and 370.

^b Change of the $\delta^{119}\text{Sn}$ value to -147.5 on dilution with CCl_4 .

^c $\delta^{119}\text{Sn}$ values for the other isomers are assigned as follows: *cis, cis, trans* (-158); *cis, trans, trans* (-142); *cis, cis, ipso* (-150); *cis, trans, ipso* (-132); *trans, trans, ipso* (-118); *cis, ipso, ipso* (-127); *trans, ipso, ipso* (-112).

^d For other conditions see review 3.

^e $\delta^{119}\text{Sn}$ values for the other isomers are assigned as follows: *cis, cis, cis, trans* (-211); *cis, cis, trans, trans* (-191); *cis, trans, trans, trans* (-175); *cis, cis, cis, ipso* (-208); *cis, cis, trans, ipso* (-187); *cis, trans, trans, ipso* (-171); *trans, trans, trans, ipso* (-157); *cis, cis, ipso, ipso* (-184); *cis, trans, ipso, ipso* (-167); *trans, trans, ipso, ipso* (-153); *cis, ipso, ipso, ipso* (-162); *trans, ipso, ipso, ipso* (-149).

^f $\delta^{119}\text{Sn}$ of the complex $[\text{Me}_2\text{Sn}(\text{C}_2\text{H})_2[\text{Co}(\text{CO})_6]_2]$: -4.2 (CDCl_3).²⁵²

^g $\delta^{119}\text{Sn}$ of the complex $[\text{Ph}_2\text{Sn}(\text{C}_2\text{H})_2[\text{Co}(\text{CO})_6]_2]$: -114.6 (CDCl_3).²⁵²

^h $\delta^{119}\text{Sn}$ of the complex $[(\text{Ph}_2\text{Sn})_2(\text{C}_2)(\text{C}_2\text{H})_2\text{Co}(\text{CO})_6]_3]$: -122 (CDCl_3).²⁵²

ⁱ Obtained by direct ^{119}Sn NMR, assignment proved by ^1H coupled ^{119}Sn -NMR spectrum; the $\delta^{119}\text{Sn}$ value -279²⁷⁷ obtained by $^1\text{H}\{^{119}\text{Sn}\}$ INDOR spectra is not correct.

^j This corrects a misprint.¹⁵⁹

2. Substituent effects and multiple substitution

The shielding of the ^{119}Sn nucleus is significantly affected by the number of various substituents present, and by their electronic and steric properties. Very often a direct comparison of substituent effects is hampered because bulky groups, either at the tin atom or at the substituent atom, are required to prevent autoassociation (e.g., fluorides or alkoxides). The bulk of the valves of $\delta^{119}\text{Sn}$ available concerns compounds containing tin atoms with coordination number 4. The qualitative application of the theory of nuclear screening predicts major changes in σ when the tetrahedral geometry is distorted and the symmetry is lowered, e.g., to C_{3v} or C_{2v} .⁸⁴ This is seen in Fig. 6, which shows the dependence of the screening of ^{119}Sn in $\text{Me}_{4-n}\text{SnX}_n$ on the number (n) of groups X. A comparison of the $\delta^{119}\text{Sn}$ values for the compounds SnX_4 (Fig. 6) reveals that there is no obvious general relationship between $\delta^{119}\text{Sn}$ and other empirical parameters. Instead it appears that a number of possibly counteracting influences should be considered: (1) electronegativity, (2) excitation energies, and (3) neighbour contributions. It seems that the evaluation of neighbour contributions, in particular, constitutes a serious problem for the interpretation of tin chemical shifts.

Bearing in mind that at present there is no way of separating the contributions to tin nuclear shielding, an exceedingly complex situation arises for the theoretical understanding of ^{119}Sn chemical shifts. This also emerges from Fig. 6, in which is seen the familiar "sagging" pattern of the $\delta^{119}\text{Sn}$ values depending on X and n ; the differing amounts of "sagging" for various ligands X reflect the aforementioned counteracting influences on tin nuclear shielding and additional features introduced by the lower symmetry around the tin atom.⁸⁵

Therefore, any simplified approach to nuclear screening such as that given in Eq. (9) is inadequate to interpret $\delta^{119}\text{Sn}$ data in more than a qualitative way. However, from a purely empirical and practical point of view, the picture in Fig. 6 is encouraging. The $\delta^{119}\text{Sn}$ values available today are indicative of the type of substituent X and of the number of substituents present. Hence, ^{119}Sn -NMR spectra may be used to prove the purity of a given tin compound and to investigate the equilibrium of this compound with other species in solution and, of course, the dynamic properties in general.³⁶⁷ Thus, it is obvious that already the large range of ^{119}Sn chemical shifts is in favour of ^{119}Sn NMR being used as a useful analytical tool. The tetra-*sec*-butyltin molecule may serve as an instructive example to demonstrate some of these points. Owing to the presence of four identical chiral centres around the tin atom, three diastereomeric compounds should exist. Neither ^1H nor ^{13}C NMR reveals reliable information. However, in the ^{119}Sn -NMR spectra three signals are found (-45.2 , -45.3 , -45.8) with relative intensities close to the predicted ratio, assuming a random distribution ($37.5:50:12.5$).^{86,87}

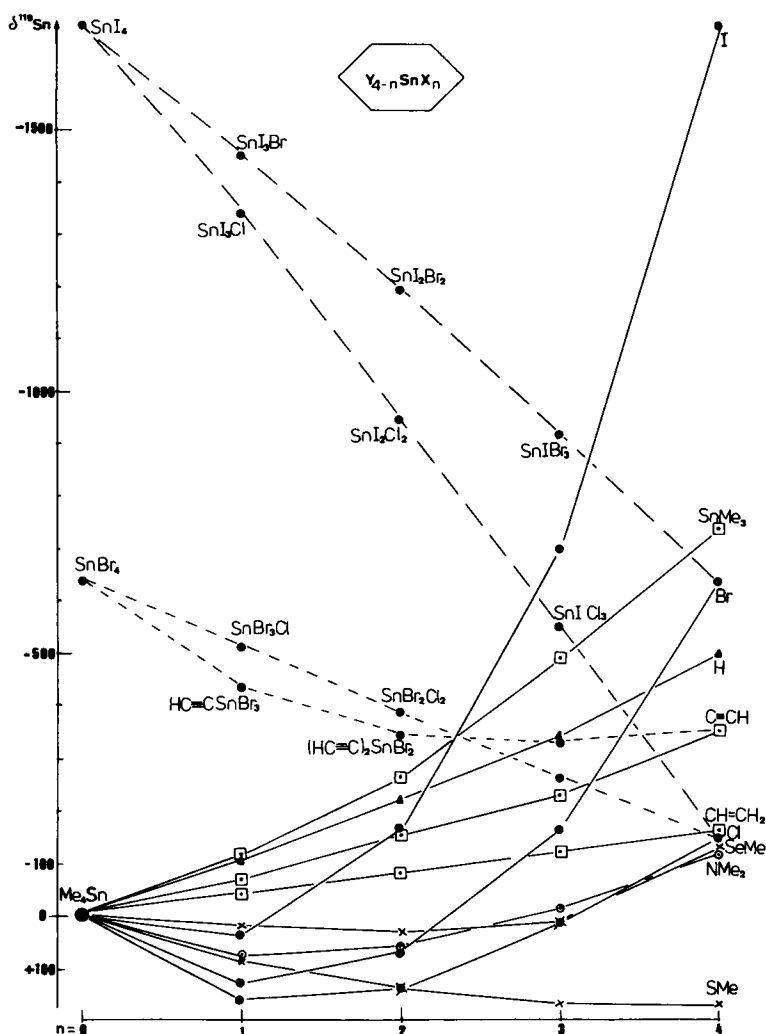
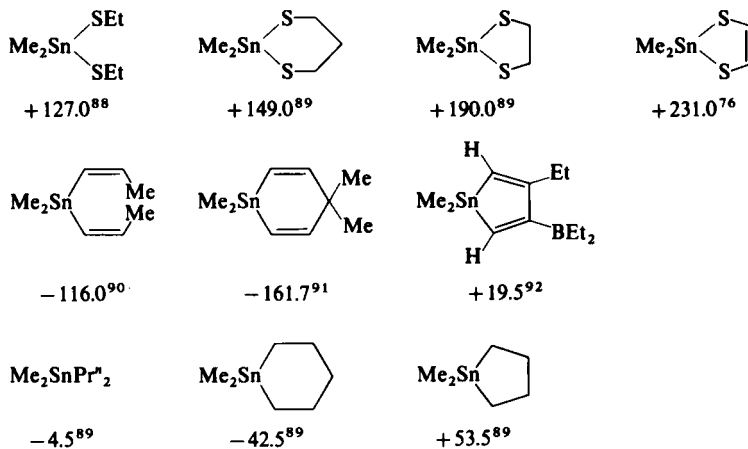


FIG. 6. Dependence of nuclear screening of ^{119}Sn on the number (n) of groups X . Compare Tables 3–9 for tetraorganylstannanes, Table 10 for tin hydrides, Tables 11–13, 20, 24 and 25 (tin—Group VII), Tables 13–18, 21, and 24 (tin—Group VI), Tables 13, 14, 18–20, and 24 (tin—Group V), Table 21 (tin—Group IV), Table 22 (tin—Group III), Table 23 (tin—lithium), and Tables 24 and 25 (tin—transition metal compounds) for more detailed information.

3. Effects of interbond angles at the tin atom

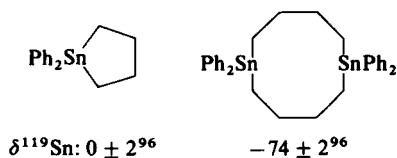
Many shielding effects, which frequently are hardly noticeable in ^{13}C NMR, are amplified in ^{119}Sn NMR. Changes in the bond angles brought upon the system by steric constraints (e.g., ring closure) are reflected by large

shifts of the ^{119}Sn resonances. This is shown, for example, with tin-sulphur and tin-carbon bonds. The ^{119}Sn resonance is shifted to significantly higher frequencies in the five-membered rings; this appears to be a general effect. A trigonal-bipyramidal five-coordination of tin in the dimethyldithiostannolane has been revealed by X-ray studies, with the molecules arranged in a



chain.^{93,94} It has been suggested⁹³ that the small bond angle ($\angle \text{S-Sn-S} = 89.6^\circ$) prevails to some extent in solution (in agreement with a $^1\text{H-D}$ NMR study)²³ and, therefore, accounts for the deshielded tin atom.⁸⁹ Similar arguments may be valid in the case of dithiastannolene in which the shielding of the tin atom is even smaller.

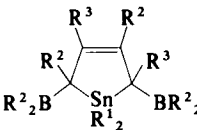
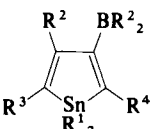
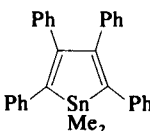
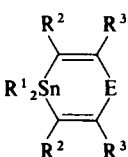
In the cyclic tetraorganylstannanes it is evident that ^{119}Sn NMR is an extremely sensitive tool for distinguishing between six-membered and five-membered cyclic compounds⁹⁵ (see Table 9). In the case of the diphenylstannolane system the presence of a 10-membered ring, the dimer, is readily shown by ^{119}Sn NMR.⁹⁶ Again, the shielding of the tin atom in the stannolane is reduced with respect to the 1,6-distannacyclodecane derivative:



This deshielding appears to be connected with the probability of excitation of σ electrons since it is frequently found for other main group nuclei (e.g., ^{11}B , ^{29}Si , ^{207}Pb) in similar bonding situations.

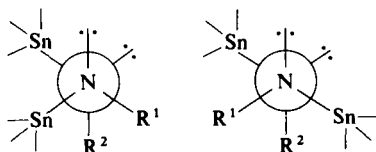
TABLE 9

Unsaturated cyclic tetraorganyl tin compounds, tin coordination number = 4

Compound	$\delta^{119}\text{Sn}$	Solvent	Reference																																																																																																																			
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4. Temperature dependence

As a result of autoassociation or covalent solvent interactions, tin nuclear shielding depends heavily on temperature. In the absence of these effects the nuclear shielding will depend on rotation, vibration, electrostatic solvent-solute interactions, and conformational equilibria within the compound under consideration.⁹⁷ It has been found that the shielding of ^{119}Sn increases roughly linearly with increasing temperature,⁹⁸⁻¹⁰⁰ although the slope of this relationship is expected to depend critically upon the type of compound and, possibly, also upon the solvent used. A recent study¹⁰⁰ shows the temperature dependence of $\delta^{119}\text{Sn}$ to indicate different conformational populations in trimethylstannylhydrazines. According to the projections, which both show the gauche conformation, the energies of the conformers depend on the nature of the substituents R^1 and R^2 (and a nonlinear change of $\delta^{119}\text{Sn}$ with temperature is observed):



5. Isotope effects

It appears¹⁰ that all claims of a significant $^{117/119}\text{Sn}$ primary isotope effect are based on inaccurate measurements. The difference in shielding $\delta^{117}\text{Sn}/\delta^{119}\text{Sn}$ (expressed in ppm) can be safely neglected.¹⁰

Secondary isotope effects on the ^{119}Sn resonance, e.g., in deuterated organotin compounds, have been measured. Direct deuteration (Me_2SnD_2)³ and indirect deuteration $[\text{Sn}(\text{CD}_3)]_4$ ³⁶ shift the ^{119}Sn resonance to lower frequency. However, no recent systematic studies on this subject have been carried out. In various studies, specifically ^2H -labeled tetraorganylstannanes have been obtained in order to determine the stereochemistry as a function of $^1J(^{119}\text{Sn}^2\text{H})$.^{87,101,102} The $\delta^{119}\text{Sn}$ values differ very little (≤ 0.1 ppm) from the values for nondeuterated compounds. Therefore, in routine ^{119}Sn -NMR spectra these effects are negligible when considering the influences of solvent, temperature changes, etc., on the ^{119}Sn resonances which are of the order of ± 0.1 ppm (even when an attempt is made to record the spectra under analogous conditions).

The isotope effect $^{12}\text{C}/^{13}\text{C} [\Delta\delta(^{13}\text{C})]$ in organotin compounds depends on the nature of the substituents. In addition to the expected effect of heavy isotopic substitution (low-frequency shift) there are examples where $\Delta\delta(^{13}\text{C}) \sim 0$ (see Fig. 7), and frequently, high-frequency shifts of the ^{119}Sn -resonances are observed.¹⁰³ $\Delta\delta(^{13}\text{C})$ in ppm¹⁰³: Me_4Sn , -0.018 ; Et_4Sn , -0.020 ; $\text{Me}_3\text{SnC}\equiv\text{CH}$, ± 0.002 (Me), -0.059 ($\text{C}\equiv$);

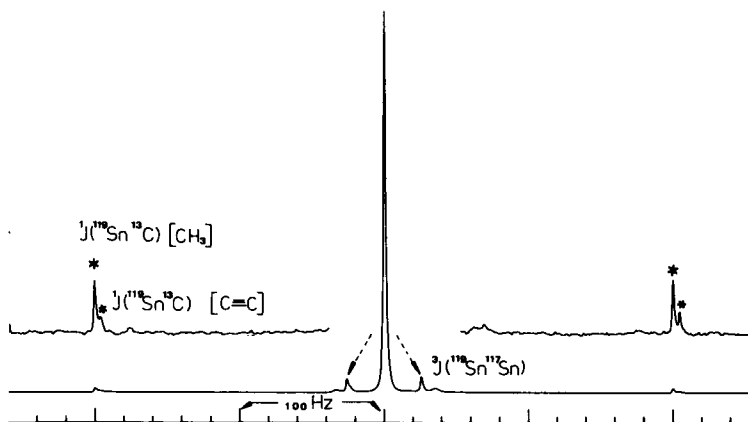
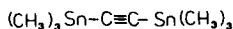


FIG. 7. ^{119}Sn -NMR spectrum at 74.63 MHz of bis(trimethylstannyl)ethyne in C_6D_6 , 20% w/v, 28°C , ^1H broadband decoupled; the centre of the $^{13}\text{CH}_3$ satellites corresponds exactly to the large ^{119}Sn resonance (± 0.2 Hz) whereas the centre of the $^{13}\text{C}\equiv$ satellites is shifted by 4 Hz = 0.054 ppm to low frequency. This is readily seen from the different intensities of the $^{13}\text{CH}_3$ and $^{13}\text{C}\equiv$ satellites and from the fact that both couplings, $^1J(^{119}\text{Sn}^{13}\text{CH}_3)$ and $^1J(^{119}\text{Sn}^{13}\text{C}\equiv)$, are of identical magnitude. The ^{13}C satellites from $^2J(^{119}\text{Sn}^{13}\text{C}\equiv)$ are masked by the ^{117}Sn satellites, $|^3J(^{119}\text{Sn}^{117}\text{Sn})| = 51$ Hz.

$\text{Me}_2\text{Sn}(\text{C}\equiv\text{CH})_2$, +0.016 (Me), -0.027 ($\text{C}\equiv$); $\text{MeSn}(\text{C}\equiv\text{CH})_3$, +0.025 (Me), -0.009 ($\text{C}\equiv$); $\text{Sn}(\text{C}\equiv\text{CH})_4$, +0.009.

C. Correlations between ^{119}Sn chemical shifts and other Group IV element chemical shifts

Since a great number of NMR parameters of Group IV elements are readily accessible (with the exception of the ^{73}Ge nucleus), comparing these data for isostructural compounds is clearly of interest. This has been done frequently, e.g., for $\delta^{13}\text{C}/\delta^{29}\text{Si}$,¹⁰⁴ for $\delta^{29}\text{Si}/\delta^{119}\text{Sn}$,¹⁰⁵ and for $\delta^{119}\text{Sn}/\delta^{207}\text{Pb}$.^{105,106} There are clearly broad parallels between the shielding of $^{29}\text{Si}/^{119}\text{Sn}$ or $^{119}\text{Sn}/^{207}\text{Pb}$, indicating that (1) the structures in solution are analogous and (2) the influences of various ligands can be compared with respect to bond polarity and excitation energies. Thus, the slopes of the straight lines resulting from the roughly linear correlations $\delta^{29}\text{Si}/\delta^{119}\text{Sn}$ and $\delta^{119}\text{Sn}/\delta^{207}\text{Pb}$ should correspond to the ratios of the radial expansion terms $\langle r^{-3} \rangle_{np}$. This is found to be the case for the correlation $\delta^{119}\text{Sn}/\delta^{29}\text{Si}$ (5.1,¹⁰⁵ to be compared with 4.5).⁴⁶ The deviation of the slope from the expected ratio of the radial expansion terms becomes much larger in the case of the $\delta^{207}\text{Pb}/\delta^{119}\text{Sn}$ correlation (slope ~ 3.0 , ratio $\langle r^{-3} \rangle_{6p}/\langle r^{-3} \rangle_{5p} = 1.4/1.9$).

It is likely that the calculation of values of $\langle r^{-3} \rangle_{np}$ becomes less reliable for heavy atoms. The correlation $\delta^{119}\text{Sn}/\delta^{207}\text{Pb}$ reported in the literature^{105,106} can be extended to include the $\delta^{119}\text{Sn}$ and $\delta^{207}\text{Pb}$ values of the polyhedral anions $[\text{Sn}_9\text{--}_n\text{Pb}_n]^{4-}$. However, the δ values of the monomeric Sn(II) and Pb(II) amides deviate considerably from the linear correlation. From the $\delta^{119}\text{Sn}$ value of bis[bis(trimethylsilyl)amino]tin(II) (+775), a $\delta^{207}\text{Pb}$ value of $\sim +1800$ to $+2400$ would be predicted for the analogous Pb(II) compound in contrast to the experimental value $\delta^{207}\text{Pb} = +4916$.⁷⁶

V. INDIRECT NUCLEAR SPIN-SPIN COUPLINGS, $^nJ(^{119}\text{SnX})$

A. General

The valence electron-mediated nuclear spin-spin coupling, J , is a scalar quantity and may be obtained directly from NMR spectra, in the present case either from ^{119}Sn - or X-NMR spectra. Since theoretical treatments of spin-spin couplings have been excellently described^{41,107-113} this summary concentrates on some aspects which are believed to be of major importance for ^{119}Sn -X spin-spin couplings.

According to Ramsey's formulation of the spin-spin coupling energies,¹⁰⁷ coupling involving electrons is described by more than one mechanism. The interaction between the nuclear magnetic moments and the electron orbital motion (spin-orbital term), and the dipolar interaction between the nuclear spins and the electron (spin-dipole term), are, in general, considered to be of minor importance in comparison to the contact term. The latter term takes into account the possibility that the electron may be found in the same place as the nucleus, as predicted by quantum mechanics. Although there is little theoretical and only limited experimental evidence, the contact term is assumed to dominate the coupling even when the heavier nuclei are involved.

As in the nuclear screening, σ , infinite summations over excited electronic states have to be taken into account in describing J . Fortunately, in contrast to σ , there is no gauge dependence problem to be considered in calculations of couplings, and the questionable reliability of results based on the difference of two more or less inaccurate parameters (σ_p and σ_d) is no problem. Therefore, most of the calculations or discussions of couplings do not suffer from too gross approximations, although we are still far from a detailed comprehension of all the data available. Various procedures have been developed to calculate couplings.^{41,113-115} However, for a more qualitative discussion, the original approach of Pople and Santry¹⁰⁹ is of advantage.

The contact term can be expressed, in Pople and Santry's MO treatment (independent electron model), as shown in Eq. (10),¹⁰⁹

$$K_{AB} = \frac{4}{9}\mu_0^2\mu_B^2\psi_A(0)^2\psi_B(0)^2\pi_{AB} \quad (10)$$

where K is the reduced coupling for nuclei A and B [$K_{AB} = (4\pi^2/h)J_{AB}(\gamma_A\gamma_B)^{-1}$], μ_0 is the permeability of free space, μ_B is Bohr's magneton, $\psi_A(0)^2$, $\psi_B(0)^2$ are the respective valence s electron densities, and π_{AB} is the mutual polarizability of the A and B s orbitals.

The mutual polarizability term (π_{AB}) represents the difference of one-electron energies. Clearly, both the magnitude and sign of K_{AB} reside in this term. By assuming constant values of singlet excitation energies, an average excitation energy, ΔE , is introduced¹⁰⁸ and π_{AB} is replaced,

$$\pi_{AB} = \Delta E^{-1} P_{S(A)S(B)}^2 \quad (11)$$

leading to values K_{AB} which are always positive and are linearly related to the " s character" ($P_{S(A)S(B)}^2$) of the A–B bond. This approach is extremely simplified and its application to nuclear spin–spin coupling involving heavy atoms, multiple bonding, or nuclei carrying lone electron pairs is not justified. Indeed, it seems that the interpretation of most of the features observed for $^1J(\text{SnX})$ requires one to consider the mutual polarizability term π_{SnX} . In addition, it has been pointed out that in the case of heavy nuclei, such as Sn or Pb, the relativistic analogue of Ramsey's theory should be used. Examples are given by calculations of spin–spin coupling tensors using a sum-over-states of relativistically parameterized extended Hückel (REX) wave functions.^{116,117} From this it appears that cautious use of nonrelativistic atomic valence s electron densities, $\psi_{\text{Sn}}(0)^2$, is advisable.¹¹⁷

The dominance of the contact energy for tin spin–spin couplings implies that the parameter $J(\text{SnX})$ is useful in discussions of structure and bonding. In this regard one is tempted to follow the well-known arguments available for a great number of carbon couplings. Accordingly, one finds many parallels between values of $J(\text{SnX})$ and $J(\text{CX})$.^{12,13} However, at the same time, there are many data pairs deviating from this concept. This indicates the additional influence of the large and polarizable ^{119}Sn nucleus leading to differing contributions to the contact interaction via the mutual polarizability term.

B. Patterns of couplings, $^1J(\text{SnX})$

1. One-bond couplings, $^1J(^{119}\text{SnX})$

There are a great number of $^1J(^{119}\text{SnX})$ values available for X taken throughout the periodic table. Reduced couplings, $^1K(^{119}\text{SnX})$, are given in Table 26 together with corresponding values of $^1K(^{13}\text{CX})$, $^1K(^{29}\text{SiX})$, and $^1K(^{207}\text{PbX})$. There are fairly regular changes of $^1K(\text{EX})$ ($\text{E} = ^{13}\text{C}$, ^{29}Si , ^{119}Sn) in the case of $\text{X} = ^1\text{H}$, ^{11}B , ^{13}C , ^{29}Si , ^{119}Sn , ^{207}Pb , ^{183}W , and the increase of $^1K(\text{EX})$ with increasing size of E corresponds to the change of valence s electron densities $\psi_E(0)^2$. This is no longer true for many values of $^1K(^{207}\text{PbX})$ ^{13,118} as a result of the large polarizability of this nucleus

together with the possible influence of relativistic effects concerning the Pb 6s electrons,¹¹⁷ which cannot be simply included in the value of $\psi_E(0)^2$. The relationship between the $^1K(\text{EX})$ values also breaks down for $\text{X} = ^{15}\text{N}$, $^{31}\text{P}(\text{III})$, $^{31}\text{P}(\text{V})$, ^{77}Se , ^{125}Te .¹² There are not enough data available for couplings to fluorine. All these X nuclei have either lone electron pairs or the Sn–X bond is much more polar [e.g., Sn–P(V)] than the corresponding C–N bond. This gives an indication that, in general, we would expect to find more negative contributions to the contact term in the case of Sn–X nuclear spin–spin couplings as compared with C–X or Si–X interactions. This means that, in all comparable compounds for which $^1K(^{13}\text{CX})$ or $^1K(^{29}\text{SiX})$ may be of either sign, a negative sign for $^1K(^{119}\text{SnX})$ is likely.

The comparison between $^1K(^{199}\text{Hg}^{119}\text{Sn})$, $^1K(^{195}\text{Pt}^{119}\text{Sn})$, and $^1K(^{199}\text{Hg}^{13}\text{C})$, $^1K(^{195}\text{Pt}^{13}\text{C})$ shows that the former values for ^1J seem to be very large, but again the ratio of the ^1K values differs very little from the ratio of the valence *s* electron densities $\psi_{^{119}\text{Sn}}(0)^2/\psi_{^{13}\text{C}}(0)^2$ (~ 8).³⁶³

a. $^1J(^{119}\text{Sn}^1\text{H})$. Values of $^1J(^{119}\text{Sn}^1\text{H})$ are listed together with the $\delta^{119}\text{Sn}$ data for some tin hydrides (Table 10). Of course, there are many more data in the literature for compounds which have not been studied by ^{119}Sn NMR.

In alkyltin hydrides the magnitude of $|^1J(^{119}\text{Sn}^1\text{H})|$ increases with *n* in the series $\text{R}_{4-n}\text{SnH}_n$ ($n = 1, 2, 3, 4$) and decreases with an increase of branching in the alkyl group:

$J(^{119}\text{Sn}^1\text{H})$ (Hz)				
R	R_3SnH	R_2SnH_2	RSnH_3	SnH_4
Me	–1744 ¹¹⁹	–1797 ¹²⁰	–1852 ¹¹⁹	–1930 ¹²⁰
Et	–1613 ¹²¹	–1690 ¹²¹	–1790 ¹⁷	—
Pr ⁱ	–1505 ¹²²	–1608 ¹²⁰	–1750 ¹²²	—
Bu ^t	—	–1554 ¹²²	—	—

In the series of phenyltin hydrides $\text{Ph}_{4-n}\text{SnH}_n$ the magnitude of $|^1J(^{119}\text{Sn}^1\text{H})|$ decreases with an increase in *n* from 1 to 3 as a result of the greater electronegativity of the phenyl group as compared with an alkyl group. These trends are very similar to those observed for the corresponding silanes¹²³ and may be attributed to rehybridization¹²⁴ at the tin atom.

b. $^1J(^{119}\text{Sn}^{13}\text{C})$. Owing to the large number of organotin compounds there is a wealth of $^1J(^{119}\text{Sn}^{13}\text{C})$ data. Therefore, only a small fraction of the results available can be addressed here. References 125–150 contain much material and should be consulted in addition to the references given in the text or in the tables for further information.

TABLE 10

Tin hydrides, tin coordination number ≥ 4

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
Me_3SnH	-104.5 (1744)	C_6H_6		9 119
Et_3SnH	-40.0 (1613.2)	C_6H_6 20% C_6H_6	<i>b</i>	9 121
Pr^n_3SnH	-89 (1600)	— Bu_2O		3 294
Bu^n_3SnH	-91.4 (1604.4)	CCl_4		279 295
	-89	—		2
	-95	—		37
Ph_3SnH	-164.5 -148 (1935.8)	— — —		4 37 296
Me_2SnH_2	-225 (1797)	10% C_6H_{12} , -20°C		170
	-229	—		3
Et_2SnH_2	-231 (1689.6)	80% C_6H_6 20% C_6H_6		9 121
Bu_2SnH_2	(1682)			122
Ph_2SnH_2	-234 (1928)	20% TMS		170 296
MeSnH_3	-346 (1852)	60% toluene, -35°C		258
EtSnH_3	-282 (1790.4)	50% in Bu^n_2O C_6H_6		9 121
PhSnH_3	-320 (1920)	—		3 170
SnH_4	-500	—	<i>c</i>	170
$[\text{SnH}_3]^+$	-186 (2960)	FSO_3H , -80°C		297

^a Values $^1J(^{119}\text{Sn}^1\text{H})$ are given in parentheses.^b Should be remeasured.^c Extrapolated value, see Fig. 5.

The sign of $^1K(^{119}\text{Sn}^{13}\text{C})$ is negative in $(\text{CH}_3)_3\text{SnLi}^{151}$ and may be assumed to be positive in most other organotin compounds. In the case of methyltin compounds, a plot of $^1J(^{119}\text{Sn}^{13}\text{C})$ against $^2J(^{119}\text{Sn}^1\text{H})$ helps to predict the magnitude of one or the other coupling.¹⁵¹

Starting from tetramethylstannane, the replacement of a methyl group by any other substituent causes significant changes in the magnitude of $^1J[^{119}\text{Sn}^{13}\text{C}(\text{CH}_3)]$. This is the result of the polarizability of the ^{119}Sn nucleus and can be ascribed to rehybridization¹²⁴ at the tin atom. Within this terminology the increase, or decrease, in $^1J(^{119}\text{Sn}^{13}\text{C})$ is attributed to the

respective change in the "*s* character" of the Sn–C bond.^{152,153} In Tables 27 and 28, values of $^1J(^{119}\text{Sn}^{13}\text{C}(\text{CH}_3))$ are collated for the compounds Me_3SnX and Me_2SnX_2 , respectively. In (alkyltrimethyl)stannanes, $\sum ^1J(^{119}\text{Sn}^{13}\text{C})$ is roughly constant.¹⁵⁴ The situation becomes more complex in the case of alkenyl stannanes^{90,155} and the relationship between $^1J(^{119}\text{Sn}^{13}\text{C})$ and the hybridization of tin and carbon atoms breaks down completely in alkynyltrimethylstannanes.^{91,156–159} With an increase in the number of electronegative ligands the ^{119}Sn nucleus becomes less polarizable and the couplings, $^1J(^{119}\text{Sn}^{13}\text{C})$, are more in agreement with the concept of the *s* character of the Sn–C bond.

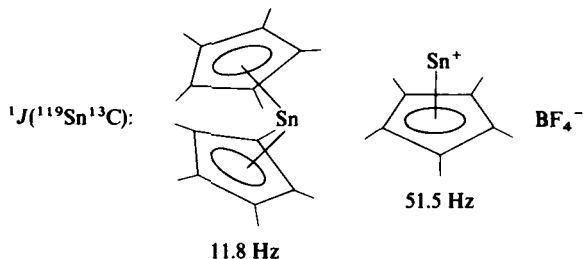
A typical example of this is found in the ratio of the following $^1J(^{119}\text{Sn}^{13}\text{C})$ values corresponding closely to the ratio of the formal Sn–C *s* character (2.0) in the case of $\text{X} = \text{Br}$, whereas this is not true if $\text{X} = \text{CH}_3$:

$^1J(^{119}\text{Sn}^{13}\text{C})$ (Hz)		
X	$\text{CH}_3\text{—SnX}_3$	$\text{HC}\equiv\text{C—SnX}_3$
CH_3	-337.8^{154}	-414.8^{103}
Br	-640.0^{160}	-1290.0^{161}

The value of $|^1J(^{119}\text{Sn}^{13}\text{C})|$ in compounds of the type R_4Sn ($\text{R} = \text{Me}, \text{Et}, \text{Pr}^i, \text{Bu}^n, \text{Bu}^t$) decreases in magnitude with increasing chain length and branching of the alkyl group.^{162,163} This shows that changes in the nature of the Sn–C bond are sensitively reflected by $^1J(^{119}\text{Sn}^{13}\text{C})$. The fairly small values of $|^1J(^{119}\text{Sn}^{13}\text{C})|$ in allyl- and benzyltin compounds may be explained in terms of σ – π conjugation.^{164,165}

The loose relationship between $^1J(^{119}\text{Sn}^{13}\text{C})$ and *s* character means that interbond angles at the tin atom in cyclic compounds are important. This is particularly noteworthy for the exocyclic $|^1J(^{119}\text{Sn}^{13}\text{C})|$ data which, in most cases, are smaller in five- and four-membered rings than in six-membered rings or analogous noncyclic compounds.

The small values of $|^1J(^{119}\text{Sn}^{13}\text{C})|$ in cyclopentadienyltin(II) compounds^{77,78} reflect the small *s* electron participation in the cluster bonding, in agreement with MO calculations⁷⁸:



In conclusion, $^1J(^{119}\text{Sn}^{13}\text{C})$ values obtained so far cover the range between +220 Hz ($\text{Me}_3\text{SnLi} \cdot 3 \text{ HMPT}$) and -1466 Hz [$\text{Cl}_2\text{Sn}(\text{C}\equiv\text{CH})_2$]. The extent of this range shows that this parameter is very useful as an analytical criterion and in discussions of structure and bonding.

c. $^1J(^{119}\text{Sn}^{29}\text{Si})$, $^1J(^{119}\text{Sn}^{119}\text{Sn})$, and $^1J(^{207}\text{Pb}^{119}\text{Sn})$. As shown in Table 21 there are only a few data available for $^1J(^{119}\text{Sn}^{29}\text{Si})$ and $^1J(^{207}\text{Pb}^{119}\text{Sn})$, whereas a great number of $^1J(^{119}\text{Sn}^{119}\text{Sn})$ values have been observed. The latter cover the enormous range between -6000 and +15,000 Hz. It is readily seen that small or even negative $^1J(^{119}\text{Sn}^{119}\text{Sn})$ couplings can be assigned either to anionic compounds (e.g., $[(\text{Me}_3\text{Sn})_3\text{Sn}]^-$) or to di- or polystannanes. The *s* overlap integral of the Sn-Sn bond is small in both types of compound as a result of the weakness of the Sn-Sn bond, for steric reasons, and because of the lone electron pair in the anionic compound.¹⁶⁶ All this may lead to additional electronic excitations, of which some make negative contributions to the mutual polarizability term π_{SnSn} . The medium-sized values of $^1J(^{119}\text{Sn}^{119}\text{Sn})$ (around +4000 Hz) are observed for distannanes with methyl or phenyl groups attached to tin,¹⁶⁷ whereas very large values of $^1J(^{119}\text{Sn}^{119}\text{Sn})$ (~11,000 to 15,000 Hz) are found in ditin complexes in which each tin atom gains a coordination number of five.^{167,168} It is believed that two effects are mainly responsible for this unexpected increase in the magnitude of $^1J(^{119}\text{Sn}^{119}\text{Sn})$:

1. The geometry at the tin atoms corresponds to trigonal bipyramids in which the heteroatoms (O, S) occupy axial positions. This increases the *s* electron participation in the equatorial positions, in particular in the Sn-Sn bond owing to the greater electronegativity of carbon as compared to tin.
2. The electronegative atoms oxygen or sulphur linked to the tin atoms greatly reduce the polarizability of the ^{119}Sn nuclei. Therefore, negative contributions to π_{SnSn} , which may be of great significance even in $\text{Me}_3\text{SnSnMe}_3$, are less likely to be important.

The ^{119}Sn -NMR spectra of naked-metal cluster anions (Table 21) reveal information on the number of tin atoms forming the polyhedron. Since these compounds are nonrigid (relative to the NMR time scale), averaged couplings $^1J(^{119}\text{Sn}^{117}\text{Sn})$ are observed. The intensity and multiplicity of the ^{117}Sn satellites show the presence of $[\text{Sn}_9]^{4-80}$ or $[\text{Sn}_4]^{2-82}$. Similar arguments lead to the assignment of $[\text{Sn}_9-n\text{Ge}_n]^{4-82}$ whereas the existence of the corresponding clusters $[\text{Sn}_9-n\text{Pb}_n]^{4-}$ is demonstrated by the values of $^1J(^{119}\text{Sn}^{117}\text{Sn})$ and $^1J(^{207}\text{Pb}^{119}\text{Sn})$.^{80,81} Furthermore, it is deduced that alloys of the composition $\text{NaSnTi}_{1.5}$ give solutions in ethylenediamine (en) containing the anion $[\text{Sn}_8\text{Ti}]^{5-82}$.

The data available leave no doubt that ^{119}Sn NMR is an attractive tool for the investigation of di- and polytin compounds. The trends observed, so far, for $^1J(^{119}\text{Sn}^{119}\text{Sn})$ should also stimulate other spectroscopic studies in order to base the interpretation of the NMR parameters on more firm ground. In an attempt to find out whether the mutual polarizability term π_{SnSn} or changes of the valence s electron density $[\psi(0)^2]$ are responsible for the large range of $^1J(^{119}\text{Sn}^{119}\text{Sn})$ data, Mössbauer isomer shifts [as a measure of $\psi_{\text{Sn}}(0)^2$] have been compared with $^1J(^{119}\text{Sn}^{119}\text{Sn})$ results.¹⁶⁹ Although this comparison may be questionable from a theoretical point of view, it indicates that π_{SnSn} is the major source of changes in the magnitude of $^1J(^{119}\text{Sn}^{119}\text{Sn})$.

d. $^1J(^{119}\text{Sn}^{11}\text{B})$. Except for $^1J(^{205}\text{Tl}^{119}\text{Sn})$ in $[(\text{Me}_3\text{Sn})_4\text{Tl}]\text{Li}$ ($-11,610$ Hz) and in $[\text{Sn}_8\text{Tl}]^{5-}$ (800 Hz), all other one-bond ^{119}Sn -Group III element couplings concern $^1J(^{119}\text{Sn}^{11}\text{B})$ (Table 22). The comparison with analogous values of $^1J(^{119}\text{Sn}^{13}\text{C})$ shows that the change in hybridization is much better reflected by $^1J(^{119}\text{Sn}^{11}\text{B})$ than by $^1J(^{119}\text{Sn}^{13}\text{C})$:

$^1J(^{119}\text{Sn}^{11}\text{B})$ (Hz) $[\text{Me}_3\text{Sn}-\text{BH}_3]^-$: -554^{18}	$(\text{Me}_3\text{Sn})_2\text{B}-\text{NMe}_2$: -657^{15}
$^1J(^{119}\text{Sn}^{13}\text{C})$ (Hz) $\text{Me}_3\text{Sn}-\text{CH}_3$: -338^{154}	$(\text{Me}_3\text{Sn})_2\text{C}=\text{CH}_2$: -298^{170}

Furthermore, the reduced couplings, $^1K(^{119}\text{Sn}^{11}\text{B})$, are larger than $^1K(^{119}\text{Sn}^{13}\text{C})$, although $\psi_{13\text{C}}(0)^2 > \psi_{11\text{B}}(0)^2$. This is evidence for the influence of the polar Sn-C bond on the mutual polarizability term π_{SnC} . Since the Sn-B bond is expected to be less polar, negative contributions to the contact energy arising from bond polarity should be of minor importance.

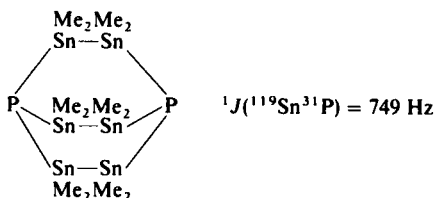
Large values of the $^1J(^{119}\text{Sn}^{11}\text{B})$ couplings hamper the direct observation of ^{119}Sn resonances, in particular for trigonal boranes, because of the broadening induced by scalar relaxation of the second kind (Section III,B). Since the couplings are so large, measurements at low temperature are not of much help either. For rapid detection of the ^{119}Sn resonances, and of the $^1J(^{119}\text{Sn}^{11}\text{B})$ data, heteronuclear double resonance experiments (e.g., $^1\text{H}\{^{119}\text{Sn}\}$) are superior to ^{119}Sn PFT NMR spectra.¹²⁻¹⁵

So far, values of $^1J(^{119}\text{Sn}^{11}\text{B})$ have been reported solely for Sn-B two electron two-centre bonds. It would clearly be of interest to obtain $^1J(^{119}\text{Sn}^{11}\text{B})$ data for polyhedral cage compounds either containing the tin atom or being attached to an organotin moiety. Both types of compound have been prepared¹⁷¹⁻¹⁷⁴ but no $^1J(^{119}\text{Sn}^{11}\text{B})$ values have been reported.

e. $^1J(^{119}\text{Sn}^{15}\text{N})$ and $^1J(^{119}\text{Sn}^{31}\text{P})$. Some $^1J(^{119}\text{Sn}^{15}\text{N})$ data are given in Table 29. The polarizability of the tin nucleus and the presence of the nitrogen lone electron pair prevent, in general, the prediction of the sign and magnitude of $^1J(^{119}\text{Sn}^{15}\text{N})$. In the case of multiple substitution it is

shown that ${}^1K({}^{119}\text{Sn}^{15}\text{N})$ increases with increasing n in the series $\text{Me}_{4-n}\text{Sn}(\text{NMePh})_n$ ($n = 1, 2, 3, 4$).¹¹⁸ This indicates that the polarizability, which is large for small n , of the ${}^{119}\text{Sn}$ nucleus produces at least some of the negative contributions to the contact energy in ${}^{119}\text{Sn}$ – ${}^{15}\text{N}$ spin–spin couplings.

Values of ${}^1J({}^{119}\text{Sn}^{31}\text{P})$ are found, together with the $\delta^{119}\text{Sn}$ values, in Table 20. Large negative contributions to the mutual polarizability term π_{SnP} in P(III) organotin compounds are reflected by the large negative values of ${}^1K({}^{119}\text{Sn}^{31}\text{P})$ [large positive ${}^1J({}^{119}\text{Sn}^{31}\text{P})$].¹⁷⁵ This mirrors the influence of the phosphorus lone electron pair. As shown in the crystal structure of dodecamethyl- $1\lambda^3, 4\lambda^3$ -diphospha-2,3,5,6,7,8-hexastannabicyclo[2.2.2]octane the bond angle $\text{Sn}–\text{P}–\text{Sn}$ is 98° and ${}^1J({}^{119}\text{Sn}^{31}\text{P})$ is -749 Hz,¹⁷⁶ which is close to the value for $(\text{Me}_3\text{Sn})_3\text{P}$ (-832 Hz):



The values of ${}^1K({}^{119}\text{Sn}^{31}\text{P})$ become less negative if the phosphorus lone electron pair is used in metal complexation.^{175,177,178} This trend is in agreement with expectations based on the accepted theory of nuclear spin–spin coupling.¹⁷⁵ However, it should be noted that values of ${}^1K({}^{31}\text{P}^{13}\text{C})$ in analogous compounds are always positive. So far no sign of ${}^1J({}^{119}\text{Sn}^{31}\text{P})$ has been determined in complexes of the type $\text{SnX}_4(\text{PR}_3)_2$, for anions $[\text{SnX}_5\text{PP}_3]^-$ ($\text{X} = \text{halogen}$; see Table 20), or for phosphine complexes of tin(II).^{59,92,179}

f. ${}^1J({}^{119}\text{Sn}^{77}\text{Se})$ and ${}^1J({}^{125}\text{Te}^{119}\text{Sn})$. Data for the couplings ${}^1J({}^{119}\text{Sn}^{77}\text{Se})$ and ${}^1J({}^{125}\text{Te}^{119}\text{Sn})$ are given, together with $\delta^{119}\text{Sn}$ values, in Tables 16–18. While the magnitude of ${}^1J({}^{119}\text{Sn}^{77}\text{Se})$ in Sn(IV) compounds does not change significantly,¹⁸⁰ ${}^1J({}^{119}\text{Sn}^{125}\text{Te})$ values appear to cover a larger range. This is in agreement with the high polarizability of both Sn and Te. Presumably, all values of ${}^1K({}^{119}\text{Sn}^{77}\text{Se})$ and ${}^1K({}^{125}\text{Te}^{119}\text{Sn})$ are negative.

In the cationic complexes of Sn(II),^{181,182} the presence of ${}^1J({}^{119}\text{Sn}^{77}\text{Se})$ shows that the exchange of the ligands ($[\text{PhSe}]^-$, $\text{chex}_3\text{P}=\text{Se}$; $\text{chex} = \text{cyclohexyl}$) is slow compared to the NMR time scale. In these complexes $|{}^1J({}^{119}\text{Sn}^{77}\text{Se})|$ is much smaller than in the Sn(IV)–selenium compounds.

g. $^1J(^{119}\text{Sn}^{19}\text{F})$. There is only a single value of $^1J(^{119}\text{Sn}^{19}\text{F})$ (+2298 Hz) for a triorganotin fluoride (Table 11) in the literature.¹⁸³ All other $^1J(^{119}\text{Sn}^{19}\text{F})$ data concern anionic complexes. For these an extensive list is already available,^{184,361} with most of the data taken from other sources.¹⁸⁵⁻¹⁸⁷ The values of $^1J(^{119}\text{Sn}^{19}\text{F})$ of peroxo complexes of the type

TABLE 11

Organotin halides, tin coordination number = 4

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
(PhCMe ₂ CH ₂) ₃ SnF	+139	CDCl ₃		183
Me ₃ SnCl	+164.2	3-20% C ₆ H ₆ or CHCl ₃	<i>a, b</i>	298
Et ₃ SnCl	+155	30% CCl ₄	<i>b</i>	277
Bu' ₃ SnCl	+50	—		4
chex ₃ SnCl	+66.2	C ₆ D ₆	<i>b, c</i>	76
CH ₂ (SnMe ₂ Cl) ₂	+160.9	CDCl ₃		170
(PhCH ₂) ₃ SnCl	+52	CDCl ₃	<i>a, b</i>	1
Ph ₃ SnCl	-44.7	CDCl ₃	<i>a</i>	299
Ph ₂ (<i>p</i> -CH ₂ =CH-C ₆ H ₄)SnCl	-44.6	C ₆ D ₆	<i>d</i>	286
(HC≡C) ₃ SnCl	-263.2	CDCl ₃		161
Me ₃ SnBr	+128	3-20% C ₆ H ₆ or CHCl ₃	<i>a, b</i>	298
Et ₃ SnBr	+148	—	<i>b</i>	277
Bu' ₃ SnBr	+74.8	C ₆ H ₆		4
CH ₂ (SnMe ₂ Br) ₂	+137.6	CDCl ₃		170
Ph ₃ SnBr	-59.8	CDCl ₃		299
(HC≡C) ₃ SnBr	-329.5	CDCl ₃		161
Me ₃ SnI	+38.6	3-20% C ₆ H ₆ or CHCl ₃		298
Bu' ₃ SnI	+82.7	C ₆ H ₆		4
Ph ₃ SnI	-114.5	CCl ₄		279
	-112.8	CDCl ₃		299
Me ₂ SnCl ₂	+137.0	30% CH ₂ Cl ₂	<i>a, e</i>	8
	+141.2	CCl ₄ , saturated		35
Et ₂ SnCl ₂	+121.0	30% CCl ₄ /CH ₂ Cl ₂	<i>a, e</i>	8
Bu' ₂ SnCl ₂	+56	CCl ₄		67
(CH ₂) ₃ SnCl ₂	-114.2	CDCl ₃		286
(CH ₂ =CH) ₂ SnCl ₂	-40.9	—		278
Ph ₂ SnCl ₂	-32.0	CH ₂ Cl ₂		8
(<i>p</i> -Me-C ₆ H ₄) <i>p</i> -CH ₂ =CH-C ₆ H ₄ SnCl ₂	-21.1	C ₆ D ₆		286

TABLE 11 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
(2-thienyl) ₂ SnCl ₂	-38.4	CCl ₄		279
(HC≡C) ₂ SnCl ₂	-194.5	CDCl ₃		161
Me ₂ SnBr ₂	+70.0	3-20% C ₆ H ₆ or CHCl ₃	<i>a, e</i>	298
Et ₂ SnBr ₂	+96.0	20% CCl ₄	<i>a, e</i>	277
Bu' ₂ SnBr ₂	+76.5	Saturated C ₆ H ₆		4
(CH ₂ =CHCH ₂) ₂ SnBr ₂	-16.8	—	<i>e</i>	279
(HC≡C) ₂ SnBr ₂	-345.6	CDCl ₃		161
Me ₂ SnI ₂	-159	3-20% C ₆ H ₆ or CHCl ₃	<i>a</i>	298
MeSnCl ₃	+21	3-20% C ₆ H ₆ or CHCl ₃	<i>a, f</i>	298
	-15.2	5 <i>M</i> CCl ₄	<i>a, f</i>	35
EtSnCl ₃	+6	30% CCl ₄	<i>a, f</i>	277
PhSnCl ₃	-63	CH ₂ Cl ₂	<i>a, g</i>	8
HC≡C—SnCl ₃	-155	CDCl ₃	<i>h</i>	161
MeSnBr ₃	-165	3-20% C ₆ H ₆ or CHCl ₃	<i>a, f</i>	183
EtSnBr ₃	-141	50% CCl ₄	<i>f</i>	277
HC≡C—SnBr ₃	-437.2	CDCl ₃		161
MeSnI ₃	-699.5	Saturated CCl ₄		288

^a For other conditions see review 3.

^b For other compounds trialkyltin halides see review 3 and reference 383.

^c Width 45 Hz; according to ¹³C NMR it is a mixture of ~93% all equatorial and ~7% axial, equatorial, equatorial chex₃SnCl.

^d (*p*-Me-C₆H₄)_x(*p*-CH₂=CH-C₆H₄)_{3-x}SnCl: $\delta^{119}\text{Sn}$, -39.6, -37.7.²⁸⁶

^e For other dialkyltin halides see review 3 and references 373 and 374.

^f For other alkyltin halides see review 3.

^g For other aryltin halides see review 3 and references 369 and 382.

^h Between -150 and -155, dependent on SnCl₄ concentration.

[SnF_{6-n}(OOH)_n]²⁻ (*n* = 1 to 5) have been reported.¹⁸⁸ The replacement of [OH]⁻ by the [OOH]⁻ group increases the value of $|^1J(^{119}\text{Sn}^{19}\text{F})|$, e.g.:

$^1J(^{119}\text{Sn}^{19}\text{F})$ (Hz)	
<i>cis</i> -[SnF ₄ (OH) ₂] ²⁻¹⁸⁵	<i>cis</i> -[SnF ₄ (OOH) ₂] ²⁻¹⁸⁸
1820 (OH, <i>trans</i>)	2064 (OOH, <i>trans</i>)
1518 (F, <i>trans</i>)	1692 (F, <i>trans</i>)

TABLE 12

Tin halides, tin coordination number = 4

Compound	$\delta^{119}\text{Sn}$	Solvent	Remarks	Reference
SnCl_4	-150	—	± 2	281
	-147.8	—		35
	-150.0	CS_2 , -30°C		64
BrSnCl_3	-260 to -267	—		281
	-265	CS_2 , -30°C		64
ISnCl_3	-543 to -557	—		281
	-543	CS_2 , -30°C		64
Br_2SnCl_2	-384 to -386	—		281
	-382	CS_2 , -30°C		64
BrISnCl_2	-663 to -672	—		281
	-663	CS_2 , -30°C		64
I_2SnCl_2	-937 to -951	—		281
	-927	CS_2 , -30°C		64
Br_3SnCl	-508 to -509	—		281
	-502	CS_2 , -30°C		64
Br_2ISnCl	-783 to -796	—		281
	-783	CS_2 , -30°C		64
BrI_2SnCl	-1060 to -1068	—		281
	-1057	CS_2 , -30°C		64
I_3SnCl	-1330 to -1347	—		281
SnBr_4	-638	CS_2	± 1	281
	-631.6	3 <i>M</i> CS_2		35
	-623	CS_2 , -30°C		64
ISnBr_3	-913 to -919	—		281
	-905	CS_2 , -30°C		64
I_2SnBr_2	-1187 to -1195	—		281
	-1176	CS_2 , -30°C		64
I_3SnBr	-1447 to -1449	—		281
	-1438	CS_2 , -30°C		64
SnI_4	-1701	CS_2	+ 2	281
	-1698.6	2 <i>M</i> CS_2		35
	-1679	CS_2 , -30°C		64

h. $^1J(^{119}\text{SnM})$ (*M* = transition metal). Spin-spin coupling between the ^{119}Sn nucleus and transition metals, *M*, has recently attracted much attention.¹⁸⁹ The bulk of the data concerns complexes with the $\text{M}-\text{SnCl}_3$ moiety, produced by insertion of SnCl_2 into the $\text{M}-\text{Cl}$ bond. The presence of $^1J(^{119}\text{SnM})$ demonstrates the kinetic stability of the $\text{M}-\text{Sn}$ bond. More recently, data have become available for the products of the well-known oxidative addition of organotin compounds to platinum(0) complexes.¹⁹⁰ Therefore, at least for platinum compounds, it is possible to compare a series

of $^1J(^{195}\text{Pt}^{119}\text{Sn})$ values:

	$^1J(^{195}\text{Pt}^{119}\text{Sn})$ (Hz)		
	$n = 0$	1	2
<i>trans</i> -[Pt(Cl)(SnMe _n Cl _{3-n})(PPh ₃) ₂]	28,052 ¹⁹¹	19,982 ¹⁹⁰	14,788 ¹⁹⁰
<i>cis</i> -[Pt(Cl)(SnMe _n Cl _{3-n})(PPh ₃) ₂]	16,321 ¹⁹¹	13,105 ¹⁹⁰	8,921 ¹⁹⁰

The trend of this and of most sets of data in Tables 24 and 25 is in accord with expectations. The magnitude of $|^1J(^{195}\text{Pt}^{119}\text{Sn})|$ depends strongly upon the polarizability of the ^{195}Pt nucleus, which in turn is partly a function of the ligand trans to the stannyl group. Thus $|J(^{195}\text{Pt}^{119}\text{Sn})|$ increases with a decreasing "trans effect." The magnitude of $|^1J(^{195}\text{Pt}^{119}\text{Sn})|$ reflects to some extent the energy of the Pt-Sn bond. Therefore, a crude relationship exists between the Pt-Sn bond length and $|^1J(^{195}\text{Pt}^{119}\text{Sn})|$.¹⁹² It should be noted that the SnCl₃ ligand is regarded as a weak σ donor and a π acceptor.¹⁹³ The balance of both properties will affect the magnitude of $^1J(^{119}\text{SnM})$. In particular, the occupation of Sn *d* orbitals by metal electron density may influence $^1J(^{119}\text{SnM})$, probably by reducing negative contributions to the contact energy term.

Although there are only two values of $^1J(^{199}\text{Hg}^{119}\text{Sn})$ available so far,¹⁹⁴ they support the argument that the polarizability of the metal plays a major role. The polarizability of both mercury and tin is reduced by replacement of the Me₃SiCH₂ group with C₆F₅ groups. This leads to an almost threefold increase in the magnitude of $|^1J(^{119}\text{Hg}^{119}\text{Sn})|$:

	$^1J(^{199}\text{Hg}^{119}\text{Sn})$ (Hz)
(Me ₃ SiCH ₂) ₃ Sn—Hg—Sn(CH ₂ SiMe ₃) ₃	6157 ¹⁹⁴
(C ₆ F ₅) ₃ Sn—Hg—Sn(C ₆ F ₅) ₃	17,550 ¹⁹⁴

A more detailed discussion requires more data on M—SnX₃ compounds.³⁷⁸⁻³⁸¹ It is evident that the nature of the transition metal-tin bond depends, in a complex way, on various factors which may be reflected to some extent by the magnitude of $^1J(^{119}\text{SnM})$. However, experience with one-bond couplings of large and polarizable nuclei shows that changes in the magnitude of these couplings are difficult to predict and even more difficult to interpret. On the other hand, this sensitivity may help in finding small differences in the bonding situation and there is clearly a need for other physical methods to prove this point when it arises from NMR measurements.

2. Geminal couplings, $^2J(\text{SnX})$

The magnitude and sign of geminal couplings, $^2J(^{119}\text{SnX})$, depend (1) on the intervening atom Z, (2) on the nature of the substituents on tin, on the

TABLE 13

Neutral and anionic complexes of tin halides and organotin halides,^{a,b} tin coordination number ≥ 4

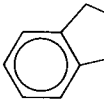
Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
Me_3SnCl —DMSO	+3	DMSO	<i>c</i>	88
Me_3SnCl —HMPT	-47.5	10% HMPT	<i>c</i>	4
Me_3SnI —DMSO	+6.5	DMSO		4
Et_3SnX —Imidazoles	<i>d</i>	CDCl_3 , -60°C	<i>d</i>	53
 SnPh(Me)Br NMe_2	-51.1	$\text{C}_6\text{D}_6/\text{CD}_2\text{Cl}_2$		259
Ph_3SnCl —DMSO	-226.8	DMSO	<i>c</i>	66
Ph_3SnCl —HMPT	-238.9	$\text{CDCl}_3/\text{HMPT}$	<i>c</i>	66
Ph_3SnCl —pyridine	-203.5	Pyridine		66
Ph_3SnBr —DMSO	-228.4	DMSO	<i>c</i>	66
Ph_3SnBr —HMPT	-239.6	$\text{CDCl}_3/\text{HMPT}$	<i>c</i>	66
Ph_3SnBr —pyridine	-224.5	Pyridine		66
Ph_3SnI —DMSO	-228.5	DMSO	<i>c</i>	66
Ph_3SnI —pyridine	-236.3	Pyridine		66
Me_2SnCl_2 (DMSO) ₂	-246	DMSO	<i>c</i>	88
Me_2SnI_2 (DMSO) ₂	-315	DMSO	<i>c</i>	4
MeSnCl_3 (DMSO) ₂	-457	DMSO	<i>c</i>	88
MeSnI_3 (DMSO) ₂	-795	DMSO	<i>c</i>	4
$\text{MeSn(OH)Cl}_2(\text{H}_2\text{O})_2$	-487	H_2O		61
<i>trans</i> -[L_2SnCl_4]	-700	CH_2Cl_2 , -30°C	<i>e</i>	65
	-622	CH_2Cl_2 , -100°C	<i>f</i>	65
<i>trans</i> -[$\text{L}_2\text{SnCl}_3\text{Br}$]	-871	CH_2Cl_2 , -30°C	<i>e</i>	65
<i>trans</i> -[$\text{L}_2\text{SnCl}_2\text{Br}_2$] (Cl, Cl- <i>trans</i>)	-1048	CH_2Cl_2 , -30°C	<i>e</i>	65
<i>trans</i> -[$\text{L}_2\text{SnCl}_2\text{Br}_2$] (Br, Br- <i>cis</i>)	-1053	CH_2Cl_2 , -30°C	<i>e</i>	101
<i>trans</i> -[$\text{L}_2\text{SnClBr}_3$]	-1260	CH_2Cl_2 , -30°C	<i>e</i>	101
<i>trans</i> -[L_2SnBr_4]	-1479	CH_2Cl_2 , -30°C	<i>e</i>	65
	-1367	CH_2Cl_2 , -100°C	<i>f</i>	
<i>cis</i> -[L_2SnCl_4]	-707	CH_2Cl_2 , -30°C	<i>e</i>	65
	-632	CH_2Cl_2 , -30°C	<i>f</i>	65
<i>cis</i> -[$\text{L}_2\text{SnCl}_3\text{Br}$] (Cl, Cl)	-881	CH_2Cl_2 , -30°C	<i>e, g</i>	65
	-790	CH_2Cl_2 , -30°C	<i>f, g</i>	65
<i>cis</i> -[$\text{L}_2\text{SnCl}_3\text{Br}$] (Cl, Br)	-887	CH_2Cl_2 , -30°C	<i>e, g</i>	65
	-813	CH_2Cl_2 , -100°C	<i>f, g</i>	65
<i>cis</i> -[$\text{L}_2\text{SnCl}_2\text{Br}_2$] (Cl, Cl)	-1040	CH_2Cl_2 , -30°C	<i>e, g</i>	65
	-958	CH_2Cl_2 , -30°C	<i>f, g</i>	65
<i>cis</i> -[$\text{L}_2\text{SnCl}_2\text{Br}_2$] (Cl, Br)	-988	CH_2Cl_2 , -100°C	<i>f, g</i>	65
<i>cis</i> -[$\text{L}_2\text{SnClBr}_3$] (Cl, Br)	-1248	CH_2Cl_2 , -30°C	<i>e, g</i>	65
	-1170	CH_2Cl_2 , -100°C	<i>f, g</i>	65
<i>cis</i> -[$\text{L}_2\text{SnClBr}_3$] (Br, Br)	-1190	CH_2Cl_2 , -100°C	<i>f, g</i>	65

TABLE 13 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
<i>cis</i> -[L ₂ SnBr ₄]	-1383	CH ₂ Cl ₂ , -100°C	<i>f</i>	65
SnF ₂	-629.0	0.462 <i>M</i> DMSO	<i>c, h</i>	5,300
	-626.1	1.58 <i>M</i> HMPT	<i>c, h</i>	5,300
SnCl ₂	-260.3	2.6 <i>M</i> dimethoxyethane	<i>h</i>	5,300
	-324.1	0.74 <i>M</i> DMF	<i>c, h</i>	5,300
	-358.2	1.09 <i>M</i> DMSO	<i>c, h</i>	5,300
	-285.2	1.7 <i>M</i> HMPT	<i>c, h</i>	5,300
	-236	THF	<i>c</i>	281
	-238	THF/C ₆ D ₆	<i>c</i>	56
SnBr ₂	-72.3	0.39 <i>M</i> dimethoxyethane	<i>h</i>	5,300
	-70.7	THF, C ₆ D ₆	<i>c</i>	56
	-202.1	0.32 <i>M</i> DMF	<i>c, h</i>	5,300
	-319.5	1.3 <i>M</i> DMSO	<i>c, h</i>	5,300
SnI ₂	-152.6	5.117 <i>M</i> DMF	<i>c, h</i>	5,300
	-586.0	1.29 <i>M</i> DMSO	<i>c, h</i>	5,300
	-174.4	1.24 <i>M</i> HMPT	<i>c, h</i>	5,300
[Ph ₃ SnBr ₂] ⁻	-239.6	0.26 <i>M</i> CD ₃ NO ₂		66
	-231.5	0.15 <i>M</i> DMSO	<i>c</i>	66
[MeSnCl ₅] ²⁻	-464	H ₂ O	<i>i</i>	8
[MeSnBr ₅] ²⁻	-662	H ₂ O	<i>i</i>	8
[Ph ₃ SnCl ₂] ⁻	-257.2	0.62 <i>M</i> CD ₃ NO ₂		66
[SnF ₆] ²⁻	-888	H ₂ O		8
[SnF ₅ Cl] ²⁻	-826	H ₂ O		4
[SnCl ₆] ²⁻	-732	CH ₂ Cl ₂ , -30°C		64
[SnCl ₅ Br] ²⁻	-912	CH ₂ Cl ₂ , -30°C		64
<i>trans</i> -[SnCl ₄ Br ₂] ²⁻	-1092	CH ₂ Cl ₂ , -30°C		64
<i>cis</i> -[SnCl ₄ Br ₂] ²⁻	-1115	CH ₂ Cl ₂ , -30°C		64
<i>mer</i> -[SnCl ₃ Br ₃] ²⁻	-1322	CH ₂ Cl ₂ , -30°C		64
<i>fac</i> -[SnCl ₃ Br ₃] ²⁻	-1336	CH ₂ Cl ₂ , -30°C		64
<i>trans</i> -[SnCl ₂ Br ₄] ²⁻	-1548	CH ₂ Cl ₂ , -30°C		64
<i>cis</i> -[SnCl ₂ Br ₄] ²⁻	-1559	CH ₂ Cl ₂ , -30°C		64
[SnClBr ₅] ²⁻	-1800	CH ₂ Cl ₂ , -30°C		64
[SnBr ₆] ²⁻	-2064	CH ₂ Cl ₂ , -30°C		64
[SnCl ₅ L] ⁻	-700	CH ₂ Cl ₂ , -50°C	<i>e</i>	65
	-668	CH ₂ Cl ₂ , -100°C	<i>f</i>	65
[SnCl ₄ BrL] ⁻ (Cl)	-880	CH ₂ Cl ₂ , -50°C	<i>e, g</i>	65
	-841	CH ₂ Cl ₂ , -100°C	<i>f, g</i>	65
[SnCl ₄ BrL] ⁻ (Br)	-883	CH ₂ Cl ₂ , -50°C	<i>e, g</i>	65
	-880	CH ₂ Cl ₂ , -100°C	<i>f, g</i>	65
[SnCl ₃ Br ₂ L] ⁻ (Cl- <i>trans</i>)	-1053	CH ₂ Cl ₂ , -50°C	<i>e, g</i>	65
	-1033	CH ₂ Cl ₂ , -100°C	<i>f, g</i>	65
[SnCl ₃ Br ₂ L] (Cl- <i>cis</i>)	-1073	CH ₂ Cl ₂ , -50°C	<i>e, g</i>	65
	-1033	CH ₂ Cl ₂ , -100°C	<i>f, g</i>	65

TABLE 13 (*cont.*)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$[\text{SnCl}_3\text{Br}_2\text{L}]^- (\text{Br})$	-1080	CH_2Cl_2 , -50°C	<i>e, g</i>	65
	-1033	CH_2Cl_2 , -100°C	<i>f, g</i>	65
$[\text{SnCl}_2\text{Br}_3\text{L}]^- (\text{Cl})$	-1270	CH_2Cl_2 , -50°C	<i>e, g</i>	65
	-1236	CH_2Cl_2 , -100°C	<i>f, g</i>	65
$[\text{SnCl}_2\text{Br}_3\text{L}]^- (\text{Br-}i{trans})$	-1283	CH_2Cl_2 , -50°C	<i>e, g</i>	65
	-1236	CH_2Cl_2 , -100°C	<i>f, g</i>	65
$[\text{SnCl}_2\text{Br}_3\text{L}]^- (\text{Br-}i{cis})$	-1284	CH_2Cl_2 , -50°C	<i>e, g</i>	65
	-1236	CH_2Cl_2 , -100°C	<i>f, g</i>	65
$[\text{SnClBr}_4\text{L}]^- (\text{Cl})$	-1501	CH_2Cl_2 , -50°C	<i>e, g</i>	65
	-1451	CH_2Cl_2 , -50°C	<i>f, g</i>	65
$[\text{SnClBr}_4\text{L}]^- (\text{Br})$	-1501	CH_2Cl_2 , -50°C	<i>e, g</i>	65
	-1451	CH_2Cl_2 , -100°C	<i>f, g</i>	65
$[\text{SnBr}_5\text{L}]^-$	-1737	CH_2Cl_2 , -50°C	<i>e, g</i>	65
	-1679	CH_2Cl_2 , -100°C	<i>f, g</i>	65
$[\text{SnCl}_3]^-$	-30	$\text{CH}_2\text{Cl}_2/\text{C}_6\text{D}_6$	<i>j</i>	56

^a For complexes with PR_3 see Table 20.

^b For more $\delta^{119}\text{Sn}$ data see reviews 1–4 and references 367 and 383–385.

^c DMSO, Dimethyl sulfoxide; HMPT, $(\text{Me}_2\text{N})_3\text{P}=\text{O}$; DMF, dimethyl formamide; THF, tetrahydrofuran.

^d No reference is given for the $\delta^{119}\text{Sn}$ data; the $\delta^{119}\text{Sn}$ values for Et_3SnX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) do not agree with literature data; there is a shift to lower frequency of the ^{119}Sn resonance in the presence of 1-ethyl and 1-vinylamidazole, indicating coordination number 5 for the tin atom. Various isomers are claimed to be present.

^e L, $\text{Bu}^n_3\text{P}=\text{O}$; $^2J(^{119}\text{SnO}^{31}\text{P})$ varies between 130 and 230 Hz.

^f L, Acetone.

^g The group *trans* to the L groups is indicated in parentheses.

^h ^{119}Sn resonances shift to higher frequency on dilution.³⁰⁰

ⁱ $\delta^{119}\text{Sn}$ depends on pH.

^j Counterion is $(\text{Bu}^t_3\text{PH})^+$.

intervening atom Z, and on X, (3) on the Sn–Z–X bond angle, and (4) on the stereochemistry of the rest of the molecule with respect to the SnZX fragment. The complex behaviour of $^2J(^{119}\text{SnX})$ is best illustrated by considering the absolute values of $|^2J(^{119}\text{Sn}^{119}\text{Sn})|$, which range between 0 and 35000 Hz; $^2J(^{119}\text{Sn}^{119}\text{Sn})$ may be of either sign. This situation may be somewhat discouraging at first sight but it has stimulated much work in the area of geminal tin couplings. Thus, a qualitatively useful picture slowly emerges which enables one to use these parameters as a diagnostic tool without attempting a quantitative theoretical analysis. A useful concept, to rationalize geminal couplings in terms of the contact energy, divides the contributions into three parts.¹⁹⁵ These describe the nature of the Sn–Z bond and the nature of the Z–X bond with respect to the transfer of nuclear spin information

TABLE 14

Organotin hydroxides, alkoxides, and related compounds,^a tin coordination number ≥ 4

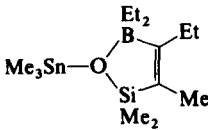
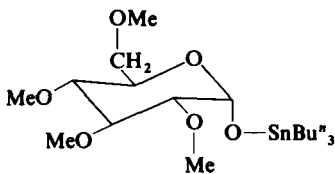
Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
Me_3SnOH	+118	Saturated CH_2Cl_2	<i>b</i>	301
Ph_3SnOH	-86	CH_2Cl_2		183
	-82.5	CDCl_3		299
Me_3SnOMe	+129	Saturated C_6H_6	<i>b</i>	51
$\text{Me}_3\text{SnOPr}^i$	+109	50% C_6H_6		51
$\text{Me}_3\text{SnOBu}^i$	+91	50% C_6H_6	<i>b</i>	51
Me_3SnOPh	+134.3	C_6H_{12}	<i>b</i>	302
$\text{Me}_3\text{Sn—Ox}$	+47.8	—	<i>c, d</i>	69
$\text{Me}_3\text{SnOSiPh}_3$	+121	Saturated CCl_4		1
	+165.7	30% CDCl_3		303
Et_3SnOMe	+100.3	CH_2Cl_2		279
$\text{Et}_3\text{Sn—Ox}$	+28.5	CDCl_3	<i>c</i>	69
$\text{Pr}^n_3\text{Sn—Ox}$	+34.9	CDCl_3	<i>c</i>	69
Bu_3SnOMe	+83	—		304
Bu_3SnOEt	+86	—		304
$\text{Bu}_3\text{SnOPr}^i$	+76	—		304
$\text{Bu}_3\text{SnOBu}^i$	+60	—		304
Bu_3SnOPh	+105	—	<i>b</i>	304
$\text{Bu}^n_3\text{Sn—Ox}$	+30.1	—	<i>c</i>	69
	+99.0	Toluene	<i>e</i>	250
$\text{Bu}^n_3\text{SnOOBu}^i$	+105	CH_2Cl_2		8
$\text{Bu}^n_3\text{SnOP(S)(OMe)}_2$	+68.4	C_6D_6		305
$\text{Bu}^n_3\text{SnOSiMe}_3$	+71	—		304
$\text{Bu}^n_3\text{SnOSiPh}_3$	+89	—		304
$(\text{PhCH}_2)_3\text{Sn—Ox}$	-98.2	CD_2Cl_2	<i>c</i>	69
$\text{Ph}_3\text{Sn—Ox}$	-190.5	CDCl_3	<i>c</i>	69
	-192	30% CHCl_3		58
	-190.1	CDCl_3		66
$\text{Ph}_3\text{SnOOBu}^i$	-91	CH_2Cl_2		8
$\text{Ph}_3\text{SnOSiPh}_3$	-103	CH_2Cl_2		8
$\text{Me}_2\text{Sn(OMe)}_2$	-126.3	C_6H_6		306

TABLE 14 (cont.)

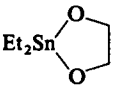
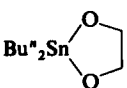
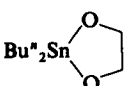
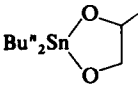
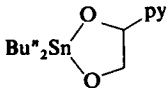
Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$\text{Me}_2\text{Sn}(\text{OEt})_2$	-125.9	C_6H_6	<i>b</i>	306
$\text{Me}_2\text{Sn}(\text{OBu}^t)_2$	-1.8	—		51
$\text{Me}_2\text{Sn}(\text{OSiPh}_3)_2$	+2.0	CH_2Cl_2		8
$\text{Me}_2\text{Sn}(\text{Ox})_2$	-237	20% CHCl_3	<i>c</i>	58
$\text{Me}_2\text{Sn}(2\text{-Me-Ox})_2$	-228	8% CH_2Cl_2	<i>c</i>	58
	-235.8	CDCl_3		69
$\text{Me}_2\text{Sn}(\text{acac})_2$	-365	15% CHCl_3	<i>f</i>	57, 58
$\text{Me}_2\text{Sn}(\text{bzac})_2$	-356	15% CH_2Cl_2	<i>g</i>	58
$\text{Me}_2\text{Sn}(\text{dbzm})_2$	-348	20% CH_2Cl_2	<i>h</i>	58
$\text{Me}_2\text{Sn}(\text{trop})_2$	-197	20% CH_2Cl_2	<i>i</i>	58
$\text{Me}_2\text{Sn}(\text{koj})_2$	-174	20% DMSO	<i>j</i>	58
$\text{Et}_2\text{Sn}(\text{OMe})_2$	-181	—		277
	-165	10% C_6H_6		277
$\text{Et}_2\text{Sn}(\text{OBu}^t)_2$	-31	—		277
$\text{Et}_2\text{Sn}(\text{Ox})_2$	-264	25% CH_2Cl_2	<i>c</i>	277
	-177	25% CDCl_3		277
$\text{Bu}^n_2\text{Sn}(\text{OMe})_2$	-159	29% CCl_4	<i>b</i>	3
$\text{Bu}^n_2\text{Sn}(\text{OEt})_2$	-154	50% CCl_4	<i>b</i>	1
$\text{Bu}^n_2\text{Sn}(\text{OBu}^t)_2$	-34	—	<i>b</i>	304
$\text{Bu}^n_2\text{Sn}(\text{OPh})_2$	-138	Saturated CCl_4 or C_6H_6	<i>b</i>	304
	-189	Saturated CHCl_3	<i>b</i>	304 71
				
— py	-144	CDCl_3		71
— dmf	-137.2	CDCl_3		71
— dmso	-144	CDCl_3		71
	-164	Saturated CHCl_3		304 71
	-146.4	CDCl_3		71

TABLE 14 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
	-155	Saturated CHCl_3		304 71
—py	-145.6	CDCl_3		71
—dmf	-144.9	CDCl_3		71
	-154	50% CCl_4		1
	-154.5	CHCl_3 , pyridine, 1:1, -40°C	<i>k</i>	245
	-216	CHCl_3	<i>l</i>	307
$\text{Bu}''_2\text{Sn}(\text{Ox})_2$	-262	30% CHCl_3	<i>c</i>	58
$\text{Bu}'_2\text{Sn}(\text{OMe})_2$	-114.7	—		4
$\text{Bu}'_2\text{Sn}(\text{OEt})_2$	-123.4	Neat, 60°C		3
$\text{Bu}'_2\text{Sn}(\text{OCH}_2\text{CH}_2)_2\text{NR}$				
R				
—				
H	-209.5	CH_2Cl_2 , 32°C	<i>m</i>	52
	-210.5	Acetone- d_6 , 32°C		
Me	-205	CH_2Cl_2 , 32°C	<i>m</i>	52
	-204	Acetone- d_6 , 32°C		52
$\text{Bu}'_2\text{Sn}(\text{acac})_2$	-486	CCl_4	<i>f</i>	67
$\text{Bu}'_2\text{Sn}(\text{trop})_2$	-326	CCl_4	<i>i</i>	67
$\text{Bu}'_2\text{Sn}(\text{Ox})_2$	-338	CCl_4	<i>c</i>	67
	-341	Saturated C_6H_6		4
$\text{Bu}'_2\text{Sn}(2\text{-Me-Ox})_2$	-311	CCl_4	<i>c</i>	67
$\text{Ph}_2\text{Sn}[\text{OP}(\text{S})(\text{OPh})_2]_2$	+58.9	CDCl_3	<i>n</i>	305
$\text{Ph}_2\text{Sn}(\text{OSiPh}_3)_2$	-188	CDCl_3		1
$\text{Ph}_2\text{Sn}(\text{Ox})_2$	-397	15% CHCl_3	<i>c</i>	58
$\text{Ph}_2\text{Sn}(\text{acac})_2$	-514	30% CHCl_3	<i>f</i>	58
$\text{MeSn}(\text{OEt})_3$	-434	50% mesitylene	<i>b</i>	51
$\text{MeSn}(\text{OBu}')_3$	-177.2	—	<i>b</i>	51

TABLE 14 (*cont.*)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$\text{MeSn}(\text{OCH}_2\text{CH}_2)_3\text{N}$	−556.7, −380.7, −375.4	CHCl_3 , −40°C	<i>o, p</i>	54 55
$\text{Bu}^n\text{Sn}(\text{OEt})_3$	−432	16% C_6H_6	<i>b</i>	98
$\text{Bu}^n\text{Sn}(\text{OBu}^i)_3$	−199	12% C_6H_6	<i>b</i>	98
$\text{Bu}^n\text{Sn}(\text{OCH}_2\text{CH}_2)_3\text{N}$	−559, −382.9, −375.9	CHCl_3 , −40°C	<i>o, p</i>	54 55
$\text{Bu}^n\text{Sn}(\text{Ox})_3$	−561	10% CHCl_3	<i>c</i>	57
$\text{Bu}^i\text{Sn}(\text{OCH}_2\text{CH}_2)_3\text{N}$	−246.4	CHCl_3 , −50°C		54 55
$\text{PhSn}(\text{OCH}_2\text{CH}_2)_3\text{N}$	−245.5, −620.5, −443.4, −433.2	CHCl_3 , +27°C CHCl_3 , −40°C	<i>o, p</i>	54 54 55
<i>o</i> -Me- $\text{C}_6\text{H}_4\text{Sn}(\text{OCH}_2\text{CH}_2)_3\text{N}$	−287	CDCl_3		55
$\text{Bu}^n_2\text{Sn}(\text{Cl})\text{Ox}$	−112	30% CHCl_3	<i>c</i>	58
$\text{Ph}_2\text{Sn}(\text{Cl})\text{Ox}$	−245	20% CHCl_3	<i>c</i>	58
$\text{Bu}^n\text{Sn}(\text{Cl})(\text{Ox})_2$	−395	30% CHCl_3	<i>c</i>	58
$[\text{Bu}^n\text{Sn}(\text{Ox})_2]_2\text{S}$	−333	15% CHCl_3	<i>c</i>	58

^a See also review 3 and references 383–389 for further $\delta^{119}\text{Sn}$ data.

^b For other conditions see review 3.

^c Ox, Oxinate.

^d $\delta^{119}\text{Sn}$ values in CD_2Cl_2 , +50.5; CDCl_3 , +50.9; C_6D_6 , +47.8; CD_3OD , +42.8 (and another broad signal at +65.8).

^e For more $\delta^{119}\text{Sn}$ data of Bu^n_3Sn ethers of carbohydrates see reference 250.

^f acac, Acetyl acetate.

^g bzac, Benzoyl acetate.

^h dbzm, Dibenzoyl methanoate.

ⁱ trop, Tropolonate.

^j koj, Kojate.

^k In reference 308 $\delta^{119}\text{Sn}$ values are given for Bu^n_2Sn derivatives of diols with a carbohydrate structure; range of $\delta^{119}\text{Sn}$ is ~ -120 to -180 ppm, indicating dimeric structures; see also references 250, 309.

^l Oligomers of the type $[(\text{Bu}^n_2\text{SnO})_2\text{O}]_n\text{C}_2\text{Ph}_2$ show $\delta^{119}\text{Sn}$ values from ca. -193 to -275 .³¹⁰

^m $\delta^{119}\text{Sn}$ shifts to lower frequencies (3–4 ppm) at -40°C .⁵²

ⁿ This may be $\text{Ph}_2\text{Sn}[\text{SP}(\text{O})(\text{OPh})_2]_2$ considering the $\delta^{119}\text{Sn}$ value.

^o For other conditions, see references 54, 55.

^p These stannatranes have a trimeric structure.^{54,55}

TABLE 15

Organotin carboxylates and thiocarboxylates,^a tin coordination number ≥ 4

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$\text{Me}_3\text{SnOC(O)H}$	+2.5	3 <i>M</i> CDCl_3		183
	+150	0.05 <i>M</i> CDCl_3		183
$\text{Me}_3\text{SnOC(O)Me}$	+129	Saturated CDCl_3		3
$\text{Et}_3\text{SnOC(O)Me}$	+102.4	CH_2Cl_2		279
$\text{Bu}^n_3\text{SnOC(O)Me}$	+96	CH_2Cl_2		8
$\text{Ph}_3\text{SnOC(O)H}$	-91.4	Saturated CDCl_3		72
$\text{Ph}_3\text{SnOC(O)Me}$	-121	<0.5 <i>M</i> CDCl_3		183
	-113.7	CDCl_3		72
$\text{Ph}_3\text{SnOC(O)Et}$	-121.0	<0.5 <i>M</i> CDCl_3		183
	-114.0	CDCl_3		72
$\text{Ph}_3\text{SnOC(O)Bu}^i$	-117.7	CDCl_3		72
$\text{Ph}_3\text{SnOC(O)Ph}$	-109.9	0.56 <i>M</i> CDCl_3		66
$\text{Ph}_3\text{SnOC(O)CF}_3$	-64.4	0.48 <i>M</i> CDCl_3		72
	-65.1	CDCl_3		183
$\text{Ph}_3\text{SnOC(O)CH}_2\text{Cl}$	-95.0	<0.5 <i>M</i> CDCl_3		183
	-89.8	Saturated CDCl_3		72
$\text{Ph}_3\text{SnOC(O)CHCl}_2$	-79	<0.5 <i>M</i> CDCl_3		183
	-75.7	Saturated CDCl_3		72
$\text{Ph}_3\text{SnOC(O)CCl}_3$	-80.0	<0.5 <i>M</i> CDCl_3		183
$\text{Ph}_3\text{SnOC(O)CH}_2\text{Br}$	-91.1	Saturated CDCl_3		72
$\text{Ph}_3\text{SnOC(O)CHBr}_2$	-77.5	Saturated CDCl_3		72
$\text{Ph}_3\text{SnOC(O)C}_6\text{H}_4\text{-}p\text{-NH}_2$	-122.6	0.55 <i>M</i> CDCl_3		66
$\text{Ph}_3\text{SnOC(O)C}_6\text{H}_4\text{-}o\text{-NH}_2$	-116.8	0.41 <i>M</i> CDCl_3		66
$\text{Ph}_3\text{SnSC(S)NEt}_2$	-189.8	0.43 <i>M</i> CDCl_3		66
	-191	30% CDCl_3		58
	-194.5	CH_2Cl_2		2
$\text{Me}_2\text{Sn[OC(O)Ph]}_2$	-125	25% CHCl_3		58
Me_2SnSAB	-150	25% CH_2Cl_2	<i>b</i>	58
$\text{Bu}^n_2\text{Sn[OC(O)Me]}_2$	-195	—		281
Ph_2SnSAB	-329	20% CHCl_3	<i>b</i>	58
$\text{Me}_2\text{Sn[SC(S)NMe}_2\text{]}_2$	-338	30% CHCl_3		58
$\text{Me}_2\text{Sn[SC(S)N(CH}_2\text{)}_4\text{]}_2$	-310	CH_2Cl_2		2
$\text{Me}_2\text{Sn[SC(S)NEt}_2\text{]}_2$	-333	30% CHCl_3		58
	-336	CH_2Cl_2		8
$\text{Bu}^n_2\text{Sn[SC(S)N(CH}_2\text{)}_4\text{]}_2$	-313	CH_2Cl_2		2
$\text{Bu}^n_2\text{Sn[SC(S)N(CH}_2\text{Ph)}_2\text{]}_2$	-340	CH_2Cl_2		2
$\text{Bu}^i_2\text{Sn[SC(S)NMe}_2\text{]}_2$	-255	CCl_4		67
$\text{Bu}^i_2\text{Sn[SC(S)NEt}_2\text{]}_2$	-262	CCl_4		67
$\text{Ph}_2\text{Sn[SC(O)Ph]}_2$	-101.2	CHCl_3		278
$\text{Ph}_2\text{Sn[SC(S)N(CH}_2\text{)}_4\text{]}_2$	-481	CH_2Cl_2		2
$\text{Ph}_2\text{Sn[SC(S)NEt}_2\text{]}_2$	-501	30% CHCl_3		58
$\text{Ph}_2\text{Sn[SC(S)N(CH}_2\text{Ph)}_2\text{]}_2$	-490	CH_2Cl_2		2
$\text{PhSn[SC(S)NMe}_2\text{]}_3$	-695	5% CHCl_3		57

TABLE 15 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$\text{Me}_2\text{Sn}(\text{Cl})[\text{SC}(\text{S})\text{NMe}_2]$	-204	30% CHCl_3		58
$\text{Me}_2\text{SnX}[\text{SC}(\text{S})\text{NEt}_2]$				
X	-201	30% CHCl_3		58
Cl	-204	CH_2Cl_2		8
Br	-233	CH_2Cl_2		8
I	-292	CH_2Cl_2		8
$\text{PhSnCl}[\text{SC}(\text{S})\text{NMe}_2]_2$	-361	10% CHCl_3		57, 58

^a For $\delta^{119}\text{Sn}$ data of other organotin carboxylates and thiocarboxylates see review 3 and reference 390.

^b SAB, Dianion of *N*-(2-hydroxyphenyl)salicylaldimine.

TABLE 16

Organotin thiolates and selenolates,^a tin coordination number ≥ 4

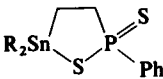
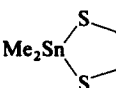
Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
Me_3SnSMe	+90	3–20% C_6H_6 or CHCl_3	<i>b</i>	298
Me_3SnSEt	+78	—		88
$\text{Me}_3\text{SnSBu}'$	+55.5	—		88
Me_3SnSPh	+90.5	—	<i>b</i>	88
				
R=Me	+191.9	CDCl_3		235
	+59.4	DMI	<i>c</i>	235
R=Bu'	+179.6	CDCl_3		235
	+96.1	DMF	<i>c</i>	235
Ph_3SnSMe	-47	30% CH_2Cl_2		288
$\text{Ph}_3\text{SnSBu}'$	-84.2	30% CH_2Cl_2		288
Me_3SnSeMe	+45.6	—		180
Me_3SnSePh	+55	—		180
Ph_3SnSeMe	-69	Saturated CH_2Cl_2		180
$\text{Me}_2\text{Sn}(\text{SMe})_2$	+144	3–20% C_6H_6 or CHCl_3	<i>b</i>	298
$\text{Me}_2\text{Sn}(\text{SEt})_2$	+127	—		88
$\text{Me}_2\text{Sn}(\text{SBu}')_2$	+75	—		88
$\text{Me}_2\text{Sn}(\text{SPh})_2$	+122.5	Neat, supercooled	<i>b</i>	88
				
	+190	Dilute CH_2Cl_2	<i>b</i>	89
	-72.6	Dilute DMSO	<i>b, c</i>	89

TABLE 16 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
	+ 149 - 56.1	Dilute CH_2Cl_2 Dilute DMSO	<i>c</i>	89 89
	+ 231.0	CDCl_3		76
$\text{Et}_2\text{Sn}(\text{SMe})_2$	+ 140	20% CCl_4		277
	+ 199	20% CH_2Cl_2 + CDCl_3		277
$\text{Bu}^n_2\text{Sn}(\text{SEt})_2$	+ 123	25% C_6H_6	<i>b</i>	1
	+ 193	25% CDCl_3		277
$\text{Ph}_2\text{Sn}(\text{SMe})_2$	+ 38.5	30% CH_2Cl_2		288
$\text{Ph}_2\text{Sn}(\text{SBu}^t)_2$	+ 30.4	30% CH_2Cl_2		288
	+ 78 - 67.7	Dilute CH_2Cl_2 Dilute DMSO	<i>c</i>	89 89
	+ 28.5 - 85.4	Dilute CH_2Cl_2 Dilute DMSO	<i>c</i>	89 89
	- 30	50% CDCl_3	<i>b</i>	1
$\text{Me}_2\text{Sn}(\text{SeMe})_2$	+ 57.1	—		180
$\text{Me}_2\text{Sn}(\text{SePh})_2$	+ 54.1	Neat, supercooled		180
$\text{Ph}_2\text{Sn}(\text{SeMe})_2$	- 20	30% CH_2Cl_2		288
$\text{MeSn}(\text{SMe})_3$	+ 167	3-20% C_6H_6 or CHCl_3		298
$\text{MeSn}(\text{SEt})_3$	+ 144	—	<i>b</i>	88
$\text{MeSn}(\text{SBu}^t)_3$	+ 65	—		88
$\text{MeSn}(\text{SPh})_3$	+ 101.5	—		88
$\text{MeSn}(\text{SCH}_2\text{CH}_2)_3\text{N}$	- 33.3	CDCl_3		55
$\text{Bu}^t\text{Sn}(\text{SCH}_2\text{CH}_2)_3\text{N}$	- 9.9	CDCl_3		55
$\text{PhSn}(\text{SMe})_3$	+ 107	30% CH_2Cl_2		288
$\text{PhSn}(\text{SBu}^t)_3$	+ 11	30% CH_2Cl_2		288
$\text{MeSn}(\text{SeMe})_3$	+ 14.8	—		180
$\text{MeSn}(\text{SePh})_3$	- 16.5	—		180
$\text{PhSn}(\text{SeMe})_3$	- 21	30% CH_2Cl_2		288

^a For more $\delta^{119}\text{Sn}$ data of organotin thiolates and selenolates see review 3.^b For other conditions see review 3.^c DMF, Dimethylformamide; DMSO, dimethyl sulfoxide.

between the ^{119}Sn nucleus ($k_{119\text{Sn}}$) and X (k_X). A third parameter, F_Z , as a function of one- and two-centre exchange integrals, describes the transfer of electron spin information between the respective geminal bonding orbitals. These parameters are related as shown by Eq. (12).

$$^2K(^{119}\text{SnZX}) = k_{119\text{Sn}}k_XF_Z \quad (12)$$

This comprises arguments 1–4 above. Since $k_{119\text{Sn}}$ or k_X represents interactions corresponding to the spin–spin coupling of directly bonded nuclei, the sign of ^2K can be predicted if the sign of F_Z is known. From various sign determinations of $^2K(^{119}\text{SnX})$ it appears that F_Z is frequently negative when the Sn–Z–X bond angle is between 90 and 110° and becomes positive when the Sn–Z–X bond angle exceeds 110°. Exceptions to this may be found if X carries a lone electron pair or pairs.

From the practical point of view, the most important geminal couplings $^2J(^{119}\text{SnX})$ are those for X = ^1H , ^{13}C , ^{31}P , or $^{117,119}\text{Sn}$, which are considered in more detail below.

a. $^2J(^{119}\text{Sn}^1\text{H})$. There is a wealth of $^2J(^{119}\text{SnC}^1\text{H})$ data available, as shown by Petrosyan.²² Therefore, no data are given here; rather, the general trends are briefly outlined. Generally, the value of $^2J(^{119}\text{Sn}^1\text{H})$ in methyltin compounds increases with the coordination number of tin and with an increasing number of electronegative ligands at the tin atom. The sign of $^2J(^{119}\text{Sn}^1\text{H})$ in methyltin compounds is positive in most cases [$^2K(^{119}\text{Sn}^1\text{H})$ has a negative sign!] except for Me_3SnLi in THF or $(\text{Me}_2\text{N})_3\text{PO}$.¹⁵¹ If the intervening atom is an sp^3 hybridized carbon the behaviour of $^2J(^{119}\text{Sn}^1\text{H})$ follows roughly the well-known pattern of $^2J(\text{HH})$, which has been rationalized using MO theory.^{196,197} Thus, in $\text{Me}_3\text{Sn}-\text{CH}_2-\text{X}$, $^2K[^{119}\text{Sn}^1\text{H}(\text{CH}_2)]$ becomes more negative if X exerts a +I effect or provides π -electron density, and it becomes more positive in the case of a –I effect.

$\text{Me}_3\text{Sn}-\text{CH}_3$	$\text{Me}_3\text{Sn}-\text{CH}_2-\text{SnMe}_3$	$\text{Me}_3\text{Sn}-\text{CH}_2-\text{Ph}$	$\text{Me}_3\text{Sn}-\text{CH}_2-\text{Cl}$
$^2J(^{119}\text{Sn}^1\text{H})$ (Hz) +54.0	+63.0	+62.7	+19.0
H–CH ₃		H–CH ₂ –Ph	H–CH ₂ –Cl
$^2J(^1\text{H}^1\text{H})$ (Hz) –12.4		–14.5	–10.8

The polarizability of the Sn–C, or of any Sn–Z, bond accounts for the sensitivity of $^2J(^{119}\text{SnZ}^1\text{H})$ toward changes in the rest of the molecule. Therefore, it is not surprising to find that $^2J(^{119}\text{Sn}^1\text{H})$ across an sp^2 hybridized carbon atom is fairly large and negative¹⁹⁸ [$^2K(^{119}\text{Sn}^1\text{H})$ is positive!], whereas the corresponding values of $^2J(\text{HH})$ are generally small and of either sign. Again, the values of $|^2J(^{119}\text{Sn}^1\text{H})|$ increase with the

coordination number of tin and with the number of electronegative ligands, e.g.:

	$^2J(^{119}\text{Sn}^1\text{H})$ (Hz)
$\text{Sn}(\text{CH}=\text{CH}_2)_4$	-99.7^{198}
	-263^{136}

In Me_3SnPPh a positive sign of $^2J(^{119}\text{SnP}^1\text{H})$ has been determined.¹⁹⁹

The magnitude of $^2J(^{119}\text{SnPt}^1\text{H})$ depends, in the usual fashion, upon the ligands at the tin atom and upon the geometrical position,²⁰⁰ cis or trans, for the ^1H relative to the ^{119}Sn nucleus.

<i>trans</i> -[PtH(SnCl ₃)(PPh ₃) ₂]	<i>trans</i> -[PtH(SnPh ₃)(Pchex ₃) ₂]
$^2J(^{119}\text{Sn}^1\text{H})$ (Hz): 1740 ²⁰¹	104 ²⁰²

In conclusion, it should be noted that the pattern of values of $^2J(^{119}\text{Sn}^1\text{H})$ is very similar to that for other $^2J(\text{M}^1\text{H})$ couplings in which $\text{M} = ^{29}\text{Si}$, ^{207}Pb , or ^{199}Hg .

b. $^2J(^{119}\text{Sn}^{13}\text{C})$. Most of the known $^2J(^{119}\text{Sn}^{13}\text{C})$ data have become available only since 1975. Sign determinations have been carried out for only a few, but, important examples.

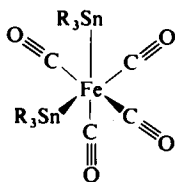
	$\text{Et}_3\text{Sn}-\text{CH}_2-\text{CH}_3$		
$^2J(^{119}\text{SnC}^{13}\text{C})$ (Hz):	+23.5 ²⁰³	+29.0 ⁹⁶	-70.0 ²⁰⁴
	$\text{Et}_3\text{Sn}-\text{C}\equiv\text{C}-\text{H}$	$\text{Me}_3\text{Sn}-\text{SnMe}_2-\text{CH}_3$	$(\text{Me}_3\text{Sn})_2\text{N}-\text{CH}_3$
$^2J(^{119}\text{SnC}^{13}\text{C})$ (Hz):	-64.7 ¹⁵⁹	-56.0 ²⁰⁵	+12.2 ²⁰⁴
$^2J(^{119}\text{SnZ}^{13}\text{C})$ (Hz):	+57.0 ²⁰⁴		

This shows that there is a fairly large range (> 125 Hz) of $^2J(^{119}\text{Sn}^{13}\text{C})$ values even in trialkyltin derivatives. The change of sign found for $^2J(^{119}\text{SnC}^{13}\text{C})$ corresponds to the observations made for $^2J(^{13}\text{CC}^1\text{H})$.²⁰⁶

As is shown later, the values and the signs of $^2J(^{119}\text{Sn}^{13}\text{C})$ are extremely useful in understanding the $^2J(^{119}\text{Sn}^{119}\text{Sn})$ data. The values of $|^2J[^{119}\text{SnC}(sp)^{13}\text{C}(sp^2)]|$ in olefins are frequently close to zero and, therefore, may be of either sign.

In five-membered cyclic organotin compounds the value of $^2J(^{119}\text{Sn}^{13}\text{C})$ reflects contributions from both geminal *and* vicinal couplings. This provides an explanation for the sign⁹⁶ and magnitude^{96,207} of the $^2J(^{119}\text{Sn}^{13}\text{C})$ data observed for these compounds.

There is clearly a need for further data, in particular for $^2J(^{119}\text{Sn}^{13}\text{C})$ values in transition metal complexes relating to coupling across the metal.^{126,208–210} Several values of $^2J[^{119}\text{Sn}^{13}\text{C}(\text{CO})]$ in carbonyl complexes have been reported. In the distorted octahedral complexes *cis*-(R_3Sn)₂Fe(CO)₄, three values of $^2J(^{119}\text{Sn}^{13}\text{C})$ have been observed in the slow exchange limit.^{208,209} It appears from the averaged value, due to fast exchange, that two couplings have the same sign and one sign is different. From the intensity of the $^{117/119}\text{Sn}$ satellites in the ^{13}C -NMR spectrum, only $^2J(^{119}\text{Sn}^{13}\text{C}^{\text{ax}})$ can be assigned with certainty. The critical dependence of the magnitude of this coupling upon geometrical changes is evident by comparing the values of $^2J(^{119}\text{Sn}^{13}\text{C})$ above with those obtained for the analogous ruthenium and osmium complexes ($\text{R} = \text{Me}$).²⁰⁸

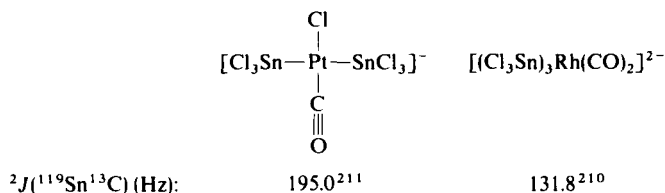


R	Me	Et	Pr	Bu	Ph	Cl
$^2J(^{119}\text{Sn}^{13}\text{C}^{\text{ax}})$ (Hz)	± 101	98	97	96	112	235
<i>trans</i> - or <i>cis</i> - $^2J(^{119}\text{Sn}^{13}\text{C}^{\text{eq}})$ (Hz)	± 65	62	65	61	80	170
	∓ 33	26	26	25	43	37

M	$^2J(^{119}\text{Sn}^{13}\text{C}^{\text{ax}})$ (Hz)	$^2J(^{119}\text{Sn}^{13}\text{C}^{\text{eq}})$ (Hz)	
		<i>trans</i>	<i>cis</i>
Ru	61	143	36
Os	54	118	40

Similarly, no clear pattern emerges so far for five-coordinate cobalt complexes $(\text{CO})_4\text{CoSnR}_3$ ($\text{R} = \text{Me}, \text{Bu}, \text{Bz}, \text{Ph}, \text{Cl}$) for which in some cases different

values of ${}^2J({}^{119}\text{Sn}^{13}\text{C}^{\text{ax}})$ and ${}^2J({}^{119}\text{Sn}^{13}\text{C}^{\text{eq}})$ have been observed (between 68 and 105 Hz).¹²⁶ Values for ${}^2J({}^{119}\text{Sn}^{13}\text{C})$ in a dianion and a monoanion have been reported and, in both cases, cis geometry has been assumed.



c. ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$. The magnitude of the geminal couplings ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$ is readily available from the ${}^{119}\text{Sn}$ -NMR spectra of the relevant compounds. In addition to the ${}^{117}\text{Sn}$ satellites [AX spin system converted to ${}^1J({}^{119}\text{Sn}^{119}\text{Sn})$ by multiplication with $\gamma({}^{119}\text{Sn})/\gamma({}^{117}\text{Sn}) = 1.0465$] the ${}^{119}\text{Sn}$ satellites (AB spin system) can be observed if the tin atoms are in different chemical surroundings. The large range of ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$ results has been mentioned already and there is clearly a need to classify these data.

A first step in this direction requires a knowledge of the sign of ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$. So far the sign of ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$ has been determined for only four compounds; $(\text{Me}_3\text{Sn})_3\text{CH}$ (-309 Hz),²¹² $(\text{Me}_3\text{Sn})_2\text{SnMe}_2$ ($+763$ Hz),²⁰⁴ $(\text{Me}_3\text{Sn})_2\text{NN}(\text{Me})\text{SnMe}_3$ (-833 Hz),²⁰⁴ and $(\text{Me}_3\text{Sn})_3\text{P}$ (-331.4 Hz).²¹³ The signs of other ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$ values can be deduced by comparison with the known signs of ${}^2J({}^{119}\text{Sn}^{13}\text{C})$ in analogous compounds.²⁰⁴ If an Me_3Sn group is replaced by a methyl group a linear correlation between ${}^2J({}^{119}\text{Sn})$ and ${}^2J({}^{119}\text{Sn}^{13}\text{C})$ emerges. This involves coupling across $Z = \text{C}, \text{Sn}, \text{N}, \text{S}$. From this a positive sign for ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$ in $(\text{Me}_3\text{Sn})_3\text{SnEt}$ is deduced showing the parallel trend for ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$ with $Z = \text{C}$ or Sn .²⁰⁴

	$\text{Me}_2\text{Z}(\text{SnMe}_3)_2$	$\text{EtZ}(\text{SnMe}_3)_3$	$\text{Z}(\text{SnMe}_3)_4$
$Z = \text{C}$	± 19	-230	-325
$Z = \text{Sn}$	$+763$	$+259$	± 20

An increasing number of Me_3Sn groups on the central atom Z leads to more negative contributions for ${}^2J({}^{119}\text{Sn}^{119}\text{Sn})$.

In bis(triorganotin) oxides the geminal couplings $|{}^2J({}^{119}\text{Sn}^{119}\text{Sn})|$ correspond to linear arrangements, SnOSn (solid state), and it is concluded that the

linear structure $[(\text{Bu}'_3\text{Sn})_2\text{O}, [(\text{PhCH}_2)_3\text{Sn}]_2\text{O}]$ prevails in solution,²¹⁴ e.g.:

	$(\text{Bu}''_3\text{Sn})_2\text{O}$	$(\text{Bu}'_3\text{Sn})_2\text{O}$	$[(\text{PhCH}_2)_3\text{Sn}]_2\text{O}$	$(\text{Ph}_3\text{Sn})_2\text{O}$
$^2J(^{119}\text{Sn}^{119}\text{Sn})$ (Hz)	440	916	617	437

Comparison with data for sulphides, which all have a bent SnSSn fragment, shows that these values of $|^2J(^{119}\text{Sn}^{119}\text{Sn})|$ lie in a narrow range,²¹⁴ e.g.:

	$(\text{Me}_3\text{Sn})_2\text{S}$	$\{(\text{PhCH}_2)_3\text{Sn}\}_2\text{S}$	$(\text{Ph}_3\text{Sn})_2\text{S}$
$^2J(^{119}\text{Sn}^{119}\text{Sn})$ (Hz)	218	230	222

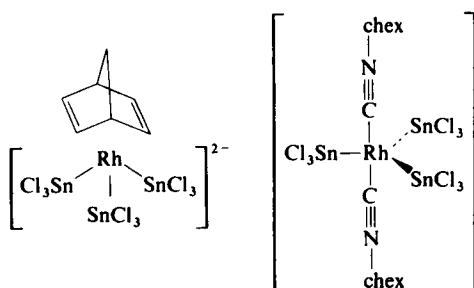
On the basis of the relationship between $^2J(^{119}\text{Sn}^{119}\text{Sn})$ and $^2J(^{119}\text{Sn}^{13}\text{C})$, a negative sign is likely for $^2J(^{119}\text{Sn}^{119}\text{Sn})$ in the sulphides.²⁰⁴ There are no $^2J(^{119}\text{Sn}^{13}\text{C})$ data available so far to deduce a sign for the $^2J(^{119}\text{Sn}^{119}\text{Sn})$ couplings in the oxides.

Strong intermolecular association of stannanes is indicated by the presence of a geminal coupling across the oxygen atom $[(\text{MeSn}(\text{OCH}_2\text{CH}_2)_3\text{N})_3]$, $^2J(^{119}\text{Sn}^{119}\text{Sn}) = 156$ Hz].⁵⁵ It should be possible to verify the ladder structure of the 1,3-dihalogeno-1,1,3,3-tetraalkyldistannoxanes on the basis of $^2J(^{119}\text{Sn}^{119}\text{Sn})$ data. However, so far only the $\delta^{119}\text{Sn}$ values are reported.⁷⁰

The most intriguing values of $^2J(^{119}\text{Sn}^{119}\text{Sn})$ are found when the intervening atom is a transition metal (Table 25). Many trichlorostannate complexes have been studied by multinuclear resonance.^{189-192,210,211,215-231} The values of $^2J(^{119}\text{Sn}^{119}\text{Sn})$ can be obtained from the ^{119}Sn -NMR spectra, provided intermolecular exchange of the SnCl_3 groups is sufficiently slow in comparison with the NMR time scale. At present, no quantitative theoretical approach is available to explain the enormous range of $|^2J(^{119}\text{Sn}^{119}\text{Sn})|$, from several hundred to $>35,000$ Hz.¹⁸⁹ However, some trends are in nice qualitative agreement with the behavior displayed, e.g., by $^2J(^{31}\text{P}^{31}\text{P})$, as far as the geometrical dependence and the dependence upon the metal itself are concerned.¹⁸⁹

In the $[\text{Pt}(\text{SnCl}_3)_5]^{3-}$ anion an average value is observed for $^2J(^{119}\text{Sn}^{119}\text{Sn}) = 6520$ Hz.^{211,217,226} Taking into account the various known data for trans $|^2J(^{119}\text{Sn}^{119}\text{Sn})|$, cis $|^2J(^{119}\text{Sn}^{119}\text{Sn})|$, and eq $|^2J(^{119}\text{Sn}^{119}\text{Sn})|$ (in trigonal-bipyramidal Pt complexes) it appears that it is necessary to assume like signs for trans ^2J and eq ^2J (probably positive) and the opposite sign for cis ^2J in order to match the observed averaged value of ^2J in the platinum-pentakis(trichlorostannate) trianion. All of these values of $^2J(^{119}\text{Sn}^{119}\text{Sn})$ show a strong dependence on geometry and on the very subtle

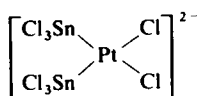
effects exerted by other ligands:



$^2J(^{119}\text{Sn}^{119}\text{Sn})$ (Hz):

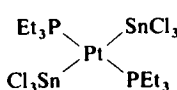
2523²¹⁰

14,141²²²

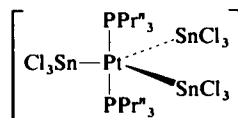


$^2J(^{119}\text{Sn}^{119}\text{Sn})$ (Hz):

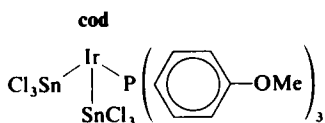
2601²²⁴



36,286¹⁹¹

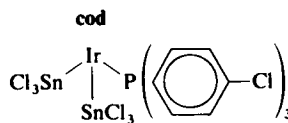


18,663¹⁹¹



$^2J(^{119}\text{Sn}^{119}\text{Sn})$ (Hz):

1831²²⁹



903²²⁹

It has been pointed out that there appears to be no relationship between $^2J(^{119}\text{Sn}^{119}\text{Sn})$ and $^1J(\text{M}^{119}\text{Sn})$ ($\text{M} = ^{195}\text{Pt}, ^{103}\text{Rh}$).^{189,210} This is not unexpected considering the various contributions that arise in particular for the two-bond coupling pathways (Section V,B,2).

d. $^2J(^{119}\text{Sn}^{31}\text{P})$. Values of $^2J(^{119}\text{Sn}^{31}\text{P})$ are reported for various types of compound where the intervening atoms are carbon, tin, oxygen, sulphur, selenium and various transition metals. Examples are given below and in Tables 24 and 25.

$^2J(^{119}\text{Sn}^{31}\text{P})$ (Hz)

$\text{Me}_3\text{P}=\text{C}(\text{SnMe}_3)_2$ 38.4 ²³³	$\text{P}(\text{Me}_2\text{Sn}=\text{SnMe}_2)_3\text{P}$ 93.0 ¹⁷⁶	$\text{trans-}[\text{SnCl}_4\{(\text{MeO})_3\text{PO}\}_2]$ 195.0 ²³⁴	$[\text{Cl}_3\text{Sn}-\text{OPBu}_3]^-$ 160.0 ⁶⁵
$[\text{Sn}[\text{XP}(\text{chex})_3]_3]^{2+}; \text{X} = \text{O} \quad \text{S} \quad \text{Se}$			
237.0, 11.0, 27.0 ¹⁸¹			

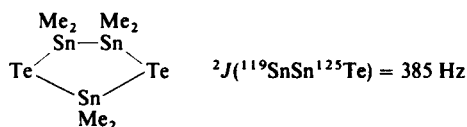
In the 1,1-dialkyl-3-phenyl-3-thio-1,2,3-stannathiophospholanes the values of $^2J(^{119}\text{Sn}^{31}\text{P})$ must be regarded as arising from contributions from $^3J(^{119}\text{SnCC}^{31}\text{P})$ and $^2J(^{119}\text{SnS}^{31}\text{P})$, for which different signs are proposed.²³⁵

		$^2J(^{119}\text{Sn}^{31}\text{P})$ (Hz)
	$R = R' = \text{Me}$	65.4 in CDCl_3
		97.1 in pyridine
		104.8 in HMPT

The solvent dependence of $^2J(^{119}\text{Sn}^{31}\text{P})$ reflects the increase in coordination number of the tin atom.

No sign of $^2J(^{119}\text{Sn}^{31}\text{P})$ has been determined so far. However, the analogy between $^2J(^{119}\text{Sn}^{31}\text{P})$, $^2J(^{119}\text{Sn}^{149}\text{Sn})$, and $^2J(^{31}\text{P}^{31}\text{P})$ in transition metal complexes (Tables 24 and 25), as far as the geometrical dependence (cis, trans) is concerned, suggests that at least the reduced couplings $^2K(^{119}\text{Sn}^{31}\text{P})$ and $^2K(^{31}\text{P}^{31}\text{P})$ (positive) for the trans coupling pathway have the same sign.¹⁸⁹ Owing to the large difference in magnitude between $|^2J(^{119}\text{Sn}^{31}\text{P})|$ cis and trans values, this parameter is valuable in the structural elucidation of transition metal complexes containing stannyl and phosphine ligands.

e. Other geminal couplings, $^2J(\text{Sn}X)$. In the five-membered tin–tellurium heterocycle, $^2J(^{119}\text{Sn}^{125}\text{Te})$ has been observed¹⁶⁸:



In polyfluoroorganotin compounds values of $|^2J(^{119}\text{Sn}^{19}\text{F})|$ range from < 10 to > 200 Hz.^{121,184,236,237}

Again, there are remarkable values of $^2J(^{119}\text{Sn}^{195}\text{Pt})$ and $^2J(^{119}\text{Sn}^{199}\text{Hg})$ in transition metal complexes:

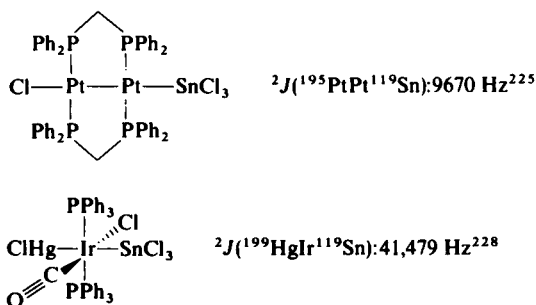


TABLE 17

Organotin chalcogenides (Sn—X—Sn),^a tin coordination number = 4

Compound	$\delta^{119}\text{Sn}^b$	Solvent	Footnotes	Reference
(Me ₃ Sn) ₂ O	+109.5	—		301
	+110.6	10% C ₆ D ₆		76
	+113.1	80% CH ₂ Cl ₂		301
	+117.1	50% CH ₂ Cl ₂		301
(Et ₃ Sn) ₂ O	+87.0	90% CH ₂ Cl ₂		9
	+86.2	CCl ₄		279
(Pr ⁿ ₃ Sn) ₂ O	+77.8	—		3
(Bu ⁿ ₃ Sn) ₂ O	+82	90% C ₆ H ₆		8
	+84.5	CCl ₄		279
	+77.8	—		3
(Bu ^t ₃ Sn) ₂ O	−39.3	Saturated C ₆ H ₆		4
[(PhCH ₂) ₃ Sn] ₂ O	+9.3	CDCl ₃		76
(Ph ₃ Sn) ₂ O	−85.5	CDCl ₃		76
(Bu ^t ₂ SnO) ₃	−84.3	CDCl ₃		311
(Am ^t ₂ SnO) ₃	−72.9	CDCl ₃		311
Ph ₂ Sn(OSnPh ₃) ₂	−109	CH ₂ Cl ₂		8
[(2,6-Et ₂ -C ₆ H ₄) ₂ SnO] ₃	−125	CCl ₄		312
(Me ₃ Sn) ₂ S	+86.5	20% CH ₂ Cl ₂		301
	+93.9	CDCl ₃		313
	+87.0	C ₆ D ₆		76
(Bu ⁿ ₃ Sn) ₂ S	+81.9	CCl ₄		279
[(C ₆ H ₅ CH ₂) ₃ Sn] ₂ S	+26.9	CDCl ₃		76
(Ph ₃ Sn) ₂ S	−53.7	CDCl ₃		76
(Me ₂ SnS) ₃	+125.6	CS ₂	c	278
	+128	C ₆ H ₆		8
	+128.6	Toluene/C ₆ D ₆		314
	+131.0	C ₆ H ₆		168
(Et ₂ SnS) ₃	+134	C ₆ H ₆		168
(Pr ^t ₂ SnS) ₃	+119	C ₆ H ₆		168
(Bu ⁿ ₂ SnS) ₃	+126.9	CCl ₄		279
(Bu ^t ₂ SnS) ₂	+123	C ₆ H ₆		168
	+124.1	CDCl ₃		76
(Ph ₂ SnS) ₃	+16.8	CDCl ₃		76

R ¹	R ²			
Me	Ph	139.1 (SnR ¹), 15.9 (SnR ²)	CDCl ₃	76
Ph	Me	15.7 (SnR ¹), 136.2 (SnR ²)	CDCl ₃	76

TABLE 17 (cont.)

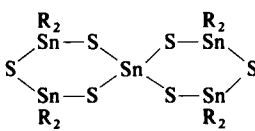
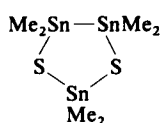
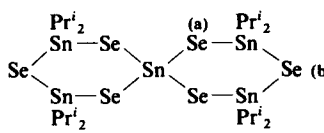
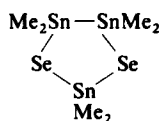
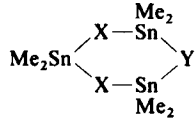
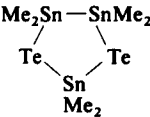
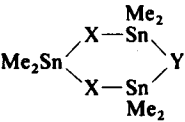
Compound	$\delta^{119}\text{Sn}^b$	Solvent	Footnotes	Reference				
								
R=Pr ⁱ	+ 89.9 (SnS ₄), + 116.4 (SnS ₂)	CDCl ₃		315				
R=Bu ⁱ	+ 84.1 (SnS ₄), + 108.4 (SnS ₂)	CDCl ₃		315				
	+ 44 (Sn) + 176 (SnS)	C ₆ D ₆		168				
(Me ₃ Sn) ₂ Se	+ 44.5 (1060)	20% CH ₂ Cl ₂		301				
	+ 42.6 (1090)	C ₆ D ₆		12				
	+ 50.7 (nr)	CDCl ₃	d	76				
[(C ₆ H ₅ CH ₂) ₃ Sn] ₂ Se	− 2.0 (1281)	CDCl ₃		313				
(Ph ₃ Sn) ₂ Se	− 78.5 (1213)	CDCl ₃		76				
	− 76 (nr)	CDCl ₃	d	76				
(Me ₂ SnSe) ₃	+ 42 (1228)	C ₆ D ₆		313				
(Ph ₂ SnSe) ₃	− 44 (1380)	CDCl ₃		168				
				76				
	− 320 (SnSe ₄) (1535), 87.1 (SnSe ₂) [1236 (a), 1339 (b)]	CDCl ₃		315				
		CDCl ₃		315				
	+ 82 (Sn) (1263), + 21 (Sn ₂) (992)	C ₆ D ₆		168				
								
<table data-bbox="113 1352 204 1413"><tr><td>X</td><td>Y</td></tr><tr><td>S</td><td>Se</td></tr></table>	X	Y	S	Se	+ 134 (SnX ₂), + 84 (SnY) (1238)	C ₆ D ₆ C ₆ D ₆		168 168
X	Y							
S	Se							

TABLE 17 (cont.)

Compound	$\delta^{119}\text{Sn}^b$	Solvent	Footnotes	Reference
Se S	+ 34 (SnX ₂) (1220), + 91 (SnY) (1245)	C ₆ D ₆		168
(Me ₃ Sn) ₂ Te	− 66.8 (1385)	80% CH ₂ Cl ₂	<i>d</i>	301
(Ph ₃ Sn) ₂ Te	− 59.3 (nr)	CDCl ₃		313
(Me ₂ SnTe) ₃	− 143.2 (nr)	CDCl ₃		313
(Me ₂ SnTe) ₃	− 195 (3098)	C ₆ D ₆		168
	− 164 (Sn) (3159), − 38 (Sn ₂) (2554)	C ₆ D ₆		168
				
X Y				
S Te	+ 148 (SnX ₂), − 32 (SnY) (3198)	C ₆ D ₆		168
Te S	− 225 (SnX ₂) (3021), − 9 (SnY) (3278)	C ₆ D ₆		168
Se Te	+ 55 (SnX ₂) (1244, Se), − 79 (SnY) (1196, Se; 3174, Te)	C ₆ D ₆		168
Te Se	− 213 (SnX ₂) (3049, Te), − 64 (SnY) (1211, Se; 3220, Te)	C ₆ D ₆		168
[(Me ₂ SnCl) ₂ O] ₂	− 81, − 128	C ₂ H ₂ Cl ₄	<i>e</i>	70
(Me ₂ SnCl) ₂ S	+ 144	20% CH ₂ Cl ₂		9

^a For more data on organotin chalcogenides see reviews 2–4.

^b ¹J(¹¹⁹Sn⁷⁷Se) or ¹J(¹¹⁹Sn¹²⁵Te) values given in parentheses.

^c For other conditions see review 4.

^d nr, Not reported.

^e $\delta^{119}\text{Sn}$ (± 4 ppm) reported relative to Me₂SnCl₂, 0.2 M in C₂H₂Cl₄ [83/29]; calculated for this table with $\delta^{119}\text{Sn}$ (Me₂SnCl₂) = + 137.

TABLE 18

Tin chalcogenides ($\text{Sn}-\text{X}-$),^a tin coordination number ≥ 4

Compound	$\delta^{119}\text{Sn}^b$	Solvent	Footnotes	Reference
$[\text{Sn}(\text{OH})_6]^{2-}$	-590	H_2O		281
$[\text{Sn}(\text{OBU}')_2]_n$	-93	Toluene, C_6D_6		316
$[\text{Sn}(\text{OSiMe}_3)_2]_2$	-221	C_6D_6		317
$[\text{Sn}_2\text{O}(\text{OSiMe}_3)_2]_2$	-136	?		317
$[\text{Sn}(\text{OSiPh}_3)_2]_2$	-339.5	Toluene, C_6D_6		316
$[\text{Sn}(\text{OPchex}_3)_2]^{2+}$	-899	SO_2 , -60°C	<i>d</i>	181
$[\text{Sn}(\text{OPchex}_3)_2]^{2+}$	-720	SO_2 , -60°C	<i>d</i>	181
$[\text{Sn}(\text{OCH}_2\text{CH}_2)_2\text{NMe}]_2$	-303	CD_2Cl_2		68
$[\text{Sn}(\text{OCH}_2\text{CH}_2)_2\text{NBu}']_2$	-314	CD_2Cl_2		68
$\text{Sn}(\text{SMe})_4$	+160	50% CH_2Cl_2		88
	+165	3-20% C_6H_6 or CHCl_3		298
	+165	—		288
$\text{Sn}(\text{SEt})_4$	+138	—		88
				288
$\text{Sn}(\text{SPr}')_4$	+106.5	—		88
				288
$\text{Sn}(\text{SBu}')_4$	+26.0	Saturated CH_2Cl_2		88
				288
$\text{Sn}(\text{SCH}_2\text{Ph})_4$	+132.0	25% CCl_4		288
$\text{Sn}(\text{SPh})_4$	+44	Saturated CH_2Cl_2		88
				288
$(\text{MeS})_3\text{SnSBu}'$	+127	15% CH_2Cl_2		
$(\text{MeS})_2\text{Sn}(\text{SBu}')_2$	+92	15% CH_2Cl_2		
$\text{MeSSn}(\text{SBu}')_3$	+58	15% CH_2Cl_2		288
$(\text{MeS})_4-n\text{SnSCH}_2\text{Ph}_n$ ($n = 0, 1, 2, 3$)	+130 to +160	5% CH_2Cl_2		288
$(\text{MeS})_3\text{SnSPh}$	+131	15% CH_2Cl_2		
$(\text{MeS})_2\text{Sn}(\text{SPh})_2$	+104	15% CH_2Cl_2		288
$\text{MeSSn}(\text{SPh})_3$	+77	15% CH_2Cl_2		
$(\text{Bu}'\text{S})_3\text{SnI}$	-210.5	30% CH_2Cl_2		
$(\text{Bu}'\text{S})_2\text{SnI}_2$	-565	30% CH_2Cl_2		288
$\text{Bu}'\text{SSnI}_3$	-1065	30% CH_2Cl_2		
$[\text{Sn}(\text{SBu}')_2]_2$	+77.7	Toluene/ C_6D_6		318
	+63.2	Toluene/ C_6D_6 /THF		
$\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{PBu}'$	-238 (903, ^{31}P)	C_6H_6		59
$[\text{Sn}(\text{SPh})_3]^-$	+125	CD_3OD , -75°C		319
	+140	CD_3OD , $+22^\circ\text{C}$		182
$[\text{Sn}(\text{SPchex}_3)_2]^{2+}$	+94	SO_2 , -60°C	<i>d</i>	181
$[\text{Sn}(\text{SPh})_2\text{SePh}]^-$	+150	CD_3OD , -75°C		182
$[\text{Sn}(\text{SPh})(\text{SePh})_2]^-$	+170	CD_3OD , -75°C		182
$[\text{Sn}(\text{SPchex}_3)_2(\text{SePchex}_3)]^{2+}$	+133	SO_2 , -60°C	<i>d</i>	181
$[\text{Sn}(\text{SPchex}_3)(\text{SePchex}_3)_2]^{2+}$	+161	SO_2 , -60°C	<i>d</i>	181
	(650)			

TABLE 18 (*cont.*)

Compound	$\delta^{119}\text{Sn}^b$	Solvent	Footnotes	Reference
$\text{Sn}(\text{SeMe})_4$	-80.5 (1520)	—		180, 288
$\text{Sn}(\text{SeBu}')_4$	-262	Saturated CH_2Cl_2		288
$\text{Sn}(\text{SePh})_4$	-135	Saturated CH_2Cl_2		288
$(\text{MeS})_3\text{SnSeMe}$	+101	20% CH_2Cl_2		
$(\text{MeS})_2\text{Sn}(\text{SeMe})_2$	+43	20% CH_2Cl_2		288
$\text{MeSSn}(\text{SeMe})_3$	-21	20% CH_2Cl_2		
$(\text{MeS})_3\text{SnSeBu}'$	+80.6	30% C_6D_6		
$(\text{MeS})_2\text{Sn}(\text{SeBu}')_2$	-18.2	30% C_6D_6		288
$\text{MeSSn}(\text{SeBu}')_3$	-129.5	30% C_6D_6		
$(\text{MeS})_3\text{SnSePh}$	+87	40% CH_2Cl_2		
$(\text{MeS})_2\text{Sn}(\text{SePh})_2$	+12.5	40% CH_2Cl_2		288
$\text{MeSSn}(\text{SePh})_3$	-61	40% CH_2Cl_2		
$[\text{Sn}(\text{SePchex}_3)_3]^{2+}$	+181 (570)	SO_2 , -60°C	<i>d</i>	181
$[\text{Sn}(\text{SePh})_3]^-$	+184 (710)	CD_3OD , -75°C		182
	+207	CD_3OD , $+22^\circ\text{C}$		182
$[\text{SnTe}_4]^{4-}$	-1828 (2804)	Ethylene diamine	<i>c</i>	82

^a See also reviews 2 and 4 and, in particular, references 288 and 391–393.

^b Values of $^1J(^{119}\text{Sn}^{77}\text{Se})$ and $^1J(^{119}\text{Sn}^{125}\text{Te})$ are given in parentheses.

^c $\delta^{119}\text{Sn}$ values given as -598 ppm relative to $[\text{Sn}_9]^{4-}$ for which a $\delta^{119}\text{Sn}$ value (-1230) relative to Me_4Sn was reported.⁸⁰

^d Referencing is not clear; $\delta^{119}\text{Sn} [\text{Sn}(\text{AsF}_6)_2(\text{SO}_2, -60^\circ\text{C})]$ is given as $+(?)1898$ relative to Me_4Sn ; shifts in this table are given relative to Me_4Sn using the data in reference 182.

3. Vicinal couplings, $^3J(\text{SnX})$

There are numerous values of $^3J(^{119}\text{SnX})$ known for various X nuclei although, at present, the main interest is probably focused on $\text{X} = ^{13}\text{C}$. In the case of $\text{X} = ^1\text{H}$, a Karplus-type²³⁸ dependence may eventually emerge. This dependence is also readily shown by the values of $^3J(^{119}\text{Sn}^{13}\text{C})$.²³⁹ It is expected that the dependence of $^3J(^{119}\text{SnX})$ on the dihedral angle will be the subject of further studies when more data for other elements for X become available. In any case, the treatment of all $^3J(^{119}\text{SnX})$ data is confined strictly to empirical use considering the complex situation involving the charge distribution in three bonds, the large polarizable ^{119}Sn nucleus, the properties of the X nucleus, and the various geometrical parameters (bond length, bond angles, and dihedral angles).

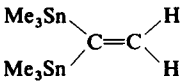
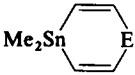
a. $^3J(^{119}\text{Sn}^1\text{H})$. A negative sign for $^3J(^{119}\text{Sn}^1\text{H})$ [positive sign for $^3K(^{119}\text{Sn}^1\text{H})!$] has been observed in all cases where it has been determined.

Many of these data have already been reviewed.²² In most cases it holds that $|^3J(^{119}\text{Sn}^1\text{H})| > |^2J(^{119}\text{Sn}^1\text{H})|$. Except for some representative examples for ethyltin and *tert*-butyltin compounds, there have been only a few attempts to use the values of $^3J(^{119}\text{SnCC}^1\text{H})$ in alkyltin compounds. This is partly a consequence of the complex ^1H -NMR spectra, which may lead to a similarly complex pattern of $^{117/119}\text{Sn}$ satellites that, in general, requires computer-assisted spectral analysis. Although it is possible, in principle, to obtain many of these data from ^{119}Sn -NMR spectra (^1H coupled),²⁴⁰ this has not attracted much interest so far. The values of $|^3J(^{119}\text{Sn}^1\text{H})|$ decrease in magnitude when the carbon atom, linked to tin in the coupling pathway $^{119}\text{Sn}-\text{C}-\text{C}-^1\text{H}$, is replaced by a heteroelement, either electropositive, e.g., Si, Sn, or Pb,^{12,13} or electronegative, e.g., N, S, or Se.^{88,127,180} Interestingly, the course of hydrostannation is readily shown using $\text{R}_3\text{Sn}-^2\text{H}$ compounds. By observing the ^1H decoupled ^{119}Sn -NMR spectra, the couplings $^3J(^{119}\text{Sn}^2\text{H})$ are resolved and the stereochemistry is deduced from the relative magnitude of $^3J(^{119}\text{Sn}^2\text{H})$.^{87,101,102}

There are plenty of data available for spin-spin coupling between the ^{119}Sn nucleus and olefinic protons. In most cases these data are readily obtained from routine ^1H -NMR spectra and their diagnostic value is highly appreciated:

$$|^3J(^{119}\text{Sn}^1\text{H})|_{\text{trans}} > |^3J(^{119}\text{Sn}^1\text{H})|_{\text{cis}} \approx |^2J(^{119}\text{Sn}^1\text{H})|$$

Similar to the behaviour of $^3J(\text{HH})_{\text{cis,trans}}$, an increase in $|^3J(^{119}\text{Sn}^1\text{H})|_{\text{cis,trans}}$ is observed when electropositive substituents are attached to the olefinic carbon atom:

	$^3J(^{119}\text{Sn}^1\text{H})$:	cis	124 Hz ²⁴¹
		trans	208 Hz ²⁴¹
	$^3J(^{119}\text{Sn}^1\text{H})_{\text{trans}}(\text{Hz})$ ²⁴²		E
	154.0		BNEt ₂
	127.0		CMe ₂
	160.6		SiMe ₂
	174.8		SnMe ₂

b. $^3J(^{119}\text{Sn}^{13}\text{C})$. The magnitude of the vicinal coupling, $^3J(^{119}\text{Sn}^{13}\text{C})$, across a C-C single bond is related to the dihedral angle ϕ between ^{119}Sn and ^{13}C by a Karplus-type dependence,^{146,154,238,239,243,244} provided that all values of $|^3J(^{119}\text{Sn}^{13}\text{C})|$ have the same relative sign, which is likely to be negative [thus $^3K(^{119}\text{Sn}^{13}\text{C})$ is positive]. Examples for $^3J(^{119}\text{Sn}^{13}\text{C})$ are given

in Table 30, and the relationship between $^3J(^{119}\text{Sn}^{13}\text{C})$ and ϕ is depicted graphically in Fig. 8.

Similarly, it has been observed that $|^3J(^{119}\text{Sn}^{13}\text{C})|_{\text{trans}} > |^3J(^{119}\text{Sn}^{13}\text{C})|_{\text{cis}}$ in olefinic compounds.⁹⁰ However, the magnitude depends critically upon the nature of the substituents:

$^3J(^{119}\text{Sn}^{13}\text{C})$			
trans 77.8 ⁹⁰	106.0 ²⁴¹	83.0 ²⁴⁵	141.5 ²⁴⁶
cis 49.3 ⁹⁰	79.0 ²⁴¹	64.3 ²⁴⁵	118.2 ²⁴⁶

Similar to the case of $^3J(^{119}\text{Sn}^1\text{H})$, an increase in the magnitude of $|^3J(^{119}\text{Sn}^{13}\text{C})|$ is observed in the presence of electropositive substituents at the C=C double bond.

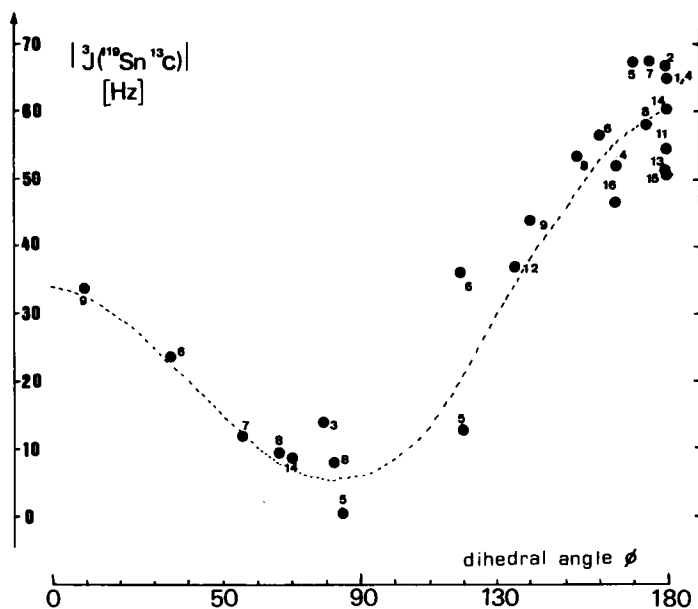
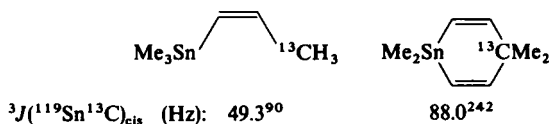


FIG. 8. Relationship between the dihedral angle ϕ and $^3J(^{119}\text{Sn}^{13}\text{C})$. The numbers correspond to the entries in Table 30.

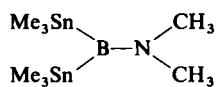
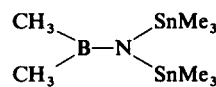
Comparison of the $^3J(^{119}\text{Sn}^{13}\text{C})$ values in trimethyl(1-propenyl)stannane and 1,1,4,4-tetramethyl-1-stanna-2,5-cyclohexadiene shows that the two equivalent coupling pathways contribute roughly additively to $^3J(\text{Sn}^{13}\text{C})$ in the latter compound.



A considerable number of $^3J(^{119}\text{Sn}^{13}\text{C})$ values are available in which the ^{13}C atom is part of an aromatic or heteroaromatic system. In general, a range of ~ 30 – 60 Hz is observed and in most cases it is found that $|^3J(^{119}\text{Sn}^{13}\text{C})| > |^2J(^{119}\text{Sn}^{13}\text{C})|$.¹²⁵

In allenyltrimethylstannanes, $^3J(^{119}\text{Sn}^{13}\text{C})$ is found to range between 45 and 70 Hz. No obvious dependence on the nature of the substituents has been derived so far.^{154,247,248}

There are plenty of examples of $^3J(^{119}\text{Sn}^{13}\text{C})$ with one or two atoms, other than carbon, in between the coupled nuclei. In most cases, no systematic study has been carried out. However, the potential of this parameter has been shown in a study of *B*- and *N*-(trimethylstannyl)aminoboranes.¹⁸ Particularly noteworthy are the two following isomeric compounds for which a barrier to rotation about the B–N bond is shown by the differing couplings¹⁸: $|^3J(^{119}\text{Sn}^{13}\text{C})|_{\text{trans}} > |^3J(^{119}\text{Sn}^{13}\text{C})|_{\text{cis}}$.

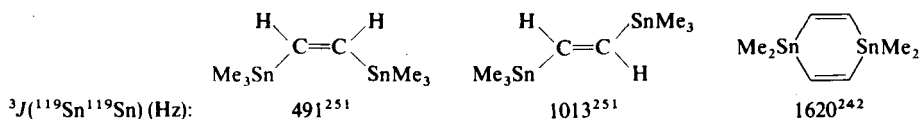
$^3J(^{119}\text{Sn}^{13}\text{C})$		
 		
trans	88.4	48.4
cis	78.9	33.0

The greater value of $|^3J(^{119}\text{Sn}^{13}\text{C})|$ is associated with the coupling path $^{119}\text{Sn}-\text{B}-\text{N}-^{13}\text{C}$. This is qualitatively in agreement with predictions that assume dominance of the contact term. The strongly polarized Sn–N bond (coupling pathway $^{119}\text{Sn}-\text{N}-\text{B}-^{13}\text{C}$) reduces the ^{119}Sn *s* electron participation as compared with the much less polar Sn–B bond.

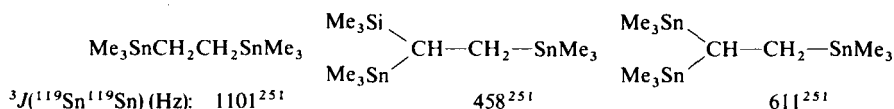
Many organotin compounds of the type $(\text{R}_3\text{Sn})_2\text{X}$ or $(\text{R}_2\text{SnX})_n$ ($\text{X} = \text{N}, \text{P}, \text{O}, \text{S}, \text{Se}, \text{Te}$) have been studied by ^{13}C NMR.^{76,143} In all cases studied the $^3J(^{119}\text{SnXSn}^{13}\text{C})$ couplings are small (< 12 Hz), and frequently they are not observed at all. The same behaviour is found for the coupling pathways $^{119}\text{Sn}-\text{C}-\text{Sn}-^{13}\text{C}$,²⁴³ $^{119}\text{Sn}-\text{Sn}-\text{Sn}-^{13}\text{C}$,¹⁶⁷ or $^{119}\text{Sn}-\text{Si}-\text{Sn}-^{13}\text{C}$.⁷⁶ This is

also observed to a lesser extent for the introduction of $X = N, O, S$ instead of carbon atoms.^{100,249,250}

c. $^3J(^{119}\text{Sn}^{119}\text{Sn})$. The rapid development of organotin chemistry has led to numerous compounds containing two or more tin atoms separated by three bonds with various intervening atoms. Changes in $|^3J(^{119}\text{Sn}^{119}\text{Sn})|$ are expected to correspond to those observed for $|^3J(^{119}\text{Sn}^{13}\text{C})|$ and, therefore, indirect structural information will become available. So far a fairly complete data set is available for $^3J(^{119}\text{Sn}^{119}\text{Sn})$ couplings across $\text{C}=\text{C}$ double bonds in methyltin derivatives. This shows that $|^3J(^{119}\text{Sn}^{119}\text{Sn})|_{\text{trans}} > |^3J(^{119}\text{Sn}^{119}\text{Sn})|_{\text{cis}}$, although the value of $|^3J(^{119}\text{Sn}^{119}\text{Sn})|$ in 1,4-dis-tannacyclohexadiene is much larger than predicted from the additivity of the two equivalent coupling pathways:



If the intervening carbon atoms are sp^3 hybridized the values of $|^3J(^{119}\text{Sn}^{119}\text{Sn})|$ become smaller when electropositive substituents are attached to the carbon atoms:



The increase in $|^3J(^{119}\text{Sn}^{119}\text{Sn})|$ in the 1,1,2-tris(trimethylstannyl)ethane as compared to the 1,2-bis(trimethylstannyl)-1-trimethylsilylethane can be traced to its dependence on dihedral angle. In the former compound there are, on average, more positions with a small or large dihedral angle between the relevant $\text{Sn}-\text{C}$ bonds than in the latter compound.

The values of $^3J(^{119}\text{Sn}^{119}\text{Sn})$ in bis(trialkylstannyl)ethynes are fairly small and solvent dependent.¹⁵⁹ Interestingly, no $\text{Sn}-\text{Sn}$ coupling is observed in the dicobalthexacarbonyl complexes of these ethynes. It is assumed that the $\text{Sn}-\text{C}-\text{C}$ bond angles ($>135^\circ$) in the complexes lead to weak electron correlation between the two $\text{Sn}-\text{C}$ bonds.²⁵²

The temperature dependence of $^3J(^{119}\text{Sn}^{119}\text{Sn})$ in 1,2-dimethyl-1,2-bis(trimethylstannyl)hydrazine (from 272 to 222 Hz between -30 and $+100^\circ\text{C}$) has been attributed to changing populations of conformations with anti and gauche arrangement of the Me_3Sn groups.¹⁰⁰

The finding of a very large value of $|^3J(^{119}\text{Sn}^{119}\text{Sn})|$ (25,430 Hz) across a $\text{Pt}-\text{Pt}$ bond in $[\text{Pt}_2(\text{SnCl}_3)_2(\mu\text{-dppm})_2]$ ²²⁵ ($\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$) fits into the somewhat abnormal behaviour of $^nJ(^{119}\text{SnX})$ data in SnCl_3 complexes.

TABLE 19

Tin nitrogen and organotin nitrogen compounds,^a tin coordination number ≥ 2

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$\text{Me}_3\text{SnNMe}_2$	+ 75.5	10% C_6H_6	<i>b</i>	320
$\text{Me}_3\text{SnNEt}_2$	+ 60	25% C_6H_6	<i>b</i>	320
$\text{Me}_3\text{SnN(H)Ph}$	+ 46.4	C_6H_6		12
$\text{Me}_3\text{SnN(Me)Ph}$	+ 73.0	C_6H_6		118
$\text{Me}_3\text{Sn}-\text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array}$	+ 72.9	C_6D_6		76
$\text{Me}_3\text{SnN(Bu')SiMe}_3$	+ 30.8	20% C_6D_6		212
MeSnN(Ph)SiMe_3	+ 64	50% C_6H_6		9
$(\text{Me}_3\text{Sn})_2\text{NMe}$	+ 81.0	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NBu'}$	+ 40.7	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NPh}$	+ 63.0	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NC}_6\text{H}_4\text{-}p\text{-Me}$	+ 62.7	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{N-C}_6\text{H}_4\text{-}o\text{-Me}$	+ 64.0	20% C_6D_6		212
$\text{Me}_3\text{SnN(SiMe}_3)_2$	+ 46.7	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NSiMe}_3$	+ 66.0	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NSiMe}_2\text{Cl}$	+ 70.8	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NSiMeCl}_2$	+ 79.1	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NSiCl}_3$	+ 87.0	20% C_6D_6		212
$\text{Me}_3\text{SnN(GeMe}_3)_2$	+ 61.4	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NGeMe}_3$	+ 73.3	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_3\text{N}$	+ 86.3	20% C_6D_6		212
$\text{Me}_3\text{SnN(Bu')PbMe}_3$	+ 47.0	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NPbMe}_3$	+ 94.3	20% C_6D_6		212
$\text{Me}_3\text{SnN(PbMe}_3)_2$	+ 103.3	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{NBMe}_2$	+ 47.5	20% C_6D_6		212
	+ 45.0	Toluene		18
$(\text{Me}_3\text{Sn})_2\text{NB} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} \text{Me}$	+ 47.0	20% C_6D_6		212
$(\text{Me}_3\text{Sn})_2\text{N-B} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} \text{Me}$	+ 61.7	20% C_6D_6		212
$\text{Me}_3\text{SnN} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} \text{Me}$	+ 45.3	C_6D_6		18
$\text{Me}_3\text{Sn-N} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \diagup \end{array} \text{Me}$	+ 44.0	C_6D_6		18

TABLE 19 (cont.)

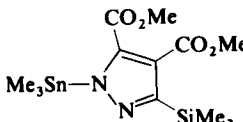
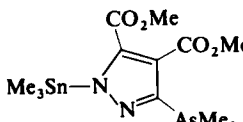
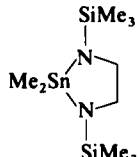
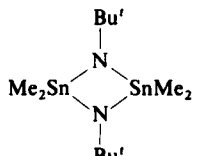
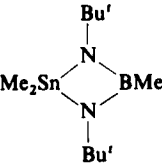
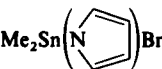
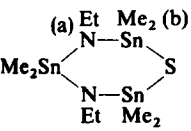
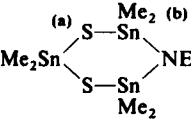
Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
$\text{Me}_3\text{SnNH—NHPh}$	+ 59.5	C_6D_6		76
$\text{Me}_3\text{SnNMe—NMeSnMe}_3$	+ 49.0	Toluene- d_8		100
$\text{Me}_3\text{SnNH—NPhSnMe}_3$	+ 64.9 (a) + 49.5 (b)	C_6D_6		76
$(\text{Me}_3\text{Sn})_2\text{N—NMe}_2$	+ 49.0	Toluene- d_8		100
$(\text{Me}_3\text{Sn})_2\text{N—NHPh}$	+ 81.0	C_6D_6		76
$(\text{Me}_3\text{Sn})_2\text{N—N(Me)SnMe}_3$	+ 61.5 (a) + 56.7 (b)	Toluene- d_8		100
$(\text{Me}_3\text{Sn})_2\text{N—N(Ph)SnMe}_3$	+ 79.5 (a) + 49.8 (b)	Toluene- d_8		100
$(\text{Me}_3\text{Sn})_2\text{N—N(SnMe}_3)_2$	+ 65.3	Toluene- d_8		100
	+ 107.1			321
	+ 101.7			321
$\text{Me}_3\text{Sn—NCO}$	+ 82.7	20% C_6H_6	<i>b</i>	322
$\text{Me}_3\text{Sn—NCS}$	+ 58.7	20% C_6H_6	<i>b</i>	322
$\text{Bu}_3\text{SnNEt}_2$	+ 36.4	—		2
$\text{Me}_2\text{Sn(NMe}_2)_2$	+ 58.8	25% C_6H_6		320
$\text{Me}_2\text{Sn(NEt}_2)_2$	+ 45	50% C_6H_6	<i>b</i>	320
$\text{Me}_2\text{Sn[N(CH}_3)_3\text{Ph]}_2$	+ 30.5	C_6H_6		118
$\text{Me}_2\text{Sn}(\text{N} \begin{smallmatrix} \diagup & \diagdown \\ & \\ \diagdown & \diagup \end{smallmatrix})_2$	+ 15.2	CDCl_3		76
$(\text{Me}_2\text{SnNMe})_3$	+ 92.1	Saturated C_6H_6		4
$(\text{Me}_2\text{SnNEt})_3$	+ 76	90% C_6H_6		4
	+ 104.2	C_6D_6		76
	+ 108.9	C_6D_6		323

TABLE 19 (cont.)

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
	+ 111.0	C_6D_6		323
$\text{Me}_2\text{Sn}[\text{N}(\text{Me})\text{C}(\text{O})\text{CH}_2]_2\text{NMe}$	- 63.3	CDCl_3		63
$\text{Me}_2\text{Sn}(\text{NCS})_2(\text{dipy})_2$	- 363	20% DMF	<i>c</i>	57
$\text{Me}_2\text{Sn}(\text{NCS})_2(2,2',2''\text{-tripyridyl})$	- 409	20% DMF		57
$\text{Et}_2\text{Sn}(\text{NMe}_2)_2$	- 67	20% CCl_4		277
$\text{Et}_2\text{Sn}(\text{NEt}_2)_2$	+ 21	—		277
$\text{Et}_2\text{Sn}[\text{N}(\text{Me})\text{C}(\text{O})\text{CH}_2]_2\text{NMe}$	- 109.2	CDCl_3		63
$\text{Bu}^n_2\text{Sn}(\text{NEt}_2)_2$	- 18	—		2
$\text{Bu}^i_2\text{Sn}[\text{N}(\text{Me})\text{C}(\text{O})\text{CH}_2]_2\text{NMe}$	- 200.7	CDCl_3		63
$\text{MeSn}(\text{NMe}_2)_3$	- 15.1	25% C_6H_6		320
$\text{MeSn}(\text{NEt}_2)_3$	- 24	25% C_6H_6		320
$\text{MeSn}[\text{N}(\text{Me})\text{Ph}]_3$	- 66.0	C_6H_6		118
$\text{BuSn}(\text{NEt}_2)_3$	- 44	—	<i>b</i>	2
$\text{Me}_2\text{Sn}(\text{NEt}_2)\text{Cl}$	+ 75	30% C_6H_6	<i>d</i>	4
	+ 44.9	CDCl_3		76
	88.3 (a) 100.7 (b) 88 (a) 100 (b)	Toluene/ C_6D_6 C_6H_6		314 8
	+ 115.7 (a) + 109.3 (b) + 114 (a) + 109 (b)	Toluene/ C_6D_6 C_6H_6		314 8
$[\text{MeSn}(\text{Cl})\text{NEt}]_3$	- 156	C_6H_6		8
$\text{Sn}(\text{NMe}_2)_4$	- 121.8 - 121.6	CH_2Cl_2 —		279 2
$\text{Sn}(\text{NEt}_2)_4$	- 122	—		2
$\text{Sn}[\text{N}(\text{Me})\text{Ph}]_4$	- 175.6	C_6H_6		118
$\{\text{Sn}[\text{N}(\text{SiMe}_3)]_2\text{BMe}\}_2$	+ 120	Pentane		324
$\text{Sn}[\text{N}(\text{SiMe}_3)]_2$	+ 767 + 776	? $\text{C}_6\text{H}_6/\text{C}_6\text{D}_6, 80^\circ\text{C}$	<i>e</i>	75 366

^a For more $\delta^{119}\text{Sn}$ of tin nitrogen compounds see reviews 3 and 4; for $^1J(^{119}\text{Sn}^{15}\text{N})$ data see Table 29.

^b For other conditions see review 4.

^c dipy, 2,2'-Dipyridyl.

^d ^{119}Sn resonance is shifted to higher frequency on dilution.

^e $\delta^{119}\text{Sn}$ given as + 720 relative to $(\text{Me}_3\text{Si})_2\text{NSnMe}_3$.⁷⁵

TABLE 20

Tin–phosphorus, tin–arsenic, tin–antimony, and tin–bismuth bonded compounds, tin coordination number = 3 or ≥ 4

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
$\text{Me}_3\text{SnPEt}_2$	− 11.1 (665.3)	C_6D_6		325
$\text{Me}_3\text{SnPBu}'_2$	− 37.8 (792)	C_6D_6		326
Me_3SnPPh	+ 18 (+ 538)	10% C_6H_6		199
				9
$\text{Me}_3\text{SnPPh}_2$	− 3.0 (+ 586)	50% C_6H_6	<i>b</i>	199
				9
	− 2.3 (+ 596)	65% C_6H_6		175
$(\text{Me}_3\text{Sn})_2\text{PEt}$	+ 25.7 (nr)	C_6H_6	<i>c</i>	325
$(\text{Me}_3\text{Sn})_2\text{PBu}'$	− 0.1 (816)	C_6D_6		326
$(\text{Me}_3\text{Sn})_2\text{PPh}$	+ 14.2 (+ 724)	90% CH_2Cl_2		175
$(\text{Me}_3\text{Sn})_3\text{P}$	+ 36.3 (+ 832.5)	65% C_6H_6		175
	+ 37.2 (829)	C_6D_6	<i>d</i>	212
	+ 38.0 (834)	C_6D_6		326
	+ 37.8 (833.7)	C_6D_6		325
$[\text{Me}_3\text{SnPBu}'_2\text{-Mn}(\text{NO})_3]$	+ 1.2 (137)	C_6D_6		326
$[\text{Me}_3\text{SnPBu}'_2\text{-Fe}(\text{CO})(\text{NO})_2]$	− 4.5 (106.6)	C_6D_6		326
$[\text{Me}_3\text{SnPBu}'_2\text{-Co}(\text{CO})_2\text{NO}]$	− 10.3 (107)	$\text{C}_6\text{D}_6/\text{THF}$		326
$[\text{Me}_3\text{SnPBu}'_2\text{-Ni}(\text{CO})_3]$	− 20.7 (149)	C_6D_6		326
$[\text{Me}_3\text{SnPPh}_2\text{-W}(\text{CO})_5]$	+ 33.7 (+ 50)	C_6H_6		175
$[(\text{Me}_3\text{Sn})_2\text{PBu}'\text{-Mn}(\text{NO})_3]$	+ 29.3 (286)	C_6D_6		326
$[(\text{Me}_3\text{Sn})_2\text{PBu}'\text{-Fe}(\text{CO})(\text{NO})_2]$	− 23.4 (264.5)	C_6D_6		326
$[(\text{Me}_3\text{Sn})_2\text{PBu}'\text{-Co}(\text{CO})_2\text{NO}]$	+ 18.1 (268)	$\text{C}_6\text{D}_6/\text{THF}$		326
$[(\text{Me}_3\text{Sn})_2\text{PBu}'\text{-Ni}(\text{CO})_3]$	+ 9.3 (304)	C_6D_6		326
$[(\text{Me}_3\text{Sn})_2\text{PPh-Cr}(\text{CO})_5]$	+ 39.7 (+ 253)	C_6H_6		175
$[(\text{Me}_3\text{Sn})_2\text{PPh-W}(\text{CO})_5]$	+ 41.6 (+ 216)	C_6H_6		175
$[(\text{Me}_3\text{Sn})_3\text{P-Cr}(\text{CO})_5]$	+ 64.2 (+ 409.5)	C_6H_6		175
$[(\text{Me}_3\text{Sn})_3\text{P-W}(\text{CO})_5]$	+ 63.4 (+ 375.5)	C_6H_6		175
$[(\text{Me}_3\text{Sn})_3\text{P-Mn}(\text{NO})_3]$	+ 62.0 (399)	$\text{C}_6\text{D}_6/\text{CDCl}_3$		326
$[(\text{Me}_3\text{Sn})_3\text{P-Fe}(\text{CO})(\text{NO})_2]$	+ 56.9 (385.7)	C_6D_6		326
$[(\text{Me}_3\text{Sn})_3\text{P-Co}(\text{CO})_2\text{NO}]$	+ 50.6 (393)	$\text{C}_6\text{D}_6/\text{THF}$		326
$[(\text{Me}_3\text{Sn})_3\text{P-Ni}(\text{CO})_3]$	+ 44.9 (429)	C_6D_6		326
$(\text{Me}_3\text{Sn})_2\text{AsPh}$	− 1.7	C_6H_6		212
$(\text{Me}_3\text{Sn})_3\text{As}$	+ 6.0	C_6D_6		327
$(\text{Me}_3\text{Sn})_3\text{Sb}$	− 90.0	C_6D_6		327
$(\text{Me}_3\text{Sn})_3\text{Bi}$	− 110.0	C_6D_6		327
$[(\text{Ph}_3\text{Sn})_2\text{P}]^-$	− 4.6 (1476)	$\text{THF}/\text{C}_6\text{D}_6$		328
$\text{Me}_2\text{Sn}(\text{PPh}_2)_2$	− 11.5 (+ 808)	C_6D_6		118
$[\text{Sn}(\text{PBu}'_2)_2]$	+ 328 (1800,t)			92, 318
	(1086,d)			
$\text{SnCl}_2\text{-PEt}_3$	− 47.3	Toluene, C_6D_6	<i>e</i>	56
$\text{SnCl}_2\text{-PBu}'_3$	− 48	Toluene, C_6D_6	<i>e</i>	56
$\text{SnCl}_2\text{-PBu}'_3$	+ 21	Toluene, C_6D_6	<i>e</i>	56
$\text{SnCl}_2\text{-P}(\text{NMe}_2)_3$	− 195		<i>e</i>	329

TABLE 20 (cont.)

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
$\text{SnCl}_4(\text{PBu}^n_3)_2$	-573 (2395)	CH_2Cl_2 , -30°C		64
$\text{SnCl}_3\text{Br}(\text{PBu}^n_3)_2$	-658 (2280)	CH_2Cl_2 , -30°C		64
$\text{SnCl}_2\text{Br}_2(\text{PBu}^n_3)_2$				
<i>trans</i>	-738 (2175)	CH_2Cl_2 , -30°C		64
<i>cis</i>	-750 (2170)	CH_2Cl_2 , -30°C		64
$\text{SnClBr}_3(\text{PBu}^n_3)_2$	-837 (2065)	CH_2Cl_2 , -30°C		64
$\text{SnBr}_4(\text{PBu}^n_3)_2$	-935 (1960)	CH_2Cl_2 , -30°C		64
$[\text{SnCl}_5\text{-PBu}^n_3]^-$	-652 (2020)	CH_2Cl_2 , -30°C		64
$[\text{SnCl}_4\text{Br-PBu}^n_3]^-$				
P,Cl- <i>trans</i>	-783 (1865)	CH_2Cl_2 , -30°C		64
P,Br- <i>trans</i>	-837 (2010)	CH_2Cl_2 , -30°C		64
$[\text{SnCl}_3\text{Br}_2\text{-PBu}^n_3]^-$				
P,Cl- <i>trans</i> ,	-913 (1720)	CH_2Cl_2 , -30°C		64
Cl,Cl- <i>trans</i>				
P,Cl- <i>trans</i> ,	-927 (1710)	CH_2Cl_2 , -30°C		64
Cl,Cl- <i>cis</i>				
$[\text{SnCl}_3\text{Br}_2\text{-PBu}^n_3]^-$				
(P,Br- <i>trans</i>)	-986 (1865)	CH_2Cl_2 , -30°C		64
$[\text{SnCl}_2\text{Br}_3\text{-PBu}^n_3]^-$				
(P,Cl- <i>trans</i>)	-1069 (1565)	CH_2Cl_2 , -30°C		64
$[\text{SnCl}_2\text{Br}_3\text{-PBu}^n_3]^-$				
P,Br- <i>trans</i> ,	-1132 (1720)	CH_2Cl_2 , -30°C		64
Br,Br- <i>trans</i>				
P,Br- <i>trans</i> ,	-1144 (1720)	CH_2Cl_2 , -30°C		64
Br,Br- <i>cis</i>				
$[\text{SnCl}_4\text{Br-PBu}^n_3]^-$				
(P,Cl- <i>trans</i>)	-1225 (1405)	CH_2Cl_2 , -30°C		64
(P,Br- <i>trans</i>)	-1301 (1555)	CH_2Cl_2 , -30°C		64
$[\text{SnBr}_5\text{-PBu}^n_3]^-$	-1470 (1415)	CH_2Cl_2 , -30°C		64

^a Values $^1J(^{119}\text{Sn}^{31}\text{P})$ are given in parentheses.^b For other conditions see review 3.^c nr, Not reported.^d Corrects a misprint (wrong sign) in reference 212.^e Rapid exchange.

d. $^3J(^{119}\text{Sn}^{11}\text{B})$. Owing to the rapid quadrupolar relaxation of the ^{11}B nucleus the scalar coupling $^3J(^{119}\text{Sn}^{11}\text{B})$ is partially relaxed in most cases. However, when the molecule is sufficiently small or when the symmetry at the ^{11}B nucleus is approximately tetrahedral the coupling may just be resolved¹³⁶ if $^3J(^{119}\text{Sn}^{11}\text{B}) \cdot T_1(^{11}\text{B}) \cdot 2\pi > 1$.

In the case of efficient scalar relaxation of the second kind, the ^{119}Sn -NMR spectra still yield information on the stereochemistry.⁹⁵ This is readily shown in Fig. 9, in which two broad ^{119}Sn resonances are observed. The broader

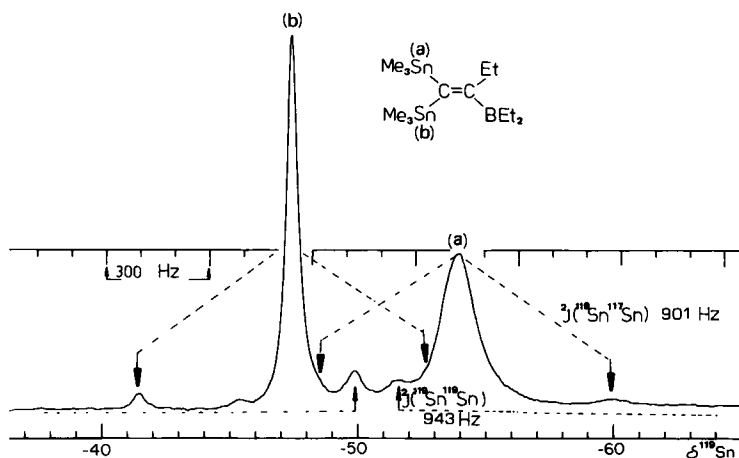


FIG. 9. $^{119}\text{Sn}\{^1\text{H}\}$ -NMR spectrum at 74.63 MHz of 1,1-bis(trimethylstannyl)-2-diethylboryl-1-butene in hexane/ C_6D_6 , 28°C .

signal can be assigned to the tin atom in the position trans to the ^{11}B nucleus, assuming that $|^3J(^{119}\text{Sn}^{11}\text{B})|_{\text{trans}} > |^3J(^{119}\text{Sn}^{11}\text{B})|_{\text{cis}}$.

Therefore, in addition to the $\delta^{119}\text{Sn}$ values, the linewidths of the ^{119}Sn resonances, in appropriate compounds, may serve as structural tools.

e. Other vicinal couplings, $^3J(\text{SnX})$. Some values of $|^3J(^{119}\text{SnX})|$ across the $\text{C}\equiv\text{C}$ triple bond in alkynylstannanes have been reported ($\text{X} = ^{29}\text{Si}$, ^{207}Pb , ^{195}Pt). These values are small in the case of $\text{X} = ^{29}\text{Si}^{157}$ or $^{207}\text{Pb}^{159}$ and fairly large for $\text{X} = ^{195}\text{Pt}^{253}$.

The $|^3J(^{119}\text{Sn}^{19}\text{F})|$ couplings are large in perfluoroethyltin compounds (220–275 Hz) ^{121} and small in perfluorovinyltin compounds, 25 (cis) and 29 Hz (trans). ^{236} No systematic study has been carried out so far. ^{184}

4. $^nJ(\text{SnX})$ couplings ($n \geq 4$)

In many cases it is possible to observe long-range couplings, $^nJ(^{119}\text{SnX})$ ($n \geq 4$). However, the data set available is insufficient for most X nuclei to reach firm conclusions regarding the structure and the bonding situation. Corresponding long-range couplings, $^nJ(^{13}\text{C}^1\text{H})$, $^nJ(^{13}\text{C}^{13}\text{C})$, $^nJ(^{29}\text{Si}^1\text{H})$, etc., have deserved only scant attention so far and in most cases analogous organotin compounds are not available or they have not been studied in detail by NMR. It is certain that developments in NMR instrumentation will facilitate the access to long-range couplings in general. In the case of organotin compounds, with the possible exception of allenyl stannanes, ^{241,245} discussion of the data should be postponed until more material is available for comparison.

TABLE 21

Tin-silicon, tin-germanium, tin-tin, and tin-lead bonded compounds, tin coordination number ≥ 4

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
$\text{Me}_3\text{Sn-SiMe}_3$	-126.7 (+ 656) (580)	90% C_6H_6		12 319
$\text{Me}_3\text{Sn-SiPh}_3$	-149	$\text{CDCl}_3/\text{dioxane}$		330
$(\text{Me}_3\text{Sn})_4\text{Si}$	-34.0 (220)	C_6D_6		212
$(\text{Me}_3\text{Sn})_3\text{SiLi}$	-1.0 (no)	$\text{C}_6\text{D}_6/\text{THF}$	<i>b</i>	212
$[\text{SnGe}_8]^{4-}$	-1233	en		82
$[\text{Sn}_9-n\text{Ge}_n] (n = 1-7)$	-1230 to -1180	en		82
$\text{Me}_3\text{Sn-SnMe}_3$	-113 (4460)	90% C_6H_6		8, 205
	-109 (no)	—	<i>b</i>	278
	-108.7 (4404)	95% C_6D_6		331, 167
	-109.0 (no)	C_6D_6	<i>b</i>	255
	-109.2 (no)	MeOH	<i>b</i>	332
^{(a) (b)} $\text{Me}_3\text{Sn-Sn(Et)Me}_2$	-107.8 (a), -92.1 (b) (no)		<i>b</i>	255
^{(a) (b)} MeSn-Sn(chex)Me_2	-107.9 (a), -95.7 (b) (no)		<i>b</i>	280
^{(a) (b)} $\text{Me}_3\text{Sn-SnEt}_3$	-109.0 (a), -62.6 (b) (no)	C_6D_6	<i>b</i>	255
	-108.1 (a), -61.8 (b) (3496)	95% C_6D_6		331 167
^{(a) (b)} $\text{Me}_3\text{Sn-SnPr}^n_3$	-108.9 (a), -88.8 (b) (3551)	95% C_6D_6		167
^{(a) (b)} $\text{Me}_3\text{Sn-SnPr}^i_3$	-105.4 (a), -32.4 (b) (2832)	95% C_6D_6		167
^{(a) (b)} $\text{Me}_3\text{Sn-SnBu}^n_3$	-108.6 (a), -82.1 (b) (3505)	95% C_6D_6		167

TABLE 21 (cont.)

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
^{(a) (b)} $\text{Me}_3\text{Sn-SnBu}^*_3$	-105.3 (a), -45.3 (b) (2810)	95% C_6D_6		331, 167
^{(a) (b)} $\text{Me}_3\text{Sn-Snchex}_3$	-103.8 (a), -78.3 (b), (2841)	95% C_6D_6		331
^{(a) (b)} $\text{Me}_3\text{Sn-SnPh}_3$	-91.5 (a), -153 (b) (4240)	CH_2Cl_2		12
	-91.5 (a), -150.6 (b) (4262)	CDCl_3		331, 167
^{(a) (b)} $(\text{Me}_3\text{Sn})_2\text{SnMe}_2$	-99.5 (a), -261.7 (b) (2873)	95% C_6D_6		167
	-100.8 (a), -263 (b) (2900)	C_6H_6		166
^{(a) (b)} $(\text{Me}_3\text{Sn})_2\text{SnEt}_2$	-99.1 (a), -199.1 (b) (2375)	95% C_6D_6		167 255
^{(a) (b)} $(\text{Me}_3\text{Sn})_2\text{SnPr}^i_2$	-97.0 (a), -139.5 (b) (1957)	95% C_6D_6		167
^{(a) (b)} $(\text{Me}_3\text{Sn})_3\text{SnMe}$	-89.5 (a), -489.7 (b) (1733)	95% C_6D_6		333
^{(a) (b)} $(\text{Me}_3\text{Sn})_3\text{SnEt}$	-89.3 (a), -440.9 (b) (1538)	95% C_6D_6		333
^{(a) (b)} $(\text{Me}_3\text{Sn})_3\text{SnBu}^n$	-90.3 (a), -459.9 (b) (1548)	95% C_6D_6		333
^{(a) (b)} $(\text{Me}_3\text{Sn})_3\text{SnBu}^i$	-90.8 (a), -480.4 (b) (1546)	95% C_6D_6		333
^{(a) (b)} $(\text{Me}_3\text{Sn})_3\text{SnC}_5\text{H}_{11}^n$	-90.1 (a), +460.5 (b) (1535)	95% C_6D_6		333
^{(a) (b)} $(\text{Me}_3\text{Sn})_3\text{SnPh}$	-83.2 (a), -434.2 (b) (1670)	95% C_6D_6		333

TABLE 21 (*cont.*)

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
$(\text{Me}_3\text{Sn})_4\text{Sn}^{(a) (b)}$	— 80 (a), — 806 (b) (no)	C_6H_6	<i>b</i>	3
	— 80 (a), — 739 (b) (881)	C_6D_6		212
$(\text{Me}_3\text{SnSnMe}_2)^{(a) (b)}$	— 96.8 (a), — 248.6 (b) (no)	C_6D_6	<i>b</i>	255
$\text{Me}_2(\text{Ph})\text{SnSn}(\text{Ph})\text{Me}_2$	— 120.2 (4153)	C_6D_6		334
$\text{Et}_3\text{Sn-SnEt}_3$	— 59.9 (2702)	95% C_6D_6		331 167
$\text{Et}_3\text{Sn-SnBu}^n_3^{(a) (b)}$	— 65.7 (a), — 79.7 (b) (2688)	95% C_6D_6		331 167
$\text{Et}_3\text{Sn-SnPh}_3^{(a) (b)}$	— 48.7 (a), — 140.4 (b) (3153)	95% C_6D_6		331 167
$(\text{Et}_3\text{Sn})_2\text{SnMe}_2^{(a) (b)}$	— 56.0 (a), — 272.8 (b) (1931)	95% C_6D_6		167
$(\text{Et}_3\text{Sn})_2\text{SnEt}_2^{(a) (b)}$	— 54.8 (a), — 205.9 (b) (1481)	95% C_6D_6		167
$(\text{Et}_3\text{Sn})_2\text{SnPr}^i_2^{(a) (b)}$	— 57.3 (a), — 139.3 (b) (1153)	95% C_6D_6		167
$(\text{Et}_3\text{Sn})_2\text{SnBu}^i_2^{(a) (b)}$	— 63.9 (a), — 214.4 (b) (no)	95% C_6D_6	<i>b</i>	167
$\text{Pr}^i_3\text{Sn-SnPr}^i_3$	— 29.1 (1208)	95% C_6D_6		331 167
	— 31.2 (1216)	?		280
$\text{Pr}^i_3\text{Sn-Sn}(\text{chex})\text{Pr}^i_2^{(a) (b)}$	— 31.9 (a), — 43.9 (b) (1226)	?		280
$(\text{Pr}^i_3\text{Sn})_2\text{SnMe}_2^{(a) (b)}$	— 34.3 (a), — 272.1 (b) (1366)	95% C_6D_6		167

TABLE 21 (cont.)

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
$(\text{Pr}^i)_3\text{Sn}_2\text{SnEt}_2^{(a) (b)}$	-31.0 (a), -206.7 (b) (no)	95% C_6D_6	<i>b</i>	167
$(\text{Pr}^i)_3\text{Sn}_2\text{SnPr}^i_2^{(a) (b)}$	-35.0 (a), -132.9 (b) (403)	95% C_6D_6		167
$\text{Pr}^i_2(\text{Bu}^i)\text{SnSn}(\text{Bu}^i)\text{Pr}^i_2$	-21.5 (764)	95% C_6D_6		331 167
$\text{Pr}^i_2(\text{chex})\text{SnSn}(\text{chex})\text{Pr}^i_2$	-44.4 (1237)	?		280
$\text{Pr}^i_2(\text{chex})\text{SnSn}(\text{Pr}^i)\text{chex}_2^{(a) (b)}$	-45.6 (a), -58.2 (b) (no)	?	<i>b</i>	280
$\text{chex}_2(\text{Pr}^i)\text{SnSn}(\text{Pr}^i)\text{chex}_2$	-57.8 (no)	?	<i>b</i>	280
$\text{Bu}^n_3\text{Sn-SnBu}^n_3$	-79.5 (no)	—	<i>b</i>	278
	-83.2 (2748)	95% C_6D_6		331 167
$\text{Bu}^i_3\text{Sn-Snchex}_3^{(a) (b)}$	-93.2 (a), -85.2 (b) (2533)	95% C_6D_6		167
$\text{Bu}^i_3\text{SnSnPh}_3^{(a) (b)}$	-86.8 (a), -146.9 (b) (3199)	CDCl_3		331 167
$(\text{Bu}^i_3\text{Sn})_2\text{SnBu}^i_2^{(a) (b)}$	-92.8 (a), -236.2 (b) (1590)	95% C_6D_6		167
$\text{Bu}^i_3\text{SnSnBu}^i_3$	-3.4 (< 60)	CDCl_3		167
$\text{chex}_3\text{SnSnPh}_3^{(a) (b)}$	-64.7 (a), -134.1 (b) (2260)	CDCl_3		167
$(\text{chex}_3\text{Sn})_2\text{SnBu}^i_2^{(a) (b)}$	-84.3 (a), -224.8 (b) (no)	95% C_6D_6	<i>b</i>	167
$\text{oct}^n_3\text{SnSnOct}^n_3$	-83.5 (2705)	95% C_6D_6		167
$\text{Ph}_3\text{SnSnPh}_3$	-143.6 (4470)	CDCl_3		167
	-144.2 (no)	C_6D_6	<i>b</i>	285

TABLE 21 (cont.)

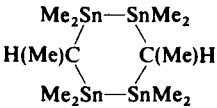
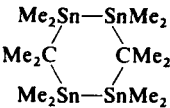
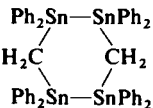
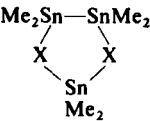
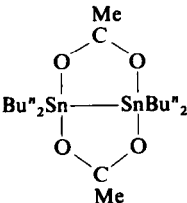
Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
(^(a) Ph_3Sn) ₂ ^(b) SnBu^t_2	-138.2, -221.0 (2273)	CDCl_3		167
	-67.1 (3567)	C_6D_6		251
	-53.1 (2878)	C_6D_6		251
	-109.3 (4159)	CDCl_3		335
$[(2,6\text{-Et}_2\text{-C}_6\text{H}_3)_2\text{Sn}]_3$	-416.5 (no)	C_6D_6	<i>b</i>	312
				
$\text{X} = \text{S}$	+44 (Sn_2) (3977), +176 (Sn)	C_6H_6		16
$\text{X} = \text{Se}$	+21 (Sn_2) (3466), +82 (Sn)	C_6H_6		168
$\text{X} = \text{Te}$	-38 (Sn_2) (2643), -164 (Sn)	C_6H_6	<i>c</i>	168
$\text{Me}_2(\text{Cl})\text{SnSn}(\text{Cl})\text{Me}_2$	+19.0 (no)	MeOH	<i>b</i>	332
	-126.8 (11,272)	CDCl_3		167

TABLE 21 (cont.)

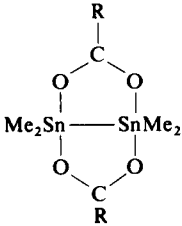
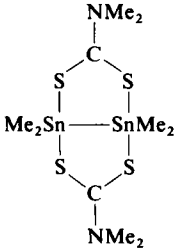
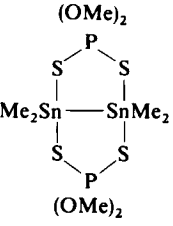
Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
$(\text{Ph}_2\text{Sn})_6$	-208 (1117)	CDCl_3 , 31°C		336
				
R				
H	-135 (no)	C_6D_6	<i>b</i>	337
	-122 (13,056)	CDCl_3		337
Me	-128 (14,980)	C_6D_6		337
	-117 (14,549)	CDCl_3		337
CH_2Cl	-95 (no)	C_6D_6	<i>b</i>	337
	-86 (no)	CDCl_3	<i>b</i>	337
CHCl_2	-57 (12,622)	C_6D_6		337
CCl_3	-15 (12,323)	C_6D_6		337
CF_3	-44 (11,424)	C_6D_6		337
				
	-72 (14,479)	C_6D_6		337

TABLE 21 (cont.)

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
	-22 (12,119)	C_6D_6		337
$[\text{Sn}_4]^{2-}$	-1895 (1281)	en		82
$[\text{Sn}_9]^{4-}$	-1230 (266)	en	<i>d</i>	80
	-1230 (no)	en	<i>e</i> <i>b</i>	81 338
$[\text{Sn}_8\text{Tl}]^{5-}$	-1167 (429, Sn) (800, Tl)	en, 30°C		82
$\text{Me}_3\text{Sn-PbMe}_3$	-57.0 (-3570)	C_6H_6		13
$\text{Ph}_3\text{Sn-PbMe}_3$	-119.5 (-2800)	C_6H_6		13
$[\text{Sn}_9-n\text{Pb}_n]^{4-}$	-1270 to -1600 (270, Sn) (560, Pb)	en	<i>f</i>	80, 81

^a Values of $^1J(^{119}\text{Sn}^{29}\text{Si})$, $^1J(^{119}\text{Sn}^{119}\text{Sn})$, or $^1J(^{207}\text{Pb}^{119}\text{Sn})$ (Hz) in parentheses.

^b no, Not observed or not reported (?).

^c Assignment of $^1J(^{119}\text{Sn}^{119}\text{Sn})$ uncertain since $^1J(^{119}\text{Sn}^{125}\text{Te})$ (2554 Hz) is in the same order of magnitude.

^d Nonrigid structure; the same ^{119}Sn -NMR spectrum was obtained at -40°C in liquid NH_3 .

^e Broad signal; the large line width (1100 Hz) is attributed to the presence of paramagnetic $[\text{Sn}_9]^{3-}$.

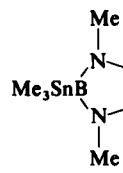
^f The shielding of the ^{119}Sn nuclei is increased fairly regularly by 42–60 ppm with increasing n .

VI. CONCLUSIONS

Many recent achievements in tin chemistry are based, at least partly, on ^{119}Sn -NMR parameters and there can be no doubt that this is a flourishing area. This is also evident from the steadily increasing number of references cited for the years 1978–1983. Although we are still far from understanding all of the trends in ^{119}Sn chemical shifts or couplings involving the ^{119}Sn nucleus, even in a qualitative sense, our general position has improved

TABLE 22

Tin-Group III element bonded compounds,* tin coordination number ≥ 4

Compound	$\delta^{119}\text{Sn}^a$	Solvent	Footnotes	Reference
$[\text{Me}_3\text{SnBH}_3]^-$	-28.5 (-554)	THF/ C_6D_6	<i>b</i>	18
$\text{Me}_3\text{SnB}(\text{Cl})\text{NMe}_2$	-139 (-1007)	—		12, 14
$\text{Me}_3\text{SnB}(\text{OMe})\text{NMe}_2$	-161.5 (-947)	C_6H_6		14
$\text{Me}_3\text{SnB}(\text{SMe})\text{NMe}_2$	-127 (-717)	C_6H_6		14
$\text{Me}_3\text{SnB}(\text{NMe}_2)_2$	-150 (-953)	C_6H_6		12, 14, 18
	-152.3 (-930)	C_6D_6		13, 14, 18
$(\text{Me}_3\text{Sn})_2\text{BNMe}_2$	-149 (-657)	Toluene		14, 18
$\text{Me}_3\text{Sn}(\text{Me}_2\text{N})\text{BB}(\text{NMe}_2)\text{SnMe}_3$	-150 (-865)	Toluene		18
$[\text{Me}_3\text{SnTlMe}_3]^-$	-376.5 (nr)	Dimethoxyethane	<i>c</i>	4
$[\text{Sn}_8\text{Tl}]^{5-}$	-1167 (429, Sn) (800, Tl)	en	<i>d</i>	82

* Broad singlets at low frequency are reported for 1-Sn-2-[SiMe_3]-R-2,3- $\text{C}_2\text{B}_4\text{H}_4$ (R = H, Me, SiMe_3).³⁶⁸^a Values of $^1J(^{119}\text{Sn}^{11}\text{B})$ and $^1J(^{119}\text{Sn}^{205}\text{Tl})$ (Hz) are given in parentheses.^b $\delta^{119}\text{Sn}$ and $^1J(^{119}\text{Sn}^{11}\text{B})$ change slightly with concentration and solvent.^c nr, Not reported; $^1J(^{205}\text{Tl}^{119}\text{Sn}) = 11,610$ Hz is given for $[(\text{Me}_3\text{Sn})_4\text{Tl}]^-$ in reference 4.^d Non-rigid structure; values of $^1J(^{119}\text{Sn}^{119}\text{Sn})$ and $^1J(^{205}\text{Tl}^{119}\text{Sn})$ (Hz) are temperature dependent; en (30 to 110°) 429–425 Hz and 793–842 Hz, respectively; liquid NH_3 (-74 to -34°C) 457–419 Hz and 927–1001 Hz, respectively.

considerably: (1) With modern equipment there are, in principle, no serious experimental difficulties in observing ^{119}Sn resonances either directly or by heteronuclear double resonance; (2) our knowledge of the ^{119}Sn relaxation behaviour is increasing, which allows for the proper choice of experimental conditions to observe the ^{119}Sn resonance (in addition to the elucidation of other features connected particularly with the relaxation mechanism); (3) $\delta^{119}\text{Sn}$ data, which become increasingly available for all kinds of tin compounds, help one to use this parameter in an empirical way and to find models for the qualitative interpretation of $\delta^{119}\text{Sn}$; (4) this also applies to couplings involving the ^{119}Sn nucleus, which have already been shown to serve as a sensitive tool in the discussion of structure and bonding.

All this concerns measurements in the liquid state. There are, of course, many applications of ^{119}Sn -NMR parameters of tin compounds, partially oriented in liquid crystal solvents. For various reasons these results have not been included here. Considering the enormous potential of solid-state NMR

TABLE 23

Tin–lithium compounds

Compound	$\delta^{119}\text{Sn}$	Solvent	Footnotes	Reference
Me_3SnLi	–183	20% THF		9
	–180.7	20% THF		339
	–179	THF		280
	–182.7	THF	<i>a</i>	340
Et_3SnLi	–99	THF	<i>a</i>	340
Pr^n_3SnLi	–130	THF		280
Pr^i_3SnLi	–13.0	THF		280
Ph_3SnLi	–109	THF (?)		280
$\text{Pr}^{(a)(b)}_3\text{SnSnPr}^n_2\text{Li}$	–123 (a), –194 (b)	THF	<i>b</i>	280
$\text{Pr}^{(a)(b)}_3\text{SnSnPr}^i_2\text{Li}$	–48.2 (a), –39.3 (b)	THF	<i>b</i>	280
$(\text{Me}_3\text{Sn})^{(a)(b)}_3\text{SnLi}$	–104.6 to –107.1 (a) –1031.2 to –1042.1 (b) –5200 to –4445 [$^1J(\text{SnSn})$] –101.7 (a) –1044 (–5737) (b)	THF THF, C_6D_6	<i>c</i>	156 212

^a Mixtures of R_3SnSnR_3 and R_3SnLi (R = Me, Et) have been studied by ^{119}Sn NMR.³⁴⁰

^b Assignment of Sn(a, b) needs confirmation.

^c Values of $\delta^{119}\text{Sn}$ and $^1J(\text{SnSn})$ (Hz) differ for two samples of different age and concentration.

and the steadily growing number of commercial instruments capable, e.g., of magic-angle sample spinning (MASS), high-power ^1H decoupling, and cross polarization (CP), it is easy to predict forthcoming applications of ^{119}Sn solid-state NMR. In addition to the interesting practical aspects we may learn more about ^{119}Sn nuclear shielding from the tensorial components of the averaged isotropic shielding.

ACKNOWLEDGMENTS

I thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for generous support of my experimental and spectroscopic studies. I am indebted to Prof. Nöth for his stimulating collaboration, and to my research students for their excellent experimental work. It is a pleasure to thank my wife for her patience and her careful work in typing the manuscript.

TABLE 24

Transition metal tin compounds (Sn—C, Sn—Sn, Sn—O, Sn—P), tin coordination number ≥ 4

Compound	$\delta^{119}\text{Sn}$	$^1J(\text{M}^{119}\text{Sn})$ (Hz)	$^2J(^{119}\text{Sn}^{31}\text{P})$ (Hz)	Solvent	Footnotes	Reference
$[(\text{cp})_2\text{Ta}(\text{H})_2\text{SnMe}_3]$	+ 53	—	—	C_6H_6		260
$[\text{cpCr}(\text{CO})_3\text{SnMe}_3]$	+ 161	—	—	C_6H_6		260
$[\text{Cr}(\text{CO})_5\text{SnCl}_2\text{—THF}]$	+ 193	—	—	C_6D_6		56
$[\text{Cr}(\text{CO})_5\text{SnCl}_2(\text{THF})_x]$	+ 55	—	—	$\text{C}_6\text{D}_6/\text{THF}$		56
$[\text{Cr}(\text{CO})_5\text{SnCl}_2\text{—PEt}_3]$	+ 228.5	—	—	C_6D_6		56
$[\text{Cr}(\text{CO})_5\text{SnCl}_2\text{—PBu}^n_3]$	+ 269	—	1514 (^1J)	C_6D_6		56
$[\text{Cr}(\text{CO})_5\text{SnCl}_2\text{—PPh}_3]$	+ 238	—	—	C_6D_6		56
$[\text{Cr}(\text{CO})_5\text{Sn}(\text{OH})_2(\text{THF})_x]$	+ 9.5	—	—	$\text{C}_6\text{D}_6/\text{THF}$		56
$[\text{Cr}(\text{CO})_5\text{Sn}(\text{OSiMe}_3)_2]$	+ 74.2	—	—	Toluene/ C_6D_6	<i>a</i>	316
$[\text{cpMo}(\text{CO})_3\text{SnMe}_3]$	+ 121	—	—	C_6H_6		260
$[(\text{cp})_2\text{Mo}(\text{H})\text{SnMe}_3]$	+ 123	—	—	C_6H_6		260
$[(\text{cp})_2\text{Mo}(\text{Cl})\text{SnMe}_3]$	+ 90	—	—	C_6H_6		260
$[(\text{cp})_2\text{Mo}(\text{Br})\text{SnMe}_3]$	+ 90	—	—	C_6H_6		260
$[(\text{cp})_2\text{Mo}(\text{I})\text{SnMe}_3]$	+ 96	—	—	C_6H_6		260
$[(\text{cp})_2\text{Mo}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\}(\text{H})\text{SnMe}_3]$	+ 119	—	—	C_6H_6		260
$[\text{cpW}(\text{CO})_3\text{SnMe}_3]$	+ 42	—	—	C_6H_6		260
	+ 43.1	150	—	C_6H_6		288
$[(\text{cp})_2\text{W}(\text{H})\text{SnMe}_3]$	— 41	—	—	C_6H_6		260
$[(\text{cp})_2\text{W}(\text{Cl})\text{SnMe}_3]$	— 70	—	—	C_6H_6		260
$[(\text{cp})_2\text{W}(\text{Br})\text{SnMe}_3]$	— 74	—	—	C_6H_6		260
$[(\text{cp})_2\text{W}(\text{I})\text{SnMe}_3]$	— 74	—	—	C_6H_6		260
$[(\text{cp})_2\text{W}\{\text{C}(\text{CO}_2\text{Me})=\text{C}(\text{CO}_2\text{Me})\}(\text{H})\text{SnMe}_3]$	— 40	—	—	C_6H_6		260
$[\text{W}(\text{CO})_5\text{SnCl}_2\text{—THF}]$	— 54.6	1440	—	C_6D_6		56
$[\text{W}(\text{CO})_5\text{SnCl}_2(\text{THF})_x]$	— 209.4	1594	—	$\text{C}_6\text{D}_6/\text{THF}$		56
$[\text{W}(\text{CO})_5\text{SnCl}_2\text{—PEt}_3]$	— 5.8	1350	—	C_6D_6		56
$[\text{W}(\text{CO})_5\text{SnCl}_2\text{—PBu}^n_3]$	+ 9.5	1490	—	C_6D_6		56

	[W(CO) ₅ SnCl ₂ —PBU' ₃]	+2.9	1470	1560 (¹ J)	C ₆ D ₆	56, 362
	[W(CO) ₅ SnBr ₂ —THF]	−2.6	1440	—	C ₆ D ₆	56
	[W(CO) ₅ SnBr ₂ (THF) _x]	−217.6	1610	—	C ₆ D ₆ /THF	56
	[W(CO) ₅ Sn(OH) ₂ (THF) _x]	−198	—	—	C ₆ D ₆ /THF	56
	[Mn(CO) ₅ SnMe ₃]	+63	—	—	C ₆ H ₆	260
		+66.3	—	—	C ₆ H ₁₂	278
	[{Mn(CO) ₅ } ₂ SnMe ₂]	+150	—	—	C ₆ H ₆	260
	[{Mn(CO) ₅ } ₃ SnMe]	+284	—	—	CDCl ₃	260
	[Re(CO) ₅ SnMe ₃]	−89	—	—	C ₆ D ₆	260
	[{Re(CO) ₅ } ₂ SnMe ₂]	−223	—	—	CDCl ₃	260
	[Fe(CO) ₄ (SnMe ₃) ₂]	+79	—	—	C ₆ H ₆	260
	[{Fe(CO) ₄ SnMe ₂ } ₂]	+257	—	—	C ₆ H ₆	260
	[cpFe(CO) ₂ SnMe ₃]	+147	—	—	C ₆ H ₆	260
	[cpFe(CO) ₂ SnPh ₃]	+58.2	—	—	C ₆ D ₆	285
	[cpFe{P(OPh) ₃ } ₂ {Sn(SnMe ₃) ₃ }]	−401 (FeSn), −103 (SnSn)	—	—	C ₆ H ₆	166
12	[Co(CO) ₄ SnMe ₃]	+151	—	—	C ₆ H ₆	260
	[{Co(CO) ₄ } ₂ SnMe ₂]	+293	—	—	C ₆ H ₆	260
	[{Co(CO) ₄ } ₃ SnMe]	+483	—	—	C ₆ H ₆	260
	[Rh(PPh ₃) ₂ (C≡CPh) ₂ SnMe ₃]	+172	—	—	CH ₂ Cl ₂	<i>b</i> 260
	[Ir(PPh ₃) ₂ (CO)(C≡CPh) ₂ SnMe ₃]	−106	—	—	CH ₂ Cl ₂	<i>b</i> 260
	[Ir(PMe ₂ Ph) ₂ (CO)(C≡CPh) ₂ SnMe ₃]	−123	—	—	CH ₂ Cl ₂	<i>b</i> 260
	[{Ni(CO) ₃ Sn(OBu') ₂ } ₂]	+79.3	—	—	Toluene/C ₆ D ₆	316
	[Ni(CO) ₃ {Sn(OSiMe ₃) ₂ } ₂]	+35.3, +24.0	—	—	Toluene/C ₆ D ₆	<i>c</i> 316
		−159, −249.8	—	—		
	<i>cis,trans</i> -[PtH(Me)(SnPh ₃) ₂ (bipy)]	−74.2	6641	—	CH ₂ Cl ₂	<i>d</i> 200
	<i>cis</i> -[Pt(SnMe ₃)(C≡CPh)(PPh ₃) ₂]	−46	—	—	CH ₂ Cl ₂	260
				1587 (<i>trans</i>) 104 (<i>cis</i>)	CH ₂ Cl ₂	

TABLE 24 (cont.)

	Compound	$\delta^{119}\text{Sn}$	$^1J(\text{M}^{119}\text{Sn})$	$^2J(^{119}\text{Sn}^{31}\text{P})$	Solvent	Footnotes	Reference
			(Hz)	(Hz)			
	<i>cis</i> -[Pt(SnMe ₃)(C≡CPh)(PPh ₂ Me) ₂]	-48	—	—	Toluene- <i>d</i> ₈		260
	<i>cis</i> -[Pt(SnMe ₃)(CF=CF ₂)(PPh ₃) ₂]	0	—	—	CDCl ₃		260
	<i>cis</i> -[Pt{Sn(CH ₂) ₄ }(Ph)(PPh ₃) ₂]	-0.3	—	1673 (<i>trans</i>)	C ₆ H ₆ /C ₆ D ₆		341
				161 (<i>cis</i>)			
	<i>cis</i> -[Pt(SnPh ₃)(Ph)(PPh ₃) ₂]	-106	12,686	1934 (<i>trans</i>)	CH ₂ Cl ₂		190
				161 (<i>cis</i>)			
	<i>cis</i> -Pt(SnPh ₂ Cl)(Ph)(PPh ₃) ₂]	+32	14,066	2398 (<i>trans</i>)	CH ₂ Cl ₂		190
				151 (<i>cis</i>)			
	<i>cis</i> -[Pt(SnPhCl ₂)(Ph)(PPh ₃) ₂]	+56	16,889	2959 (<i>trans</i>)	CH ₂ Cl ₂		190
				195 (<i>cis</i>)			
	<i>cis</i> -[Pt(SnPh ₂ Br)(Ph)(PPh ₃) ₂]	+29	13,940	2398 (<i>trans</i>)	CH ₂ Cl ₂		190
				152 (<i>cis</i>)			
	<i>cis</i> -[Pt(SnPhBr ₂)(Ph)(PPh ₃) ₂]	+47	16,241	2954 (<i>trans</i>)	CH ₂ Cl ₂		190
				183 (<i>cis</i>)			
	<i>cis</i> -[Pt(SnPh ₂ I)(Ph)(PPh ₃) ₂]	+2	13,735	2380 (<i>trans</i>)	CH ₂ Cl ₂		190
				153 (<i>cis</i>)			
	<i>cis</i> -[Pt(SnPh ₂ SCH ₂ Ph)(Ph)(PPh ₃) ₂]	-7	13,416	2167 (<i>trans</i>)	CH ₂ Cl ₂		190
				159 (<i>cis</i>)			
	<i>cis</i> -[Pt(SnPh ₂ SPh)(Ph)(PPh ₃) ₂]	-4	13,306	2185 (<i>trans</i>)	CH ₂ Cl ₂		190
				153 (<i>cis</i>)			
	<i>cis</i> -[Pt(SnPh ₂ NCS)(Ph)(PPh ₃) ₂]	-17	14,050	2375 (<i>trans</i>)	CH ₂ Cl ₂		190
				159 (<i>cis</i>)			
	<i>cis</i> -[PtCl(SnMe ₂ Cl)(PPh ₃) ₂]	+196	8,921	2267 (<i>trans</i>)	CH ₂ Cl ₂		190
				65 (<i>cis</i>)			
	<i>cis</i> -[PtCl(SnBu ⁿ ₂ Cl)(PPh ₃) ₂]	+116	8,821	204 (<i>trans</i>)	CH ₂ Cl ₂		190
				43 (<i>cis</i>)			
	<i>cis</i> -[PtCl(SnBu ^t ₂ Cl)(PPh ₃) ₂]	+81	8,800	1853 (<i>trans</i>)	CH ₂ Cl ₂		190
				21 (<i>cis</i>)			

	<i>cis</i> -[PtCl(SnMeCl ₂)(PPh ₃) ₂]	+ 77	13,105	3119 (<i>trans</i>) 128 (<i>cis</i>)	CH ₂ Cl ₂	190
	<i>cis</i> -[PtCl(SnBu ^a Cl ₂)(PPh ₃) ₂]	+ 67	12,320	2911 (<i>trans</i>) 105 (<i>cis</i>)	CH ₂ Cl ₂	190
	<i>cis</i> -[PtCl(SnPhCl ₂)(PPh ₃) ₂]	- 31	13,940	3223 (<i>trans</i>) 122 (<i>cis</i>)	CH ₂ Cl ₂	190
	<i>cis</i> -[PtBr(SnMe ₂ Br)(PPh ₃) ₂]	+ 98	8,928	2264 (<i>trans</i>) 49 (<i>cis</i>)	CH ₂ Cl ₂	190
	<i>cis</i> -[PtBr(SnBu ^a ₂ Br)(PPh ₃) ₂]	+ 113	8,191	2039 (<i>trans</i>) 24 (<i>cis</i>)	CH ₂ Cl ₂	190
	<i>cis</i> -[PtBr(SnMeBr ₂)(PPh ₃) ₂]	+ 38	11,896	3082 (<i>trans</i>) 104 (<i>cis</i>)	CH ₂ Cl ₂	190
	<i>cis</i> -[PtBr(SnBu ^a Br ₂)(PPh ₃) ₂]	+ 44	11,156	2881 (<i>trans</i>) 80 (<i>cis</i>)	CH ₂ Cl ₂	190
	<i>cis</i> -[PtBr(SnPhBr ₂)(PPh ₃) ₂]	+ 32	12,361	3195 (<i>trans</i>) 101 (<i>cis</i>)	CH ₂ Cl ₂	190
16	<i>trans</i> -[PtCl(SnMe ₂ Cl)(PPh ₃) ₂]	+ 120	14,788	131	CH ₂ Cl ₂	190
	<i>trans</i> -[PtCl(SnBu ^a ₂ Cl)(PPh ₃) ₂]	+ 81	13,294	119	CH ₂ Cl ₂	190
	<i>trans</i> -[PtCl(SnMeCl ₂)(PPh ₃) ₂]	- 18	19,982	165	CH ₂ Cl ₂	190
	<i>trans</i> -[PtCl(SnBuCl ₂)(PPh ₃) ₂]	- 2	18,534	155	CH ₂ Cl ₂	190
	<i>trans</i> -[PtCl(SnPhCl ₂)(PPh ₃) ₂]	+ 60	8,020	244	CH ₂ Cl ₂	190
	<i>trans</i> -[PtBr(SnMe ₂ Br)(PPh ₃) ₂]	+ 29	14,654	128	CH ₂ Cl ₂	190
	<i>trans</i> -[PtBr(SnBu ^a ₂ Br)(PPh ₃) ₂]	+ 78	13,062	116	CH ₂ Cl ₂	190
	<i>trans</i> -[PtBr(SnMeBr ₂)(PPh ₃) ₂]	- 63	18,361	153	CH ₂ Cl ₂	190
	<i>trans</i> -[PtBr(SnBu ^a Br ₂)(PPh ₃) ₂]	+ 26	17,877	140	CH ₂ Cl ₂	190
	<i>trans</i> -[PtBr(SnPhBr ₂)(PPh ₃) ₂]	- 57	7,880	223	CH ₂ Cl ₂	190

^a Other signals: $\delta^{119}\text{Sn}$ + 61.5, + 44.4, and more.

^b Undefined stereochemistry

^c Undefined structure.

^d bipy, Bipyridyl.

TABLE 25

Transition metal tin halides, tin coordination number ≥ 4

Compound	^{119}Sn	$^1J(\text{M}^{119}\text{Sn})$ (Hz)	$^2J(^{119}\text{Sn}^{119}\text{Sn})$ (Hz)	$^2J(^{119}\text{Sn}^{31}\text{P})$ (Hz)	Solvent	Footnotes	Reference
$[\text{Ru}(\text{SnCl}_3)_6]^{4-}$	-34.6	—	2474 (<i>cis</i>) 13,460 (<i>trans</i>)	—	3 M HCl		222
$(\text{Ru}(\text{SnCl}_3)_3\text{Cl})^{4-}$	-167.9 (eq) -149.2 (ax)	846 (eq)	3075 (<i>cis</i> , eq, eq) 2701 (<i>cis</i> , eq, ax) 22,242 (<i>trans</i> , eq, eq)	—	CH_3NO_2		227 221
$[\text{Ru}(\text{SnCl}_3)_3(\text{MeCN})]^{2-}$	-70.6 (eq) -103.9 (ax)	—	2760 (<i>cis</i> , eq, eq) 2817 (<i>cis</i> , eq, ax) 18,296 (<i>trans</i> , eq, eq)	—	CH_3NO_2		227
$[\text{Os}(\text{SnCl}_3)_3\text{Cl}]^{4-}$	-531.8 (eq) -581.8 (ax)	1290 (eq)	2270 (<i>cis</i> , eq, eq) 1614 (<i>cis</i> , eq, ax) 19,465 (<i>trans</i> , eq, eq)	—	CH_3NO_2		227
$[\text{Rh}(\text{SnCl}_3)_3]^{4-}$	+8.5	806	3803	—	3 M HCl		219
$[\text{Rh}(\text{SnCl}_3)_3\text{Cl}]^{3-}$	-100.5	547	2043	—	3 M HCl	<i>a</i>	219
$[\text{Rh}(\text{SnCl}_3)_3\text{Cl}_2]^{3-}$	-204.3	590	2258	—	3 M HCl		219
$[\text{Rh}(\text{SnCl}_3)_3\text{Cl}_3]^{3-}$	-411.1	718	2934	—	3 M HCl	<i>b</i>	219
	-395.4	708	2972		12 M HCl		219
$[\text{Rh}(\text{SnCl}_3)_2\text{Cl}_4]^{3-}$	-654.4	796	—	—	3 M HCl		219
	-626	780	3235		12 M HCl		219
$[\text{Rh}(\text{SnCl}_3)_2\text{Cl}_3]^{3-}$	-991.6	864	—	—	3 M HCl		219
	-914.1	850	—		12 M HCl		
$[\text{Rh}(\text{SnCl}_3)_2(\text{nbd})]^{2-}$	+38.8	758	2523	—	CDCl_3	<i>c</i>	210
$[\text{Rh}(\text{SnCl}_3)_2(1,5\text{-cod})]^{2-}$	+25.7	651	1759	—	CDCl_3	<i>d</i>	210
$[\text{Rh}(\text{SnCl}_3)_2(\text{chexCN})_2]^{2-}$	+50.2	986	14,141	—	Acetone- d_6 , -50°C		210
$[\text{Rh}(\text{SnCl}_3)_2(\text{CO})_2]^{2-}$	+89.1	864	9775	—	CDCl_3		210
$[\text{Rh}(\text{SnCl}_3)_2(\text{nbd})_2]$	+156.7	845	—	—	CDCl_3	<i>c</i>	210
$[\text{Rh}(\text{SnCl}_3)_2(\text{nbd})(\text{PPh}_3)]^{-}$	+66.6	757	1329	349	CDCl_3	<i>c</i>	229
$[\text{Rh}(\text{SnCl}_3)_2(\text{nbd})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OMe})_3\}]^{-}$	+65.0	757	1700	352	Acetone, -50°C	<i>c</i>	229
$[\text{Rh}(\text{SnCl}_3)_2(\text{nbd})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3\}]^{-}$	+71.8	757	1124	349	Acetone, -50°C	<i>c</i>	229
$[\text{Rh}(\text{SnCl}_3)_2(\text{nbd})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Cl})_3\}]^{-}$	+66.8	757	932	344	Acetone, -50°C	<i>c</i>	229
$[\text{Rh}(\text{SnCl}_3)_2(1,5\text{-cod})(\text{PPh}_3)]^{-}$	+38.3	674	2875	350	Acetone, -50°C	<i>d</i>	229
$[\text{Rh}(\text{SnCl}_3)_2(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-OMe})_3\}]^{-}$	+34.8	684	3538	358	Acetone, -50°C	<i>d</i>	229
$[\text{Rh}(\text{SnCl}_3)_2(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-F})_3\}]^{-}$	+44.1	671	2772	346	Acetone, -50°C	<i>d</i>	229
$[\text{Rh}(\text{SnCl}_3)_2(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-Cl})_3\}]^{-}$	+39.1	671	3295	344	Acetone, -50°C	<i>d</i>	229
$[\text{Ir}(\text{SnCl}_3)_3(\text{nbd})]^{2-}$	-268.7	—	1572	—	Acetone- d_6 , -50°C	<i>c</i>	210
$[\text{Ir}(\text{SnCl}_3)_3(1,5\text{-cod})]^{2-}$	-216.5	—	1583	—	CDCl_3	<i>d</i>	210

$[\text{Ir}(\text{SnCl}_3)(\text{nbdl})_2]$	-226.6	—	—	—	CDCl_3	<i>c</i>	210
$[\text{Ir}(\text{SnCl}_3)(1,5\text{-cod})_2]$	-292.9	—	—	—	CDCl_3	<i>d</i>	210
$[\text{Ir}(\text{SnCl}_3)(\text{nbdl})(1,5\text{-cod})]$	-266.2	—	—	—	CDCl_3	<i>c, d</i>	210
$[\text{Ir}(\text{SnCl}_3)_2(1,5\text{-cod})(\text{PPh}_3)_2]^-$	-217.6	—	1418	280	Acetone, -50°C		229
$[\text{Ir}(\text{SnCl}_3)_2(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{OMe})_2\}]^-$	-220.2	—	1916	287	Acetone, -50°C	<i>d</i>	229
$[\text{Ir}(\text{SnCl}_3)_2(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{F})_2\}]^-$	-210.1	—	1342	273	Acetone, -50°C	<i>d</i>	229
$[\text{Ir}(\text{SnCl}_3)_2(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{Cl})_2\}]^-$	-208.4	—	945	271	Acetone, -50°C	<i>d</i>	229
$[\text{Ir}(\text{SnCl}_3)(\text{CO})(1,5\text{-cod})(\text{PPh}_3)_2]$	-204.0	—	—	196	CDCl_3	<i>d</i>	229
$[\text{Ir}(\text{SnCl}_3)(\text{CO})(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{OMe})_2\}]$	-208.4	—	—	209	CDCl_3	<i>d</i>	229
$[\text{Ir}(\text{SnCl}_3)(\text{CO})(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{F})_2\}]$	-198.4	—	—	199	CDCl_3	<i>d</i>	229
$[\text{Ir}(\text{SnCl}_3)(\text{CO})(1,5\text{-cod})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{Cl})_2\}]$	-196.6	—	—	186	CDCl_3	<i>d</i>	229
$[\text{Ir}(\text{SnCl}_3)\text{Cl}(\text{HgCl})(\text{CO})(\text{PPh}_3)_2]$	-197	—	—	167	CDCl_3	<i>e, f</i>	228
$[\text{Ir}(\text{SnCl}_3)\text{Cl}(\text{HgCl})(\text{CO})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{OMe})_2\}_2]$	-192	—	—	166	CDCl_3	<i>e, g</i>	228
$[\text{Ir}(\text{SnCl}_3)\text{Cl}(\text{HgCl})(\text{CO})\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{F})_2\}_2]$	-176	—	—	172	CDCl_3	<i>e, h</i>	228
$[\text{Ir}(\text{SnBr}_3)\text{Br}(\text{HgBr})(\text{CO})(\text{PPh}_3)_2]$	-170	—	—	148	CDCl_3	<i>e, i</i>	228
$[\text{Pd}(\text{SnCl}_3)_3(1,5\text{-cod})]^-$	+33.2	—	1143	—	CDCl_3		210
$[\text{Pd}(\text{SnCl}_3)_3(\text{PEt}_3)_2]^-$	+13	—	21,966	314	Acetone, -90°C		191
$[\text{Pd}(\text{SnCl}_3)\{\text{P}(\text{C}_6\text{H}_4\text{-}o\text{-}\text{AsPh}_2)_3\}]$	+15	—	—	3649	$\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$		191
<i>trans</i> - $[\text{Pd}(\text{SnCl}_3)_3(\text{AsEt}_3)_2]$	+11	—	38,982	—	$\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$, $\sim 75^\circ\text{C}$		191
<i>trans</i> - $[\text{PdCl}(\text{SnCl}_3)(\text{PEt}_3)_2]$	-75	—	—	231	CDCl_3 , 0°C		191
<i>trans</i> - $[\text{PdCl}(\text{SnCl}_3)\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{Me})_2\}_2]$	-113	—	—	188	CDCl_3 , -40°C		191
<i>trans</i> - $\text{PdCl}(\text{SnCl}_3)(\text{AsEt}_3)_2]$	-70	—	—	—	CH_2Cl_2 , CD_2Cl_2 , $\sim 75^\circ\text{C}$		191
<i>cis</i> - $[\text{PdCl}(\text{SnCl}_3)\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}\text{Me})_2\}_2]$	-131	—	—	4848 (<i>trans</i>)	CDCl_3 , -40°C		191
$[\text{Pt}(\text{SnCl}_3)_3]^{2-}$	-142	16,024	6520	—	Acetone- <i>d</i> ₆ , -90°C		217, 226
	-121.2	15,995	6473	—	Acetone, -60°C		211
$[\text{Pt}(\text{SnCl}_3)_3(\text{PEt}_3)_2]^-$	-83	20,410	19,027	277	Acetone		191
	-77	20,239	18,638	274	MeOH , -80°C		191
$[\text{Pt}(\text{SnCl}_3)_3(\text{PPR}^n)_3]^-$	-73	20,422	18,663	274	MeOH , -80°C		191
$[\text{Pt}(\text{SnCl}_3)_3\{\text{P}(\text{OEt})_2\}_2]^-$	-117	19,049	17,271	317	Acetone, -30°C		191
$[\text{Pt}(\text{SnCl}_3)_3(\text{AsMe}_3)_2]^-$	-67	19,031	18,318	—	CDCl_3 , -40°C		191
$[\text{Pt}(\text{SnCl}_3)_3(\text{AsEt}_3)_2]^-$	-79	19,788	18,957	—	Acetone, -70°C		191
$[\text{Pt}(\text{SnCl}_3)_3(\text{nbdl})]^-$	-209.8	16,4553	729	—	CDCl_3 , -50°C	<i>c</i>	210
$[\text{Pt}(\text{SnCl}_3)_3(1,5\text{-cod})]^-$	-132.5	13,840	648	—	CDCl_3 , -50°C	<i>d</i>	210
$[\text{Pt}(\text{SnCl}_3)_3(\text{C}_6\text{Me}_6)]^-$	-143.0	21,692	2503	—	CDCl_3 , -40°C		191
$[\text{Pt}(\text{SnCl}_3)_3(\text{CO})]^-$	-144.8	14,678	6003	—	CDCl_3 , -50°C		210
$[\text{Pt}(\text{SnCl}_3)\{\text{P}(\text{C}_6\text{H}_4\text{-}o\text{-}\text{AsPh}_2)_3\}]$	-205	13,745	—	3044 (<i>trans</i>)	$\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$		191
$[\text{Pt}(\text{SnCl}_3)\{\text{As}(\text{C}_6\text{H}_4\text{-}o\text{-}\text{PPh}_2)_3\}]$	-232	16,913	—	271 (<i>cis</i>)	$\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$		191
<i>cis</i> - $[\text{PtCl}_2(\text{SnCl}_3)]^{2-}$	-142	27,640	2485	—	Acetone- <i>d</i> ₆		76
<i>trans</i> - $[\text{PtCl}(\text{SnCl}_3)(\text{PEt}_3)_2]$	-270	30,537	—	277	Acetone, -83°C	<i>j</i>	216
	-84.9	20,585	—	250			
	-199	29,077	—	235	$\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$, -75°C	<i>k</i>	191

TABLE 25 (cont.)

Compound	^{119}Sn	$^1J(\text{M}^{119}\text{Sn})$ (Hz)	$^2J(^{119}\text{Sn}^{119}\text{Sn})$ (Hz)	$^2J(^{119}\text{Sn}^{31}\text{P})$ (Hz)	Solvent	Footnotes	Reference
<i>trans</i> -[PtCl(SnCl ₃)(PPr ₃) ₂]	-201	29,272	—	237	CH ₂ Cl ₂ /CD ₂ Cl ₂ , -75°C	<i>k</i>	191
<i>trans</i> -[PtCl(SnCl ₃){P(C ₆ H ₄ - <i>p</i> -Cl) ₃ }] ₂	-222	28,052	—	226	CDCl ₃ , -40°C		191
<i>trans</i> -[PtCl(SnCl ₃)(AsEt ₃) ₂]	-221	27,536	—	—	CH ₂ Cl ₂ , CD ₂ Cl ₂ , -75°C		191
<i>trans</i> -[PtCl(SnCl ₃)(As(C ₆ H ₄ - <i>p</i> -Me) ₃) ₂]	-250	27,222	—	—	CDCl ₃ , -25°C		191
<i>cis</i> -[PtCl(SnCl ₃){P(C ₆ H ₄ - <i>p</i> -Me) ₃ }] ₂	-59	16,321	—	4298 (<i>trans</i>) 216 (<i>cis</i>)	CDCl ₃ , -25°C		191
<i>cis</i> -[PtCl(SnCl ₃){P(C ₆ H ₄ - <i>p</i> -Cl) ₃ }] ₂	-72	16,931	—	4296 (<i>trans</i>) 219 (<i>cis</i>)	CDCl ₃ , -40°C		191
[PtCl(SnCl ₃)(As(C ₆ H ₄ - <i>p</i> -Me) ₃){P(C ₆ H ₄ - <i>p</i> -Me) ₃ }]	-131	22,314	—	207 (<i>cis</i>)	CDCl ₃ , -25°C		191
<i>cis</i> -[PtCl(SnCl ₃)(As(C ₆ H ₄ - <i>p</i> -Me) ₃) ₂]	-136	20,043	—	—	CDCl ₃ , -25°C		191
[PtCl(SnCl ₃)(1,5-cod)]	-115.8	25,964	—	—	CDCl ₃ , -50°C	<i>d</i>	210
<i>trans</i> -[Pt(SnCl ₃) ₂ (PEt ₃) ₂]	-235.7 -88.4 -41.0	30,537 20,585 23,517	— — 36,286	250 276 244	Acetone, -83°C CH ₂ Cl ₂ /CD ₂ Cl ₂ , -75°C	<i>j</i>	216 191
<i>trans</i> -[Pt(SnCl ₃) ₂ (PPr _n) ₂]	-40	23,682	36,408	247	CH ₂ Cl ₂ /CD ₂ Cl ₂ , -75°C		191
<i>trans</i> -[Pt(SnCl ₃) ₂ (AsEt ₃) ₂]	-39.0	22,364	36,722	—	CH ₂ Cl ₂ /CD ₂ Cl ₂ , -75°C		191
<i>trans</i> -[PtCl(SnCl ₃) ₂ (PPh ₃) ₂] ⁻	-109.4	18,600	—	250	Acetone, -60°C	<i>l</i>	211, 230
<i>trans</i> -[PtCl(SnCl ₃) ₂ (CO)] ⁻	-141.6	14,960	6081	—	Acetone, -60°C	<i>m</i>	211

^a $^2J(\text{SnSn})(\text{Hz})$ in (Me₂N)₂PO solution.^b $^2J(\text{SnSn}) = 2043 \text{ Hz}$ in (Me₂N)₂PO solution.^c nbd, Norbornadiene.^d 1,5-cod, 1,5-Cyclooctadiene.^e SnCl₃/HgCl and the phosphines are mutually in *trans* positions.^f $^2J(^{199}\text{Hg}^{119}\text{Sn})$, 41,479 Hz.^g $^2J(^{199}\text{Hg}^{119}\text{Sn})$, 42,688 Hz.^h $^2J(^{199}\text{Hg}^{119}\text{Sn})$, 39,916 Hz.ⁱ $^2J(^{199}\text{Hg}^{119}\text{Sn})$, 39,294 Hz.^j $\delta^{119}\text{Sn}$ values are dependent on SnCl₃ concentration; the observation of two signals is not accounted for.^k $^2J(^{119}\text{Sn}^{31}\text{P})(\text{Hz})$ in CDCl₃, -40°C.^l $^2J(\text{SnSn})$ not observed; the resonances are observed only in the presence of other major species.^m The value of $^2J(\text{SnSn})$ is rather small for mutually *trans* positions of the SnCl₃ groups, although the value of $^1J(^{195}\text{Pt}^{13}\text{C})$ (1794 Hz) points to a *trans* arrangement of ¹³CO and Cl.

TABLE 26

Comparison of reduced couplings $^1K(\text{EX})$ ($10^{20} \text{ NA}^{-2} \text{ m}^{-3}$) for $\text{E} = {}^{13}\text{C}$, ${}^{29}\text{Si}$, ${}^{119}\text{Sn}$, and ${}^{207}\text{Pb}^a$

Compound	X	$^1J({}^{119}\text{SnX})$	$^1K({}^{119}\text{SnX})$	$^1K({}^{13}\text{CX})$	$^1K({}^{29}\text{SiX})$	$^1K({}^{207}\text{PbX})$
$\text{Me}_3\text{E}-\text{H}$	${}^1\text{H}$	-1744^{119}	+39.0	$+4.14^{342}$	$+7.69^{123}$	$+106.7^{120}$
$\text{Me}_3\text{E}-\text{BH}_3$	${}^{11}\text{B}$	-554^{15}	+38.6	$+5.16^{155}$	$+9.67^{15}$	—
$\text{Me}_3\text{E}-\text{CH}_3$	${}^{13}\text{C}$	-340^{22}	+30.2	$+4.80^{342}$	$+8.38^{123}$	$+39.6^{351}$
$\text{Me}_3\text{E}-\text{CH}=\text{CHMe}^b$	${}^{13}\text{C}$	-446.6^{90}	+39.7	$+5.83^{343}$	$+10.7^{123}$	$+56.8^{352}$
$\text{Me}_3\text{E}-\text{C}\equiv\text{C}-\text{H}$	${}^{13}\text{C}$	-415.5^{76}	+36.9	$+8.18^{157}$	$+14.2^{76}$	-9.34^{c159}
$\text{Me}_3\text{E}-\text{SiMe}_3$	${}^{29}\text{Si}$	$+656^{12}$	+73.8	$+9.5^{344}$	$+17.9^d$	—
$\text{Me}_3\text{E}-\text{SnMe}_3$	${}^{119}\text{Sn}$	$+4460^{205}$	+267.3	$+38.8^{154}$	$+73.8^{12}$	$+381.2^{13}$
$\text{Me}_3\text{E}-\text{N}(\text{Me})\text{Ph}$	${}^{15}\text{N}$	$+2.2^{13}$	+0.5	$(+)3.37^e 345$	$(+)3.47^f 76$	-102.8^{13}
$\text{Me}_3\text{E}-\text{PPh}_2$	${}^{31}\text{P}$	$+596^{330}$	-32.9	-1.20^{342}	-2.22^{123}	-131.3^{13}
$\text{Me}_3\text{E}-\text{SeCH}_3$	${}^{77}\text{Se}$	$+1015^{180}$	-118.9	$-17.0^g 346$	$-24.3^h 348$	-244.2^{13}
$(\text{Me}_3\text{E})_2\text{Te}$	${}^{125}\text{Te}$	-1385^{301}	-97.9	$-8.5^i 346$	—	—
$(\text{Me}_2\text{PhCCH}_2)_3\text{E}-\text{F}$	${}^{19}\text{F}$	$+2298^{183}$	-54.6	$-9.3^j 342$	$-12.2^k 349$	—
$[(\text{Me}_3\text{SiCH}_2)_3\text{Sn}]_2\text{Hg}$	${}^{199}\text{Hg}$	$(-)6157^{194}$	$(+)771.3$	$+128.5^l 342$	$(+)228.5^m 350$	—
<i>cis</i> - $[\text{Pt}(\text{Ph}_3\text{E})\text{Ph}(\text{PPh}_3)_2]$	${}^{195}\text{Pt}$	$(-)12,686^{190}$	$(+)1318$	$(+)91.5^n 347$	—	$(+)3403^{353}$
$\text{Me}_3\text{EW}(\text{CO})_3(\text{C}_5\text{H}_5)$	${}^{183}\text{W}$	-150^{12}	+80.5	$(+)7.6^{12}$	—	—

^a $^1K(\text{EX}) = (4\pi^2/h)(\gamma_{\text{E}}\gamma_{\text{X}})^{-1}^1J(\text{EX})$.^b Cis compound.^c Value for $\text{Et}_3\text{Pb}-\text{C}\equiv\text{C}-\text{H}$.^d Estimated from various values for compounds $\text{Me}_3\text{Si}-\text{SiMe}_2\text{R}$.^e Value for PhNHMe .^f Value for $\text{Me}_3\text{SiNC}_4\text{H}_4$.^g Value for Me_2Se .^h Value for $(\text{H}_3\text{Si})_2\text{Se}$.ⁱ Value for Me_2Te .^j Value for Me_3CF .^k Value for Me_3SiF .^l Value for Me_2Hg .^m Value for $[(\text{Me}_3\text{SiCH}_2)\text{Me}_2\text{Si}]_2\text{Hg}$.ⁿ Value for *cis*- $[\text{PtPh}_2(\text{PEt}_3)_2]_2$.

TABLE 27

Selected coupling constants $^1J(^{119}\text{Sn}^{13}\text{C})$, $^2J(^{119}\text{Sn}^1\text{H})$, and $^1J(^{119}\text{SnX})$ of trimethyltin compounds (Me_3SnX)

Compound	$^1J(^{119}\text{Sn}^{13}\text{C})_{\text{Me}}$ (Hz)	$^2J(^{119}\text{Sn}^1\text{H})_{\text{Me}}^a$ (Hz)	$^1J(^{119}\text{SnX})$ (Hz)	X	Solvent	Reference
$\text{Me}_3\text{Sn}-\text{CH}_3^b$	-337.8	+54.3	-337.8	^{13}C	—	154
$\text{Me}_3\text{Sn}-\text{CH}_2\text{Me}$	-320.8	+52.8	-374.2	^{13}C	—	154
$\text{Me}_3\text{Sn}-\text{CHMe}_2$	-306.7	+50.8	-410.2	^{13}C	—	154
$\text{Me}_3\text{Sn}-\text{CMe}_3$	-295.7	+50.0	-436.9	^{13}C	—	154
$\text{Me}_3\text{Sn}-\text{CH}(\text{CH}_2)_2$	-341.6	—	-502.8	^{13}C	—	154
$\text{Me}_3\text{Sn}-\text{CH}(\text{CH}_2)_3$	-313.5	—	-389.7	^{13}C	—	154
$\text{Me}_3\text{Sn}-\text{CH}(\text{CH}_2)_4$	-311.8	51.4	-405.6	^{13}C	—	154
$\text{Me}_3\text{Sn}-\text{CH}(\text{CH}_2)_5$	-303.9	+50.8	-407.4	^{13}C	—	154
(equatorial)	-299.4	—	-403.8	^{13}C	CD_2Cl_2 , -69°C	354
(axial)	-295.5	—	—	—	CD_2Cl_2 , -69°C	354
$\text{Me}_3\text{Sn}-\text{CH}_2\text{Bu}^t$	-318.6	—	-369	^{13}C	—	154
$\text{Me}_3\text{Sn}-\text{CH}_2\text{SiMe}_3$	-331	—	-250	^{13}C	CDCl_3	170
$\text{Me}_3\text{Sn}-\text{CH}_2\text{SnMe}_3$	-330	63.0	-287	^{13}C	CDCl_3	355
$\text{Me}_3\text{Sn}-\text{CH}(\text{SnMe}_3)_2$	-323	—	-192	^{13}C	CDCl_3	243
$\text{Me}_3\text{Sn}-\text{C}(\text{SnMe}_3)_3$	-318	—	-107	^{13}C	CDCl_3	243
$\text{Me}_3\text{Sn}-\text{CH}=\text{CHMe}$						
(cis)	-346.9	—	-464.6	^{13}C	CDCl_3	90
(trans)	-352.0	—	-478.4	^{13}C	CDCl_3	90
$\text{Me}_3\text{Sn}-\text{C}_6\text{H}_5$	-347.5	+54.6	-474.4	^{13}C	CDCl_3	356
$\text{Me}_3\text{SnCH}=\text{C}=\text{CH}_2$	-356.0	—	-382.0	^{13}C	—	354
$(\text{Me}_3\text{Sn})_2\text{C}=\text{C}=\text{C}(\text{SnMe}_3)_2$	-344.0	—	-296.0	^{13}C	—	248
$\text{Me}_3\text{Sn}-\text{C}\equiv\text{C}-\text{Me}$	-404.1	+60.5 ^c	-502.9	^{13}C	C_6D_6	159
$\text{Me}_3\text{SnC}(\text{CO}_2\text{Et})\text{N}_2$	-385.2	—	-300	^{13}C	C_6D_6 , 38°C	357
$(\text{Me}_3\text{Sn})_2\text{CN}_2$	-365	—	-217	^{13}C	C_6D_6	275
$(\text{Me}_3\text{Sn})_2\text{CPMe}_3$	-324.7	—	no ^d	^{13}C	C_6D_6	233
$\text{Me}_3\text{Sn}-\text{SiMe}_3$	-245.8	+46.7	+656	^{29}Si	90% C_6H_6	12

(Me ₃ Sn) ₄ Si	-261.0		+ 220	²⁹ Si	C ₆ D ₆	212
Me ₃ Sn—GeMe ₃	255.1		—	—	?	249
Me ₃ Sn—SnMe ₃	-244.2	+ 48.3	+ 4460	¹¹⁹ Sn	C ₆ H ₆	205
Me ₃ Sn—H	-352	+ 56.5	-1744	¹ H	CDCl ₃	162
Me ₃ Sn—Cl	-379.7	+ 58.1	—	—	CCl ₄	358
Me ₃ Sn—Br	-368.9	+ 57.8	—	—	CCl ₄	358
Me ₃ Sn—OMe	-398.0	+ 57.8	—	—	CDCl ₃	249
Me ₃ Sn—SCH ₃	-355.8	+ 56.9	—	—	?	249
Me ₃ Sn—SeSnMe ₃	-340.0	+ 56.1	+ 1060	⁷⁷ Se	80% CH ₂ Cl ₂	301
Me ₃ Sn—NMe ₂	-381.2	+ 55.3	—	¹⁵ N	?	249
Me ₃ Sn—NEt ₂	-378.8	+ 55.2	< 1 ^e	¹⁵ N	?	249
Me ₃ Sn—N(SnMe ₃) ₂	-366.2	—	79.6 ^e	¹⁵ N	C ₆ D ₆	76
(Me ₃ Sn) ₂ NN(SnMe ₃) ₂	-349.6	—	—	—	Toluene- <i>d</i> ₈	100
Me ₃ Sn—P(SnMe ₃) ₂	-301.8	+ 52.5	- 833.7	³¹ P	C ₆ D ₆	325
Me ₃ Sn—As(Ph)SnMe ₃	-283.2	—	—	—	CDCl ₃	271
Me ₃ Sn—Bi(SnMe ₃) ₂	-220	+ 47.0 ^f	—	—	C ₆ D ₆	327
[Me ₃ Sn—BH ₃] ⁻	-110	+ 32.0 ^g	- 554	¹¹ B	THF/C ₆ D ₆	15
Me ₃ Sn—B(NMe ₂) ₂	-230.4	+ 42.3	- 953	¹¹ B	Toluene- <i>d</i> ₈	15
Me ₃ SnLi·3THF	+ 155	- 6.2	—	—	25% THF	151
<i>cis</i> -[Fe(CO) ₄ (SnMe ₃) ₂]	-274	—	—	—	CD ₂ Cl ₂	209
<i>cis</i> -[Ru(CO) ₄ (SnMe ₃) ₂]	-207	—	—	—	Neat	208
<i>cis</i> -[Os(CO) ₄ (SnMe ₃) ₂]	-278	—	—	—	CD ₂ Cl ₂	208

^a Data taken from reference 22 if not otherwise indicated.

^b Various values for ¹*J*(¹¹⁹Sn¹³C) are reported between 335 to 340 Hz.³⁵⁸

^c Reference 95.

^d no, Not observed.

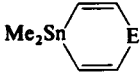
^e Direct ¹⁵N measurement in C₆D₆ (90%).⁷⁶

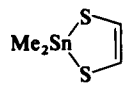
^f Reference 327.

^g Reference 15.

TABLE 28

Selected coupling constants (Hz) $^1J(^{119}\text{Sn}^{13}\text{C})$, $^2J(^{119}\text{Sn}^1\text{H})$, and $^1J(^{119}\text{SnX})$ of dimethyltin compounds (Me_2SnX_2)

Compound	$^1J(^{119}\text{Sn}^{13}\text{C})_{\text{Me}}$ (Hz)	$^2J(^{119}\text{Sn}^1\text{H})_{\text{Me}}^a$ (Hz)	$^1J(^{119}\text{SnX})$ (Hz)	X	Solvent	Reference
$\text{Me}_2\text{Sn}(\text{CH}_3)_2^b$	-337.8	+54.3	-337.8	^{13}C	—	154
$\text{Me}_2\text{Sn}(\text{CH}_2\text{Me})_2$	-302.5	+49.8	-354.7	^{13}C	CDCl_3	155
$\text{Me}_2\text{Sn}(\text{CH}_2\text{Bu}')_2$	-297.0	—	-346.0	^{13}C	CDCl_3	170
$\text{Me}_2\text{Sn}(\text{CH}_2\text{SiMe}_3)_2$	-325.0	—	-246	^{13}C	CDCl_3	170
$\text{Me}_2\text{Sn}(\text{CH}_2)_4$	-300.6	+54.9	-334.8	^{13}C	—	154
$\text{Me}_2\text{Sn}(\text{CH}_2)_5$	-306.9	—	-322.1	^{13}C	—	154
$\text{Me}_2\text{Sn}(\text{CH}_2)_6$	-300.4	+51.3	-339.7	^{13}C	—	154
$\text{Me}_2\text{Sn}(\text{CH}=\text{CHMe})_2^c$	-357.2	—	(c)	^{13}C	CDCl_3	90
172  Me_2Sn 						
<u>E</u>						
CMe_2	-379.2	+59.5 ^d	-440.0	^{13}C	C_6D_6	242
SiMe_2	-354.0	+55.5 ^d	-470.0	^{13}C	C_6D_6	242
SnMe_2	-349.0	+54.1 ^d	-495.6	^{13}C	C_6D_6	242
PPh	-328.0	+59.5 ^d	-438.0	^{13}C	C_6D_6	242
		+61.0 ^d				
BNEt_2	-355	+59.0 ^d	-455	^{13}C	C_6D_6	242
$\text{Me}_2\text{Sn}(\text{C}\equiv\text{C}-\text{H})$	-501.2	+70.0 ^e	-606.7 ^f	^{13}C	C_6D_6	159
$\text{Me}_2\text{Sn}(\text{SnMe}_3)_2$	-179.4	—	+2873	^{119}Sn	95% C_6H_6	167
Me_2SnH_2	—	+58.0	-1797.0	^1H	C_6D_6	76
Me_2SnCl_2	-468.4	+68.2 ^g	—	—	CCl_4	358
Me_2SnBr_2	-442.7	+66.7 ^g	—	—	CCl_4	358

	-368.7	+61.4 ^h	—	—	CDCl ₃	76
(Me ₂ SnS) ₃	-407.0	—	—	—	CDCl ₃	76
(Me ₂ SnSe) ₃	-360.0	+61.0 ⁱ	1228	⁷⁷ Se	?	359
Me ₂ Sn(NEt ₂) ₂	-472	+59.4	—	—	CCl ₄	320
(Me ₂ SnNEt) ₃	-430	—	—	—	C ₆ D ₆	76

^a Data taken from reference 22 if not indicated otherwise.

^b Various values for ¹J(¹¹⁹Sn¹³C) are reported between 335 and 340 Hz.³⁵⁸

^c The cis,cis isomer, ¹J(¹¹⁹Sn¹³C=), ranges from 480 to 494 Hz.

^d Reference 242.

^e Reference 95.

^f Reference 360 gives 504—494 Hz [¹J(¹¹⁹Sn¹³C)_{Me}] and 598 Hz [¹J(¹¹⁹Sn¹³C=)]; no solvent is reported.

^g Reference 358.

^h Reference 76.

ⁱ Reference 359.

TABLE 29

Some $^1J(^{119}\text{Sn}^{15}\text{N})$ data

Compound	$^1J(^{119}\text{Sn}^{15}\text{N})$ (Hz)	Solvent	Reference
$\text{Me}_3\text{Sn}-\text{NEt}_2$	< 1.0	C_6D_6	76
$\text{Me}_3\text{Sn}-\text{NHPh}$	-26.3	C_6H_6	12
$\text{Me}_3\text{Sn}-\text{NMePh}$	+2.2	C_6H_6	118
$(\text{Me}_3\text{Sn})_2\text{NBu}'$	(-)38.0	C_6D_6	76
$(\text{Me}_3\text{Sn})_2\text{NPh}$	-41.4	C_6H_6	118
$(\text{Me}_3\text{Sn})_2\text{NGeMe}_3$	(-)68.4	C_6D_6	76
$(\text{Me}_3\text{Sn})_3\text{N}$	(-)79.6	C_6D_6	76
$(\text{Me}_3\text{Sn})_2\text{N}-\text{NMe}_2$	46.0	C_6D_6	76
$\text{Me}_3\text{Sn}-\text{N}$ 	6.4	C_6D_6	76
$\text{Me}_3\text{Sn}-\text{N}(\text{PMe}_2)\text{Ph}$	+9.5	C_6H_6	118
$\text{Me}_3\text{Sn}-\text{N}[\text{P}(\text{S})\text{Me}_2]\text{Ph}$	-21.0	C_6H_6	118
$\text{Me}_2\text{Sn}(\text{NMePh})_2$	+24.0	C_6H_6	118
$\text{MeSn}(\text{NMePh})_3$	+87.0	C_6H_6	118
$[\text{MeSn}(\text{OCH}_2\text{CH}_2)_3\text{N}]_3$	75.6, 110.0	CDCl_3	54
$\text{Bu}'\text{Sn}(\text{OCH}_2\text{CH}_2)_3\text{N}$	69.9	CDCl_3 , -20°C	54
$\text{Sn}(\text{NMePh})_4$	+175.0	C_6H_6	118
$\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$	344 ^a	C_6D_6 , 80°C	76

^a $^1J(^{119}\text{Sn}^{14}\text{N}) = 245 \pm 10 \text{ Hz}$

TABLE 30

Some $J(^{119}\text{Sn}^{13}\text{C})$ data for organotrimethylstannanes with a rigid geometry of the hydrocarbon framework

Number	Compound ^a	$^1J(^{119}\text{Sn}^{13}\text{C})\text{Me}$ (Hz)	$^1J(^{119}\text{Sn}^{13}\text{C})$ (Hz)	$^2J(^{119}\text{Sn}^{13}\text{C})$ (Hz)	$^3J(^{119}\text{Sn}^{13}\text{C})$ (Hz)	Footnotes	Reference
1	Me_3Sn —chex (eq)	299.4	403.8	no	65.0	<i>b, c</i>	354
2	1- Me_3Sn —4-Bu ^t -chex (eq)	304.5	408.1	13.6	66.6		129
3	1- Me_3Sn —4-Bu ^t -chex (ax)	301.3	402.5	12.0	13.8		129
4	1- Me_3Sn —norbornane	313.8	459.0	17.3 (2, 6) 13.0 (7)	51.9 (3, 5) 65.8 (4)	<i>d</i>	239
5	2- Me_3Sn —norbornane (<i>exo</i>)	306.0	407.0	9.8 (1) 23.4 (3)	12.7 (4) 67.4 (6) — (7)	<i>d</i>	146
6	2- Me_3Sn —norbornane (<i>endo</i>)	306.0	432.0	10.0 (1) no (3)	23.4 (4) 36 (6) 56.6 (7)	<i>b, d</i>	146
7	7- Me_3Sn —norbornane	314.2	405.6	no	11.9 (2, 3) 67.5 (5, 6)	<i>b, d</i>	239
8	3- Me_3Sn —nortricyclane	313.9	411.8	6.0 (2) 12.4 (4)	53.6 (1) 9.7 (5) 8.0 (6) 57.8 (7)	<i>d</i>	239
9	7,7-(Me_3Sn) ₂ —norcarane	318.0	332.0	24.0	34 (Sn, <i>endo</i>) 44 (Sn, <i>exo</i>)		243

TABLE 30 (cont.)

Number	Compound ^a	¹ J(¹¹⁹ Sn ¹³ C)Me (Hz)	¹ J(¹¹⁹ Sn ¹³ C) (Hz)	² J(¹¹⁹ Sn ¹³ C) (Hz)	³ J(¹¹⁹ Sn ¹³ C) (Hz)	Footnotes	Reference
10	1-Me ₃ Sn—tricyclo[4.1.1.0 ^{2,7}]heptane ^c	343	463.3	17.1 (2) 21.5 (7)	no	<i>b, d, e</i>	244
11	1-Me ₃ Sn—bicyclo[2.2.2]-octane	292	459	no	54	<i>b, e</i>	244
12	1-Me ₃ Sn—cubane	313.2	no	24.6	37.4	<i>b, e</i>	244
13	1-Me ₃ Sn—adamantane	290.4	451.7	12.2	51.1		239
14	2-Me ₃ Sn—adamantane	295.8	406.6	12.3	8.5 (4, 9) 60.0 (8, 10)	<i>d</i>	164
15	1-Me ₃ Sn—4-Me-1,4-ethano- 1,2,3,4-tetrahydronaphthalene	312.5 312.5	no	no (2) 4.6 (9)	50.8 (3) 36.0 (10)	<i>b</i>	164
16	4-Me ₃ Sn—quinuclidine	307.0	no	9.0	46.0	<i>b</i>	128

^a Structure numbers correspond to the entries in Fig. 8; ³J(¹¹⁹Sn¹³C) against the dihedral angle ϕ .

^b no, Not observed, or not reported.

^c CD₂Cl₂, -69°C.

^d Numbers in parentheses indicate the positions of the carbon atoms.

^e All values of J(Sn¹³C) are given as the average of ^{119/117}Sn-¹³C coupling.²⁴⁴

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Isomerization Processes Involving N—X Bonds

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I. INTRODUCTION

Considerable spectrometer time has been devoted in the last 20 years to dynamic NMR experiments, and among the very abundant literature concerning this subject the problem of the isomerization processes involving N—X bonds occupies a privileged place. This may be partly explained by the fact that the barrier heights, especially in compounds wherein the nitrogen lone pair is delocalized, correspond to coalescence figures, which frequently occur in a convenient temperature range and may be easily interpreted. On the other hand, the problem of isomerization about N—X bonds is of general concern in chemistry and biochemistry. In this respect much attention has

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been given to the amide structure on the basis of its importance as a unit of the backbone of peptides and protein molecules.

In spite of the improvement in NMR methodology the determination of activation parameters remains a relatively long and tedious task and the problem of accuracy is frequently a critical one. In this article, therefore, we insist on the importance of using appropriate and complementary methods for determining reliable values of enthalpy (ΔH^*) and entropy (ΔS^*). Numerous investigations of isomerization barriers have been published since the last review on this topic, which appeared in this series in 1971.¹ We present, following Section IV, 40 tables giving the values of activation parameters in typical series of compounds. Only a brief analysis of the results is given and we do not enter into a detailed discussion of the dynamic behaviour of each type of structure. Instead, we provide the reader with some information concerning possible theoretical interpretations and discussions in terms of correlations with substituent and NMR parameters.

Much is now known about the problems of isomerization, and for several years this subject has no longer constituted a particularly expanding field of NMR. No great development is expected in the future regarding the quantity of structures investigated, but efforts may still be devoted to a deeper interpretation of the fundamental mechanisms that control the variations of the enthalpy and entropy parameters. For this reason it is essential that the experimental values may be used with complete confidence, a situation which is still not generally the case.

II. METHODS OF INVESTIGATION

In spite of the considerable literature devoted to the investigation of dynamic processes since the introduction of NMR, much uncertainty still remains concerning the accuracy and therefore validity of dynamic parameters which are currently published. In fact, whereas it is generally accepted that the values of the activation energies $\Delta G^\ddagger$ measured at the coalescence temperature T_c are accurate parameters, severe problems exist when values of the activation enthalpies and entropies are desired. Determining such parameters, which is expected to provide a better understanding of the exchange mechanisms, requires time-consuming variable-temperature experiments, and therefore a critical insight into the potential and limitations of the experimental methods is of prime importance. It is beyond the scope of this review to give a detailed presentation of the theoretical and experimental aspects of dynamic NMR. However, with a view to limiting the risk of time wastage associated with insufficiently accurate determinations of kinetic parameters, attention will be drawn to the various complementary methods that are at our disposal for obtaining rate constants in suitable conditions.

A. Total line-shape analysis and one-parameter methods

Analysis of line-shape variation as a function of temperature in ^1H -NMR spectroscopy has been used extensively for the investigation of isomerization processes around X—N bonds. In fact, when exchange between two uncoupled, equally populated sites is considered, recourse to a full line-shape analysis by means of an appropriate computer program is not necessary and the rate constants can be derived from the measurement of single parameters such as the distance between the maxima of absorption, the half-height line width, or the signal intensity.

We shall not examine here the usual methods of dynamic NMR. The reader is referred, for example, to Chapter 8 of reference 2 for a presentation of the various formulas and theoretical frameworks which apply to the different types of spectra. We shall restrict ourselves to several points of particular importance for obtaining accurate results and appreciating the reliability of published results.

A survey of the literature (see Tables 1–40) shows that a majority of studies are concerned with the rotation of $(\text{CH}_3)_2\text{N}$ groups. Although this type of exchange benefits from the advantage of simplicity it is certainly not the most favourable from the point of view of the accuracy of the results. In fact, in most cases the dynamic parameters are deduced solely from a line-shape analysis or from one-parameter treatments of the ^1H -NMR spectra. The latter methods, which were proposed in the early years of NMR,³ have been the subject of considerable criticism. However, the major source of error seems to result in this case from the use of one-parameter formulas in situations where they are not strictly applicable: unequal values of the transverse relaxation times, existence of long-range couplings, etc.² It is now recognized that, when applied in appropriate conditions, several of these methods lead to an accuracy which may be comparable to that of a total line-shape analysis.⁴ But whichever method is considered, it should be noted that the sensitivity of the shape of the spectrum to variations in the lifetimes is less favourable for the simple two-site spectrum associated with the *N,N*-dimethyl probe (especially when the chemical shift separation is small), than for more complicated spectra. A total line-shape analysis is likely to provide better results when coalescence patterns, which involve coupled systems and extend over a large temperature range, are considered.^{5,6} Such analyses are now made relatively easy since computer programs enabling simulations, and eventually iterations, over strongly coupled multispin ^1H spectra are readily available.^{2a,b-11}

An important point to consider in the derivation of rate constants from the study of line-shape modifications is the possible occurrence of variations in the chemical shift separation ($\Delta\nu$) between the exchanging nuclei. This parameter is sometimes considered as an additional variable in the iterative

computer programs, but, when two-site exchanges are concerned, it seems preferable not to iterate over too great a number of variables and an independent estimation of $\Delta\nu$ is recommended. This can be achieved in many cases by measuring $\Delta\nu$ at several temperatures in the slow exchange domain and extrapolating the curve $\Delta\nu = f(T)$, which is frequently found to be linear, to the desired temperature.

Similarly, treatments by a total bandshape method or by single-parameter formulas require a careful estimation of the transverse relaxation times of the exchanging nuclei at each temperature. This estimation can be made by considering the behaviour of the half-height line width of a reference signal. When possible, this reference signal should preferably pertain to the same molecule as that which undergoes the exchange phenomenon.¹² A double-fitting treatment based on a logarithmic temperature dependence of the line-shape parameters has also been developed.¹³ In principle, the above considerations apply indifferently to the line-shape analysis of ^1H and ^{13}C or heteroatom NMR spectra.¹⁴ However, whereas ^{13}C dynamic NMR, for example, offers the advantage of generally higher diastereotopy of the exchanging sites and therefore of a better dynamic ability, its use is limited by the low sensitivity of ^{13}C , which is a severe impediment to the investigation of total line-shape variations in the case of dilute samples. Moreover, the possible influence of differences in the relaxation times and in the nuclear Overhauser effects (NOE) of the exchanging nuclei must be taken into account when Fourier transform (FT) NMR spectra in the broadband decoupled mode are studied.

It should be noted that the investigation of dynamic processes is sometimes rendered difficult or impossible by the fact that the chemical shift difference between the exchanging sites, $\Delta\nu$, is very small or accidentally zero. This difficulty can be overcome in certain cases by recourse to lanthanide reagents for increasing the $\Delta\nu$ value.^{15-18,440} For instance, no splitting of the $\text{N}(\text{CH}_3)_2$ ^1H signal of *N,N*-dimethylcarbamate, $(\text{CH}_3)_2\text{NCOOCH}_3$, is observed in CCl_4 at probe temperature. But, through progressive addition of $\text{Eu}(\text{fod})_3$ ($\text{fod} = 1,1,1,2,2,3,3$ -heptafluoro-7,7-dimethyl-4,6-octanedionato) at 300 K, the methyl signal broadens and splits into two peaks that undergo increasing separation accompanied by signal sharpening.¹⁹ A line-shape analysis of these results, obtained at constant temperature, reveals a dependence of the rate constant on the concentration of the lanthanide reagent. Extrapolation to zero concentration gives a value which is expected to be the true rate constant of the rotation process in CCl_4 at 300 K. In fact, as shown by the study of the isomerization process involving the C–N bond of *boc*-Gly- OCH_3 - d_3 (*boc* = *t*-butoxycarbonyl), performed by complete line-shape analyses at four different concentrations of $\text{Eu}(\text{fod})_3$, the observed barrier of rotation $\Delta G^\ddagger_{\text{Z} \rightarrow \text{E}} = 66.8 \text{ kJ mol}^{-1}$ correctly reflects the barrier of the uncomplexed

substrate.²⁰ However, preferential complexation with the shift reagent may introduce variations in the relative amounts of the conformational isomers.²⁰

In another approach it has been shown that optically active lanthanide reagents such as (+)Eu(hfbc)₃ (hfbc = 3-heptafluorobutyryl *d*-camphorato) may be used for separating the signals of enantiomers or of enantiotopic groups, thus enabling enantiomerization rate constants to be determined by line-shape analyses.^{21,22} This method has provided the activation parameters for rotation about the aniline bond of nitrosamines, ArN(CH₂R)NO, in which the substituted N-aryl ring is twisted out of the N—N=O plane.⁴³⁹

In this section we have drawn attention to several sources of error in the derivation of rate constants. However, it should be emphasized that the problems of the control and measurement of temperature are often the most critical factors in the determination of reliable activation parameters whatever method is used for deriving the rate constants. Various techniques, of which the majority are reviewed in reference 2c, have been proposed in order to attempt to solve this problem in different isothermal situations. In addition, the varytemp method, which links temperature variation to an easily controlled time variation, offers an alternative approach.²³

B. Multicoalescence experiments

It has been recognized that combining coalescence experiments which involve several nuclei (¹H, ¹³C, etc.) engaged in a given dynamic process is likely to provide a powerful method for obtaining accurate activation parameters.^{24,25} Similarly, when several NMR spectrometers are available it is interesting to perform coalescence measurements at different nominal frequencies for a given nucleus.²⁶ These procedures result in several advantages; first they limit tedious line-shape measurements and analyses since the determinations may be restricted to the coalescence points. Second, the values of the rate constants at the coalescence temperatures are frequently accessible with good accuracy due to the usual sensitivity of the coalescence region to variations in the life times. In fact, since the ¹H-decoupled ¹³C spectra of NR₂ fragments generally consist of pairs of single, equally intense lines, the multicoalescence method makes full use of the simple familiar equation $k_c = \pi\Delta\nu/\sqrt{2}$, which gives the rate constant at the coalescence point for two exchanging groups characterized by a shift difference, $\Delta\nu$, much larger than the line width. This equation is reputed for readily providing good values of the rate constants. Third, on condition that reliable coalescence parameters are determined, an important improvement in the accuracy of the dynamic results can be attained by access to a wider active temperature range.^{2b}

However, it should be emphasized that in these experiments careful measurement of the coalescence temperature is required since a relatively

small error (± 2 K) may introduce an error of several J mol^{-1} in $\Delta S^\ddagger$. When multinuclear experiments are performed it is therefore necessary to implement accurate methods for calibrating the temperature at different nominal resonance frequencies and eventually for different probes and different spectrometers.^{26,27}

C. Methods which refer to longitudinal relaxation

The investigation of relaxation rates in exchanging systems may, in certain cases, increase significantly the range of the activation barriers accessible by conventional dynamic methods. We shall recall only briefly here that the rates of fast internal rotations, occurring at frequencies of the same order of magnitude as those which characterize the overall molecular reorientations, can be obtained in conventional relaxation experiments. Taking into account internal motions in the expression of the effective correlation times, in terms of the components of the diffusion tensor, an analysis of the experimental results allows small rotational barriers ($< 20 \text{ kJ mol}^{-1}$) to be determined.²⁸ Similarly, information on internal motion can be obtained through measurements of rotating frame spin-lattice relaxation in the presence of an off-resonance radiofrequency irradiation,²⁹ $T_{1\rho}^{\text{off}}$. However, since the rotational barriers around N-X partial double bonds are usually relatively high, these methods are of limited applicability. By contrast, determinations of rotational rate constants, which are of the order of magnitude of the relaxation times, may be achieved in various types of relaxation measurements. These methods are very useful for extending the range of accessible activation parameters and for improving their accuracy.

If we consider the simple case of an exchange between two uncoupled sites, A and X, the magnetization transfer due to exchange can be simply introduced into the Bloch equations for relaxation. Neglecting the cross-relaxation, it is easily shown that, after a given perturbation, the A and X magnetizations $M_{zA}(t)$ and $M_{zX}(t)$ recover according to biexponential laws [Eqs. (1) and (2)].

$$M_{zA}(t) = M_A^\infty + C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t} \quad (1)$$

$$M_{zX}(t) = M_X^\infty + C_1 a e^{-\lambda_1 t} + C_2 b e^{-\lambda_2 t} \quad (2)$$

If M_A^0 , M_X^0 and M_A^∞ , M_X^∞ denote the initial and final magnetizations, respectively, and $\tau_{1A}^{-1} = T_{1A}^{-1} + \tau_A^{-1}$ and $\tau_{1X}^{-1} = T_{1X}^{-1} + \tau_X^{-1}$, then the various coefficients in Eqs. (1) and (2) may be written as follows:

$$\lambda_{1,2} = \frac{1}{2} \{ (\tau_{1A}^{-1} + \tau_{1X}^{-1}) \pm [(\tau_{1A}^{-1} - \tau_{1X}^{-1})^2 + 4\tau_A^{-1}\tau_X^{-1}]^{1/2} \}$$

$$a = -\tau_X(\lambda_1 - \tau_{1A}^{-1}) \quad \text{and} \quad b = -\tau_X(\lambda_2 - \tau_{1A}^{-1})$$

$$C_1 = -C_2 + M_A^0 - M_A^\infty$$

$$C_2 = \tau_X^{-1}(\lambda_1 - \lambda_2)^{-1} [\tau_X(\lambda_1 - \tau_{1A}^{-1})(M_A^0 - M_A^\infty) + (M_X^0 - M_X^\infty)]$$

where τ_A and τ_X are the lifetimes of sites A and X, respectively, and T_{1A} and T_{1X} are the corresponding longitudinal relaxation times.

It appears that if the τ_A , τ_X values are either very large or very small with respect to the relaxation times T_{1A} , T_{1X} then Eqs. (1) and (2) reduce to monoexponential recoveries independent of τ_A , τ_X . Relaxation measurements of the A and X signals are therefore likely to provide access to the exchange parameters only when relaxation and exchange occur with comparable rates.

Different types of experiments which are based on the study of relaxation behaviour can be used for determining the exchange rate constants. These are discussed in the following sections.

1. *The conventional IRFT method*

First it should be noted that if the exchanging sites have equal relaxation times, $T_{1A} = T_{1X} = T_1$, a conventional inversion recovery FT (IRFT) experiment leads to monoexponential behaviour of the relaxation characterized by the time constant T_1 . The lifetimes are not accessible in such conditions. On the other hand, if the intrinsic relaxation times are different the phenomenon is governed by nonexponential equations in which the initial conditions of the IRFT method are introduced. A multiparameter double-exponential analysis of the relaxation curves then allows, in principle, the parameters T_{1A} , T_{1X} , τ_A , and τ_X to be determined. The influence of the exchange phenomenon on the relaxation behaviour of two equally populated sites characterized by the intrinsic relaxation times $T_{1A} = 20$ seconds and $T_{1X} = 10$ seconds is illustrated in Fig. 1. It appears that whereas A and X relax independently with their own relaxation rates T_{1A} and T_{1X} when τ is much higher than T_{1A} , T_{1X} ($\tau = 500$ seconds), the recoveries behave more similarly when $\tau = 15$ seconds. A monoexponential treatment of the results would lead in this case to apparent relaxation times $\tau_{\text{eff}}(\text{A}) = 16.1$ seconds and $\tau_{\text{eff}}(\text{X}) = 11.6$ seconds. A detailed analysis of ^{13}C IRFT experiments has been performed in the case of dimethylformamide,³⁰ which is characterized by methyl relaxation times $T_{1A} = 17.8$ seconds and $T_{1X} = 10.5$ seconds at 25°C. At 56°C, for example, whereas an exponential treatment of the recoveries leads to apparent relaxation times of 18.1 seconds for A and 15.6 seconds for B, the suitable biexponential analysis of the results provides the following values: $T_{1A} = 25.2$ seconds, $T_{1X} = 12.0$ seconds, and $\tau_A = \tau_X = 9$ seconds.

2. *The IRFT method in the presence of selective saturation*

This method is derived from the CW experiments first introduced by Forsen and Hoffman.³¹ In ^{13}C NMR the method consists of applying a nonselective IRFT sequence in which the A signal is observed while the X signal is

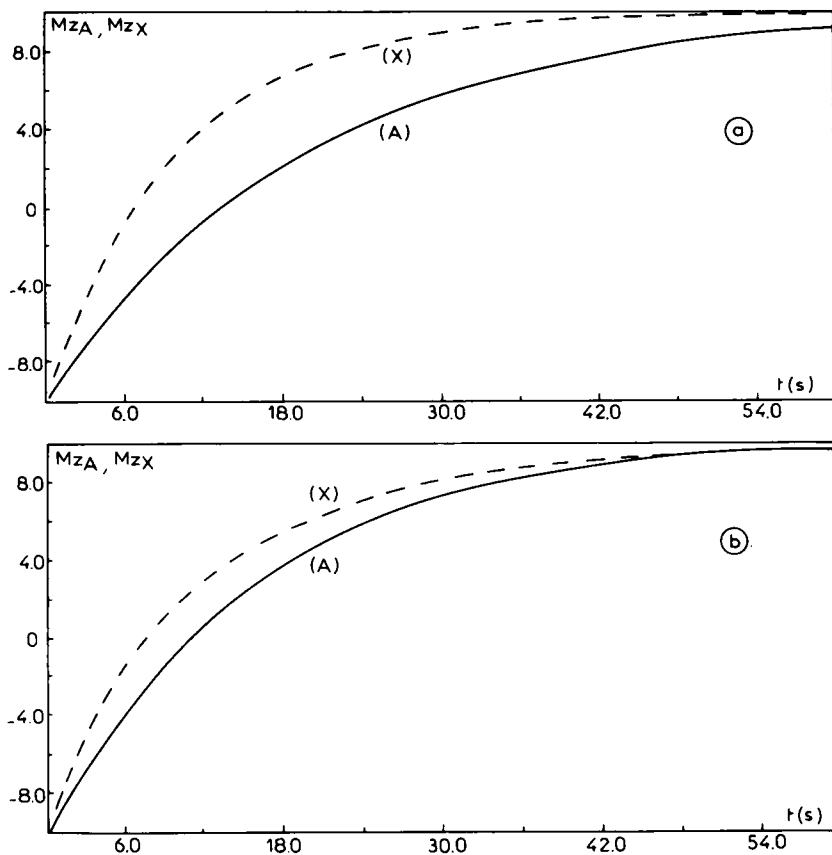


FIG. 1. Influence of exchange on the relaxation recoveries of two equally populated sites A and X characterized by the relaxation times $T_{1A} = 20$ seconds and $T_{1X} = 10$ seconds. The lifetimes in sites A and X are (a) $\tau_A = \tau_X = 500$ seconds, (b) $\tau_A = \tau_X = 15$ seconds.

selectively saturated outside the acquisition period and the protons are simultaneously decoupled.^{2d} Under these conditions the magnetization in site X is cancelled and the A magnetization recovers according to a monoexponential law [Eq. (3)]

$$M_{zA} = M_{zA}^X [1 - 2 \exp(-t/\tau_{1A})] \quad (3)$$

characterized by the rate constant $\tau_{1A}^{-1} = T_{1A}^{-1} + \tau_A^{-1}$. The exchange parameters can then be determined on condition that a complementary relation between T_{1A} and τ_A is obtained in other types of experiments (Section IID). The analysis is the same as that which applies to the IRFT results but the method suffers from a dynamic range, $2M_{zA}^X$, which is smaller since the

equilibrium magnetization of A in the presence of a saturation of X, M_{zA}^X , is decreased with respect to M_A^0 in proportions which depend on the relative values of τ_A and T_{1A} [Eq. (4)]. Relatively low exchange rates are accessible by this technique. Thus, in the case of *N,N*-dimethylformamide in dimethyl sulphoxide, a value of $k = 0.017 \text{ sec}^{-1}$ is measured at 313.7 K whereas line-shape analyses enable values of 9.4 to 210 sec^{-1} to be calculated between 384 and 433 K.³²

3. The selective inversion method

In the case of an exchange between two ^{13}C sites A and X, for example, a selective inversion of the A signal by means of a weak pulse of duration $P_w = \pi/\gamma B_1$ applied in the presence of broadband ^1H decoupling gives rise to nonexponential recoveries of the A and X signals.^{2d,33,34} While the A magnetization recovers from $-M_A^0$ to $+M_A^0$, the magnetization in site X, which starts from $+M_X^0$, goes through a minimum which depends on the relative values of the relaxation and exchange rates, and tends again toward $+M_X^0$ (Fig. 2). A biexponential multiparameter regression analysis of Eqs. (1) and (2) gives the values of T_{1A} , T_{1X} , τ_A , and τ_X . Such selective inversions have been applied, for example, to the determination of the exchange parameters for the isomerization of the dipeptide glycylsarcosine.³³ In these experiments the resonance of the trans methylene protons is inverted; an iterative treatment of the relaxation behaviour observed at 318 and 338 K, for

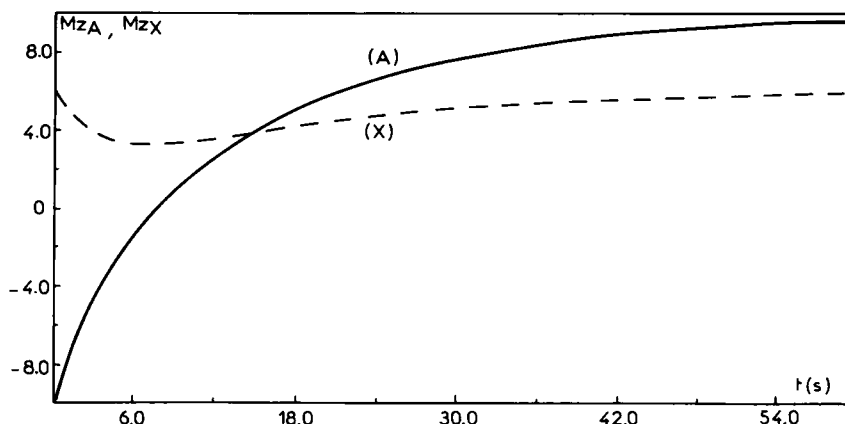


FIG. 2. Selective inversion in the presence of an exchange process for two unequally populated sites A ($p_A = 0.625$) and X ($p_X = 0.375$) characterized by relaxation times $T_{1A} = 20$ seconds, $T_{1X} = 10$ seconds, and lifetimes $\tau_A = 18$ seconds and $\tau_X = 9$ seconds. The A signal has been selectively inverted and both signals are observed.

example, leads, respectively, to $T_1(\text{trans}) = 2.1$ seconds, $T_1(\text{cis}) = 2.0$ seconds, $\tau(\text{trans}) = 5.6$ seconds, and $T_1(\text{trans}) = 2.7$ seconds, $T_1(\text{cis}) = 3.2$ seconds, $\tau(\text{trans}) = 1.1$ seconds.

This method is applicable in ^1H NMR but cross-relaxation effects must then be considered.³⁵

D. Equilibrium saturation transfer experiments

When a sufficiently strong irradiation is selectively applied at the resonance frequency of a given site X, the populations of the energy levels involved in this transition tend to equalize and $M_{zX} = 0$. This saturation may then be transferred to the other sites which exchange with X.³¹ Thus, for a system of two independent sites in which X is saturated, the equilibrium magnetization at site A is given by

$$M_{zA}^X = M_A^0 [\tau_A / (\tau_A + T_{1A})] \quad (4)$$

A saturation transfer factor, S_A^X , may be defined as in Eq. (5).

$$S_A^X = (M_A^0 - M_{zA}^X) / M_A^0 \quad (5)$$

This factor can be used, for example, in conjunction with a relaxation measurement performed in the presence of saturation of X in order to derive the values of the exchange parameters. In ^{13}C $\{^{13}\text{C}\}$ $\{^1\text{H}\}$ experiments, the recourse to an auxiliary frequency synthesizer for providing the homonuclear double irradiation can be avoided by simply introducing a mixing of the ^{13}C radiofrequency with an audio frequency which enables the irradiation offset to be accurately monitored.⁴

In ^1H systems in which cross-relaxation between A and X cannot be neglected³⁵ the equilibrium magnetization is given by

$$M_{zA}^X = \frac{(1 + \eta_A K) R_A}{R_A + k_{AX}} M_A^0 \quad (6)$$

in which η_A is the Overhauser enhancement factor, K the equilibrium constant, and R_A the self-relaxation rate at site A, which is related to the transition probabilities between the energy levels of the system ($R_A = 2W_{1A} + W_2 + W_0$).

As in the case with relaxation methods, measurements of saturation transfers can be used for the determination of kinetic parameters only in a range of lifetimes which are comparable to the relaxation times (about $50 > T_1/\tau > 0.1$). For example, in the case of *N,N*-dimethylnitrosamine the saturation factor of the more shielded methyl carbon X is deduced from the signal intensity of X perturbed by a homonuclear irradiation of methyl A, M_{zX}^A , and from the equilibrium intensity M_X^0 measured while the irradiation frequency is applied at a value far from any carbon signal.^{2c} At 368 K, a value

$S_X^A = 0.55$ is obtained. By combining this result with the value of the apparent relaxation time $\tau_{1X} = 13$ seconds, measured in the experiment described in Section II,C,2, the rate constant $k = 0.042 \text{ sec}^{-1}$ is calculated. Such experiments, which extend the range of the accessible lifetimes between rotational motions toward the slow exchange limit, may be performed in $^1\text{H}^{36}$ or in ^{13}C -NMR spectroscopy either in the CW^{31,37} or in the FT³² mode. The potential of pulsed saturation transfer experiments is well illustrated by the investigation of the solvent exchange and rotation processes which take place in primary amides in aqueous solution at different pH values.³⁸

E. Methods which refer to transverse relaxation times or to rotating frame longitudinal relaxation times

In conventional dynamic NMR, based on the study of line-shape modifications, the lifetimes τ are accessible only in a temperature range where the broadening due to exchange is larger than the effect of field inhomogeneity. By contrast, in a measurement of transverse relaxation, the effects due to exchange can be detected as soon as they exceed those of the intrinsic relaxation rates.

1. Spin-echo experiments

In a spin-echo experiment^{2f,39,40} the echo amplitude depends not only on the transverse relaxation rate but also on the rate constant for the exchange.⁴¹⁻⁴⁵ A study of the decay of the echoes in a Carr-Purcell sequence allows an apparent relaxation rate to be determined which is a function of the pulse interval, t_{ep} . For an exchange between two equally populated sites, a fast pulse repetition gives, at the limit, the natural relaxation time. The investigation of the dependency of the apparent relaxation time as a function of t_{ep} provides values of the lifetimes, which may be situated before or after the coalescence point and extend over a temperature range which is wider than that of the line-shape analysis method. These types of experiments (which are usually performed in the nonselective mode) have been claimed to yield unreliable results. Thus, in the case of the isomerization of *N,N*-dimethylcarbamoyl chloride, the kinetic parameters derived from spin-echo measurements do not agree satisfactorily with the results of line-shape analysis.⁴² In addition to the experimental sources of error inherent in the spin-echo technique,^{42,46,47} the neglect of the influence of scalar relaxation introduced by quadrupolar relaxation of the ^{14}N nucleus in R—N fragments probably results in noticeable discrepancies. Thus, when this effect is considered in the study of rotation around the C—N bond of *N,N*-dimethylcarbamoyl chloride, the results obtained by the spin-echo method compare favourably with those of line-shape analysis.⁴⁸

The spin-echo method combined with FT is of more general use since apparent individual spin-spin relaxation times in multisite exchanging systems may then be measured. For an AX two-site exchange, discarding the initial echoes, simple exponentials with identical time constants are obtained for peaks A and X even if both lifetimes and natural spin-spin relaxation times are different.⁴⁹ The apparent relaxation rate $T_{2\text{exp}}^{-1}$ may then be determined for various values of the pulse interval t_{cp} , and these results can be fitted to the theoretical equation relating $T_{2\text{exp}}^{-1}$ to t_{cp} ^{49,50} in order to obtain the exchange lifetimes. The spin-echo method offers the advantage of providing chemical rate constants without the need for temperature variations. Applied to the investigation of the hindered rotation process in *N,N*-dimethylbenzamide (1.65 *M* CDCl₃), it enables chemical lifetimes to be evaluated at very different temperatures.⁴⁹ Thus, at 318 K (fast exchange) $\tau = 3.0 \times 10^{-3}$ seconds, at 298 K (intermediate situation) $\tau = 1.2 \times 10^{-2}$ seconds, and at 278 K (slow exchange) $\tau = 8.8 \times 10^{-2}$ seconds. These values give an activation energy of 62 kJ mol⁻¹, in satisfactory agreement with other determinations (Table 8).

2. Measurement of spin-lattice relaxation in the rotating frame

It is also possible to derive the dynamic parameters from measurements of the relaxation time in the rotating frame ($T_{1\rho}$).^{28,43b,51-53} For an exchange between two equally populated sites characterized by the lifetime τ , the spin-locking experiment leads to

$$\frac{1}{T_{1\rho}} = \frac{1}{T_1} + (\pi\Delta\nu)^2 \frac{\tau/2}{1 + (\gamma B_1)^2(\tau/2)^2} \quad (7)$$

in which T_1^{-1} corresponds to relaxation processes other than those due to exchange and $\Delta\nu$ is the difference in the resonance frequencies at the two sites. In this type of experiment care must be taken to fulfill the appropriate technical requirements: absence of noise decoupling during the spin-locking period, suitable intensities of the radio-frequency field, etc. This technique enables values of the rate constants to be determined in a range of temperatures significantly higher than the coalescence temperature.⁵³⁻⁵⁵

The method has also been extended to slow exchange conditions. Thus, in the case of two equally populated sites separated by the chemical shift difference $\Delta\nu$ (given in Hz), the rate constant is accessible from the joint investigation of the signal decays, $s = f(t)$, in two types of experiments.⁵⁶ In the first, a spin locking of duration t is normally achieved for both sites immediately after the $\pi/2$ pulse. In a second, modified, experiment, a delay $\tau = (2\Delta\nu)^{-1}$ is introduced between the $\pi/2$ pulse, applied at the resonance frequency of one line and the period t , during which the two magnetizations

are spin locked. In suitable conditions $2k$ is obtained directly from the difference between the time constants of the exponential decays in the two types of experiment.

F. Two-dimensional NMR spectroscopy

The two-dimensional (2D)-exchange methods should be considered powerful tools for studying simple or complex isomerization phenomena.⁵⁷⁻⁵⁹ In the basic 2D-exchange experiments, the exchange process produces a magnetization transfer during a variable mixing time, t_m , introduced into a sequence of three 90° pulses; $\pi/2 - t_1$ (evolution), $\pi/2 - t_m$ (mixing time), and $\pi/2 - t_2$ (detection time). In order to obtain quantitative results it is often necessary to record a series of 2D (ω_1, ω_2) spectra for different values of t_m and this renders the method very time consuming. The "accordion" method⁶⁰ is based on the same sequence but uses a variable mixing time, t_m , which is stepped together with t_1 : $t_1 \cdot t_m = kt_1$. A Fourier transformation with respect to t_1 is at the same time a Fourier transformation with respect to t_m , and ω_1, ω_m axes run in parallel but with scales that differ by the factor k . The accordion spectrum resembles a normal 2D-exchange spectrum characterized by cross-peaks at the intersections of the ω_1 and ω_2 coordinates of the exchanging sites, ω_A and ω_X , for example. However, the line shapes of the diagonal and cross-peaks, which appear in the cross-sections at $\omega_2 = \omega_A$ and $\omega_2 = \omega_X$ and must be measured in units of the ω_m frequency, are characteristic of both the relaxation rates and the exchange rate constants. These parameters can therefore be extracted from an appropriate line-shape analysis of the figure obtained in a single experiment.⁶⁰

The effects of the cross-relaxation and chemical-exchange phenomena intervening simultaneously at several temperatures in the proton 2D spectra of *N,N*-dimethylformamide have been analysed and the technique appears to be promising for the study of cross-relaxation in macromolecules.⁶¹

G. Equilibration methods

In some cases a given rotational isomer can be obtained in a pure or enriched form. The isomerization rate constants are then accessible through the measurement of the time dependency of the concentrations of the equilibrating isomers.^{62,63} For example, it is possible to isolate the *Z* isomer of *N*-benzyl-*N*,2,4,6-tetramethylbenzamide, and the ^1H spectra, recorded after dissolution of the crystals in a 1:1 mixture of 1-chloronaphthalene and benzotrichloride at 306 K, enable the decrease of the signals associated with the *Z* isomer and the increase of the signals corresponding to the *E* form to be observed within a period of about 200 minutes.⁶² From the rate equation of the concentration variations, the rate constants $k_{Z \rightarrow E} = 2.6 \times 10^4 \text{ sec}^{-1}$ and

$k_{E \rightarrow Z} = 6.5 \times 10^4 \text{ sec}^{-1}$ can be derived. In favourable cases, such as the isomerization processes involving the N–N bond of nitrosamines,⁶⁴ the rate constants can be obtained in equilibration measurements at a low temperature whereas line-shape analyses of the same system at equilibrium provide values of the rate constant at higher temperatures^{65–71} (Table 30). The time for the equilibration techniques can be reduced by using the varytemp method developed for the study of nonisothermal kinetics.^{23,441} In practice, thermal equilibration sometimes offers a very helpful tool not only for improving the reliability of activation parameters obtained in the active temperature range of exchange phenomena,^{72,73} but also for studying slow interconversions, in aqueous media, for example. Thus a value $\Delta G^\ddagger_{\text{cis} \rightarrow \text{trans}} = 92.8 \text{ kJ mol}^{-1}$ is obtained for the isomerization of L-Pro–L-4Hyp (Hyp = hydroxyproline) in D₂O by dissolving the pure cis dipeptide at 288 K and following the evolution of the ¹³C signals.⁷⁴

III. DYNAMIC NMR RESULTS

A large number of dynamic parameters have been determined since the early days of NMR, and the problem of the isomerization about N–X bonds has already been considered in several reviews.^{1,75–79,442,443} A critical survey of the relevant literature in this field was provided by Sutherland¹ in Volume 4 of this series in 1971. Consequently, apart from the typical cases of *N,N*-dimethylformamide and –acetamide, we shall restrict ourselves, in a tabular format, to results obtained since 1970. Although the bibliography is probably not completely exhaustive we think that Tables 1–40 (at the end of the text, following Section IV) provide a rather comprehensive view of the behaviour of the isomerization parameters in different classes of N–X-containing compounds.

Since the energy barrier is often considered as being solvent dependent, the nature and concentration of the solvent are indicated whenever possible. The value, in hertz, of the chemical shift difference ($\Delta\nu$) between the interconverting sites, which controls the temperature T_c at which the coalescence is observed, is given in each table. However, this value, which either corresponds to a temperature well below coalescence or sometimes is the result of an extrapolation to T_c , provides only a rough indication of the diastereotopy, since it may be, to a variable extent, temperature dependent.

Information on the technical conditions of the experiment and methods used for analysing the results are given in the tables as footnotes, which are defined in Table 1. However, it should be noted that criteria such as the year of publication, the frequency of the spectrometer, or even the type of analysis performed sometimes offer insufficient information for interpreting the reliability of the results.

IV. INTERPRETATION OF DYNAMIC NMR RESULTS

A. Solvent effects on the dynamic parameters

Before attempting an explanation of the variations in activation parameters in terms of structural effects of the substituents, the importance of solvent effects must be appreciated. Some examples showing the influence of the nature and concentration of the solvent can be found in the tables following this section. However, when the results have been obtained by different authors they may lack the guarantee of accuracy necessary for a detailed interpretation. Whereas it is sometimes, more or less explicitly, considered that the solvent plays a minor role, relatively large variations of the free energy of activation, $\Delta G^\ddagger$, have been measured in a number of cases and several specific investigations of the solvent effects have been performed.^{13,454} In *N,N*-dimethylacetamide, for example, the value of $\Delta G^\ddagger$, which is 65.5 kJ mol⁻¹ in the gas phase¹²¹ and 75.2 kJ mol⁻¹ in acetone, reaches 80.7 kJ mol⁻¹ in water and in formamide.¹¹⁵ Similarly, in *N*-methyl-*N*-benzyl-*o*-chlorobenzamide, $\Delta G^\ddagger$ increases from about 78.2 to 87.6 kJ mol⁻¹ when phenol (0 to 2.8 *M*) is added to a 0.6 *M* solution of amide in *o*-dichlorobenzene.⁷² As regards the variations in $\Delta G^\ddagger$ accompanying the change from gas state to liquid state, the effect of the internal pressure of the solvent should be considered.^{121,387}

More generally, such variations are discussed in terms of various properties of the solvent.³⁸⁸ In amides and thioamides, for example, relationships concerning a limited number of solvents are observed between $\Delta G^\ddagger$ and a function of the dielectric constant.^{155,214} An increase in solvent polarity leads to an increase in the stability of the more polar ground state relative to the less polar excited state of benzamides, for example, and this results in an increase in the rotational barrier.¹⁵⁵ Similarly, hydrogen bonding involving the carbonyl oxygen stabilizes the ground state and enhances the barrier height. In this respect a satisfactory correlation is observed for *N,N*-dimethylbenzamide between $\Delta G^\ddagger_{298}$ and the E_T solvent parameter,³⁸⁹ which represents both polarity and hydrogen bond properties of the solvent.^{390,391} However, more complex effects are exhibited by dimethylaminonitroethylene, for example, and the lack of correlation with E_T or a function of the dielectric constant may indicate a particular behaviour of the given solvents.²⁴²

Due to the difficulty of determining sufficiently accurate values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$, discussion of solvent effects is usually restricted to $\Delta G^\ddagger$, and $\Delta S^\ddagger$ is frequently considered to be close to zero for torsional barriers in tertiary amides (even when protic solvents are used). This behaviour is attributed to the fact that the hydrogen bonds between the amide carbonyl and the solvent protons are not broken in the internal rotation. By contrast the large value of $\Delta S^\ddagger$ (37.6 kJ mol⁻¹) found for acetamide in dimethylformamide has been

attributed to the breaking of hydrogen bonds between the NH group of the solute and the solvent carbonyl group in the rotational process.¹⁷⁵

It should also be noted that a quantum chemical approach to the electrostatic interactions involving the amide structure is expected to provide a deeper insight into the mechanisms of the solvation effects.³⁹²

B. Theoretical interpretations

1. Quantum mechanical treatments

A number of attempts have been made in order to predict the magnitude of rotational barriers and to explain their variation as a function of substituents, solvents, etc., on a theoretical basis. Most of these investigations consist of calculating, in the framework of a more or less elaborate theory, the energy difference between the molecular ground state, which is frequently planar, and the rotational transition state, which usually involves a perpendicular geometry. Thus, in order to compare the effects of substituents in various conjugated systems, correlations have been tested with parameters produced by simple Hückel molecular orbital approaches. In this respect, good correlations are observed between the activation energy for rotation around the C–N bond of para-substituted benzamides and cinnamamides and, ΔE_π , the difference between the π -electron energies of an all-planar ground state and of the transition state, both characterized by the same molecular parameters but with a vanishing resonance integral for the C–N bond in the transition state.¹⁵⁵ Similarly, the activation energies are satisfactorily correlated with the π bond order, p_{C-N} , in these series^{155,241} and in other structures such as anilines.^{257,261}

In principle an improvement may be expected when all-valence electron methods such as EHT,^{115,393–396} CNDO,^{394–398} MNDO,⁴⁸⁰ INDO,^{246,256,399,400} or PCILO, the perturbational analogue of CNDO,^{194,270,401} are considered. Thus the EHT procedure has been claimed to be well suited for rationalizing the preference for a trans geometry of the amide group in peptides and predicting the rotational barriers.³⁹⁶ As far as the problem of the syn–anti isomerization of imines ($\text{CH}_2=\text{N}-\text{X}$) is concerned, the EHT calculations have been considered to rationalize the influence of the nitrogen substituent on the basis of a lateral shift mechanism.⁴⁰²

The CNDO/2 formalism gives satisfactory results in the calculations of rotational parameters in many amides,^{394–396,403–405} in dithiocarbamate esters,⁴⁰⁶ in dimethylaminooxa- and -thiadiazoles,⁴⁰⁷ and in guanidine and related compounds,^{283,291,408} such as *N*-methylcreatine.³¹⁵ This method, applied to the determination of the effect of heteroatoms on barriers to syn–anti isomerization about an imino $\text{C}=\text{N}$ double bond, via both inversion

and torsion,^{308,408} has led to a preference for a torsional contribution to the transition state in $(\text{NH}_2)_2\text{C}=\text{NH}$.⁴⁰⁸ By contrast, CNDO/2 calculations suggest that an out of plane rotational mechanism is unlikely for the isomerization of the oxime anion $(\text{CH}_3)_2\text{C}=\text{NO}^-$ ⁹⁵ and a lateral shift mechanism is also favoured for the imine structure $\text{CH}_2=\text{NH}$.⁴⁰⁸

Molecular orbital calculations in the INDO approximation predict a barrier of 62.7 kJ mol^{-1} for the rotation of the amino group in 2-aminoacetophenone. Considering the hypotheses made on the conformation of the carbonyl group, the neglect of solvent effects, etc., this value agrees satisfactorily with the experimental one (44.3 kJ mol^{-1}).²⁵⁶ However, the INDO (and CNDO/2) calculations overestimate the CN rotational barriers of nitrones by a factor of about two.⁴⁰⁹ For the PCILO method,⁴⁰¹ energy computations confirm conformational hypotheses concerning dialkylaminopyrimidines.²⁷⁰

It should also be noted that perturbation theory has been employed in the CNDO formalism in order to calculate the energy interaction between a filled donor orbital and the lowest empty acceptor orbital of *N,N*-dimethylbenzamide and its thio and seleno analogues.^{228,410} Similarly, a perturbational molecular orbital approach has enabled a rationalization of the observed variations of the rotational barriers in thiazoylcarbamides, thiocarbamides and their furyl and thienyl analogues (Tables 8 and 17),¹⁷¹ and in sulphenamides.²⁷⁴

The more recent development of complete *ab initio* methods has led to an expectation of a higher degree of reliability in the calculation of molecular parameters. Thus the total energy of a molecule can be explicitly computed, and *ab initio* determinations of the rotation barriers in various amide, imine, and guanidine derivatives have been achieved.^{117,254,284,411–419} The correct orders of magnitude are usually deduced from these calculations and the simple π -electron origin of the barrier in amide structures is confirmed.⁴¹³ Similarly the conformational preference of formamide for a planar *E,Z* conformation in the vapour state is corroborated with a barrier height of 52 kJ mol^{-1} calculated with the STO-3G basis for the conversion *E,Z* $\rightarrow$ *E,E*.⁴²⁰ This value is very close to the experimental value, 52.7 kJ mol^{-1} , measured in acetone.¹⁸⁷ From an *ab initio* SCF treatment further insight is also gained into the problem of "y aromaticity" in guanidines^{416,421} and interpretations of the origin of the P—N isomerization barriers in aminophosphines have been attempted. Whereas calculations concerning $\text{H}_2\text{N}-\text{PH}_2$ indicate that the nitrogen atom adopts a trigonal planar geometry, regardless of the presence or absence of *d*-type functions in the basis set,^{422,423} it is concluded that the topomerization of aminophosphines is best described as a hybrid process that involves both N—P rotation and pyramidal inversion at nitrogen.⁴⁵⁵

It should be noted that calculation of the total energies for both the planar and perpendicular structures of the rotating fragment requires previous

knowledge of bond lengths and bond angles. These parameters are frequently selected on the basis of experimental results but theoretical optimisations of the geometry are also carried out in certain cases.^{413,415}

2. Empirical methods

It has been claimed that calculations of the conformational energies by means of empirical methods, based on a summation of physically relevant contributions, may be as successful as those founded on quantum mechanical methods. Thus good agreement is obtained for diformamide and *N*-vinylformamide⁴¹⁵ for the results of an *ab initio* treatment and those deduced from the partition of energy method (PEM), which considers a summation of electrostatic van der Waals and torsional terms.⁴²⁴ Similarly, when the energetics of rotation about the N-C_α bond of peptides is considered, empirical force field calculations of the rotational potential surface are in reasonable agreement with the experimental results and with those of *ab initio* quantum mechanical computations.⁴²⁵

C. Correlations with substituent parameters

In order to identify and quantify the effects of substituents in typical series of conjugated compounds containing a C—N fragment, correlations are frequently attempted with various parameters liable to characterize, more or less satisfactorily, inductive and resonance electronic effects or steric requirements.

A frequently discussed correlation uses the Hammett-type substituent parameters. In anilines, for example (Table 26), $\Delta G^\ddagger$ is found to follow a simple relationship with the Hammett constant σ ,^{257,259}

$$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = 28.9 + 21.4 \sigma \quad (8)$$

Para-substituted benzamides^{163,426} or enamines¹³⁴ are particularly good models for investigating the electronic contributions of substituents.^{154,156} Thus when nine primary substituents on benzamides are considered, a dual substituent parameter relationship applies.¹⁶³

$$\Delta\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = -5.44\sigma_1 - 9.03\sigma_{R^+} + 1.28 \quad (R = 0.958) \quad (9)$$

Where σ_1 and σ_{R^+} are the inductive and resonance Taft constants⁴²⁷ and $\Delta\Delta G^\ddagger$ refers to the value for *N,N*-dimethylbenzamide. This analysis enables the substituent effects of the bromomethyl groups to be compared. In the ortho-substituted compounds a third parameter, the van der Waals radius of the substituent, has been introduced in order to characterize the steric effect and it is shown that $\Delta\Delta G^\ddagger$ is dominated by the steric contribution and that the inductive effect is larger than the resonance effect.¹⁶⁰

Linear correlations of $\Delta G^\ddagger$ with the constants, σ , σ^+ ,⁴²⁸ or σ^n ⁴²⁹ are observed for *trans*-*N,N*-dimethylcinnamamides $[(\text{CH}_3)_2\text{NCOCH}=\text{CH}-\text{C}_6\text{H}_4\text{X}]$,¹⁵⁶ as follows.

$$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = 67.1 + 3.55\sigma \quad (R = 0.953) \quad (10)$$

$$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = 67.0 + 3.84\sigma^n \quad (R = 0.952) \quad (11)$$

$$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = 67.6 + 2.51\sigma^+ \quad (R = 0.902) \quad (12)$$

The fact that, contrary to benzamides, the correlation for the dimethylcinnamamides is better with σ and σ^n than with σ^+ indicates a lesser contribution of conjugation in the transmittance of the polar effect for cinnamamides. The values of the slopes, ρ , also show that the sensitivity of the barrier toward substituent effects is smaller for cinnamamides than for benzamides by a factor of two despite the fact that the deviation from planarity is greater in the latter. Similarly, in thiobenzoylpiperidines and cinnamoylthiopiperidines, correlations [Eqs. (13) and (14), respectively] with the Hammett constant σ are found²⁴¹ (Table 22).

$$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = 68.34 + 9.44\sigma \quad (R = 0.903) \quad (13)$$

$$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = 65.19 + 2.92\sigma \quad (R = 0.970) \quad (14)$$

The same trends of sensitivity to electronic effects as in the analogous amide structures are thought to be operative.

Linear multiple correlations of $\Delta G^\ddagger$ with several types of substituent parameters can be obtained for 14-alkyl- and halo-substituted *N,N*-dimethylacetamides.¹³³ The inductive and resonance effects are represented by the Taft constants σ_1 and σ_R and the steric effects by Charton's ν parameters,⁴³⁰ the Taft E_s constants, or the van der Waals radii, calculated for different conformations of the substituents. For the nine derivatives of the halogen series a combination of σ_1 and ν is sufficient to account for the results ($R = 0.993$). When a larger variety of substituents,²² is considered a direct resonance interaction intervenes for the substituents that contain unsaturation or lone pairs and a correlation with σ_1 , ν , and the resonance parameter σ_{R-} ⁴²⁷ is found ($R = 0.903$) [Eq. (15)].

$$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = 8.255\sigma_1 - 19.48\nu + 30.10\sigma_{R-} + 79.0 \quad (15)$$

The effects of substituents on the nitrogen atom of amides are also conveniently described by multiple regressions with steric, inductive, and resonance parameters.⁴³¹ With 12 acetamide groups the significance of the correlation is maximized by using ν as the steric parameter and σ^* as the inductive parameter⁴³² [Eq. (16)].

$$\Delta G^\ddagger \text{ (kJ mol}^{-1}\text{)} = -13.3\nu + 5.77\sigma^* + 0.25\sigma_R + 90.4 \quad (R = 0.941) \quad (16)$$

As in the case of substitution on the carbonyl group, the steric effect strongly affects the rotational barrier. As far as steric effects are concerned it should be noted that in certain classes of sterically hindered compounds the ground state conformation is no longer the usual planar, or nearly planar, structure but is built from perpendicular moieties. This explains the opposite behaviour of the activation parameters as a function of steric parameters. Thus, whereas increasing steric interactions destabilize a nearly planar ground state and decrease the rotational barrier,¹²² this barrier is enhanced by larger substituents when the perpendicular ground state is preferred since the energy of the coplanar transition state is then increased.

In aromatic pentamethylguanidinium iodides the barriers are linearly correlated with the Hammett constants of parasubstituents in aryl groups, for the C—N bond both β and γ to the aryl ring.²⁷⁴ From a related point of view the relationship between barriers of aminophosphines and lone-pair ionization potentials, deduced from photoelectron spectra is discussed in order to clarify the origins of the barriers.⁴³³

D. Correlations with NMR parameters

In order to rationalize further the behaviour of the rotational barriers, their variations are sometimes compared with those of other parameters obtained from NMR measurements. In this respect it is observed that the barrier heights in thioamides (20 compounds) and in the corresponding amides are well correlated¹⁶⁷ [Eq. (17)].

$$\Delta G^\ddagger \text{ (thioamides)} = 4.72 + 1.11\Delta G^\ddagger \text{ (amides)} \quad (R = 0.97) \quad (17)$$

Due probably to a common dependence on the positive charge carried by the nitrogen atom, linear correlations between the free energies of activation and the $^1J(\text{C—H})$ couplings of the N-methyl group are observed in *N,N*-dimethylaminopyrimidines.²⁷²

More generally, correlations between barrier heights and various chemical shift parameters have also been investigated. In aromatic compounds, such as para-substituted *N,N*-dimethylbenzamides, in which carbon probes relatively remote from the site of substitution can be selected, correlations between $\Delta G^\ddagger$ and $\delta^{13}\text{C}$ are exhibited by the carbon atom para to the substituent.⁴³⁴ Although poorer, a correlation also holds for the carbonyl carbon in this series. However, when changes in the substituent linked directly to the C=O group of amides are considered, the electronic modifications transmitted through the carbonyl group introduce complex variations of the chemical shift. Then $\Delta G^\ddagger$ and $\delta^{13}\text{C}=\text{O}$ are usually uncorrelated or correlated only loosely.

By contrast, larger variations may be exhibited by the ^{15}N chemical shift in the >N—C= fragment and good correlations have been observed, for

constant substituents at the nitrogen, in certain series of compounds such as amides,^{435,436} enamines and enaminones,⁴³⁷ anilines, aminopyridines,⁴³⁸ and compounds containing the N—N=X fragment.³⁴² The investigation of such correlations enables the extent of delocalization of the nitrogen lone pair to be better appreciated. In addition, a lack of correlation may indicate the particular behaviour either of the ¹⁵N chemical shift or of the rotational process. Thus in the case of guanidinium ions, anomalies are observed which are explained by the existence of a propeller-like ground state associated with strong steric effects in the rotational transition state.²⁷³ In such structures, the variations in the barrier heights no longer reflect the variations in the extent of electron delocalization. By contrast, the fact that OR and SR substituents behave very differently with respect to $\Delta G^\ddagger$ and $\delta^{15}\text{N}$ may be attributed to the influence of large differences in the electronic excitation energies on the nitrogen nuclear shielding. Although no general correlation can be expected to apply, the joint consideration of the energy barriers and of the ¹⁵N chemical shifts in appropriate series of compounds may therefore be the source of valuable information on the problem of the delocalization of the nitrogen lone pair in conjugated systems.^{197,273,342,435,437,541}

TABLES

See Section III for a discussion of results presented in Tables 1–40. Typical results for isomerization about N—X bonds, given in the tables, are presented as follows:

Table number	General formula	
1	(CH ₃) ₂ N—COH	
2	(CH ₃) ₂ N—COCH ₃	
3	(CH ₃) ₂ N—COR	(R = hydrocarbon residue)
4	(CH ₃) ₂ N—COAR	(A = O, S)
5	(CH ₃) ₂ N—COX	
6	(CH ₃) ₂ N—COR	R = >C=C< , $\text{—C}\equiv\text{C—}$
7	(CH ₃) ₂ N—CO—C ₆ H ₄ X	
8	(CH ₃) ₂ N—COAr	
9	H ₂ N—COR	
10	R ₂ N—COR'	
11	RNHCOR'	
12	R ¹ R ² NCOR ³	
13	R ¹ R ² N—CONR ³ R ⁴	
14	 N—COR	

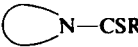
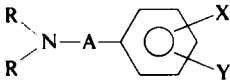
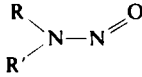
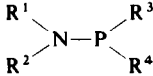
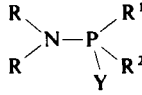
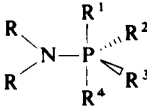
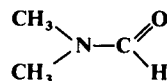
Table number	General formula	
15	$(\text{CH}_3)_2\text{N}-\text{CSR}$	
16	$(\text{CH}_3)_2\text{N}-\text{CSAR}$	$\text{A} = \text{O}, \text{S}$
17	$(\text{CH}_3)_2\text{N}-\text{CSAr}$	
18	$\text{R}_2\text{N}-\text{CAR}'$	$\text{A} = \text{S}, \text{Se}, \text{Te}$
19	$\text{R}_2\text{N}-\text{CSNR}'\text{R}''$	
20	$\text{RNHCSNR}'\text{R}''$	
21	$\text{R}^1\text{R}^2\text{N}-\text{CSR}^3$	
22	 $\text{N}-\text{CSR}$	
23	$(\text{CH}_3)_2\text{N}-\text{CR}^1=\text{CR}^2\text{R}^3$	
24	$\text{R}^1\text{R}^2\text{N}-\text{CH}=\text{CR}^3\text{R}^4$	
25	$\text{R}_2\text{N}-\text{CR}^1=\text{NR}^2$	
26	$\text{>N}-\text{Ar}$	
27	$(\text{CH}_3)_2\text{N}-\text{C}^+\text{XY}, \text{B}^-$	
28	Miscellaneous examples of isomerization processes involving $\text{>C}-\text{N}'$ and $\text{>C}-\text{N}''$ bonds	
29	$\text{R}_2\text{C}=\text{NR}'$	
30	$\text{R}^1\text{R}^2\text{C}=\text{NR}^3$	
31	Miscellaneous examples of isomerization processes involving $\text{>C}=\text{N}$ and $\text{>C}^+-\text{N}$ bonds	
32	Miscellaneous examples of isomerization processes involving $\text{>N}-\text{C}$ bonds	
33	 $(\text{A} = \text{S}, \text{Se})$	
34		
35	$\text{R}^1\text{R}^2\text{N}-\text{N}=\text{CR}^3\text{R}^4$	
36	Miscellaneous examples of isomerization processes involving $\text{>N}-\text{N}''$, $\text{>N}-\text{N}'$, and $\text{>N}-\text{S}$ bonds	
37		
38	 and 	
39	Miscellaneous examples of isomerization processes involving $\text{>N}-\text{P}$, $\text{>N}-\text{P}^+$, $\text{>N}-\text{P}''$, and $\text{>N}-\text{P}'''$ bonds	
40	Miscellaneous examples of isomerization processes involving N-X bonds ($\text{X} = \text{Si}, \text{B}, \text{Pd}, \text{As}, \text{O}$)	

TABLE 1*



Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log A	Reference
Neat		60 ^f	8.1	386				117.9	17.2	105
		100 ^f	16	389	90.7 ^d			92.0	13	106
		60 ^f	10.1	395		99.4	28	102.4		107
		17.7 ^f	3.2	372	92 ^c			29.3		3
		60 ^f	9	391	86.9 ^c			96.1		109
		60 ^f	9.4	422	87.8 ^d			76.5	10.8	110
		56.4 ^f	8.7	394.5				66.5		111
		60 ^a	9.8	392				85.7	12.7	112
		60 ^f	8	386	87.8 ^e		46.0	108.7	15	113
		60 ^a	9.4	392	87.9 ^c	84.4	-7.1	85.7	12.7	114
		60 ^a	9.4	392	87.4 ^d	85.7	-5.9	89		115
		220 ^a	36.6	413.5	87.2 ^c	87.3	0			26
		60 ^a	10.4					40.1	6.5	116
		60 ^a				86.9	0			47
HMDs	0.06 M	56.4 ^f	2.9	≈ 383				39.3		111
CHCl ₂ CHCl ₂	0.6 M	60 ^f	8.0	395	87.8 ^e		46.0	108.7	15	113
CHCl ₂ CHCl ₂	0.025 M	60 ^f	4.1	388	92.0 ^e		-29.3	83.6	12	113
CHCl ₂ CHCl ₂		100 ^a	11.3	400	88.2 ^e	84.0	-10	87.4	12.8	118
CHCl ₂ CHCl ₂	5 mol%	60 ^f	5	387	87.8 ^c					15
CHCl ₂ CHCl ₂	4 mol%	60 ^f	5.6	388		27.2	-226	25.9	4.6	108
CHCl ₂ CHCl ₂ + Eu(fod) ₃	5 mol%	60 ^f ($\rho = 0.1$)	14.0	404.5	88.5 ^c					15
CHCl ₂ CHCl ₂ + Eu(fod) ₃	5 mol%	60 ^f ($\rho = 0.6$)	76.0	440.5	90.4 ^c					15
C ₂ HCl ₅	0.2 M	60 ^f	5.4	386.4	87.8 ^e		25.1	100.3	14	113
C ₄ Cl ₆		60		378	85.3 ^c					119
	0.6 M	60 ^a	20.9	401	86.1 ^c					62
(CD ₃) ₂ CO	0.09 M	56.4 ^f	8.2					70.2		111
CFCl ₃	0.1 M	56.4 ^f	6.4	390				47.2		111
CH ₂ OHCH ₂ OH	0.2 M	60 ^f	8.3	405	87.8 ^e		54.3	112.9	16	113
C ₆ H ₁₁ OH	0.2 M	60 ^f	16	394.9	83.6 ^e		46.0	104.5	16	113
Cyclohexanone	0.2 M	60 ^f	15	394.3	87.8 ^e		33.4	104.5	15	113

TABLE 1 (cont.)

Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log A	Reference
Cyclohexylamine	0.2 M	60 ^f	16	389.1	87.8 ^a		33.4	104.5	16	113
H ₂ NCHO	0.2 M	60 ^f	16	406.6	92.0 ^a		46.0	112.9	16	113
Decalin	10 mol%	60 ^a	4.9	373	84.9 ^d	81.9	-10.0	85.3		115
C ₂ Cl ₄	10 mol%	60 ^a	6.2	382	86.5 ^d	86.9	1.7	90.3		115
H ₂ O + Be ²⁺	30%, 1/20	60 ^a		397				151.7	21.3	117
H ₂ SO ₄	0.4 M	60 ^a	6.7	403				53.1	8	116
CF ₃ COOH + BF ₃	0.3 M	60 ^f	8.2	372	90.3 ^d			108.7	16	106
CHCl ₂ CHCl ₂	4 mol%	60 ^f	7.1	408		49.3	-230	60.6	9.1	108
(CH ₃) ₂ NCDO neat		60 ^a	9	397.5	91.1 ^d		26.3	101.6	14.6	120
		60 ^f	8	398.5	96.1 ^d			114.5	16	106
		40 ^a	7			90.3	4			47

* It should be noted that the enthalpies ($\Delta H^\ddagger$) and entropies ($\Delta S^\ddagger$) of activation undergo well-correlated variations. This enthalpy-entropy compensation effect mainly illustrates the problems of accuracy encountered in dynamic measurements. See also references 444, 520 (dimethylformamide), and 535: a gas-phase value of the free activation energy is determined (81.1 kJ mol⁻¹), which is about 6 kJ mol⁻¹ lower than the values obtained for the neat liquid; $\Delta H^\ddagger = 82.3 (\pm 1.2)$ kJ mol⁻¹ and $\Delta S^\ddagger = 4.2 (\pm 3.3)$ J. mol⁻¹ K⁻¹.

^a Total line-shape analysis (see Section II,B).

^b Formula at coalescence (see Section II,B).

^c $\Delta G^\ddagger$ is determined at the coalescence temperature.

^d At 298 K.

^e At 400 K.

^f One-parameter methods (see Section II,A).

^g Multicoalescence experiments (see Section II,B).

^h Relaxation and magnetization transfer experiments (see Sections II,C and II,D).

ⁱ At 373 K.

^j At 450 K.

^k Equilibration experiments (see Section II,G).

^l Spin-echo experiments (see Section II,E).

^m At 290 K.

ⁿ At about 300 K.

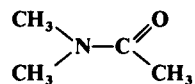
^o At 345 K.

^p The first value is for CH₃ trans to CS.

^q 4×10^{-4} mol in 0.17 g phenol, 0.45 g CH₃NO₂.

^r See also reference 80.

^s For signal assignments in tertiary amides, see references 81 and 82.

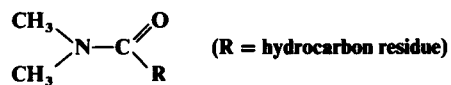
TABLE 2^a

Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger_T$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log A	Reference
Gas		360 ^a	17	305	65.4 ^d					121
Neat		60 ^f				78.6	6.7	81.5		107
		100 ^f				79.4	12.1	82.3		107
		100 ^a			75.7	79.4	12.1	82.3	13.9	122
		60 ^a	10.7	342	75.7 ^d	76.5	2.9	79.4		115
		60 ^a			77.7 ^d	83.6	19.6	92.2	14.3	123
		17.7	4	325	79.4 ^c			50	8.5	3
		60 ^f	10.6	360	72.7 ^d			48.5	8.4	124
		60 ^f	10.1	346	75.2 ^e		46	96.1	16	113
		220 ^a	40.5	360	75.2 ^c	75.2	0			26
		60 ^f	10.1	343				84.4	16.1	105
C ₂ HCl ₃	0.2	60 ^f	6.3	309.4	66.9 ^e		25.1	79.4	16	113
CCl ₄	15 mol%	100 ^a		339	72.4 ^d	68.0	-15	70.4		125
	15% v/v	60 ^a	10	331	71.1	66.9	-8.8	71.1		126
CHCl ₂ CHCl ₂	0.2	60 ^f	5.8	340.1	75.2 ^e		33.4	92.0	15	113
		25.2(¹³ C) ^b	77.1	376	76.5 ^c					127
		60 ^b	5	340	76.8 ^c					15
CHCl ₂ CHCl ₂ + Pr(fod) ₃	27.5 mol%	60 ^b ($\rho = 0.512$)	146	361	80.0 ^c					15
C ₄ Cl ₆		60		323	71.5 ^c					119
<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μ l	60 ^a		≥ 318	77.3 ^c					128
C ₆ H ₁₂	5% v/v	60 ^b		319	71.1 ^d					115
(CH ₃) ₂ CO	10 mol%	60 ^a	10.5	339	75.2 ^d	79.4	13.0	82.0		115
CH ₂ OHCH ₂ OH	0.2	60 ^f	8.9	363.2	79.4 ^e		8.4	87.8	14	113
Cyclohexanol	0.2	60 ^f	8.1	348.1	79.4 ^e		12.5	87.8	14	113
(CD ₃) ₂ SO	9.5 mol%	60 ^f	9.7	343	73.8 ^c	84.9	25.5	87.8		107

TABLE 2 (cont.)

Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger_T$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i>	Reference
(CD ₃) ₂ SO	9.5 mol%	100 ^f				88.6	32.6	91.5		107
	6.2 <i>M</i>	25.1(¹³ C) ^a	127			85.2	-6.2			32
D ₂ O	10 mol%	60 ^a	9.6	364	80.7 ^d	79.8	-3.3	82.8		115
H ₂ NCHO	0.6	60 ^f	9.5	350.4	79.4 ^e	79.8	-8.4	79.4	13	113
SbCl ₅										
CHCl ₂ CHCl ₂	0.4/0.8 <i>M</i>				> 87.8 ^d					52
					(CH ₃) ₂ N—CO—CD ₃					
Neat		60	10		76.1 ^d	79.4	11.3	81.9	13.8	123
Isooctane	2.6 mol%	60 ^a			72.3 ^d		2.1	75.2	13.3	129
CCl ₄	1.7 mol%	60 ^a			72.7 ^d		4.6	76.5	13.5	129
(CD ₃) ₂ SO	9.5 mol%	60 ^a	9.4		77.3 ^d	82.3	17.1	84.9	14.1	130
		60 ^a	9.5		77.7 ^d	83.6	19.6	86.1	14.3	123
		100 ^f				88.6	32.6	91.5		107
H ₂ NCHO	9.8 mol%	60 ^a			81.1 ^d		18.4	89.0	14.2	124
	10 mol%	60 ^f						103.2	16.4	131
D ₂ O	1.04 <i>M</i>	60 ^a		366	80.7	84.8	11.3	87.8	13.9	132
AgNO ₃										
D ₂ O	1/4.4 <i>M</i>	60 ^a		337	74.8	76.9	5.8	79.4	13.6	132

^a For explanations to footnotes see Table 1. An enthalpy-entropy compensation effect is also apparent from these results. See also references 444, 460, 461, and 555.

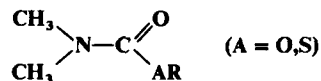
TABLE 3^a

R (s)	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (kJ mol ⁻¹)	E_a (kJ mol ⁻¹)	log A	Reference
CH ₂ CH ₃	Neat		60		327	71.1 ^c		33.4	87.8	15	113
	Neat		60 ^a	9.1	326	71.9 ^d	66.9	-17.1	69.4		115
	Neat		100 ^a			71.9	76.1	13.0	79.0	13.9	122
	Neat		220 ^a	38.3	342.3	71.5 ^c	71.6	0			26
	CCl ₄	10%	60 ^a		325.4	71.9 ^c	68.1	-12.5	70.6		133
	CHCl ₂ CHCl ₂		25.2(¹³ C) ^b	45.6	350	72.7 ^c					127
	CHCl ₂ CHCl ₂		100 ^b	8.7	330	72.7 ^c					127
	CHCl ₂ CHCl ₂	5 mol%	60 ^b	4.4	324	73.4 ^c					15
	CHCl ₂ CHCl ₂		60 ^b	22.0	347	74.1 ^c					15
	+ Eu(fod) ₃	0.15									
CH(CH ₃) ₂	(CH ₃) ₂ CO	10 mol%	60 ^a	8.6	323	71.1 ^d	64.4	-22.2	67.3		115
	Neat		60 ^a	13.4	318	69.0 ^d	66.0	-10.0	68.6		115
	CHCl ₂ CHCl ₂		100 ^b	14.5	325	70.2 ^c					127
	CHCl ₂ CHCl ₂		25.2(¹³ C) ^b	40	340	70.6 ^c					127
	(CH ₃) ₂ CO	10 mol%	60 ^a	13.0	316	69.0 ^d	65.6	-10.5	68.6		115
C(CH ₃) ₃	C ₆ H ₅ Cl	10%	60 ^a		304.5	69.4 ^c	58.5	-33.4	61		133
	C ₆ H ₅ CH ₃	30%	60 ^a		210.3	46.8 ^c	56.4	41.8	58.9		133
	(CH ₃) ₂ CO	10 mol%	60 ^a	20.5	223	48.1 ^d	46.8	-4.2	48.5		115
CH ₂ CH ₂ C ₆ H ₅	CHCl ₂ CHCl ₂		100 ^b	6.0	323	73.6 ^c					134
	Neat		60 ^a	17.6	320	68.6 ^c	70.3	10.0	71.1		134
	CDCl ₃	5%	60 ^f	27.0	327.5	69.4 ^c					18
	+ Eu(fod) ₃	0.10									
	CDCl ₃	0.25 M	100 ^a	21.3	326	69.6 ^c	73.6	12.1			136

TABLE 3 (cont.)

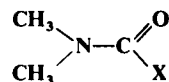
R (s)	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (kJ mol ⁻¹)	E_a (kJ mol ⁻¹)	log A	Reference
 C ₆ H ₅											
<i>trans</i>	CDCl ₃	0.25 M	100 ^a	13.5	327	70.9 ^c	76.1	15.9			136
<i>cis</i>	CDCl ₃	0.25 M	100 ^a	25.7	—	73.8 ^d	81.5	25.7			136
 C ₆ H ₄ NO ₂ - <i>p</i>											
(<i>trans</i>)	CDCl ₃	0.25 M	100 ^a	31.4	332	72.0 ^c	79.6	22.8			136
	Neat		60 ^a	4.5	321	72.4 ^c	66.9	-17.2	69.5		135
	Neat		60 ^a	12.5	326	71.7 ^c	63.6	-22.2	66.9		135
	CDCl ₃	10%	60 ^b	8	325	73.4 ^c			76.1		137
	Neat		60 ^a	11	321	70.3 ^c	64.9	-10.5	67.8		135
	CDCl ₃	10%	60 ^b	7.6	314.5	71.1 ^c			73.6		137
	CDCl ₃	10%	60 ^b	5.2	281	64.1 ^c			66.4		137
	CDCl ₃	10%	60 ^b	5.0	269.5	61.5 ^c			63.7		137

^a For explanations to footnotes see Table 1. See reference 545 for investigations of *N,N*-dimethylamides by high-pressure NMR.

TABLE 4^a

AR	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i>	Reference
A = O											
215	OCH ₃	CCl ₄	60 ^a			75.2 ^d					19
		+ Eu(fod) ₃									
		CDCl ₃	10%	60 ^a	1.8	63.5		-20.9	59.8		138
		CHCl ₃		60 ^a		65.6 ^d	48.9	-55.2	51.4		139
		CDCl ₃	50% v/v	100 ^a	1.8	277.6	64.5 ^c	0.7			4
		C ₆ H ₅ Cl	30% v/v	60 ^a	3.7	283.2	61.9		60.2	12.5	141
	OCH ₂ CH ₃	CDCl ₃ /C ₆ D ₆	1 M	60 ^a			64.8 ^d	58.9	-19.2		52
	→ SbCl ₅	CHCl ₂ CHCl ₂	0.4/0.8 M	60 ^a			> 75				52
	OC ₆ H ₅	HCONH ₂	80 ^f			61.9	69.0	23.8			142
		C ₆ H ₅ Br		100 (<i>p</i> = 0.3)	51.5	335	69.0 ^c				143, 451
		+ Eu(fod) ₃									
	OC ₆ H ₄ NO ₂ p	C ₆ H ₅ Br		100 (<i>p</i> = 0.3)	58.0	347	71.5 ^c				143, 451
		+ Eu(fod) ₃									
	O-naphthyl	CCl ₄	0.13 M	80 ^f	18.2	59.4 ^d	64.3	16.3			142
		HCONH ₂	0.15 M	80 ^f	18.0	61.9 ^d	69.0	23.0			142
	OC(CH ₃) ₃	CHCl ₃	10 mol%	60 ^a	0.5	51.0 ^c					139
	OSi(CH ₃) ₃	<i>n</i> -Hexane	11 mol%	60 ^a		67.3 ^d	60.2	-23.8	62.7	12	139, 140
A = S											
	SCH ₃	CHCl ₃	60 ^a			60.6 ^d	67.7	21.3	69.4		140
		CHCl ₃	60 ^a			62.7 ^d	51.8	-36.8	54.3		139
	SC ₆ H ₅	C ₆ H ₅ Br	100 (<i>p</i> = 0.35)	60.0	305	62.3					143
		+ Eu(fod) ₃									
	SC(CH ₃) ₃	CHCl ₃	10 mol%	60 ^a	1.1	59.4 ^d	49.7	-32.6	52.2		139
	SGe(CH ₃) ₃	CHCl ₃	10 mol%	60 ^a		66.9 ^d	60.2	-23.4	62.7		139
	SSn(CH ₃) ₃	CHCl ₃	10 mol%		12.7	315	68.1 ^d	80.7	38	83.2	140
		<i>n</i> -Hexane	10 mol%		13.4	315	68.6 ^d	68.6	0.8	71.1	140
	SPb(CH ₃) ₃	CHCl ₃		14.0		66.5 ^d	64.8	-5.1	67.3		139

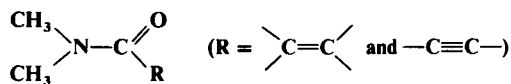
^a For explanations to footnotes see Table 1.

TABLE 5^a

X (s)	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i>	Reference
Cl	Neat		60 ^f		326	69.0 ^c			30.5	6.1	110
	Neat		60 ^a			70.2 ^d			70.6	12.9	144
	Neat		60 ^a	6.8		70.2 ^d	71.5	3.3	73.6		145
	Neat		15.1 (¹³ C) ^a	27.1	333	70.9 ^d	74.7	12.7	77.2	13.9	146
	Neat		100 ^a			71.5	75.2	12.5	69.8	13.9	122
			60 ^f	6.7	314		67.7	-2.5	70.2		107
	CCl ₄	6 mol%	60 ^a	7.1		69.0 ^d	69.0	-2.5	71.5		145
		10.4 mol%	60 ^a	7.1		68.1 ^d			74.0	13.8	147
	CDCl ₃	50 mol%	100 ^{a,h}				69.5	-0.4	72	13.2	48
		5 mol%	100 ^{a,h}				68.2	-2.5	71	13.1	48
Br	Neat		60 ^a	5.4		65.6 ^d	61.4	-13.8	64.0		145
F	CCl ₄	16.5 mol%	100 ^a	2		75.7 ^d	74.0	-5.9	76.5	12.9	148
CCl(CH ₃) ₂	C ₆ H ₅ Cl	30%	60 ^a		264.4	56.4 ^c	55.6	-4.2	58.1		133
CCl ₂ CH ₃	C ₆ H ₅ Cl	30%	60 ^a		302.5	64.4 ^c	66.5	8.4	69		133
CH ₂ Cl	C ₆ H ₅ Cl	10%	60 ^a		293.5	69.0 ^c	64.4	-16.7	66.9		133
CHCl ₂	C ₆ H ₅ Cl	30%	60 ^a		319.9	73.2 ^c	77.3	12.5	79.8		133

CCl ₃	Neat		100 ^a		62.7	67.3	15.5	69.8	14.0	122
	Neat		100 ^a	29.6	62.7	63.1	1.3	65.6	13.3	149
	C ₆ H ₅ Cl	10%	60 ^a	285.3	61.9 ^c	61.4	1.7	64.0		133
	CF ₂ BrCF ₂ Br	70%	22.6 (¹³ C) ^a	288	73.6 ^c			69.4		150
					63.0 ^d	64.5	5.4			13
CH ₂ Br	C ₆ H ₅ Cl	30%	60 ^a	292.2	65.2 ^c	69.8	12.5	72.3		133
CHBr ₂	C ₆ H ₅ Cl	30%	60 ^a	317.5	71.9 ^c	66.5	−20.9	68.6		133
CBr ₃	(CH ₃) ₂ CO	30%	60 ^a	277.9	56.0 ^c	54.3	−12.5	56.8		133
CH ₂ F	C ₆ H ₅ Cl	30%	60 ^b	317.5	71.1 ^c					133
CHF ₂	C ₆ H ₅ Cl	30%	60 ^b	348.1	78.6 ^c					133
CF ₃	CHCl ₂ CHCl ₂	4% w/w	100 ^a	9.3	78.6 ^a	80.3	4.6	83.2	13.5	151
	CCl ₄	11 mol%	100 ^a		75.5 ^d	70.2	−17.6	72.7		125
CN	CHCl ₂ CHCl ₂	5.6 mol%	100 ^a	25.0	89.5 ^d	89.9	2.1	92.4		145
		18 mol%	100 ^a		91.5 ^d	92.8	4.2	95.3		145
N=C=S	<i>n</i> -Octane	10 mol%	100 ^a	8.0	76.9 ^d	76.1	−3.8	78.6		145
N ₃	CCl ₄	10 mol%	100 ^a	1.8	74.0 ^d	73.6	−1.3	76.1		145

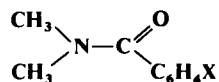
^a For explanations to footnotes see Table 1. See also references 445 and 476 (for X = Cl and X = I); see reference 554 for rotation around the amide bond in 1-(N,N-dimethylcarbamoyl)-*o*- and -*m*-carboranes.

TABLE 6^a

R (s)	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ J mol ⁻¹ K ⁻¹	E_a (kJ mol ⁻¹)	log A	Reference
CH=CH ₂	CHCl ₃	5 mol%	100			69.8 ^d	67.7	-7.1	70.2		152
	CDCl ₃	5%	60 ^f	40	338.5	70.6 ^c					18
	+ Eu(fod) ₃	0.08									
CH=CHCH ₃	CDCl ₃	0.5 M	60 ^a		267	59.8 ^c	37.6	-83.6	40.1	8.8	153
(CH=CH) ₂ CH ₃	CDCl ₃	0.5 M	60 ^a		300	67.7 ^c	74.0	20.9	76.5	14.3	153
CH=CHC ₆ H ₅	CDCl ₃	0.5 M	60 ^a		304	68.1 ^c	73.1	12.5	75.7	14.1	153
	CDCl ₃	0.25 M	100 ^a	11.0	312	68.3 ^c	72.0	11.5			154, 155
	CDCl ₃	0.5 M	60 ^a	6.7	303.8	67.7 ^c	58.9	-28.4			156
	CDCl ₃	5%	60 ^f	56.8	336	69.0 ^c					18
	+ Eu(fod) ₃	0.16									
CH=CHC ₆ H ₄ X											
X = CN- <i>p</i>	CDCl ₃	0.25 M	100 ^a	12.9	319	69.8 ^c	72.7	9.2			154, 155
Br- <i>p</i>	CDCl ₃	0.25 M	100 ^a	11.2	314	68.9 ^c	73.0	13.1			154, 155
Cl- <i>p</i>	CDCl ₃	0.25 M	100 ^a	11.3	313	68.8 ^c	71.7	9.0			154, 155
	CDCl ₃	0.5 M	60 ^a	7.0	305.5	67.7 ^c	74.8	23.4			156
CH ₃ - <i>p</i>	CDCl ₃	0.25 M	100 ^a	10.8	309	67.8 ^c	75.4	24.6			154, 155
	CDCl ₃	0.5 M	60 ^a	9.0	297.3	65.6 ^c	71.5	20.1			156
OCH ₃ - <i>p</i>	CDCl ₃	0.25 M	100 ^a	11.0	305	67.0 ^c	74.4	24.4			154, 155
	CDCl ₃	0.5 M	60 ^a	6.4	298.4	66.6 ^c	70.6	14.2			
F- <i>p</i>	CDCl ₃	0.25 M	100 ^a	11.5	312	68.5 ^c	71.3	8.8			154, 155
NO ₂ - <i>p</i>	CDCl ₃	0.25 M	100 ^a	13.8	323	70.4 ^c	75.8	16.7			154, 155
	CDCl ₃	0.5 M	60 ^a	8.3	318.4	70.2 ^c	70.6	1.7			156

X = Cl- <i>m</i>	CDCl ₃	0.5 <i>M</i>	60 ^a	7.4	308.2	68.6 ^c	58.5	-32.2	156
OCH ₃ - <i>m</i>	CDCl ₃	0.5 <i>M</i>	60 ^a	7.0	304.1	67.7 ^c	60.2	-24.7	156
NO ₂ - <i>m</i>	CDCl ₃	0.5 <i>M</i>	60 ^a	9.2	313.5	69.4 ^c	69.0	-0.4	156
CH=CHX									
X = Cl, <i>cis</i>	C ₂ Cl ₄		100 ^b	10.7	331	72.5 ^c			158
<i>trans</i>	CDCl ₃		100 ^b	17.0	314	67.5 ^c			158
X = Br, <i>cis</i>	C ₂ Cl ₄		100 ^b	10.4	331	72.5 ^c			158
<i>trans</i>	CCl ₄		100 ^b	15.5	311	67.0 ^c			158
X = I, <i>cis</i>	CCl ₄		100 ^b	8.8	330	72.9 ^c			158
<i>trans</i>	C ₂ Cl ₄		100 ^b	18.6	300	64.1 ^c			158
CH=CHCON(CH ₃) ₂	CDCl ₃	5%	60 ^f	6.0	336	74.4 ^c			18
(<i>trans</i>)	+ Eu(fod) ₃	0.12	60 ^f	13.8	341.5	74.0 ^c			18
CH=CH- 	C ₂ D ₂ Cl ₄		90 ^b	10.8	315	68.8 ^c			159
C(CH ₃)=CH ₂	CDCl ₃		60 ^f	4.5	289.5	65.2 ^c			18
	CDCl ₃	5%	60 ^f	31	314	66.0 ^c			18
	+ Eu(fod) ₃	0.09							
CH=CHN(CH ₃) ₂	(CD ₃) ₂ CO		25.2 (¹³ C) ^b	45.3	253	51.8 ^c			134
(<i>trans</i>)									
C≡CH	CDCl ₃	0.5 <i>M</i>	60 ^a	16.2	377	81.9 ^c			157
C≡CCH ₃	CDCl ₃	0.5 <i>M</i>	60 ^a	15.0	363	78.2 ^c			157
C≡CC ₆ H ₅	CDCl ₃	0.5 <i>M</i>	60 ^a	15.6	367	79.8 ^c			157
	CHCl ₂ CHCl ₂		100 ^b	27	373	80.7 ^c			134

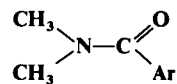
^a For explanations to footnotes see Table 1.

TABLE 7^a

X (s)	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i>	Reference
H			60 ^f				70.6	20.5	73.1		107
	CS ₂	2 mol%	100 ^a			61.9 ^d	56.0	-19.6	58.5		125
	CDCl ₃	0.25 <i>M</i>	90 ^a			64.4 ⁱ	71.2	18.3			160
				10.5	290.7	64.0 ^d					452
	CDCl ₃	0.5 <i>M</i>	60 ^a		297	65.2 ^d					153
	CDCl ₃	0.5 <i>M</i>	60 ^f	7.8	303	64.8 ^d					161
	CDCl ₃	0.25 <i>M</i>	100 ^a	13.1	303	65.4 ^c	70.0	15.3			154, 155
	CDCl ₃	15% w/w	60 ^a	8.5	283	61.5 ^d			64	13.2	162
	CDCl ₃	0.25 <i>M</i>	90 ^a			65.3 ^d					163
	CDCl ₃		20 (¹³ C) ^b	98.9	319	64.0 ^c					164
	CDCl ₃	0.5 <i>M</i>	60 ^a	7.8	301.2	66.5 ^d					165
	Cyclopentane	0.2 mol/dm ³	80 ^a			65.2 ^m					166
	CHCl ₂ CHCl ₂		100 ^b	13.8	305	65.6 ^c					127
			25.2 (¹³ C) ^b	108	326	65.2 ^c					127
	C ₆ H ₄ Cl ₂ - <i>o</i>	1 <i>M</i>	60 ^b		286.5	61.9 ^c					167
	CD ₃ CN		90 ^a			63.5 ⁱ	70.3	18.4			160
	CD ₃ NO ₂	20 mol%	22.6 (¹³ C) ^g	10.2	322.5	64.6 ^c	63.6	-3.7	66.2	30.0	168
Para substituents	CH ₃										
	CDCl ₃	0.25 <i>M</i>	90			62.1 ^d	82.4	67.9			163
	CDCl ₃		20 (¹³ C) ^b	98.8	311	62.2 ^c					164
	Cyclopentane	0.2 mol/dm ³	80 ^a			64.1 ^m					166
	CDCl ₃	0.25 <i>M</i>	90 ^a			62.0 ^d	87.2	84.3			163
	CDCl ₃	0.25 <i>M</i>	100 ^a		298						154
	Cyclopentane	0.2 mol/dm ³	80 ^a			65.6 ^m					166
	CDCl ₃	0.25 <i>M</i>	100 ^a	11.7	299	65.1 ^c	70.6	18.4			154, 155
	Cyclopentane	0.2 mol/dm ³	80 ^a			65.5 ^m					166
	CDCl ₃	0.5 <i>M</i>	60 ^a		295	65.2 ^d					153
I	Cyclopentane	0.2 mol/dm ³	80 ^a			65.5 ^m					166

F	CDCl ₃	0.25 <i>M</i>	100 ^a	10.3	293	63.8 ^c	71.3	25.4	154, 155
	Cyclopentane	0.2 mol/dm ³	80 ^a			64.5 ^m			166
CN	CDCl ₃	0.25 <i>M</i>	100 ^a	15.6	314	67.4 ^c	74.0	21.1	154, 155
NO ₂	CDCl ₃	0.25 <i>M</i>	100 ^a	16.1	317	68.1 ^c	73.0	15.8	154, 155
	Cyclopentane	0.2 mol/dm ³	80 ^a			68.5 ^m			166
OH	CDCl ₃			4.2	279.2	65.3 ^d			452
OCH ₃	CDCl ₃	0.25 <i>M</i>	100 ^a	6.2	277	61.3 ^c	70.3	32.7	154, 155
	Cyclopentane	0.2 mol/dm ³	80 ^a			60.4 ^m			166
CH ₂ Br	CDCl ₃	0.25 <i>M</i>	90 ^a			64.4 ^d	82.5	60.6	163
CHBr ₂	CDCl ₃	0.25 <i>M</i>	90 ^a	11.7		64.6 ^d	82.4	59.7	163
CBr ₃	CDCl ₃	0.25 <i>M</i>	90 ^a			65.3 ^d	79.5	47.7	163
CON(CH ₃) ₂	CDCl ₃	0.5 <i>M</i>	60 ^a	8.4	298	65.6 ^c			157
Ortho substituents									
CH ₃	CDCl ₃	0.25 <i>M</i>	90 ^a			72.1 ⁱ	92.1	53.4	160
	CDCl ₃	5%	60 ^f	18	349	75.2 ^c			18
	CD ₃ CN	0.25 <i>M</i>	90 ^a			73.9 ⁱ	74.9	2.6	160
	CHCl ₂ CHCl ₂			19.3	343.8	72.4 ^d			452
F	CDCl ₃	0.25 <i>M</i>	90 ^a			73.5 ⁱ	84.0	28.1	160
	CD ₃ CN	0.25 <i>M</i>	90 ^a			73.7 ⁱ	80.7	19.0	160
Cl	CDCl ₃	0.25 <i>M</i>	90 ^a			79.7 ⁱ	88.2	22.7	160
	CD ₃ CN	0.25 <i>M</i>	90 ^a			80.0 ⁱ	81.2	3.2	160
Br	CHCl ₂ CHCl ₂			16.2	375.2	76.6 ^d			452
	CDCl ₃	0.25 <i>M</i>	90 ^a			80.6 ⁱ	78.1	−6.7	160
I	CD ₃ CN	0.25 <i>M</i>	90 ^a		90 ^a	81.3 ⁱ	77.6	−10.0	160
	CDCl ₃	0.25 <i>M</i>	90 ^a			80.8 ⁱ	81.5	0.7	160
OH	CD ₃ CN	0.25 <i>M</i>	90 ^a			81.3 ⁱ	85.8	12.0	160
	CH ₂ Cl ₂			6.5	232.9	53.1 ^d			452
CON(CH ₃) ₂	CDCl ₂		20 (¹³ C) ^b	86.4	318	65.1 ^c			164
	CDCl ₃	0.5 <i>M</i>	60 ^a	8.3	319	70.6 ^c			157
Meta substituents									
OCH ₃	CDCl ₃	0.5 <i>M</i>	60 ^a	7.0	304.1	67.8 ^c	60.2	−24.1	156
NO ₂	CDCl ₃	0.5 <i>M</i>	60 ^a	9.2	313.5	69.3 ^c	69.0	0.4	156
CON(CH ₃) ₂	CDCl ₃	0.5 <i>M</i>	60 ^a	7.8	295	65.2 ^c			157

^a For explanations to footnotes see Table I. See reference 527 for an investigation of the isomerization processes in protonated orthosubstituted benzamides.

TABLE 8^a

Ar	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i>	Reference
	CDCl ₃	15% w/v	60 ^a	3.4	319	74.9 ^d			92.9	15.9	162
	CDCl ₃	15% w/v	60 ^a	6.6	298	66.6 ^d			79.1	14.9	162
	CDCl ₃	1%	90 ^b	10	301	65.8 ^c					159
	C ₂ D ₂ Cl ₄	1%	90 ^b	10	304	66.5 ^c					159
	H ₂ O	1 <i>M</i>	100 ^a	7.9	344	83.3 ^d	80.7	-8.7			169
	CDCl ₃	15% w/v	60 ^a	10.8	318	69.5 ^d			78.7	14.4	162
	CDCl ₃	0.5 <i>M</i>	60 ^f	7.2	319	66.9 ^d					161
X, X' = OEt, OEt	CDCl ₃		<i>b</i>	12	328	71.5 ^c					170
X, X' = Cl, Cl	C ₆ Cl ₆		<i>b</i>	12	363	79.4 ^c					170
X, X' = CH ₃ , H	C ₂ D ₂ Cl ₄		90 ^b	26.4	345	73.1 ^c					159
X, X' = CH ₃ , CH ₃	C ₂ D ₂ Cl ₄	1%	90 ^b	24.9	340	72.3 ^c					159
	CDCl ₃		20 (¹³ C) ^b	79.8	361	73.4 ^c					164



A = O

CS ₂		60 ^a	19.2	273	58.1 ^c	53.9	−15.9	56.4	171
CDCl ₃		60 ^a	12.0	282.5	61.4 ^c				171
CDCl ₃	0.5 M	60 ^a	11.6	289	63.1 ^d				165
CDCl ₃ + Eu (fod) ₃	5% 0.13	60 ^f	42.5	299	70.2 ^c				16
A = S		60 ^a	16.4	363	53.5 ^c	50.6	−13.0	52.7	171
A = S		60 ^a	9.4	264	57.7 ^c				171
CDCl ₃	0.5 M	60 ^a	9.5	274	60.6 ^d				165
CDCl ₃ + Eu (fod) ₃	5% 0.15	60 ^f	41.5	285	58.9 ^c				16
A = Se		60 ^f	8.0	268.2	59.4 ^c				16
+ Eu (fod) ₃	0.08	60 ^f	46.6	284	58.5 ^c				16
A = Te		60 ^f	8.0	262	57.7 ^c				16
+ Eu (fod) ₃	0.17	60 ^f	98.8	286.8	57.3 ^c				16



A = O

CS ₂		60 ^a	10.0	272	59.4 ^c	60.6	5.0	62.7	171
CDCl ₃	0.5 M	60 ^a	5.9	286	63.5 ^d				165
A = S		60 ^a	9.7	260	57.0 ^c	53.1	−15.0	55.2	171



C ₂ Cl ₄		60 ^a	30.9	339.5	71.5 ^c	70.6	−2.9	73.2	171



CS ₂		60 ^a	12.9	309.5	66.9 ^c	65.2	−4.6	68.0	171

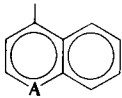


CS ₂		60 ^a	11.4	273.5	59.8 ^c	56.0	−12.5	58.1	171

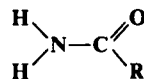


C ₂ Cl ₄		60 ^a	16.7	349	75.2 ^c	67.7	−22.2	70.6	171

TABLE 8 (cont.)

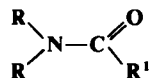
Ar	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i>	Reference
 A = CH A = N	CDCl ₃	0.5 <i>M</i>	60 ^f	28.8	339	69.4 ^d					161
	CDCl ₃	0.5 <i>M</i>	60 ^f	28.8	359	71.9 ^d					161
	CDCl ₃	0.5 <i>M</i>	60 ^a	12.0	278	60.2 ^d					165
	CDCl ₃	0.5 <i>M</i>	60 ^a	9.2	279	61.0 ^d					165

^a For explanations to footnotes see Table 1.

TABLE 9^a

R	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log A	Reference
H (¹⁵ N)	C ₃ H ₇ COCH ₃	9.4 mol%	60 ^a			74.2 ^d	77.3	11.3	80.3	13.9	172
	Diglyme	14.1 mol%	60 ^a			74.4 ^d	79.4	16.7	82.3	14.2	172
CH ₃ (¹⁵ N)	(CH ₃) ₂ SO		90 ^f						66.9		173
	(CH ₃) ₂ CO	1 M	90 ^f						71.1		173
	H ₂ O	1 M	90 ^f						62.7		173
	Dioxane	5.7 mol%	60 ^a			70.1	85.6	51.9	88.0	15.9	174
(14N)	(CH ₃) ₂ CO	0.5 M	100 ^a	56	333	69.8 ^d	76.1	20.9			175
	(CH ₃)NCHO	1.5 M	100 ^a	66	346	72.3 ^d	84.0	37.6			175
	(CD ₃) ₂ NCDO	7 mol%	100 ^b	62.5	345	70.6 ^c					176
	[EtO(CH ₂) ₂] ₂ O	2.1 mol%	100 ^b	34.5	328	68.6 ^c					176
	(CH ₃) ₂ SO	6 mol%	60 ^a			72.7 ^d	78.3	19.0	81.0	14.3	174
	(CD ₃) ₂ NCDO	7 mol%	100 ^b	54	335	69.0 ^c					176
	(CH ₃) ₂ CO	5 mol%	100 ^b	42	325	67.7 ^c					176
	[EtO(CH ₂) ₂] ₂ O	2.1 mol%	100 ^b	16	312.5	67.3 ^c					176
CF ₃ (¹⁵ N)	Dioxane		60 ^a		341	74.0 ^d	74.5	2.1	76.5	13.4	177
C(CH ₃) ₃	(CD ₃) ₂ NCDO	7 mol%	100 ^b	35.5	322.5	67.3 ^c					176
	(CH ₃) ₂ CO	5 mol%	100 ^b	30	313	65.6 ^c					176
C ₆ H ₅	(CD ₃) ₂ NCDO	7 mol%	100 ^b	71.5	325	66 ^c					176
	(CH ₃) ₂ CO	5 mol%	100 ^b	46.5	317	65.6 ^c					176
CH ₂ F	(CH ₃) ₂ NCHO		94.1 (¹⁹ F) ^a				64.0	-17.2	66.1		178
CHF ₂	(CH ₃) ₂ NCHO		94.1 (¹⁹ F) ^a				78.3	+6.3	81.2		178

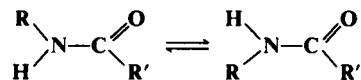
^a For explanations to footnotes see Table 1. See reference 493 for *ab initio* molecular orbital calculations of the structure of formamide.

TABLE 10^a

R ¹	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (kJ mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
R = CH₂CH₃										
H	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μ l	60 ^a (CH ₂)		≥ 389	87.4 ^c				128
CH ₃	CHCl ₂ CHCl ₂		25.2 (¹³ C) (CH ₂)	72.9	370.5	75.4 ^c				127
	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μ l	60 ^a (CH ₂)		≥ 330	74.0 ^c				128
CH ₂ CH ₂ CH ₃	CHCl ₂ CHCl ₂		25.2 (¹³ C) (CH ₂)	50.1	345	71.3 ^c				127
C ₆ H ₅			60 ^f				63.1	17.1	65.2	107
	Cyclopentane	0.5 mol/dm ³	80 ^a			62.9 ^m				166
	CD ₃ CN	0.5 M	100 ^a			62.6 ^d	62.0	-0.1		179
	Diglyme- <i>d</i> ₁₄	20 mol%	90 ^a (CH ₂)	24.1	282	59.5 ^c	60.6	+3.4	63.0	72
C ₆ H ₄ OCH ₃ - <i>p</i>	Cyclopentane	0.5 mol/dm ³	80 ^a			57.8 ^m				166
C ₆ H ₄ CH ₃ - <i>p</i>	Cyclopentane	0.5 mol/dm ³	80 ^a			61.7 ^m				166
C ₆ H ₄ F- <i>p</i>	Cyclopentane	0.5 mol/dm ³	80 ^a			62.1 ^m				166
C ₆ H ₄ NO ₂ - <i>p</i>	Cyclopentane	0.5 mol/dm ³	80 ^a			66.8 ^m				166
 C₆H₅										
<i>trans</i>	<i>o</i> -C ₆ H ₄ Cl ₂	60% w/w	25.1 (¹³ C) ^a (CH ₂)	27.3		73.5 ^d	76.9	11.7		180
<i>cis</i>	<i>o</i> -C ₆ H ₄ Cl ₂	60% w/w	25.1 (¹³ C) ^a (CH ₂)	39.2		70.6 ^d	69.8	-2.5		180

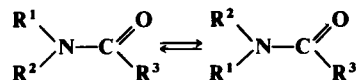
				R = CH(CH₃)₂					
H	C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH)	≥ 393	86.1 ^c				128
CH ₃	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₃)	≥ 313	68.1 ^c				128
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f (CH ₃)	293		69.8	− 18.0	72.3	181
C ₆ H ₅	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f (CH ₃)	281		61.9	− 10.9	64.4	181
CH ₂ C ₆ H ₅	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f (CH ₃)	338		71.1	− 8.4	73.6	181
				R = CH₂CH(CH₃)₂					
H	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₂)	≥ 387	87.8 ^c				128
	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₃)	≥ 373	87.8 ^c				128
CH ₃	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₂)	≥ 333	73.6 ^c				128
				R = Si(CH₃)₃					
H	C ₆ H ₅ Cl	20%	60 ^b	12.1	227	48.5 ^c			182
CH ₃	C ₆ H ₅ Cl	30% v/v	60 ^a	8.1	284	64.0 ^d		51.0	183
CH(CH ₃) ₂	C ₆ H ₅ Cl	20%	60 ^b	5.8	284	63.5 ^c			182
C(CH ₃) ₃	C ₆ H ₅ Cl	20%	60 ^b	1.3	332	78.6 ^c			182
CF ₃	C ₆ H ₅ Cl	20%	60 ^b	2.8	398	92.4 ^c			182

^a For explanations to footnotes see Table 1. See also reference 446 for dynamic processes in orthosubstituted *N,N*-diethylbenzamides. See references 534 and 535 for gas-phase kinetic studies of *N,N*-dialkylformamides.

TABLE 11^a

R	R'	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Log A	Reference
CH ₃	H	Neat		60 ^a			(A) 92.0 ^d (B) 86.5 ^d			98.6 99.0	14.0 15.0	184 184 185
		CH ₂ ClCH ₂ Cl		250 ^{a,k}			81.4 87.4	86.1 92.4	18.4 18.8			
		CH ₂ ClCH ₂ Cl	10 mol%	<i>a</i> (CH ₃)			74.4 86.1	73.2 93.6	-16.7 +20.9			186
		CH ₂ ClCH ₂ Cl	35 mol%	<i>a</i>			75.2 86.9	82.8 94.5	20.9 20.9			186
	CH ₃	H ₂ O	20 mol%	<i>a</i>			78.6 89.0	82.8 97.0	12.5 20.9			186
C(CH ₃) ₃	H	C ₆ H ₅ Cl	30% v/v	60 ^a (CH ₃)	12	362	(A) 85.3 ^d (B) 82.8 ^d			99.5 94.5	15.3 14.9	183
Si(CH ₃) ₃	H	C ₆ H ₅ Cl	30% v/v	60 ^a (CH ₃)	7.5	322	(A) 75.9 ^d (B) 73.2 ^d			86.9 82.8	14.7 14.5	183
CH ₂ C ₆ H ₅	CF ₃	CDCl ₂ CDCl ₂	2 M	100 ^{a,k}			79.0 (315 K)	93.2	41			37
CH ₂ COOCH ₃	OC(CH ₃) ₃	C ₂ D ₂ Cl ₄ + Eu(fod) ₃	0.4 M	90 ^a			(A) 66.8	65.7	4.7			20
CHO	H	(CH ₃) ₂ CO		60 ^a (EZ → EE)		250	52.7 ^c					187
COCH ₃	CH ₃			60 ^a (CH ₃)	17.7	213	(EZ) 45.1 ^c					187

^a For explanations to footnotes see Table 1. See also references 484 and 524 for the structure of the rotational isomers in *N*-methylpropionamide and *N*-methylisobutyroamide; see reference 521 for an investigation of cis-trans isomerism and keto-enol tautomerism in 2-acetamido derivatives of 4-methylpyridine and -pyrimidine.

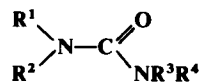
TABLE 12^a

R ¹	R ²	R ³	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
CH ₃	CH ₂ CH ₃	CH ₃	Neat		100 ^a			75.2	84.0	29.3	86.9	122
	C ₆ H ₅ - <i>n</i>	CH ₃	Neat		100 ^a			74.8	79.8	17.1	82.3	122
	CH(CH ₃) ₂	CH ₃	Neat		100 ^a			71.1	73.1	6.7	75.7	122
	C ₆ H ₁₁	CH ₃	Neat		100 ^a			71.5	76.5	16.3	79.0	122
	Si(CH ₃) ₃	H	C ₆ H ₅ Cl	30% v/v	60 ^a (CH ₃) ₃	6.2	344	(A) 82.8 (B) 77.3 ^r				183
	Si(CH ₃) ₃	H	C ₆ H ₅ Cl	30% v/v	60 ^a (CH ₃) ₃	8.8	270	(A) 60.2 (B) 66.0 ^r				183
	F	H	(CD ₃) ₂ CO		60 ^a			(A) 44.7 (B) 46.8 ^d				100
			CFCl ₃	10% v/v	60 ^a	4.8		(A) 47.7 (B) 45.1 ^d				100
		H	CH ₂ ClCH ₂ Cl	2% w/v	60 ^a (CH ₃)	4.5	333	(A) 72.0 ^d				189
	CH ₂ CH=CH ₂	OCH ₂ CH ₃			250 ^a (CH ₂)	3.0		62.0 ^r				188
	CH ₂ C ₆ H ₅	C ₆ H ₄ Cl- <i>o</i>	<i>o</i> -C ₆ H ₄ Cl ₂	0.6 M	60 ^{a,d} (CH ₃)			(A) 77.3 (B) 79.0				72
	COCH ₃	CH ₃			60 ^a	9.2	160	(E, Z) 34.3 ^r				187
CH ₂ CH ₃ C(CH ₃) ₃ <i>n</i> -C ₃ H ₇ <i>n</i> -C ₄ H ₉ CH ₂ CH(CH ₃) ₂	C ₆ H ₅ NO ₂ - <i>p</i>	H	C ₆ H ₅ Cl	5%	60 ^r (CH ₃)	13.2	309	(A) 71.5 ^r				190
	C ₆ H ₅ OCH ₃ - <i>p</i>	H	C ₆ H ₅ Cl	5%	60 ^r (CH ₃)	12.5	342	(A) 79.4 ^r				190
	CH=CHC ₆ H ₅	CH ₃ (<i>cis</i>)	CDCl ₃		60 ^b (CH ₃)	5.5	312	70.6, 74.8 ^r				191
		(<i>trans</i>)	CDCl ₃		60 ^b (CH ₃)	4	311	71.9, 73.6 ^r				191
	OH	H	CDCl ₃		60 (CH)	27.2	324	68.6 ^r				192
	CH ₂ SO ₂ C ₆ H ₄ CH ₃ - <i>p</i>	OCH ₃	CDCl ₃	6.6 mol%	60 ^a			68.1, 68.9 ^d	64.6	-11.6	67.1	193
	CH ₂ SC ₆ H ₄ CH ₃ - <i>p</i>	OCH ₃	CDCl ₃	7.4 mol%	60 ^a			66.0, 66.7 ^d	61.9	-13.2	64.5	193
	C ₆ H ₅	H	C ₆ H ₅ Cl	5%	60 ^r	23.8	337	(A) 76.5 ^r				190
	C ₆ H ₅	H	C ₆ H ₅ Cl	5%	60 ^r	16.3	342	(A) 76.9 ^r				190
	OC ₂ H ₅	OC ₂ H ₅	CDCl ₃	10-20%	80 ^a (CH ₂ N)	2.9		63.2 ^r				188
	CH ₃	OC ₂ H ₅	CDCl ₃	10-20%	80 ^a (CH ₃)	1.2		62.8 ^r				188
	CH ₂ C ₆ H ₄ OCH ₃ - <i>o</i>	CH ₃	CDBr ₃		80 ^a (CH ₂ N)		339	74.9 ^r	137.3	183.9		194
	CH ₃	OC ₂ H ₅	CDCl ₃		80 ^a (CH ₂ N)	2.4		64.5 ^r				188
	CH ₂ CH ₃	OC ₂ H ₅	CDCl ₃		80 ^a (CH ₂ N)	2.7		63.6 ^r				188

TABLE 12 (cont.)

R ¹	R ²	R ³	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
CH ₂ CH(CH ₃) ₂		H	CHCl ₂ CHCl ₂	400 mg/0.2 ml	60 ^a (CHO) (CH ₂)	6 10.6	341 348	(A) 78.8 ^c (A) 79.3 ^c				189
		H	CHCl ₂ CHCl ₂	400 mg/0.2 ml	60 ^a (CHO) (CH ₂)	4.3 8.7	360 364	(A) 81.3 ^c (A) 81.9 ^c	67.3 66.0	-37.6 -41.8	70.2 69.0	189
		H	C ₂ Cl ₄	200 mg/0.2 ml	60 ^a (CHO) (CH ₂)	7.7 8.8	358 359	(A) 79.4 ^c (A) 80.7 ^c	68.1	-35.5	71.1	189
CH ₂ C ₆ H ₅	CH ₂ NC ₂ H ₁₀	H	(CH ₃) ₂ SO		60 ^b (CHO)	12.0	372	83.2, 86.1 ^c				191
C ₆ H ₅	CH ₂ NC ₂ H ₁₀	H	CDCl ₃		60 ^b (CH ₂)	17.4	338	74.4, 79.0 ^c				191
C ₆ H ₅	CH=CHC ₆ H ₅ (cis)	CH ₃	CDCl ₃		60 ^b (CH ₃)	6	270	60.2 ^c				191
CH ₂ CH=CH ₂	CH ₃	OC ₂ H ₅	CDCl ₃	10-20%	80 ^a (CH ₂ N)	3.0		62.0 ^c				188
	CH ₂ CH ₃	OC ₂ H ₅	CDCl ₃		80 ^a (CH ₂ N)	5.4		60.7 ^c				188
	CH(CH ₃) ₂	OC ₂ H ₅	CDCl ₃		80 ^a (CH ₃)	2.8		60.3-59.5 ^c				188
	C ₆ H ₁₁	OC ₂ H ₅	CDCl ₃		80 ^a (CH ₂ N)	7.0		63.0-60.7 ^c				188
	C ₆ H ₅	OC ₂ H ₅	CDCl ₃		80 ^a (CH ₃)	10.8		55.3-54.8 ^c				188
CH ₂ C=CH ₂	CH ₃	OC ₂ H ₅	CDCl ₃	10-20%	80 ^a (CH ₂ N)	2.4		65.3 ^c				188
CH ₃	CH ₂ CH ₃	OC ₂ H ₅	CDCl ₃		80 ^a (CH ₂ N)	2.7		64.9-64.5 ^c				188
	CH(CH ₃) ₂	OC ₂ H ₅	CDCl ₃		80 ^a			64.5-63.6 ^c				188
	C ₆ H ₅	OC ₂ H ₅	CDCl ₃		80 ^a			59.0-57.8 ^c				188

^a For explanations to footnotes see Table 1. See also reference 461 for aminoacids, 462 for nicotinamides, 539 for glycinester derivatives, 515 for hindered rotation in *N*-aryl-*N*-benzyl alkylcarbamates, and 531 for the rotational barrier in a triamide *N*-acetylformimide.

TABLE 13^a

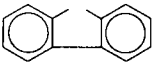
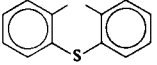
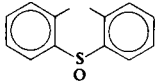
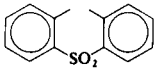
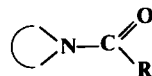
R ¹	R ²	R ³	R ⁴	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	Reference
H	H	H	H	(CH ₃) ₂ CO + TMU		60 ^a			47.7			195
				(CD ₃) ₂ CO/(CD ₃) ₂ NCDO		100 ^b	48	225	46.0 ^c			196
			H	CH ₃ OH		100 ^a		≈ 220	≈ 41 ^c			197
			CH ₃	(CD ₃) ₂ CO		250 ^a	60	211	40.9 ^c			197
		CH ₂ CH ₃	CH ₂ CH ₃	(CD ₃) ₂ CO		250 ^a	140	205	39.7			197
			H	(CD ₃) ₂ CO		250 ^a	22.5	211	44.5 ^c			197
		H	→ BF ₃	CH ₂ Cl ₂ /CH ₃ NO ₂	0.5 M	60 ^b (CH ₃)	1.2	276	65.2 ^c			198
			CH ₃	(CD ₃) ₂ CO		100			< 37			197
		CH ₃	CH ₃	CHFCl ₂ /CHF ₂ Cl		200 ^{b,d}	25	132	26.7			199
				CHFCl ₂ , CDCl ₃	15%	25.2 ^a (¹³ C)	91	123	25.5			55
		H	→ BCl ₃	neat		60 ^b	3.0	212	47.9 ^c			200
			CH(CH ₃) ₂	CHFCl ₂	0.6 M	100 ^a	29		40.5 ^d	34.3	-18.4	201
		CH ₂ CH ₃	→ SbCl ₅	CD ₂ Cl ₂	0.3 M				54.8 ^d	64.0	30.1	52
			CH ₂ CH ₃	CD ₂ Cl ₂		100			< 33			197
		C ₆ H ₅	→ TiCl ₄	CD ₂ Cl ₂		250 ^a	≈ 100	253	53.1 ^c			197
			C ₆ H ₅	CH ₂ Cl ₂	10% w/v	60 ^b	22.8	197	41.0 ^c			202
			+ CF ₃ COOH		10% w/v	60 ^b	27.6	228	47.0 ^c			202
				CH ₂ Cl ₂	10% w/v	60 ^b	16.2	223	47.0 ^c			202
			+ CF ₃ COOH		10% w/v	60 ^b	17.4	258	55.0 ^c			202
				CH ₂ Cl ₂	10% w/v	60 ^b	25.2	192	39.0 ^c			202
				+ CF ₃ COOH	10% w/v	60 ^b	34.2	221	45.0 ^c			202

TABLE 13 (cont.).

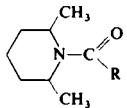
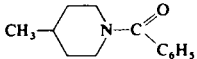
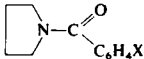
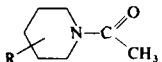
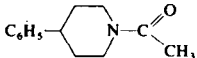
R ¹	R ²	R ³	R ⁴	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	Reference
				CH ₂ Cl ₂ + CF ₃ COOH	10 ⁻⁶ w/v 10 ⁻⁶ w/v	60 ^b 60 ^b	24.0 24.6	253 288	53.0 ^c 60.0 ^c			202 202
				CH ₂ Cl ₂ + CF ₃ COOH	10 ⁻⁶ w/v 10 ⁻⁶ w/v	60 ^b 60 ^b	24.0 24.6	262 282	55.5 ^c 59.0 ^c			202 202
CH ₂ CH ₃	CH ₂ CH ₃	H	H →BF ₃	(CD ₃) ₂ CO		250 ^a (CH ₃)	21.2	205	43.0 ^c			197
		CH ₃	CH ₃	CHCl ₃ /CH ₃ NO ₂	0.5 M	60 ^a (CH ₃)	3.2	287	65.6 ^c			198
		CH ₂ CH ₃	CH ₂ CH ₃	CD ₂ Cl ₂		100			< 33.4			197
		H	H	CD ₂ Cl ₂					< 33.4			197
H	CH ₃	H	CH ₃	CH ₃ OH		100 ^a		253	55.2 ^c			197
		H	CH ₃ →BF ₃	CH ₂ Cl ₂ /CH ₃ NO ₂	0.5 M	60 ^a (CH ₃)	1.7	288	67.3 ^c			198
H	CH ₂ CH ₃	H	CH ₃ →SbCl ₅	CH ₂ Cl ₂	0.5 M	100 ^a (CH ₃)	10.8	303	67.0 ^c	62.7	-14.5	203
		H	CH ₂ CH ₃ →BF ₃	CH ₂ Cl ₂ /CH ₃ NO ₂	0.5 M	60 ^a (CH ₃)	3.6	287	65.2 ^c			198

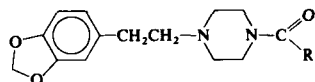
^a For explanations to footnotes see Table 1. See also reference 541 for a discussion of activation energy barriers in alkylureas.

TABLE 14^a

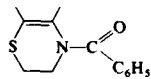
	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
233										
	R = C ₆ H ₅									
	<i>o</i> -C ₆ H ₄ Cl ₂	1 M	60 ^b		281	58.9 ^c				167
	CDCl ₃		60 ^a (Hz)		292	61.9 ^c				204
	CDCl ₃		25.2 (¹³ C) ^a (C α)		316	62.4 ^c				204
	CDCl ₃		20 (¹³ C) ^b (C β)	114.4	309	62.8 ^c				164
	CH ₂ Cl ₂		25.2 (¹³ C)(g)		223	49.7 ^c				204
	<i>o</i> -C ₆ H ₄ Cl ₂	1 M	60 ^b		344.5	69.4 ^c				167
	<i>o</i> -C ₆ H ₄ Cl ₂	1 M	60 ^b		297.5	62.3 ^c				167
	CDCl ₃		20 (¹³ C) ^b (C β)	125.2	323	64.1 ^c				164
	<i>o</i> -C ₆ H ₄ Cl ₂	1 M	60 ^b		256	54.3 ^c				167
	CDCl ₃	1 M	22.6 (¹³ C) ^b	130.9	300	59.3 ^c				205
	R = H									
	CDCl ₃	≈ 1 M	100 ^b (Hz)	19.0	384	82.8 ^c				206
	CHCl ₂ F	≈ 1 M	100 ^b (Hz)	9.2	315	69.4 ^c				206
	CHCl ₂ F	≈ 1 M	100 ^b (Hz)	20.0	283	60.2 ^c				206
	CDCl ₃		25.2 (¹³ C) (C α)		305	60.2 ^c				204
	CDCl ₃		20 (¹³ C)	114.4	300	59.6 ^c				164
	CDCl ₃	1 M	22.6 (¹³ C) ^b	130.9	306	60.6 ^c				205
	CDCl ₃		60 ^a (Hz)		273	58.4 ^c				204
			25.2 (¹³ C) ^a (C α)		303	59.9				204
	CDCl ₃		25.2 (¹³ C) ^a (C α)		310	61.2 ^c				204
			(C β)		284	61.2 ^c				204

TABLE 14 (cont.)

	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
234										
	R = CH ₃	CDCl ₃	25.16 (¹³ C) ^a			57.7				207
	C ₆ H ₅	CDCl ₃	60 ^a (Hz)		263	55.0 ^c				204
		CHF ₂ Cl	25.16 (¹³ C) ^a			50.6				207
		CDCl ₃	60 ^a (Hz ax) (Hz eq)		285 308	61.7 ^c 63.0 ^c				204 204
										
	X = CH ₃ ^p	CDCl ₃	20 (¹³ C) ^b	78.4	315	63.7 ^c				164
	NO ₂ ^p	CDCl ₃	20 (¹³ C) ^b	60.8	354	72.7 ^c				164
										
	R = 2-CH ₃	Toluene- <i>d</i> ₈	0.5 M	100 ^b (CH ₃) (CH ₃ CO)	12.8 4.5	290.5 279	63.0 ^c 62.7 ^c			208 208
	2,2,6,6-CH ₃	CHF ₂ Cl		25.16 (¹³ C) ^a			28.0			207
		Toluene- <i>d</i> ₈	0.5 M	100 ^b (H ₂)	150	357	70.7 ^c			208

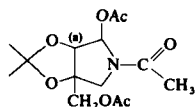


R = C ₆ H ₅	(CD ₃) ₂ CO	0.25 M	60° (CH ₂)	16.2		61.5 ^d	62.1	2.1	209
C ₆ H ₄ Clp	(CD ₃) ₂ CO	0.25 M	60° (CH ₂)	15.6		60.8 ^d	59.9	-3.1	209
C ₆ H ₄ OCH ₂ p	(CD ₃) ₂ CO	0.25 M	60° (CH ₂)	6.0		57.6 ^d	57.6	-0.2	209
C ₆ H ₄ NO ₂ p	(CD ₃) ₂ CO	0.25 M	60° (CH ₂)	25.2		63.5 ^d	62.6	-3.1	209

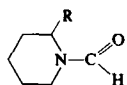


(A)

CD ₃ CN	0.8 M	200°				(A) 61.4°	58.9	-9.2	61.9	210
						(B) 59.8°	58.5	-5.0	61.0	

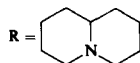


(CD ₃) ₂ NCDO		(Ha) ^{a,4}	0.19 (ppm)			75.2°	76.1	2.5	79.0	71
						73.6°	75.2	5.0	78.2	71

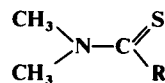


(A)

(CH ₃) ₂ SO	0.8 M	60° (CHO)	5.1	366		82.8°				211
+ HBr	0.8 M	60° (CHO)	5.0	359		81.5°				211

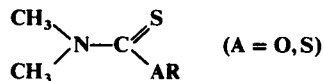


^a For explanations to footnotes see Table 1. See also reference 83 for C-N rotational barriers in *N*-acetyl and *N*-benzoyl derivatives of bicyclic amines with high nitrogen inversion barriers, and 463 for results concerning tetrahydropyridines. See also 503 and 505 (for *N*-vinylamides), 540 (for 2,2-dichloro-1'-formyl-3',4'-dihydrospiro[cyclopropane-1,2'-(1'*H*)-quinoline] and related compounds).

TABLE 15^a

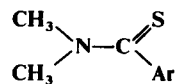
R	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i>	Reference
H	Gas		100 ^a	9	420	94.05 ^c					212
	Neat		100 ^a	12	473	106.6 ^c					212
	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μ l	60 ^a		≥ 433	100.7 ^c					128
	<i>m</i> -C ₆ H ₄ Cl ₂	0.1 <i>M</i>	100	14	443	102.8 ^c					212
CH ₃	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μ l	60 ^a		≥ 409	91.1 ^c					128
CD ₃	(CD ₃) ₂ SO	8.1 mol%	60 ^a	7		97.8 ^d	105.8	26.3	108.3	14.6	130
	Decalin	1.6 mol%	60 ^a			84.9 ^d		2.5	88.2	13.4	129
CH ₂ C ₆ H ₅	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f	22.9	403		86.1	-1.7	89.5		107
CN	CHCl ₂ CHCl ₂	1.9 mol%	100 ^a			98.2 ^d	102.8	15.9	105.3		213
	<i>o</i> -C ₆ H ₄ Cl ₂	8.6% w/w	100 ^a	14	445	97.0 ^j		100.3	145.9	18.6	214
	C ₆ H ₅ NO ₂	9.2% w/w	100 ^a	12	457	100.7 ^j		86.5	143.4	17.9	214
	CHCl ₂ CHCl ₂	18.2 mol%	100 ^a			86.5 ^d	86.9	0.84	89.4		213
F	CCl ₄	20 mol%	100 ^a			78.2 ^d	74.0	-13.8	76.5		213
COOCH ₃	<i>o</i> -C ₆ H ₄ Cl ₂	9.6% w/w	100 ^a	13	441	96.6 ^j		68.6	131.3	17.0	214
	Naphthalene	10.3% w/w	100 ^a	40	456	97.8 ^j		51.8	124.6	16.1	214
CSN(CH ₃) ₂	C ₆ H ₅ NO ₂	10% w/w	100 ^a	8.0	446	99.1 ^j		133.8	163	20.4	214
	<i>o</i> -C ₆ H ₄ Cl ₂	5.8% w/w	100 ^a	19.5	458	99.5 ^j		39.3	120.8	15.5	214
	Naphthalene	8.7% w/w	100 ^a	48	466	99.8 ^j		42.2	122.9	15.6	214
	C ₆ H ₅ NO ₂	9.1% w/w	100 ^a	14	460	101.2 ^j		15.9	112.0	14.2	214

^a For explanations to footnotes see Table 1. See also references 447 and 552 (for molecular mechanics calculations).

TABLE 16^a

AR	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Log A	Reference
OCH ₃	Neat		60 ^a	11.9		75.2		-62.7	56.8		138
			60 ^a			72.7 ^d	58.1	-48.9	60.6	10.7	139, 215
			60 ^a			74.8 ^d	75.7	2.9	78.2		139
	CHCl ₃	10 mol%	60 ^a	15.0		74		-54.3	58.1		138
	CH ₂ Cl ₂	50% v/v	250 ^{a,h}	57	360.5	74.2 ^c	72.3	-4.4			4
OSi(CH ₃) ₃	C ₆ H ₁₂	1.5 mol%	60 ^a			71.5 ^d	56.8	-48.9	59.4	10.6	139, 215
	Neat		60 ^a			82.3 ^d	84.4	7.1	86.9	13.6	139, 216
	n-Hexane	37 mol%	60 ^a			80.7 ^d	79.0	-5.4	81.5	12.9	139, 216
	CHCl ₃		60 ^a			76.1 ^d	53.5	-75.2	56.0		139
	n-Hexane		60 ^a	10.4		61.4 ^d	52.2	-30.9	54.3	11.6	215
SCH ₃	CHCl ₃		60 ^a			66.5 ^d	71.5	17.6	74.0		139
	C ₆ H ₅ Cl	0.1 M	100 ^a	39.4	311	66.5 ^d	63.1	-5.9			217
	+ I ₂	+ 0.2 M	100 ^a	40.6	334	75.7 ^d					217
	CDCl ₃	10%	80 ^a	14.4	308	66.5 ^d	81.5	-59.4	83.2		218
	n-Hexane	10 mol%	60 ^a	6.0		60.2 ^d	46.4	-45.1	48.9		139
SC(CH ₃) ₃	CHCl ₃	10 mol%	60 ^a	8.1		61.9 ^d	59.4	-7.5	62.3		139
SCH ₂ SCSN(CH ₃) ₂	C ₆ D ₅ CD ₃		90 ^b	45	318	65.6					219
SCH=CH ₂	CDCl ₃	10%	80 ^a	12.8	308	67.7 ^d	76.5	-28.4	75.2		218
SCH=CHC ₆ H ₅	CDCl ₃	10%	80 ^a	14.4	311	66.9 ^d	77.3	-33.2	77.3		218
SCH=CHCOC ₆ H ₅	CDCl ₃	10%	80 ^a	4.8	315	71.5 ^d	70.2	6.0	70.6		218
SC(C ₆ H ₅)=CHCOCH ₃	CDCl ₃	10%	80 ^a	13.6	308	66.5 ^d	86.5	64.3	88.2		218
SC(C ₆ H ₅)=CHCOC ₆ H ₅	CDCl ₃	10%	80 ^a	9.6	308	67.3 ^d	84.9	58.5	87.4		218
SSi(CH ₃) ₃	CHCl ₃		60 ^a			62.3 ^d	49.3	-42.6	51.8		139
SGe(CH ₃) ₃	CHCl ₃		60 ^a			61.9 ^d	52.7	-31.4	55.2		139
SCSN(CH ₃) ₂	CDCl ₃	0.7 M	100 ^a	8.1		66.9 ^d	66.5	-1.7	69.0		220
SSCSN(CH ₃) ₂	CDCl ₃	0.7 M	100 ^a	3.5		64.0 ^d	62.7	-3.8	65.2		220

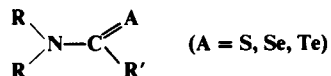
^a For explanations to footnotes see Table 1.

TABLE 17^a

Ar	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
C ₆ H ₄ X X = H X = <i>p</i> -OH <i>p</i> -OCH ₃ ortho-substituents <i>o</i> -OH <i>o</i> -OCH ₃ <i>o</i> -CH ₂ COC ₆ H ₄ OCH ₃ - <i>p</i>	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f	32.6			79.0	-5.4	81.9	107
	<i>o</i> -C ₆ H ₄ Cl ₂		100 ^f				79.4	12.5	82.8	107
	<i>o</i> -(CD ₃) ₂ SO		60 ^a	19.4	343.6	73.6 ^c				221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a	26.2	335.3	71.1 ^c				221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a	25.5	302.5	64 ^c				221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a	32.3	440	93.7 ^c				221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^{a,f}			97.2 ^a	100.3	7.1		222
	Pyridine- <i>d</i> ₅		60 ^a	19.0	298.1	63.6 ^c				221
	CDCl ₃		60 ^a	13.9	258.7	55.6 ^c	57	4		221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a	31.3	431.2	91.6 ^c				221
C ₆ H ₃ XY X = <i>o</i> -OH, Y = <i>p</i> -OCH ₃ X = <i>o</i> -OCH ₃ , Y = <i>p</i> -OH X = <i>o</i> -OCH ₃ , Y = <i>p</i> -OCH ₃ C ₆ H ₂ X ₂ Y X = <i>m</i> -Bu [†] , Y = <i>p</i> -OH	(CD ₃) ₂ SO		60 ^a	27.4	428.9	91.6 ^c				221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a	30.6	419.5	89.1 ^c				221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a	24.4	331.1	70.3 ^c				221
			60 ^a	51.5	458.9	95.8 ^c				221
			60 ^a	48.4	441.0	92.5 ^c				221
			60 ^a	48.5	405.6	84.5 ^c				221
			60 ^a							221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a							221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a							221
	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^a							221

X = H	$\alpha\text{-C}_6\text{H}_4\text{Cl}_2$		60 ^a	34.2	358.7	75.3 ^c			221
X = OH	$\alpha\text{-C}_6\text{H}_4\text{Cl}_2 + \text{C}_6\text{H}_5\text{F}$		60 ^a	26.8	258.1	54.0 ^c	51.0	−10	221
	CS_2		60 ^a	10.0	271	58.9 ^c	56	−10.8	171
	C_2Cl_4		60 ^a	6.5	287.5	63.5 ^c	62.3	−4.6	171
	CS_2		60 ^a	9	295	64.8 ^c			171
	C_2Cl_4		60 ^a	11	344.5	75.2 ^c	70.6	−13.8	171
	C_2Cl_4		60 ^a	10.9	344.5	76.1 ^c	75.2	−1.7	171
R = H	$\alpha\text{-C}_6\text{H}_4\text{Cl}_2$	0.5 M	100 ^{a,b}	28.8	339.8	71.8			12
CH ₃	$\alpha\text{-C}_6\text{H}_4\text{Cl}_2$	0.5 M	100 ^{a,b}	29.8	341.2	72.0			12
C ₆ H ₅	$\alpha\text{-C}_6\text{H}_4\text{Cl}_2$	0.5 M	100 ^{a,b}	25.0	350.2	74.5			12

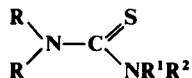
^a For explanations to footnotes see Table 1.

TABLE 18^a

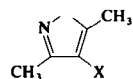
R'	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
A = S, R = H										
H	(CH ₃) ₂ NCHO	7 mol%	100 ^b	≈ 15	> 391	> 84.9 ^c				176
CH ₃	(CH ₃) ₂ NCHO	7 mol%	100 ^b	10.5	> 404	> 88.6 ^c				176
	[EtO(CH ₂) ₂] ₂ O	21 mol%	100 ^b	17.8	392	84.4 ^c				176
CH(CH ₃) ₂	[EtO(CH ₂) ₂] ₂ O	21 mol%	100 ^b	29	388	82.3 ^c				176
C(CH ₃) ₃	(CH ₃) ₂ NCHO	7 mol%	100 ^b	54.5	396	81.9 ^c				176
	[EtO(CH ₂) ₂] ₂ O	21 mol%	100 ^b	82	383	77.7 ^c				176
C ₆ H ₅	(CD ₃) ₂ NCDO	7 mol%	100 ^b	22.0	367	78.6 ^c				176
	[EtO(CH ₂) ₂] ₂ O	21 mol%	100 ^b	32	361	76.1 ^c				176
<i>p</i> -C ₆ H ₄ OCH ₃	[EtO(CH ₂) ₂] ₂ O	21 mol%	100 ^b	27	345	73.2 ^c				176
<i>p</i> -C ₆ H ₄ NO ₂	[EtO(CH ₂) ₂] ₂ O	21 mol%	100 ^b	35	365	76.9 ^c				176
240 SCH ₃	CDCl ₃		270 ^a	229	292	56.8 ^c	41.0	-54.3	43.0	223
A = S, R = CH₂CH₃										
H	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₂ N)		≥ 445	102.4 ^c				128
CH ₃	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₂ N)		≥ 397	86.1 ^c				128
	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₃)		≥ 384	86.5 ^c				128
C ₆ H ₅	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f (CH ₂)	47.5			79.0	11.7	81.9	107
	<i>o</i> -C ₆ H ₄ Cl ₂		100 ^f				82.3	27.2	85.3	107
Cl	Neat		100 ^b (CH ₂ N)	8.0	354	78.6 ^c				224
	C ₆ D ₆	0.01	100 ^b (CH ₂ N)	12.7	356.5	77.8 ^c				224
		0.01	100 ^b (CH ₃)	2.1	328	76.2 ^c				224
		0.03	100 ^b (CH ₂ N)	15.2	360	78.1 ^c				224
		0.03	100 ^b (CH ₃)	4.6	335	75.8 ^c				224
SCH ₃	CDCl ₃	4 M	100 ^a (CH ₂)	26.8	305.5	64.5 ^c				225
SFe(CO) ₂ Cp	CDCl ₃	1.5 M	100 ^a (CH ₃)	8.6	288.5	63.4 ^c				225
SSCSNEt ₂	CDCl ₃	1.5 M	100 ^a (CH ₃)	19.2	302	64.5 ^c				225
SSCSNEt ₂	CDCl ₃	0.7 M	100 ^b (CH ₃)		302	62.7 ^c	61.4	-3.3	64.0	220
	CDCl ₃		60 ^b (CH ₃)	11.6	294	65.7 ^c				226
A = S, R = <i>n</i>-C₃H₇										
Cl	CDCl ₃		60 ^b (CH ₂ N)	7.8	350	77.7 ^c				226
SSCSN(C ₃ H ₇) ₂	CDCl ₃		60 ^b (CH ₃)	6.8	290	66.0 ^c				226

241	H	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	A = S, R = CH(CH ₃) ₂		60 ^a (CH ₃)	≥427	102.8 ^c			128
	CH ₃	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f (CH ₃)		363			84.4	19.7	181
		<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH)		≥387	80.3 ^c				128
	C ₆ H ₅	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f (CH ₃)	46	333		69.4	−5.0	71.9	181
	CH ₂ C ₆ H ₅	<i>o</i> -C ₆ H ₄ Cl ₂		60 ^f (CH ₃)	40	378		82.8	11.7	85.3	181
					A = S, R = <i>n</i> -C ₄ H ₉						
	SSCSN(C ₄ H ₉) ₂	CDCl ₃		60 (CH ₃)	3.7	287	66.7 ^c				226
					A = S, R = <i>i</i> -C ₄ H ₉						
	H	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₃)		≥444	102.8 ^c				128
	CH ₃	<i>o</i> -C ₆ H ₄ Cl ₂	100 mg/500 μl	60 ^a (CH ₂)		≥384	84.9 ^c				128
	Cl	CDCl ₃		60 ^b (CH ₂)	7.3	337	74.9 ^c				226
	SSCSN(<i>i</i> -C ₄ H ₉) ₂	CDCl ₃		60 ^b (CH ₃)	6.7	279	63.5 ^c				226
					A = Se, R = H						
NH ₂	CH ₃ OH		60 ^b	6	239	51.8 ^c				453	
	(CD ₃) ₂ CO/(CD ₃) ₂ NCDO		100 ^b	34	257	53.5 ^c				196	
				A = Se, R = CH ₃							
SeCH ₂ SeCSeN(CH ₃) ₂	C ₆ D ₅ CD ₃		90 ^b	61	348	71.1				219	
NH ₂	CDCl ₃	0.94 mol%	100 ^a			60.9 ^d	57.3	−12.0	59.8	227	
				A = Te, R = CH ₃							
C ₆ H ₅	<i>o</i> -C ₆ H ₄ Cl ₂		<i>a</i>	0.95 ppm		80.5				228	

^a For explanations to footnotes see Table 1. See also references 543 and 550.

TABLE 19^a

R ¹	R ²	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
R = H											
H	H ^c	(CD ₃) ₂ CDO	3 mol%	100 ^b	43	264	54.3 ^c				196
		Pyridine- <i>d</i> ₅	1 M	60 ^a			57.3 ^c				229
		CH ₃ OH		60	10.2	227	47.2 ^c	41.4	-25		230
H	CH ₃	Pyridine- <i>d</i> ₅	1 M	60 ^{a,b}	53.9	273	55.6 ^{c,p}				229
		Pyridine- <i>d</i> ₅	1 M	60 ^{a,b}	55.6	223	45.1 ^{c,p}				229
		CH ₃ OH		60 ^a	18.6	203	42.6 ^c				230
H	C ₆ H ₅	(CD ₃) ₂ CO		60 ^a	48	253	51.8 ^c				230
H	COCH ₃	CH ₃ OH		60 ^a	120	> 403	> 82.3				230
H	CH ₂ CH ₃	Pyridine- <i>d</i> ₅	1 M	60 ^{a,b}	54.6	270	55.2 ^{c,p}				229
		Pyridine- <i>d</i> ₅	1 M	60 ^a	58.2	230	46.8 ^{c,p}				229
H	C(CH ₃) ₃	Pyridine- <i>d</i> ₅	0.5 M	60 ^{a,b}	102.9	251	49.7 ^{c,p}				229
		Pyridine- <i>d</i> ₅	0.5 M	60 ^a	83.6	228	45.6 ^{c,p}				229
CH ₃	CH ₃	(CD ₃) ₂ CO		60 ^a (CH ₃)	20.4	239	50.6 ^c	48.1	-12.5		230
		Pyridine- <i>d</i> ₅	1 M	60 ^a			50.2 ^c				229
R = CH₃											
H	H	CH ₃ OH		60 ^a	16.8	268	57.3 ^c	49.3	-29.3		230
		CHCl ₃ CHCl ₂	3.6 mol%	100 ^a	30		58.1 ^d	54.8	-11.6	57.3	213
		CF ₃ COOH		60 ^a		308	69.8 ^c				230
		Pyridine- <i>d</i> ₅		60 ^a			52.7 ^c				229
		Pyridine		60	28.0	248	51.8 ^c				231
H	CH ₃	CDCl ₃		60 ^b		211	44.3 ^c				232
		Pyridine- <i>d</i> ₅		60 ^a			44.7 ^c				229
H	C ₆ H ₅	CDCl ₃	0.7 M	60 ^a	27		48.1 (217 K)				232
H	<i>p</i> -C ₆ H ₄ NO ₂	Pyridine	0.9 M	60 ^a	23		48.1 (222 K)				232
H	<i>p</i> -C ₆ H ₄ Cl	Pyridine	2.6 M	60 ^a	33		43.9 (210 K)				232
H	<i>p</i> -C ₆ H ₄ CH ₃	(CD ₃) ₂ CO		60 ^a	6	213	45.1 ^c	36.4	-4		230
H	CH ₂ SO ₂ CH ₂ Ph	(CD ₃) ₂ SO		60	30	256	53.5 ^c				233
CH ₃	CH ₃	CH ₂ Cl ₂ /CHF ₂ Cl		50.3 ^b	55	134	26.3 ^c				199
CH ₃	C ₆ H ₅	CHCl ₃ F		60 ^b		193	39.8 ^c				232
C ₆ H ₅	C ₆ H ₅	CH ₂ Cl ₂	10% w/v	60 ^b	33	239	49.0 ^c				202



X = H
CH₃
Cl
NO₂

o-C₆H₄Cl₂
o-C₆H₄Cl₂
o-C₆H₄Cl₂
o-C₆H₄Cl₂

10% v/v
10% v/v
10% v/v
10% v/v

60^a
60^a
60^a
60^a

24.4
22.2
23.6
29.4

336.9
329.4
339.2
389.6

71.5^c
70.2^c
72.3^c
82.8^c

234
234
234
234



X = H
C(CH₃)₃

o-C₆H₄Cl₂
o-C₆H₄Cl₂

10% v/v
10% v/v

60^a
60^a

10.4
36.6

293.2
437

64.0^c
92.4^c

234
234



X = H
C₆H₅

o-C₆H₄Cl₂
o-C₆H₄Cl₂

10% v/v
10% v/v

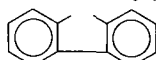
60^a
60^a

10.2
18.5

295.2
340.6

64.4^c
73.2^c

234
234



CH₂Cl₂

10% v/v

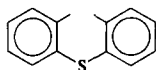
60^b

20

308

64.0^c

202



CH₂Cl₂

10% v/v

60^b

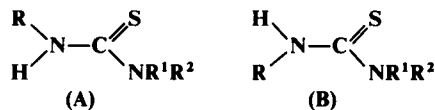
19.2

197

41.0^c

202

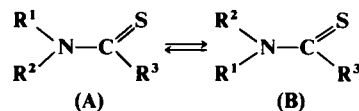
^a For explanations to footnotes see Table 1. See also reference 464 for metal complexes of Et₂NCXNHCO₂C₆H₅ (X = S, Se); see 80 for thiourea in ethylacetate and acetonitrile.

TABLE 20^a

R ¹	R ²	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
R = CH ₃											
H	H	CH ₃ OH	1 M	60 ^a (CH ₃)	12	285	63.1 ^c	63	−0.4	65.6	235
		Pyridine- <i>d</i> ₅		60 ^a (NH)	36.5	294	61.4 ^c				229
H	CH ₃	CH ₃ OH		60	≈ 232	≈ 49.3	235				
		Pyridine- <i>d</i> ₅		60 ^a		53.1 ^c	229				
R = CH ₂ CH ₃											
H	H	Pyridine- <i>d</i> ₅	1 M	60 ^a (NH)	33.3	282	58.9 ^c				229
H	C ₂ H ₅	Pyridine- <i>d</i> ₅		60		48.9 ^c	229				
R = CH(CH ₃) ₂											
H	CH(CH ₃) ₂	CH ₂ Cl ₂		60 ^b (CH ₃)	3.5	205	46.0 ^c				236
		Pyridine- <i>d</i> ₅		60 ^a		48.1 ^c	229				
R = C(CH ₃) ₃											
H	H	Pyridine	0.5 M	60	13.0	248	53.5 ^c	42.2	−16.7		231
		Pyridine- <i>d</i> ₅		60 (NH)	12.9	247	53.1 ^c				229
H	CH ₃	Pyridine- <i>d</i> ₅	1 M	60 ^a			48.9 ^c				229
H	C(CH ₃) ₃	CH ₂ Cl ₂		60 ^{a,c} (CH ₃)	10.8	223	46.4 ^c				230
		CDCl ₃	5%	60 ^a (CH ₃)	13	217	46.4 ^c				237

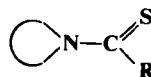
H	H	CD ₃ CN	60	$R = CH_2C(CH_3)_3$ 267 300	63.1 ^c			231
H	C ₆ H ₅	CDCl ₃	60 ^b (NH)	$R = C_6H_5$ 38 215	43.9 ^c			236
H	<i>p</i> -C ₆ H ₄ CH ₃	(CD ₃) ₂ CO	60 ^a (CH ₃)	$R = p-C_6H_4CH_3$ 12 223	46.4 ^c	42.6	- 16.7	230
H	<i>o</i> -C ₆ H ₄ CH ₃	CDCl ₃	60 ^b (CH ₃)	$R = o-C_6H_4CH_3$ 13 231	48.5 ^c			236
H	<i>o,o</i> -C ₆ H ₃ (CH ₃) ₂	CDCl ₃	60 ^b (CH ₃)	$R = o,o-C_6H_3(CH_3)_2$ 12.5 323	70.2 ^c			236
H	<i>o,o,p</i> -C ₆ H ₂ Pr ⁱ ₃	Decalin	60 ^b (Hm)	$R = o,o,p-C_6H_2Pr^i_3$ 12.0 397	87.4 ^c			236

^a For explanations to footnotes see Table 1. See also reference 542 for the structure of the conformational isomers in alkylated thioureas.

TABLE 21^a

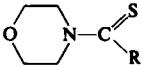
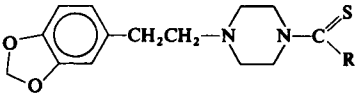
R ¹	R ²	R ³	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Log A	Reference
H	CH ₃	H	C ₆ D ₆	7.5 mol%	60 ^{f,k}			(A) 99.6, (B) 96.6 ^d					69
			CDCl ₃ -C ₆ D ₆	3 mol%	60 ^{f,k}			(A) 102.4, (B) 97 ^d	99.5	-9.6	102	12.7	69
H	CH ₂ C(CH ₃) ₃	H	CCl ₄	14 mol%	60 ^{f,k}			(A) 102.4, (B) 101.2 ^d	102.8	0.84	105.3	13.3	69
			C ₆ H ₄ Cl _{2-o}	14 mol%	60 ^{g,h} (CH)	31.5	447	(A) 103.2, (B) 102.0 ^d	116.6	44.7	119.1	15.6	69
H	CH ₂ C ₆ H ₅	H	CDCl ₃	10 mol%	60 ^{f,k}			(A) 101.2, (B) 97 ^d	86.1	-50.2	88.6	10.6	69
H			C ₆ D ₆	3 mol%	60 ^{f,k}			(A) 99.9, (B) 96.1 ^d	106.6	21.3	108.7	14.4	69
H	C ₆ H ₄ N(CH ₃) _{2-p}	SCH ₃	CDCl ₃	0.5 M	100 ^a (CH ₃ S)	11.4	267	(A) 61.9 ^c					238
H	C ₆ H ₄ OCH _{3-p}	SCH ₃	CDCl ₃	0.5 M	100 ^a (CH ₃ S)	10.8	256	(A) 60.2 ^c					238
	C ₆ H ₄ N(CH ₃) _{2-p}	OCH ₃	CDCl ₃	0.5 M	60 ^a (CH ₃ O)	3.5	288	(A) 68.1 ^c					238
H	CH ₂ C ₆ H ₄ OCH _{3-p}	OCH ₃	C ₂ Cl ₄		100 ^a			73.2 (329 K)	64.0	-25.1			239
H	CH ₂ CH ₂ C ₆ H ₅	OCH ₂ C ₆ H ₅	C ₂ Cl ₄		100 ^a			72.7 (320 K)					239
CH ₃	CH ₂ C ₆ H ₅	SSCN-CH ₃ S-CH ₂ C ₆ H ₅	CDCl ₃		60 ^b CH ₂ C ₆ H ₅	8.2	289	65.3 ^c					226
	CH ₂ C ₆ H ₅	C ₆ H ₄ Cl _{2-o}	C ₆ H ₄ Cl _{2-o}	0.6 M	60 ^b CH ₃ 60 ^{g,h}	4.8	283	65.2 ^c 99 (325 K)					226 72
CH ₂ CH ₃	CH ₂ C ₆ H ₅	SSCN-C ₂ H ₅ S-CH ₂ C ₆ H ₅	CDCl ₃		60 ^b CH ₂ C ₆ H ₅	9.9	289	64.9 ^c					226
CH ₂ C=CH ₂ CH ₃	CH ₃	SC ₂ H ₅	(CH ₃) ₂ SO		60 ^b CH ₃ CH ₂ N ^b	11.0 25.6	289 327	64.6 ^c 69.5 ^c					226 240
	CH ₂ CH ₃	SC ₂ H ₅	(CH ₃) ₂ SO		CH ₂ N ^b		29.0	321	67.8 ^c				240
	CH(CH ₃) ₂	SC ₂ H ₅	(CH ₃) ₂ SO		$p_A - p_B$ = 0.1 CH ₂ N ^b		24.7	315	68.2 67.0 ^c				240
					$p_A - p_B$ = 0.18 CH ₂ N ^b				67.8 79.8 ^c				240
OCH ₃	CH ₃	OC ₆ H ₅	(CD ₃) ₂ SO		60 (CH)	15.6	368	81.9 ^c					192
OCH ₃	C ₆ H ₅	H	CDCl ₃		60 (CH)	7.0	233	69.4 ^c					192
OH	CH ₃	CH ₃	(CD ₃) ₂ SO		60 (CH ₃ N)	3.0	374	86.5 ^c					192

^a For explanations to footnotes see Table 1. See also references 516 and 498 for ¹H and ¹³C NMR parameters of thioamide and thioxamide derivatives.

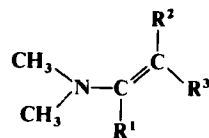
TABLE 22^a

R	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	Reference
 R = CH ₂ C ₆ H ₅ C ₆ H ₅ <i>p</i> -C ₆ H ₄ NO ₂ <i>p</i> -C ₆ H ₄ Cl <i>p</i> -C ₆ H ₄ OCH ₃ CH=CHC ₆ H ₅ <i>p</i> -CH=CHC ₆ H ₄ Cl <i>p</i> -CH=CHC ₆ H ₄ OCH ₃	<i>o</i> -C ₆ H ₄ Cl ₂	1 <i>M</i>	60 ^b	50.5	388	80.7 ^c			167
	<i>o</i> -C ₆ H ₄ Cl ₂	0.3 <i>M</i>	80 ^b (CH ₂ N)	65.0	389.2	80.4 ^c			241
	<i>o</i> -C ₆ H ₄ Cl ₂	0.3 <i>M</i>	80 ^b (CH ₂ N)	76.0	353.5	72.0 ^c			241
	<i>o</i> -C ₆ H ₄ Cl ₂	1 <i>M</i>	60 ^b	58.0	352	72.3 ^c			167
			22.6 (¹³ C) ^b	59.0	353	72.6 ^c			167
	<i>o</i> -C ₆ H ₄ Cl ₂	Saturated	60 ^b	57.0	362	74.8 ^c			167
	<i>o</i> -C ₆ H ₄ Cl ₂	1 <i>M</i>	60 ^b	55.5	347	71.5 ^c			167
	<i>o</i> -C ₆ H ₄ Cl ₂	1 <i>M</i>	60 ^b	51.0	324	66.9 ^c			167
	<i>o</i> -C ₆ H ₄ Cl ₂	0.3 <i>M</i>	80 ^b (CH ₂ N)	47.0	317.5	65.7 ^c			241
	<i>o</i> -C ₆ H ₄ Cl ₂	0.3 <i>M</i>	80 ^b (CH ₂ N)	48.5	318.7	65.8 ^c			241
	<i>o</i> -C ₆ H ₄ Cl ₂	0.3 <i>M</i>	80 ^b (CH ₂ N)	50.0	312.7	64.5 ^c			241
SSCSN	CDCl ₃	0.7 <i>M</i>	100 ^a (CH ₂ N)	13.4	268.5	58.1 ^c			220
SCSN	CDCl ₃	0.7 <i>M</i>	100 ^a (CH ₂ N)	39.3	307	64.0 ^c			220

TABLE 22 (cont.)

R	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	Reference
									
R = C ₆ H ₅	<i>o</i> -C ₆ H ₄ Cl ₂	Saturated	22.6 (¹³ C) ^b	67.5	338	69.0 ^c			167
C ₆ H ₄ NO ₂ - <i>p</i>	<i>o</i> -C ₆ H ₄ Cl ₂	Saturated	22.6 (¹³ C) ^b	51.0	347	71.9 ^c			167
C ₆ H ₄ OCH ₃ - <i>p</i>	<i>o</i> -C ₆ H ₄ Cl ₂	Saturated	22.6 (¹³ C) ^b	63.0	312	63.5 ^c			167
									
R = C ₆ H ₅	CDCl ₃	0.25 M	60 ^a (CH ₂ - <i>o</i>)	59.4		72.6 ^d	71.8	-3.0	209
<i>p</i> -C ₆ H ₄ Cl	Pyridine- <i>d</i> ₅	0.25 M	60 ^a (CH ₂ - <i>o</i>)	56.4		73.5 ^d	74.0	1.6	209
<i>p</i> -C ₆ H ₄ OCH ₃	Pyridine- <i>d</i> ₅	0.25 M	60 ^a (CH ₂ - <i>o</i>)	56.4		68.2 ^d	68.1	-0.3	209
<i>p</i> -C ₆ H ₄ NO ₂	Pyridine- <i>d</i> ₅	0.25 M	60 ^a (CH ₂ - <i>o</i>)	57.0		76.2 ^d	76.4	0.7	209

^a For explanations to footnotes see Table 1. See reference 486 for an interpretation of coalescence phenomena in *N*-thiobenzoylmorpholines.

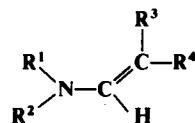
TABLE 23^a

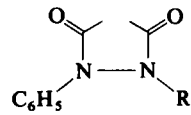
R ¹	R ²	R ³	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
H	H	H	(CH ₃) ₂ O		25.2 (¹³ C) ^b	199	183	34.7 ^c				134
H	H	NO ₂	Pyridine		90 ^a	27.5			53.1	54.7	55.6	242
H	H	NO ₂	CHCl ₃		90 ^a	29.5			60.2	29.7	62.7	242
H	H	NO ₂	(CD ₃) ₂ SO		90 ^a	29.5			74.0	4.2	76.9	242
H	H		C ₂ D ₂ Cl ₄	1%	90 ^b	19.9	308	65.7 ^c				159
H	H	CSCl ₃	CDCl ₃	6%	100 ^b		325	68.6 ^c				243
H	H	N(CH ₃) ₂	(CD ₃) ₂ CO		25.2 (¹³ C) ^b	184	253	48.9 ^c				134
H	H	C ₆ H ₅	(CH ₃) ₂ O		25.2 (¹³ C) ^b	209	186	35.1 ^c				134
H	H	CH=C(CO ₂ CH ₃) ₂	CD ₃ OD	0.65 M	100 ^{b,f}	20.5	286	61.0 ^c				244
H	H	CH=C(NO ₂)CO ₂ CH ₃	CH ₃ CN	0.65 M	100 ^b	17.1	331	71.7 ^c				244
H	C ₆ H ₅	CSCl ₃	CDCl ₃		80 ^b	49.8	300	57.3 ^c				245
H	CO ₂ CH ₃	CO ₂ CH ₃	CD ₃ OD	0.65 M	100 ^b	38.1	266	55.0 ^c				244
	COCH ₃	COCH ₃	CDCl ₃	0.65 M	100 ^f	55.1	265	53.9 ^c				246
H			C ₆ F ₅ CF ₃		90 ^a	19.5			87.4	107.8	89.4	242
			(CH ₃) ₂ CO		90 ^a				55.6	-10.4	58.1	242
H												

TABLE 23 (cont.)

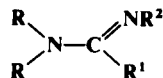
R ¹	R ²	R ³	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
		R = H	(C ₆ H ₅) ₂ O		60 ^b	22	402	86.2 ^c				65
		CH ₃	(C ₆ H ₅) ₂ O		60 ^b	48.5	419	87.6 ^c				65
			(C ₆ H ₅) ₂ O		60 ^a			88.8 ^c				65
		C ₆ H ₅	(C ₆ H ₅) ₂ O		60 ^b	56	433	90.0 ^c				65
		COCH ₃	(C ₆ H ₅) ₂ O		60 ^b	45.5	445	92.9 ^c				65
CH ₃	COOC ₂ H ₅	CN	CD ₂ Cl ₂		60 ^a	9	230	44.9 ^d	62.2	58.1	64.7	247
	CN	COOC ₂ H ₅	CD ₂ Cl ₂		60 ^a	8.4	258	55.3 ^d	64.2	33.4	66.7	247
C ₆ H ₅	H	CH=C(NO ₂)CO ₂ CH ₃	CDCl ₃	0.65 M	100 ^b	36.7	306	64.0 ^c				244
N(CH ₃) ₂	COOCH ₃	CN	C ₆ H ₅ F		100 ^a	51		59.4				248
N(CH ₃) ₂	CN	COOCH ₃	C ₆ H ₅ F		100 ^a	28.7		57.3				248
N(CH ₃) ₂	CN	CN	CDCl ₃		60 ^b	15.0	202.6	43.0 ^c				248
N(CH ₃) ₂	C ₆ H ₅	COCH ₃	CDCl ₃ /CS ₂	1/1 v/v	60 ^b	14.5	295	63.5 ^c				248
N(CH ₃) ₂	C ₆ H ₅	CN	C ₆ H ₅ F		100 ^a	58		51.2 ^d	42.2	-20.5	44.3	248
N(CH ₃) ₂	CN	C ₆ H ₅			100 ^a	15		54.5 ^d	38.9	-47.6	40.5	248

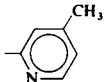
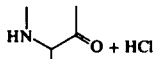
^a For explanations to footnotes see Table 1. See also references 496 and 517 for solvent and substituent effects on the rotational barriers in substituted phenyl- β -dimethylamino vinylthioketones; see reference 499 for bis(dimethylamino)polymethinium salts.

TABLE 24^a

R ¹	R ²	R ³	R ⁴	Solvent	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	Reference
CH ₂ CH ₃	CH ₂ CH ₃	C ₆ H ₅	CSC ₆ H ₅	CDCl ₃	80 ^b	33.9	283	58.9 ^c	245
CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	C ₆ H ₅	CSC ₆ H ₅	CDCl ₃	80 ^b	28.6	268	56.0 ^c	245
		C ₆ H ₅	CSC ₆ H ₅	CDCl ₃	80 ^b	57.2	242	48.9 ^c	245
		C ₆ H ₅	CSC ₆ H ₅	CDCl ₃	80 ^b	44.3	273	56.0 ^c	245
		C ₆ H ₅	CSC ₆ H ₅	CDCl ₃	80 ^b	70.9	303	61.4 ^c	245
CH ₃	CH ₂ C ₆ H ₅								
(E)	CH ₂ C ₆ H ₅	R = CH ₃			(C ₆ H ₅) ₂ O	60 ^b	416	87.5 ^c	65
(Z)	CH ₂ C ₆ H ₅				(C ₆ H ₅) ₂ O	60 ^b		86.8 ^c	65
(E)	CH ₂ C ₆ H ₅	C ₆ H ₅			CDCl ₃	60 ^k		91.5 ^e	65
(Z)	CH ₂ C ₆ H ₅	C ₆ H ₅			CDCl ₃	60 ^k		90.2 ^e	65
(E)	CH ₂ C ₆ H ₅	H			C ₂ HCl ₅	60 ^b	31.5	85.3 ^c	65
(Z)	CH ₂ C ₆ H ₅	H				60 ^b		84.5 ^c	65

^a For explanations to footnotes see Table 1. See also reference 518 for (R)₂NCH=CHCSAr; see 522 for a study of the structural properties of the conformational isomers of enamino-ketones-esters and -amides by nitrogen NMR.

TABLE 25^a

R ¹	R ²	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Log <i>A</i>	Reference
R = CH ₃												
C ₃ H ₄ N- α	COCF ₃	CHCl ₃	0.75%	100 ^a	8	318	70 ^c	117.7	35			249
C ₃ H ₄ N- γ	COCF ₃	CHCl ₃	0.75%	100 ^a	17.6	325	69.6 ^c	76.3	5			249
CH ₃	COCF ₃	CCl ₄	10%	100 ^a	16	335	71.9 ^c	70.2	-4	72.7	12.2	250
C ₆ H ₅	COCF ₃	CHCl ₃	0.5%	100 ^a	5.2	367	75.7 ^c	69.4	-16.7	71.9	12.3	250
H	COCl ₃	CCl ₄	0.5%	100 ^a	4.2	398	90.7 ^c	45.3	-117	47.6	6.8	250
C ₆ H ₅	COCl ₃	C ₂ Cl ₄	10%	100 ^a	34	323	67.3	60.6	+21	63.1	12.0	250
C ₃ H ₄ N- β	COCl ₃	CHCl ₃	0.75%	100 ^a	11.2	308	67.5 ^c	84.2	13			249
252												
H		(CD ₃) ₂ SO	60 ^b	4.5	351	79.8 ^c						251
H		CDCl ₃	60 ^b	4.0	322	73.2 ^c						251
CH ₃		CDCl ₃	60 ^b	4.5	246	55.2 ^c						251
253												
C ₆ H ₅	H	CHF ₂ Cl		60 ^a	14.8	214	46.0 ^c	47.7	8.8	49.7	13.6	252
C ₆ H ₅	PS(OCH ₃) ₂	(CD ₃) ₂ SO		^b	22	353	75.2 ^c					253
H	C ₆ H ₅ (<i>E</i>)	CDCl ₃	40% v/v	25.2 (¹³ C) ^b	145	318	62.3 ^c					24
				100 ^b	7.8	278	61.4 ^c					24
CH ₂ CH ₃	C ₆ H ₅ (<i>E</i>)	CH ₂ =CCl ₂	40% v/v	25.2 (¹³ C) ^b	11	213	46.0 ^c					24
C ₆ H ₅	C ₆ H ₅ (<i>E</i>)	CDCl ₃	40% v/v	25.2 (¹³ C) ^b	53	261	53.5 ^c					24
CH=CHCH ₃ (<i>E</i>)	C ₆ H ₅ (<i>E</i>)	CH ₂ =CCl ₂	40% v/v	25.2 (¹³ C) ^b	20	233	49.3 ^c					24
	(<i>Z</i>)	CH ₂ =CCl ₂	40% v/v	25.2 (¹³ C) ^b	24	176	36.4 ^c					24
254												
				D ₂ O	0.1 <i>M</i>	100 ^b	11	298.7	65.3 ^c			254
				D ₂ O	0.1 <i>M</i>	100 ^b	2.6	320	74.1 ^c			254

H	C ₆ H ₅ (E)	CH ₂ =CCl ₂	40% v/v	25.2 (¹³ C) ^a (CH ₂)	R = CH₂CH₃		59.8 ^c			24
H		CH ₂ =CCl ₂	40% v/v	100 ^b	160	304	58.9 ^c			24
					16.8	275				
					R = CH(CH₃)₂					
C ₆ H ₅	C ₆ H ₅	CDCl ₃		60 ^f	54	259	52.7 ^c	52.7	0	255
C ₆ H ₅	C ₆ H ₅ NO ₂ -p	CDCl ₃		60 ^f	48	283	58.1 ^c	55.6	0	255
					R,R = 					
C ₆ H ₅	C ₆ H ₅	CDCl ₃		60 ^f	65	251	50.6 ^c	51.4	0	255
C ₆ H ₅	C ₆ H ₅ NO ₂ -p	CDCl ₃		60 ^f	55.5	268	54.8 ^c	74.0	71	255
C ₆ H ₅	C ₆ H ₅ OCH ₃ -p	CDCl ₃		60 ^f	66	256	51.4 ^c	67.7	62.7	255
C ₆ H ₅ OCH ₃ -p	C ₆ H ₅	CDCl ₃		60 ^f	62	243	48.9 ^c	37.2	46.0	255
					R,R = 					
CH ₃	C ₆ H ₅	CS ₂		25.16 (¹³ C) ^a			45.7			207
C ₆ H ₅	C ₆ H ₅	CHF ₂ Cl		25.16 (¹³ C) ^a			43.5			207

^a For explanations to footnotes see Table 1. See also references 465 and 477.

TABLE 26^a

Compound			Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
R ¹	R ²	X, Y										
254	H	H	<i>r</i> -NO ₂ , <i>o</i> -OCH ₃	C ₆ D ₅ CD ₃	15 mol%	100 ^b	336	236	44.3 ^c			256
			<i>o</i> -NO ₂ , <i>p</i> -OCH ₃	(CD ₃) ₂ CO		60 ^b	36	188	38.9 ^c			257
			<i>p</i> -NO ₂ , <i>o</i> -CH ₃	(CD ₃) ₂ CO		60 ^b	30	187	38.9 ^c			257
			<i>o</i> -NO ₂ , <i>p</i> -NO ₂	(CD ₃) ₂ CO		60 ^b	48	197	40.5 ^c			257
			<i>o</i> -NO ₂ , <i>p</i> -NO ₂	(CD ₃) ₂ CO		60 ^b	12	233	51.4 ^c			257
			<i>o</i> -CN	(CD ₃) ₂ CO		60 ^b			35.9 ^c			257
	CH ₃	H	(CH ₃) ₂ O		25.16 (¹³ C) ^b (H α)	150	158	30.3	31.8	8.4		258
			CHFCl ₂ /CHF ₂ Cl		50.3 (¹³ C) ^b (H α)	278	138	25.5				199
		<i>p</i> -OCH ₃	CHF ₂ Cl		25.16 (¹³ C) ^b			23.8				259
		<i>p</i> -F	(CH ₃) ₂ O		25.16 (¹³ C) ^a			28.8				259
		<i>p</i> -Cl	(CH ₃) ₂ O		25.16 (¹³ C) ^b			32.2				259
		<i>p</i> -COCH ₃	(CH ₃) ₂ O		25.16 (¹³ C) ^b			39.5				259
		<i>p</i> -NO ₂	(CD ₃) ₂ CO		25.16 (¹³ C) ^b			46.4				258
			(CD ₃) ₂ CO		50.3 (¹³ C) ^b (H α)	320	243	45.6				199
	NH ₂	H	(CH ₃) ₂ O		25.16 (¹³ C) ^a (H α)	93.1		28.8				260
	CH ₂ CH ₃	H	(CH ₃) ₂ O		25.16 (¹³ C) ^b			30.1				259
		<i>o,o,p</i> -(NO ₂) ₃	CH ₂ Cl ₂		60 ^a (Ar)	27.2		43.9 ^d	58.1	48.5	60.7	261
	CH(CH ₃) ₂	H	(CH ₃) ₂ O		25.16 (¹³ C) ^b (H α)			28.4				259
		<i>o,o,p</i> -(NO ₂) ₃	CH ₂ Cl ₂		60 ^a (Ar)	30.8		38.5 ^d	52.2	46.0	54.7	261
	<i>n</i> -C ₄ H ₉	<i>o,o,p</i> -(NO ₂) ₃	CH ₂ Cl ₂		60 ^a (Ar)	26.9		45.1 ^d	57.3	41.8	59.8	262
	C(CH ₃) ₃	H	CCl ₂ F/CHFCl ₂		25.16 (¹³ C) ^b (H α)			26.3				259
	CH ₃	<i>o</i> -NO ₂ , <i>p</i> -CO ₂ CH ₃	CHF ₂ Cl		25.16 (¹³ C) ^b	100	136	26.3				263
	CH ₃	NO	C ₆ D ₅ CD ₃ /CH ₂ =CHCl		100 ^b	7.1	185.5	41.4 ^c				264
	CH ₃	CHO	C ₆ D ₅ CD ₃ /CH ₂ =CHCl		100 ^b	5.4	148	32.6 ^c				264
		COCH ₃	C ₆ D ₅ CD ₃ /CH ₂ =CHCl		100 ^b	8.2	139	30.1 ^c				264

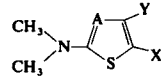
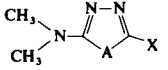
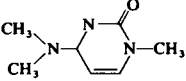
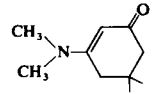
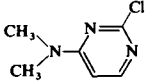
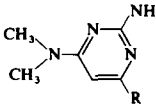
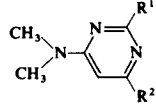
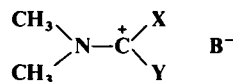
											
A	Y	X									
CH	NO ₂	H	CHF ₂ Cl	25.16 (¹³ C) ^a	67	130	25.5 ^c				263
		CO ₂ CH ₃	CHF ₂ Cl	25.16 (¹³ C) ^a	56	161	32.2 ^c				263
		COCH ₃	CHF ₂ Cl	25.16 (¹³ C) ^a	50	173	35.5 ^c				263
		NO ₂	CHF ₂ Cl	100 ^a	4.2	167	36.8 ^c				263
	H	NO ₂	CHF ₂ Cl	100 ^a	1.4	168	38.9 ^c				263
N	H	H	CHF ₂ Cl	60 ^a	7.7	149.5	32.2 ^c				265
		Br	CHF ₂ Cl	60 ^a	9.9	151	32.2 ^c				265
		NO ₂	CHF ₂ Cl	60 ^a	12.4	241.5	51.8 ^c	49.3	− 12.5	51.4	265
											
A	X										
O	NO ₂		Pyridine- <i>d</i> ₅ /CD ₂ Cl ₂ , 2/1	60 ^a	11.0	205.2	44.3 ^c	35.1			266
	CN		Pyridine- <i>d</i> ₅ /CD ₂ Cl ₂ , 2/1	60 ^a	13.4	201.7	43.1 ^c	33.9	− 44.7		266
	CO ₂ C ₂ H ₅		Pyridine- <i>d</i> ₅ /CD ₂ Cl ₂ , 2/1	60 ^a	18.2	187.6	39.3 ^c	30.9			266
S	NO ₂		Pyridine- <i>d</i> ₅ /CD ₂ Cl ₂ , 2/1	60 ^a	19.2	224.9	47.7 ^c	38.0	− 42.6		266
	CN		Pyridine- <i>d</i> ₅ /CD ₂ Cl ₂ , 2/1	60 ^a	20.7	214.1	45.1 ^c	35.9			266
	CO ₂ C ₂ H ₅		Pyridine- <i>d</i> ₅ /CD ₂ Cl ₂ , 2/1	60 ^a	25.4	203.0	42.2 ^c	33.4			266
											
			CDCl ₃	0.4 M	60 ^a	8.6	283	62.3 ^c	31.3	73.6	267
			CD ₃ OH	0.4 M	60 ^a	3.4	278	63.1 ^c	0.8	65.6	268
											
			CD ₂ Cl ₂	10% w/w	60 ^a	8.8		51.4 ^d	67.5	55.3	269
			(CD ₃) ₂ CO	5% w/w	60 ^a	13.3	240	50.6 ^c		69.9	269

TABLE 26 (cont.)

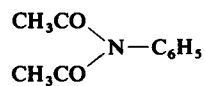
Compound	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
	CH ₂ Cl ₂ /CDCl ₃		100 ^a	15.6	264	56.4 ^c				270
										
R = CH ₃	CDCl ₃		90 ^a		276	61.4 ^c	75.2	50		271
Cl	CDCl ₃		90 ^a		243	52.8 ^c	44.8	-33		271
OH	CDCl ₃		90 ^a		230	52.7 ^c	41.6	-48		271
NH ₂	CD ₃ OD		90 ^a		190	52.3 ^c	23.3	-153		271
										
R ¹	R ²									
H	H		100 ^{a,d}	13.4	247	53.5 ^c	52	-8		272
Cl	H		100 ^a	10.2	268	58.6 ^c	59	4		272
Cl	NO ₂		100 ^f	42.6	253	51.9 ^c				272
N(CH ₃) ₂	H		100 ^f (CH ₃ N)	15.2	232	49.4 ^c				272

^a For explanations to footnotes see Table 1. See also reference 466 for *N,N*-dimethylaminopyrimidine hydrochlorides and reference 467 for *N*-acetyl-*N*-ethoxycarbonylmethyl-2-amino-5-nitrothiophen. See reference 504 for solvent effects on the rotational barrier about the Ar-NO bond in nitrosoanilines; 538 for CNDO/2 computations on aniline; 494 for 3-aryl-2-benzyl-4(3*H*)-quinazolinones; 506 for rotational barriers about the Ar-NO bond in dialkylaminonitrosobenzenes; 482 for isomerization processes in 1,8-bisdimethylamino- and 1-benzylmethylamino-8-dimethylaminonaphthalene; 547 for rotational barriers about the C-N bond in *N*-aryl imides; 483 for solvent effects on the rotation barrier in *N*-methylaniline; 489 for experimental and theoretical values of the energy barriers for rotation of the *N,N*-dimethylamino group in aromatic and hetero aromatic systems.

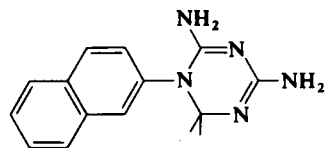
TABLE 27^a

X	Y	B	Solvent	C	ν_0 (MHz) nucleus Analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Log A	Reference
NH ₂	CD ₃	NO ₃	(CD ₃) ₂ SO	3.1 mol%	60 ^a			89.8 ^d	86.5	-10.9	89	12.7	130
NH ₂	CD ₃	NO ₃	CHCl ₂ CHCl ₂	0.4 mol%	60 ^a			92.4 ^d		19.2	100.3	14.2	129
NH ₂	CD ₃	Cl	(CD ₃) ₂ SO	7.4 mol%	60 ^a			91.1 ^d	92.8	5.9	95.3	13.5	130
			CHCl ₂ CHCl ₂	0.4 mol%	60 ^a			90.7 ^d		7.9	95.3	13.6	129
N(CH ₃) ₂	H	Cl	CDCl ₃	2 M	25.2 (¹³ C) ^b	159.4	337	64.4 ^e					273
N(CH ₃) ₂	CH ₃	CH ₃ SO ₃	CDCl ₃	1.5 M	25.2 (¹³ C) ^b	67.0	227	44.2 ^e					273
N(CH ₃) ₂	OCH ₃	OSO ₂ F	CDCl ₃	1.5 M	25.2 (¹³ C) ^b	34.5	213	42.6 ^e					273
N(CH ₃) ₂	SCH ₃	OSO ₂ F	CDCl ₃	1.5 M	25.2 (¹³ C) ^b	26.0	195.5	39.3 ^e					273
N(CH ₃) ₂	SCH ₃	I	CH ₂ Cl ₂	10% w/v	60 ^b	7.2	198	43 ^e					202
N(CH ₃) ₂	NHC ₆ H ₅	Cl	CDCl ₃	1 M	60 ^b	29.5	229	47.5 ^e					273
N(CH ₃) ₂	N(CH ₃)C ₆ H ₄ R	I											
	R = H		CD ₃ NO ₂		60 ^b	16	301	64.8 ^e					274
	Cl		CD ₃ NO ₂		60 ^b	16	304	65.6 ^e					274
	N(CH ₃) ₂		CD ₃ NO ₂		60 ^b	14	282	60.4 ^e					274
	CN		CD ₃ NO ₂		60 ^b	17	325	69.8 ^e					274
	NO ₂		CD ₃ NO ₂		60 ^b	18	328	71.1 ^e					274
N(CH ₃) ₂	N(CH ₂ C ₆ H ₄ R) ₂	Cl											
	R = H		CDCl ₃		60 ^b	3.0	276	61.0 ^e					275
	p-CH ₃		CDCl ₃		60 ^b	4.0	298.7	65.6 ^e					275
	o-CH ₃		CDCl ₃		60 ^b	9.0	297	63.1 ^e					275
N(C ₂ H ₅) ₂	H	Cl	CDCl ₃	2 M	25.2 (¹³ C) ^b	192.0	342	66.8 ^e					273
N(C ₂ H ₅) ₂	OCH ₃	OSO ₂ F	CDCl ₃	1 M	25.2 (¹³ C) ^b	32	199	41.0 ^e					273
N(C ₂ H ₅) ₂	N(CH ₃) ₂	Cl	CH ₂ Cl ₂	0.8 M	60 ^b	4.6	301	66.0 ^e					273
N(C ₂ H ₅) ₂	N(C ₂ H ₅) ₂	Cl	CDCl ₃	1.5 M	25.2 (¹³ C) ^b	14.0	308	64.0 ^e					273

^a For explanations to footnotes see Table 1. See also reference 485 for 1-dimethylamino-3-dimethyliminio-2- (parasubstituted phenyl) propene perchlorates. See 519 for DNMR investigations of uronium and thiuronium salts.

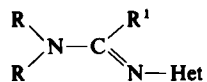
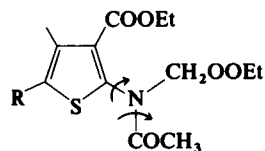
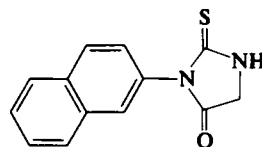
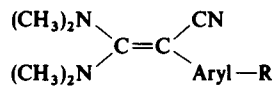
TABLE 28^a

and protonated forms (276)

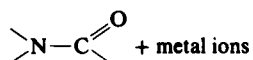
 $\Delta G^\ddagger = 96.6$ (277)

L-Pro-L-4-Hyp

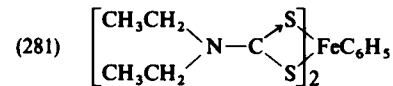
(74)

R = CH₃, C₂H₅ R¹ = H, CH₃ (251)R = COCH₃, COEt
 $\Delta G^\ddagger = 52-56$ and $71-76$ (278) $\Delta G^\ddagger = 90.7$ (277)

Thiamin and 2-(1-hydroxyethyl)thiamin (282)

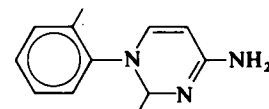


(117, 283-285)

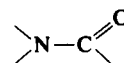


(281)

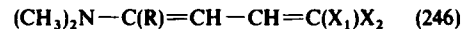
(89)



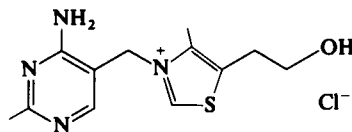
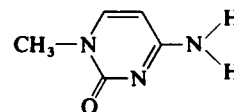
HCl (63)



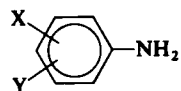
on carboranes (289)



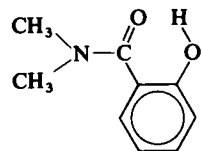
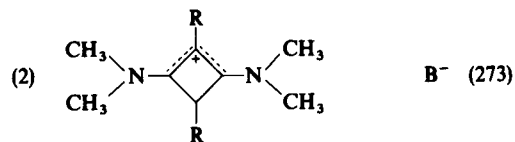
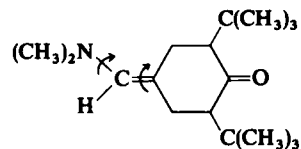
(246)

H₂O, low pH (286)

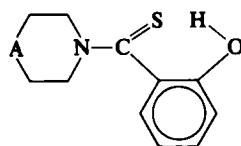
(290)



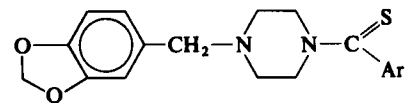
$$\Delta G^\ddagger \approx 33-52 \quad (257)$$



and Li salt $(279, 280)$

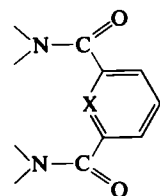


$A = CH_2, O \quad (287, 288)$

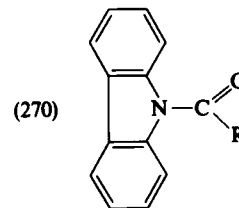
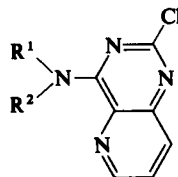


corresponding N—CO in Table 14 (209)

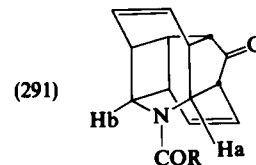
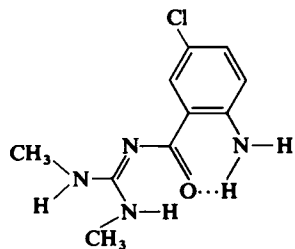
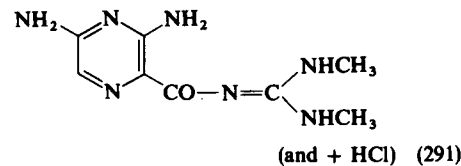
259



$X = N, CH, CNO_2 \quad (164)$

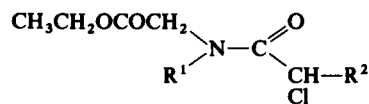


$R = H, CH_3, C_2H_5, i-C_3H_7, i-C_4H_9, CF_3, C_6H_5$
 $\Delta G^\ddagger = 29.7-62.7 \quad (294)$

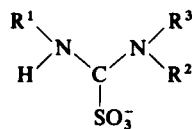


$R = H, CH_3, OC_2H_5$
 $\Delta G^\ddagger = 79-96 \quad (295)$

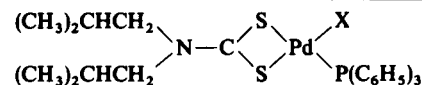
TABLE 28 (cont.)



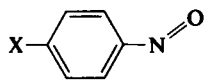
$$\begin{aligned} \text{R}^2 &= \text{H, Cl} \\ \text{R}^1 &= \text{alkyl} \\ \Delta G^\ddagger &= 74.6\text{--}78.2 \quad (292) \end{aligned}$$



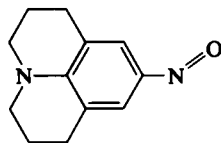
$$\begin{aligned} \text{R}^1 &= \text{alkyl, CH}_2\text{Ar}; \text{R}^2 = \text{CH}_3 \\ \text{R}^3 &= \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5, i\text{-C}_3\text{H}_7 \end{aligned}$$



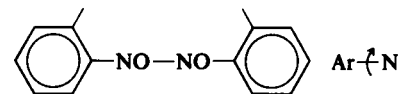
$$\begin{aligned} \text{X} &= \text{Cl, Br, I} \\ \Delta G^\ddagger \quad (\text{X} = \text{Cl}) &= 91.5 \quad (296) \end{aligned}$$



$$\begin{aligned} \text{X} &= \text{H} \quad \Delta G^\ddagger = 31.8 \quad (260) \\ \text{X} &= \text{N}(\text{CH}_3)_2 \quad \Delta H^\ddagger = 60.6 \quad (180) \end{aligned}$$

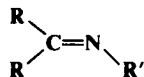


$$\Delta G^\ddagger = 59.3 \quad (293)$$



$$(297)$$

^a $\Delta G^\ddagger$ is in kJ mol^{-1} . High-pressure experiments enabled values of the free energies of activation ($\Delta G^\ddagger$) and of the activation volumes ($\Delta V^\ddagger$) to be determined for the rotation of the amide group in dimethylbenzamides⁸⁴ and other series of amides.⁸⁵ See also reference 10: hindered rotation about N–CS and N–CSe bonds of metal complexes of 1,1-diethyl-3-benzoylthio- and selenourea; 87: rotational isomerization of 6-dimethylaminofulvene tungsten tricarbonyl in acidic media (protonation of the nitrogen atom and of the tungsten atom in weakly and highly acidic solutions, respectively); 88: restricted rotation about N–C and Ar–CS bonds in hindered thioamides; 89: $\text{Fe}[\text{RR}'(\text{dtc})]_3$, $\text{Fe}[\text{RR}'(\text{dtc})]_2$ phen complexes; 90, 91, and 92 N–CS₂ bond rotation in $\text{Fe}(\text{R}^1\text{R}^2\text{dtc})_2(\text{S}_2\text{C}_2\text{R}_2)$ complexes; 93: $\text{M}(\text{NO})_2(\text{S}_2\text{CNMe}_2)_2$ with M = Mo or W; 478: $\text{Me}_2\text{AuS}_2\text{CN}(\text{CH}_3)\text{C}_6\text{H}_5$; 491: substituted 1-aryl-1, 2-dihydro-s-triazines; 526: theoretical study of vinylamine; 501: observation of restricted rotation in 6-methylaminopurine and analogues; 532: conformation of the dimethylaminogroup in pyrimidine and cytosine derivatives; 493: rotational barriers in *N,N*-dimethylaminopyrylium cations; 530: rotational barriers in $\text{R}_2\text{N}-\text{CS}-\text{SO}_2\text{R}'$, $(\text{CH}_3)_2\text{N}-\text{CO}-\text{SO}_2\text{R}$, and $(\text{CH}_3)_2-\text{CO}-\text{S}-\text{SO}_2\text{Ar}$.

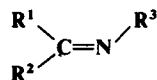
TABLE 29^a

R	R'	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Log A	Reference
H	<i>o</i> -SC ₆ H ₄ NO ₂	C ₆ H ₅ Cl		60 ^b (CH)	24.0	273	56.4 ^c					298
		CDCl ₃		60 ^b	18.6	274	56.9 ^c					299
CH ₃	N(C ₆ H ₅) ₂	C ₄ Cl ₆		100 ^b (CH ₃)	27.0	> 443	> 94.5					300
CH ₃	N(CH ₂ C ₆ H ₅) ₂	C ₄ Cl ₆		100 ^b (CH ₃)	16	416	90.3 ^c					300
CH ₃	N(CH ₃)C ₆ H ₅	C ₄ Cl ₆		100 ^b (CH ₃)	18	407	88.2 ^c					300
	SC ₆ H ₅			(CH ₃) ^b	6	378	84.8 (313 K)					301
	<i>p</i> -SC ₆ H ₄ Cl			(CH ₃) ^b	6.3	383	86.1 (313 K)					301
	<i>p</i> -SC ₆ H ₄ NO ₂			(CH ₃) ^b	7.3	389	86.9 (313 K)					301
	<i>o,p</i> -SC ₆ H ₃ (NO ₂) ₂	CDCl ₃		100 ^b	2.0	352	82.2 ^c					299
<i>i</i> -C ₃ H ₇	<i>o,p</i> -SC ₆ H ₃ (NO ₂) ₂	C ₆ H ₅ Cl		60 ^b (CH)	4.6	371	84.4 ^c					298
CF ₃	C ₆ H ₅	Pyridine	33% v/v	56.4 ^a (CF ₃)			64.6 ^d	58.5	-20.5	61.0	12.2	302
CF ₃	<i>p</i> -C ₆ H ₄ Cl	Pyridine	33% v/v	56.4 ^a (CF ₃)			64.9 ^d	63.5	-4.6	66.0	13.0	302
CF ₃	<i>p</i> -C ₆ H ₄ F	Pyridine	33% v/v	56.4 ^a (CF ₃)			64.2 ^d	63.1	-3.8	65.6	13.0	302
CF ₃	<i>p</i> -C ₆ H ₄ OCH ₃	Pyridine	33% v/v	56.4 ^a (CF ₃)			60.0 ^d	56.4	-12.1	58.9	12.6	302
CF ₃	<i>p</i> -C ₆ H ₄ NO ₂	Pyridine	33% v/v	56.4 ^a (CF ₃)			62.3 ^d	56.8	-17.6	59.4	12.3	302
CF ₃	CF(CF ₃) ₂	Neat		56.4 (1 ⁹ F) ^b						54.3		303
CF ₃	<i>o</i> -SC ₆ H ₄ NO ₂	CDCl ₃		56.4 (1 ⁹ F) ^b	87.4	305	61.5 ^c					299
CH ₂ C ₆ H ₅	<i>o</i> -SC ₆ H ₄ NO ₂	C ₆ H ₅ Cl		60 ^b (CH ₂)	7.5	374	83.6 ^c					298
CH ₂ Cl	<i>o</i> -SC ₆ H ₄ NO ₂	C ₆ H ₅ Cl		220 ^b	1.3	326	77.0 ^c					299
<i>p</i> -C ₆ H ₄ CH ₃	SC ₆ H ₅	C ₆ H ₅ Cl		60 ^b	5.1	345	77.8 ^c					299
	<i>o</i> -SC ₆ H ₄ NO ₂	C ₆ H ₅ Cl		60 ^b	4.0	335	76.4 ^c					299
	SCH ₃	C ₆ H ₅ Cl		60 ^b	4.7	342	77.4 ^c					299
	CCl ₃	C ₆ H ₅ Cl		60 ^b	3.0	270	61.9 ^c					299
	SO ₂ C ₆ H ₅	C ₆ H ₅ Cl		60 ^b	4.5	250	56.1 ^c					299
	<i>o,p</i> -SC ₆ H ₃ (NO ₂) ₂	CDCl ₃		60 ^b (CH ₃)	4.0	340	73.3 ^c					298
	<i>p</i> -SC ₆ H ₄ Cl	CDCl ₃		60 ^b (CH ₃)	4.9	345	77.7 ^c					298

TABLE 29 (cont.)

R	R'	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Log <i>A</i>	Reference
CO ₂ CH ₃	N(CH ₃) ₂	C ₆ Cl ₆		100 ^a (OCH ₃)	6.3	429	97.0 ^c					300
	N(CH ₂ C ₆ H ₅) ₂	C ₆ Cl ₆		100 ^a (OCH ₃)	31.6	419	88.6 ^c					300
	N(CH ₃)C ₆ H ₅	C ₆ Cl ₆		100 ^a (OCH ₃)	5.0	430	97.8 ^c					300
OCH ₃	C ₆ H ₅	CDCl ₃	0.3 <i>M</i>	60 ^a	10.5	275.5	59.8 ^c					304
OCH ₃	C ₆ H ₅	CH ₃ OD	0.3 <i>M</i>	60 ^a	8.8	280	61.4 ^c					304
	<i>p</i> -C ₆ H ₄ OCH ₃	(CD ₃) ₂ CO	0.3 <i>M</i>	60 ^a	4.0	283	64.0 ^c					304
	<i>p</i> -C ₆ H ₄ Cl	(CD ₃) ₂ CO	0.3 <i>M</i>	60 ^a	6.1	268	59.6 ^c					304
	<i>p</i> -C ₆ H ₄ NO ₂	(CD ₃) ₂ CO	0.3 <i>M</i>	60 ^a	6.4	232	50.6 ^c					304
SCH ₃	C ₆ H ₅	CDCl ₃	0.3 <i>M</i>	60 ^a	2.6	248	56.8 ^c					304
	C ₆ H ₅ F	C ₆ H ₅ F		100 ^a	14	271	58.5 ^c					305
	<i>p</i> -C ₆ H ₄ F	(CD ₃) ₂ CO	0.3 <i>M</i>	60 ^a	3.0	261	59.8 ^c					304
	<i>p</i> -C ₆ H ₄ NO ₂	(CD ₃) ₂ CO	0.3 <i>M</i>	60 ^a	5.6	223	49.3 ^c					304
	<i>p</i> -C ₆ H ₄ NO ₂	C ₆ H ₅ F	0.3 <i>M</i>	100 ^a	12.3	232	54.8 ^d					305
	N(CH ₃) ₂	C ₆ H ₅ F		100 ^a	14.8	286	62.7 ^d					305
	OCH ₃	C ₆ H ₅ F		100 ^a	14.8	283	62.7 ^c	49.3	-46.4			305

^a For explanations to footnotes see Table 1.

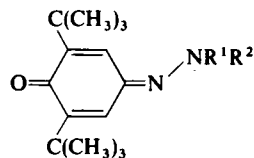
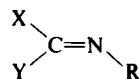
TABLE 30^a

R ¹	R ²	R ³	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	Reference
OCH ₃	C ₆ H ₅	CH ₃	<i>q</i>		60 ^b	18	367	(Z) 79.1 ^c			306
OCH ₃	C ₆ H ₅	<i>i</i> -C ₃ H ₇	<i>q</i>		60 ^b	17.5	362	(Z) 78.2 ^c			306
SCH ₃	C ₆ H ₅	CH ₃	C ₆ H ₅ NO ₂		60 ^b	21.5	393	(Z) 84.5 ^c			306
SCH ₃	C ₆ H ₅	<i>i</i> -C ₃ H ₇	CHBr ₃		60 ^b	18	378	(Z) 81.6 ^c			306
SCH ₃	<i>o</i> -C ₆ H ₄ F	<i>i</i> -C ₃ H ₇	C ₆ H ₅ NO ₂		60 ^b	23.5	406.5	(Z) 87.0 ^c			306
SCH ₃	<i>o</i> -C ₆ H ₄ I	<i>i</i> -C ₃ H ₇	C ₆ H ₅ NO ₂		60 ^b	32.5	415	87.9 ^c			306
SCH ₃	CH ₂ CH ₃	CH ₂ CH ₃			<i>f</i>			81.1 (352 K)	81.1	-9.2	307
C ₆ H ₅	<i>p</i> -C ₆ H ₄ CF ₃	Ge(CH ₃) ₃	(CH ₃) ₂ O	20% v/v	60 ^b	1.1	165	38.5 ^c			308
H	9-anthryl	CH ₃ (Z)	C ₆ D ₆		<i>k</i>			92.8 (315 K)			66
		(E)	C ₆ D ₆		<i>k</i>			99.5 (315 K)			66
H	9-anthryl	CH ₃ (Z)	(C ₆ H ₅) ₂		<i>a</i>			112.4 (473 K)			66
		(E)	(C ₆ H ₅) ₂		<i>a</i>		> 473	120.4 (473 K)			66
C ₆ H ₅	<i>p</i> -C ₆ H ₄ N(CH ₃) ₂	CH ₃ (Z)	(C ₆ H ₅) ₂ O	0.33 M	100 ^{a,b}			108.7 (308 K)	106.2	-7.9	67
		(E)						110.6 (308 K)	107.8	-8.8	67
C ₆ H ₅	<i>p</i> -C ₆ H ₄ NO ₂	CH ₃ (Z)	(C ₆ H ₅) ₂ O	0.33 M	100 ^{a,b}			107.2 (308 K)	107.0	+0.8	67
		(E)						108.9 (308 K)	107.4	-4.2	67
C ₆ H ₅	<i>p</i> -C ₆ H ₄ NO ₂	<i>t</i> -C ₄ H ₉ (Z)	<i>t</i> -C ₄ H ₉ OH	0.5 M	100 ^{a,b}			122.5 (333 K)	120.8	-4.2	67
		(E)						125.0 (333 K)	119.1	-16.7	67
CH ₃	1-naphthyl	CH(CH ₃) ₂			(CH ₃) ₂ ^a	11.0	182	(Z) 103.2 ^c			309
	C(CH ₃)=C(CH ₃) ₂	SO ₂ C ₆ H ₅			60 ^{a,b}			68.1	65.6	-8.3	68
N(CH ₃) ₂	N(CH ₃)CH ₂ C ₆ H ₅	C ₆ H ₅	CS ₂ /CDCl ₃		60 ^b N(CH ₃) ₂	23	243	51.2 ^c			274
	N(CH ₃)CH ₂ C ₆ H ₅	C ₆ H ₅ (<i>i</i> -Pr) ₃ - <i>o,o,p</i>	CS ₂ /CDCl ₃		60 ^b N(CH ₃) ₂	18.5	224	48.9 ^c			274, 310
N(CH ₃) ₂	N(CH ₃) ₂	OCH ₃	(C ₆ H ₅) ₂ O	0.3 M	60 ^b N(CH ₃) ₂	11.4	> 473	104.5			311
N(CH ₃) ₂	N(CH ₃) ₂	CH ₂ C ₆ H ₅	CCl ₄	0.3 M	60 ^b N(CH ₃) ₂	5.5	202	77.3 ^c			311
N(CH ₃) ₂	N(CH ₃) ₂	C ₆ H ₅	CS ₂ /CDCl ₃	0.3 M	60 ^b N(CH ₃) ₂	19.3	238	50.7 ^c			311
		OCH ₃	(C ₆ H ₅) ₂ O		60 ^b NCH ₃	11	438	97.0 ^c			311
		N(CH ₃) ₂	(C ₆ H ₅) ₂ O	0.05 M	60 ^b NCH ₃	27.8	410	87.8 ^c			311
		CH ₂ C ₆ H ₅	CH ₂ Cl ₂	0.3 M	60 ^b NCH ₃	12.6	227	48.9 ^c			311

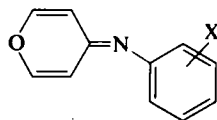
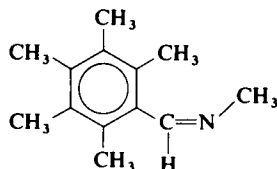
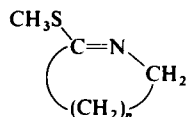
^a For explanations to footnotes see Table 1. See also references 468 and 551 (for a ¹³C investigation of *E/Z* mixtures of *N*-methylthiobenzimidates).

TABLE 31^a

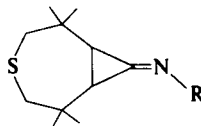
264


 $R^1, R^2 = \text{CH}_3, \text{C}_6\text{H}_5 \quad (312)$


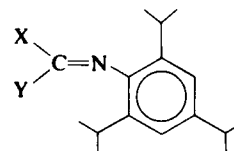
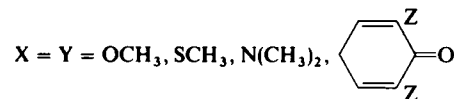
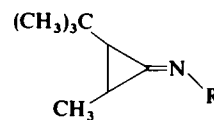
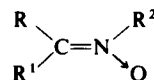
Y = 1-naphthyl, C_6H_5 , C_2H_5 , OCH_3
 X = CH_3 , C_2H_5 , C_6H_5 (309, 313)
 R = CH_3 , $i\text{-C}_3\text{H}_7$, $\text{CH}_2\text{C}_6\text{H}_5$, $t\text{-C}_4\text{H}_9$

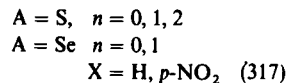
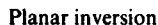
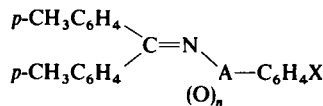
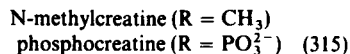
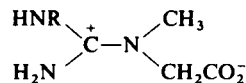
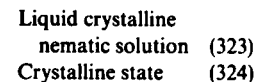
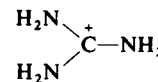
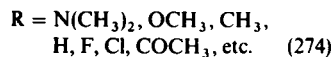
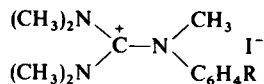
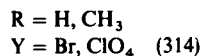
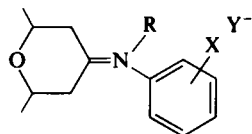

 $\Delta G^\ddagger = 61-85 \quad (314)$

 $(E) \rightarrow (Z): \Delta G^\ddagger = 125.4 \quad (67)$


$n = 7-13$
 $\Delta G^\ddagger = 78.6-90.7 \quad (307)$

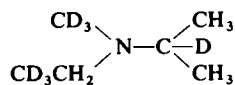
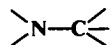


R = C_6H_5 , $p\text{-C}_6\text{H}_4\text{NO}_2$, cyclohexyl
 R = C_6H_5 : $\Delta G^\ddagger = 78.2 \quad (316)$

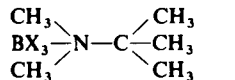
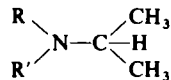
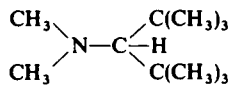

 $\text{X Y} = \text{N}(\text{CH}_3)_2, \text{N}(\text{CH}_3)\text{CH}_2\text{C}_6\text{H}_5 \quad (318)$

 $\text{R} = \text{CH}_3, \text{C}(\text{CH}_3)_3 \quad (319)$

 $(320-322)$



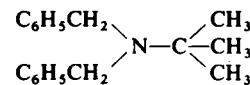
^a $\Delta G^\ddagger$ is in kJ mol⁻¹. Several mechanisms have been invoked for explaining the *E/Z* isomerization of imines and their derivatives. Thus a planar inversion at nitrogen (lateral shifts), a torsion around the C=N bond, or an intermediate mechanism has been considered. A number of papers discuss this problem in relation with the σ or π electronic factors which control the energy barriers. Typical examples are given in Tables 29 to 31 and other results of syn/anti isomerization can be found in references 94, 95, 456, 457, 469, and 470. See also 509 for an investigation of tautomerism and hindered rotation in *N,N'*-dimethylformamidine and its cationic and anionic forms.

TABLE 32^a

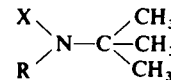
(325)


 $\text{X} = \text{H}, \text{D}$
 $\Delta G^\ddagger = 41.8$ (326)

 $\text{R}, \text{R}' = \text{CH(CH}_3)_2, \text{CH}_3,$
 $\text{CH}_2\text{C}_6\text{H}_5, \text{CD}_2\text{CD}_3$ (330)

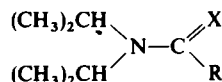
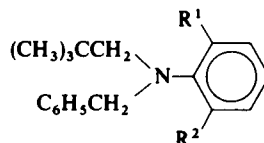
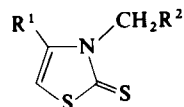
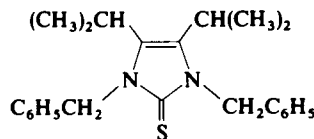
(329)



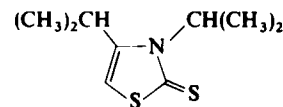
(331)


 $\text{R}, \text{X} = \text{CH}_3, \text{CH}_3; \text{CH}_3, \text{CH}_2\text{C}_6\text{H}_5; \text{Cl},$
 $\text{CH}_2\text{C}_6\text{H}_5; \text{Cl}, \text{CH}_2\text{CD}_3; \text{Br},$
 $\text{CH}_3; \text{Cl}, \text{CH}_3; \text{Cl}, \text{Cl}$
 $\Delta G^\ddagger = 25-40$ (96-99)

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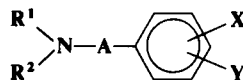

 $\text{X} = \text{O}, \text{S}, \text{Se}$ (327)
(331) $\text{X}_2\text{Sn}[\text{Y}_2\text{CN}(\text{Pr}-i)_2]_2$
 $\text{X} = \text{Cl}, \text{CH}_3; \text{Y} = \text{S}, \text{Se}$ (333)

 $\text{R}^1 = \text{CH}_3, t\text{-C}_4\text{H}_9$
 $\text{R}^2 = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7$
 $\Delta G^\ddagger = 29-48$ (328)


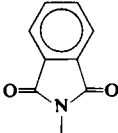
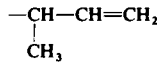
(332)



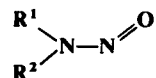
(334)

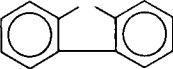
^a $\Delta G^\ddagger$ is in kJ mol^{-1} . Relatively high conformational barriers involving >N-C< bonds may be found in various crowded structures. The mechanisms of internal rotation of isopropyl, ethyl, or benzyl groups in particular have been elucidated in typical examples. An unambiguous distinction between nitrogen inversion and rotation about a C-N bond could be made in favorable cases.⁹⁶⁻¹⁰⁰ See also reference 101 for a review on pyramidal inversion. See also 533, 544 for internal rotation around the isopropyl nitrogen bond of $[\text{X}(\text{CH}_2)_n\text{XCN}(i\text{-Pr})_2]^+ \text{Y}^-$ with $\text{X} = \text{S}$ or Se ; 510 for hindered rotations around glycosidic bonds; 487 for activation parameters in $(\text{RCH}_2)_2\text{N-CX-R}'$ and force-field calculations; 556 for a discussion of N-inversion and C-N rotation processes in tertiary isopropylamines.

TABLE 33^a

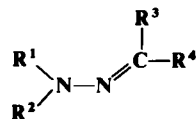
R ¹	R ²	X, Y	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	Reference
A = S									
CH(CH ₃) ₂	SO ₂ C ₆ H ₅	H, H	Toluene- <i>d</i> ₈	10%	60 ^a (CH ₃)	18.2	266	56.8 ^c	335
CH(CH ₃) ₂	SO ₂ C ₆ H ₅	<i>p</i> -NO ₂ , H	Toluene- <i>d</i> ₈	10%	60 ^a (CH ₃)	19.2	308	66.0 ^c	335
CH(CH ₃) ₂	CH(CH ₃) ₂	<i>o,p</i> -NO ₂	C ₆ H ₅ NO ₂	20 mg/0.3 ml	60 (CH ₃)	4.9	380	86.2 ^c	336
CH(CH ₃) ₂	CH(CH ₃) ₂	<i>o,p</i> -NO ₂	Toluene- <i>d</i> ₈	2–4 mol%	60 (CH ₃)	5.0	378	86.1 ^c	70
CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	<i>o,p</i> -NO ₂	Toluene- <i>d</i> ₈	2–4 mol%	270 ^b (CH ₂)	29.7	318	65.9 ^c	336
CH ₃	CH ₂ C ₆ H ₅	<i>o,p</i> -NO ₂	Toluene- <i>d</i> ₈	2–4 mol%	270 ^b (CH ₂)	21.6	308	64.1 ^c	336
CH ₂ C ₆ H ₅	CHO	H, <i>p</i> -Cl	Toluene- <i>d</i> ₈	7–10%	100 ^a (CH ₂)	159	227	43.9 ^c	337
CH ₂ C ₆ H ₅	COC ₆ H ₅	H, <i>p</i> -Cl	Toluene- <i>d</i> ₈	7–10%	100 ^a (CH ₂)	155	210	40.5 ^c	337
CH ₂ C ₆ H ₅	COOCH ₃	H, <i>p</i> -Cl	Toluene- <i>d</i> ₈	7–10%	100 ^a (CH ₂)	154	205	39.7 ^c	337
CH ₂ C ₆ H ₅	COOCH ₃	H, <i>p</i> -OCH ₃	Toluene- <i>d</i> ₈	7–10%	100 ^a (CH ₂)	136	188	36.4 ^c	337
CH ₂ C ₆ H ₅	COOCH ₃	<i>o,p</i> -NO ₂	Toluene- <i>d</i> ₈	7–10%	100 ^a (CH ₂)	47	331	67.7 ^c	337
CH ₂ C ₆ H ₅	CH(CH ₃) ₂	<i>o,p</i> -NO ₂	CDCl ₃		(CH ₃)		≈ 337	71.1 ^c	338
CH ₂ C ₆ H ₅	CH(CH ₃) ₂	NO ₂ , H	CDCl ₃					62.7 ^c	338
		<i>o,p</i> -NO ₂			220 (H _o)	15.4	≈ 312	70.2 ^c	338
CH(CH ₃)C ₆ H ₅	SO ₂ C ₆ H ₅	NO ₂ , H	CDCl ₃	10–20%	60 ^a (CH ₃)	16.5	256	61.0 ^c	338
		H, H						54.3 ^c	339
A = Se									
CH(CH ₃) ₂	CH(CH ₃) ₂	<i>o,p</i> -NO ₂	Toluene- <i>d</i> ₈	20 mg/0.3 ml	60 ^b (CH ₃)	5.5	355	80 ^c	336
CH ₂ C ₆ H ₅	CH ₂ C ₆ H ₅	<i>o,p</i> -NO ₂	Toluene- <i>d</i> ₈	20 mg/0.3 ml	270 ^b (CH ₂)	26.4	292	60.4 ^c	336
CH ₂ C ₆ H ₅	CH(CH ₃) ₂	<i>o,p</i> -NO ₂	CDCl ₃	20 mg/0.3 ml	270 ^b (CH ₃)	47	325	67.3 ^c	336
CH ₃	CH ₂ C ₆ H ₅	<i>o,p</i> -NO ₂	Toluene- <i>d</i> ₈	20 mg/0.3 ml	270 ^b (CH ₂)	39.4	292	59.9 ^c	336
C ₆ H ₅	CH ₂ C ₆ H ₅	<i>o,p</i> -NO ₂	CDCl ₃	20 mg/0.3 ml	60 ^b (CH ₂)	29.4	320	66.0 ^c	336

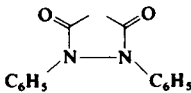
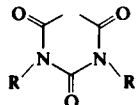
^a For explanations to footnotes see Table 1.

TABLE 34^a

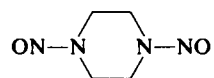
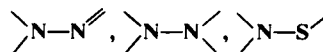
R ¹	R ²	Solvent	C	ν_0 (MH ₂) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	log <i>A</i>	Reference
CH ₃	CH ₃	Neat		60 ^b			97.0 ^j	120.0	4.6	106	13.6	340
CH ₂ CH ₃	CH ₂ CH ₃	C ₆ H ₅ NO ₂		60 ^a			97.0	96.6	1.3	99.9		341
<i>n</i> -C ₃ H ₇	<i>n</i> -C ₃ H ₇	Neat		60 ^b		443	94.1 ^c					342
CH(CH ₃) ₂	CH(CH ₃) ₂	C ₆ H ₅ NO ₂		60 ^a			98.2	98.2	0.6	102		341
C ₆ H ₅	C ₆ H ₅	(CD ₃) ₂ SO		(¹³ C) ^a			79.8 ^c					343
		Neat		100 ^a (CH ₂ α)	76.4	463	99.5 ^d	95.3	-13.8	97.8	12.5	344
		Neat		100 ^a (CH ₂ α)	47.8	453	94.9 ^d	97.8	-7.5	100.3	12.8	344
		Neat		60 ^b			93.0 (450 K)					340
		C ₂ Cl ₄		60 ^a			81.9	77.3	-12.1	80.7		341
		CHFC1 ₂		25.2 ^b			81.9 ^c					345
		(CD ₃) ₂ SO		(¹³ C) ^a			70.4	73.2	8.4			343
		(CD ₃) ₂ SO	1 M	200 ^b	57	351	72 ^c					346
CH ₃	CH ₂ CN	(CCl ₃) ₂ CO	5% w/w	100 ^a (CH ₂)	74	412	(<i>E</i> → <i>Z</i>) (<i>Z</i> → <i>E</i>)	79.1 80.0	-15.5 -14.2			347 347
CH ₂ CH ₃	CH ₂ C ₆ H ₅	Neat		60 ^b (CH ₂)	26.4	447	95.7 ^c					342
CH ₂ CH ₃	(CH ₂) ₂ OH	Neat		60 ^b (CH ₃)	18.4	446	97.0					342

^a For explanations to footnotes see Table 1. See also reference 537 for line-shape analyses of dynamic NMR spectra of CH₃N(NO)CH₃C¹⁵N and CH₃N(NO)CH₂C¹⁴N; 289 for an investigation of internal rotation of the nitroso group in nitrosoanilines.

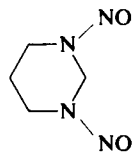
TABLE 35^a

R ¹	R ²	R ³	R ⁴	Solvent	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	E_a (kJ mol ⁻¹)	Reference
CH ₃	CH ₃	H	H	CHF ₂ Cl	25.2 (¹³ C) ^(b)			22.6 ^(c)				345
CH ₃	CH ₃			(C ₆ H ₅) ₂ O C ₆ H ₅ NO ₂	60 ^(b) (CH ₃) 100 ^(b) (CH ₃)	23 29	346 350	73.7 ^(c) 74.2 ^(c)				65 65
CH ₃	CH ₃		R = C ₆ H ₅ , CH ₃	(C ₆ H ₅) ₂ O C ₆ H ₅ NO ₂	100 ^(b) (CH ₃) 100 ^(b) (CH ₃)	12 20.5	320 314	70.0 ^(c) 67.0 ^(c)				65 65
		CH ₃	CH ₃	C ₂ Cl ₄	60 ^(a) (CH ₃ pip.)	23.1	327.5	69.8	71.9	6.3	74.4	341
				C ₆ H ₅ NO ₂	60 ^(a) (CH ₃ pip.)	24.0	326	69.0	71.1	5.8	73.6	341
				CHF ₂ Cl	25.2 (¹³ C) ^(b)			65.2 ^(c)				345
		H	H	CHF ₂ Cl	100 ^(a) (CH ₃ pip.)	26.0	152	31.4				341
				CS ₂	60 ^(a) (CH ₃ pip.)	13.5	226	48.5	48.1	0.8	50.2	341
				C ₂ Cl ₄	60 ^(a) (CH ₃ pip.)	23.1	352	75.2	74.8	-1.7	77.7	341
				C ₂ Cl ₄	60 ^(a) (CH ₃ pip.)	20.0	335	71.9	72.7	2.1	75.2	341
		CH ₃	C ₆ H ₅	CDCl ₃	60 ^(a) (CH ₃) ₂	25.2	309	65.2 ^(c)	58.9	0.1		348
		CH ₃	4-pyridyl	CDCl ₃	60 ^(a) (CH ₃) ₂	26.2	279.5	58.9 ^(c)	58.9	0.4	61.0	348
			3-pyridyl	CDCl ₃	60 ^(a) (CH ₃) ₂	25.5	295	62.3 ^(c)	65.2	10.4	67.7	348
			2-thienyl	CDCl ₃	60 ^(a) (CH ₃) ₂	23.4	285	60.2 ^(c)				348
			β -naphthyl	CDCl ₃	60 ^(a) (CH ₃) ₂	24.6	316	66.9 ^(c)				348
		H	H	CHF ₂ Cl	25.2 (¹³ C) ^(b)			20.9 ^(c)				345

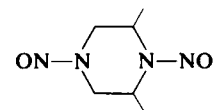
^a For explanations to footnotes see Table 1. pip, Piperidine.

TABLE 36^a

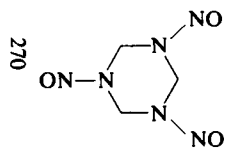
(349)



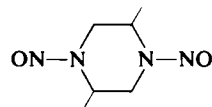
(340)



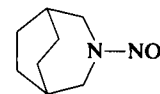
(349)



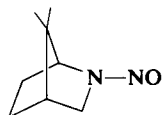
(340, 349)



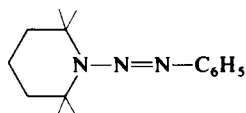
(349)



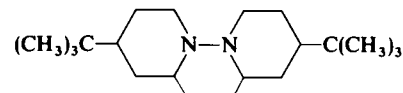
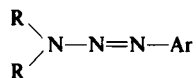
(344)



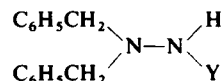
(344)



(350)

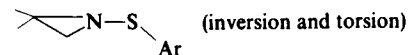
 $\Delta G^\ddagger = 79$ (352)

(350)



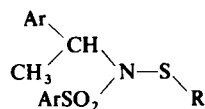
Y = Ar, COCH₃
 Y = o, p-C₆H₃(NO₂)₂: $\Delta G^\ddagger = 69.4$

(351)



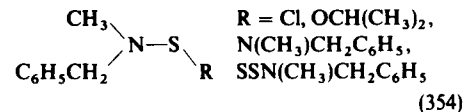
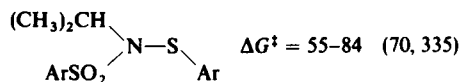
(inversion and torsion)

(353)



R = CCl₃, Ar (339)

R = CCl₃, Ar = C₆H₅^{a,t}: $\Delta H^\ddagger = 61.4$
 $\Delta S^\ddagger = -35.5$



(degenerative racemization)

^a $\Delta G^\ddagger$ is in kJ mol⁻¹. See also reference 104 for barriers to rotation about the N-N bonds of C₆H₅CH₂N(R)N(R)CH₂C₆H₅; 102: (CH₃)₂Si(X)N(CH₃)N(CH₃)Si(X)(CH₃)₂ with X = Cl, Br; 471: sulfenamide and amide barriers in C₆H₅CH₂N(SAr)COR'; 103: hindrance of rotation around N-N and C-N in RCONHNHNR'¹R²; 472: R₂NSOX; 479: R₂N-N=S=O; 473: cyclic nitrosamines; 497: rotation around the N-N bond in (CH₃)₂N-N(R)-C(R')=N'OR; 553: rotational barriers about the N-N single bond of silyltriazene [(CH₃)₃Si]₂N-N=N-Ph; 511: restricted torsion around the N-S bond of halogeno-sulphinamides R₂NSOX; 512: N,N-dimethylsulphinamides; 546: free energies of activation for rotation about the N-N bond of N' derivatives of N-amino[2.2.1]bicyclo-5-heptene-2,3-endo-dicarboximide; 513: discussion of the influence of N-S torsion and halogen exchange in halogenosulphenamides R₂NSX; 502: rotational barriers in compounds R₂NX with X = SO₂Cl, SOCl, SCl, SCl₃; 536: barriers to torsion about the N-S bond of trinitrobenzene sulfenamides and perhalobenzene sulfenamides; 548 and 549: free energies of activation to rotation about the exocyclic N-N bond in fragments of

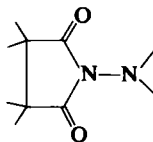
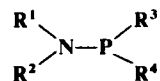
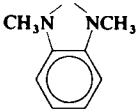
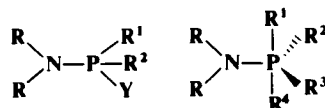


TABLE 37^a

R ¹	R ²	R ³	R ⁴	Solvent	C	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G_T^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	Reference
CH ₃	CH ₃	Cl	Cl	CHFC1 ₂		100 ^a			35.1 (160 K)		355
		CF ₃	CF ₃	CF ₂ Cl ₂		100 ^a			37.6 (172 K)		355
		CH[Si(CH ₃) ₃] ₂	Cl	CH ₂ Cl ₂	15%	90 ^f (CH ₃ N)	12	220	47.2 ^c		356
		CH ₃	Cl	CH ₂ =CHCl	13% w/w	<i>a</i>	10	233	49.3 ^c		357
		C ₆ H ₅	Cl	CFC1 ₃		100 ^a	53	233	45.6 ^c		358
				CS ₂			33	219	45.1 ^c		359
				CS ₂		22.6 (¹³ C) ^b	122	233	45.6 ^c		360
		<i>t</i> -C ₄ H ₉	Cl	CHCl ₂ F		100 ^a		189	39.7		361
		<i>t</i> -C ₄ H ₉	Cl	CH ₂ =CHCl	10% w/w	<i>a</i>	17	188		39.3	357
		CH ₂ Cl	Cl	CH ₂ =CHCl	33% w/w	<i>a</i>	16	229	47.7 ^c		357
		C ₆ H ₅	OCH ₃	CFC1 ₃ /CF ₂ Cl ₂		60 ^b (CH ₃)	42.9	174	35.1 ^c		359
		Cl	Cl	CHFC1 ₂		100 ^a	4	160	35.1 ^c		358
		CF ₃	CF ₃	CF ₂ Cl ₂		100 ^a	7	168	36.4 ^c		358
				CHFC1 ₂		100 ^{a,g}	80	197	38.0 ^c		362
				C ₆ D ₆ /CHFC1 ₂		100 ^b		161	31.8 ^c		363

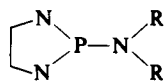
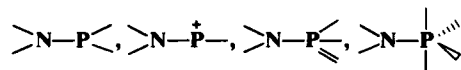
<i>i</i> -C ₃ H ₇	<i>i</i> -C ₃ H ₇	CH[Si(CH ₃) ₂] ₂	Cl	CH ₂ Cl ₂	15%	90 ^f (CHN)	20	248	53.1 ^c	356
		C(CH ₃) ₃	Cl	CH ₂ Cl ₂	15%	90 ^f (CHN)	18	222	46.4 ^c	356
		CH ₃	Cl	Toluene- <i>d</i> ₈	15%	60 ^a (CH ₃)		265	57.2 ^c	361
		CH ₃	Cl	CH ₂ =CHCl	20% w/w	<i>a</i>		253	56.0 ^c	357
		C ₆ H ₅	Cl	CFCl ₃		100 ^a	20	258	53.5 ^c	358
		C(CH ₃) ₃	Cl	CHCl ₂ F		100 ^a		273	58.9 ^c	361
		CH ₃	F	CH ₂ =CHCl	20% w/w	<i>a</i>		213	45.6 ^c	357
		CF ₃	CF ₃			<i>b</i>			61.9 ^c	364
		Cl	Cl	CS ₂ /(CD ₃) ₂ CO		22.6 (¹³ C) ^b (CH)	80	225	44.7 ^c	360
						(CH ₃)	105	228	44.7 ^c	360
<i>sec</i> -C ₄ H ₉	<i>sec</i> -C ₄ H ₉	C ₆ H ₅	Cl	CS ₂		22.6 (¹³ C) ^b (CH ₂)	100	280	55.6 ^c	360
		Cl	Cl	CS ₂ /(CD ₃) ₂ CO		22.6 (¹³ C) ^b (CH ₂)	90	225	44.7 ^c	360
<i>t</i> -C ₄ H ₉	<i>t</i> -C ₄ H ₉	F	F	Toluene	20%		10.4	226	48.9 ^c	365
		Cl	Cl	Toluene	20%		15.3	338	73.2 ^c	365
		Br	Br	Toluene	20%		17.0	346	74.4 ^c	365
Si(CH ₃) ₃	Si(CH ₃) ₃	C(CH ₃) ₃	Cl	CH ₂ Cl ₂	15%	90 ^f (CH ₃ Si)	5	200	44.3 ^c	356
		CF ₃	CF ₃			60 ^b	3.7		64.0 ^c	144
		Cl	Cl						41.8	364
Si(CH ₃) ₃	<i>t</i> -C ₄ H ₉	CF ₃	CF ₃			60 ^b (CH ₃) ₃		383	86.9 ^c	144

^a For explanations to footnotes see Table 1. See also reference 474.

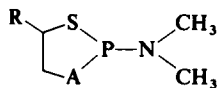
TABLE 38^a

R ¹	R ²	Y or R ³ , R ⁴	Solvent	ν_0 (MHz) nucleus analysis	$\Delta\nu$ (Hz)	T_c (K)	$\Delta G^\ddagger$ (kJ mol ⁻¹)	$\Delta H^\ddagger$ (kJ mol ⁻¹)	$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)	Reference
R = H										
F	NH ₂	F, F	CH ₃ CN/CH ₂ Cl ₂	84.7 (¹⁹ F) ^a			51.2 (250 K)	44.5	-26.8	366
R = CH(CH₃)₂										
C ₆ H ₅	Cl	O	CHCl ₂ F				39.3 (194 K)			367
CH ₃	Cl	S	CHCl ₂ F	100 ^a (CH ₃)		207	43.1 ^c	40.2	-4	361
C ₆ H ₅	Cl	S	CHCl ₂ F	100 ^a (CH ₃)		208	42.2 ^c	37.2	-20.9	361
<i>i</i> -C ₄ H ₉	Cl	S	CHCl ₂ F	100 ^a (CH ₃)		244	52.7 ^c			361
		S	CD ₂ Cl ₂	(CH ₃)		215	44.3 ^c			368

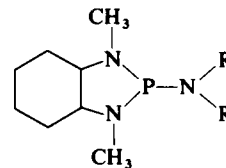
^a For explanations to footnotes see Table 1. See also references 448 and 449.

TABLE 39^a

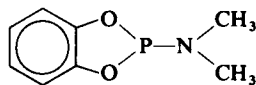
R = CH₂CH₃, CH(CH₃)₂
 $\Delta G^\ddagger = 34$ and 42.2 (369)



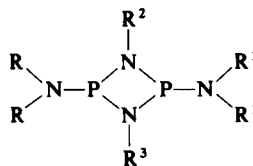
A = O, S
 R = H, CH₃ (363)



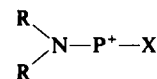
R = CH₃, CH₂CH₃, CH(CH₃)₂
 $\Delta G^\ddagger = 37.2\text{--}55.2$ (362)



$\Delta G^\ddagger$ (CFCl₃/CF₂Cl₂) = 32.6 (359)

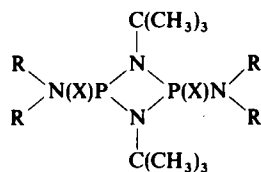


R = R¹ = CH₃, C₂H₅, etc.
 R², R³ = CH₃, *t*-C₄H₉, C₆H₅, etc.
 For R = R¹ = CH₃ and
 R² = R³ = *t*-C₄H₉, $T_c = 327\text{ K}$ (C₆H₆)
 and $\Delta G^\ddagger = 73.6$ (373)



R = CH₃, CH(CH₃)₂
 X = Cl, NR₂ (375)
 For R = CH₃, X = N(*i*-C₃H₇)₂
 $\Delta G^\ddagger$ [N(CH₃)₂] = 52.7 ,
 $\Delta G^\ddagger$ [N(*i*-C₃H₇)₂] = 48.1

TABLE 39 (cont.)



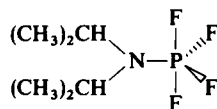
X = O, S, Se

R = CH₃, C₂H₅

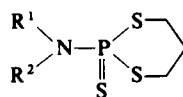
For *cis*, R = CH₃, X = O

T_c = 213 K (CH₂Cl₂), ΔG[‡] = 48.5

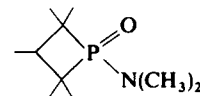
(370, 371)



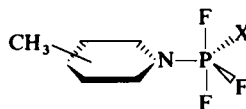
(limit) (372)



R¹, R² = CH₃, *i*-C₃H₇, *t*-C₄H₉ (368)



(376)



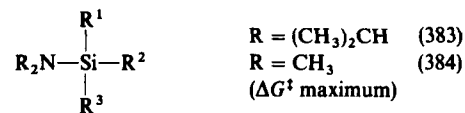
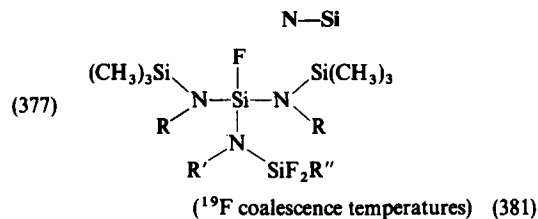
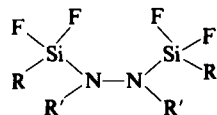
(qualitative)

X = F, hydrocarbon (374)

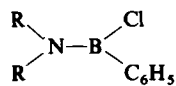
^a ΔG[‡] is in kJ mol⁻¹. See also reference 475 for variable-temperature experiments on X₂PNR₂PX₂; 488 for an investigation of hindered rotation about the N-P and N-N bonds in F₂PN(CH₃)N(CH₃)PF₂.

TABLE 40^a

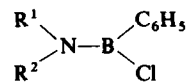
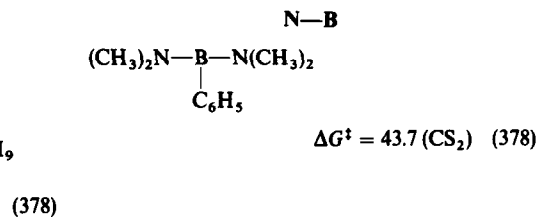
N—X (X = Si, B, O, As, Pd, Sb)



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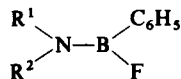


R = CH₃, C₂H₅, *n*-C₄H₉, *i*-C₃H₇, *sec*-C₄H₉
 ΔG[‡] = 71–84.8



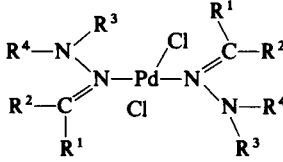
R¹ = R² = *n*-C₃H₇, *n*-C₄H₉, CH₂CH=CH₂
 R¹ = C₂H₅, R² = C₆H₅
 ΔG[‡] = 77–83

(385)



R¹ = R² = CH₃, C₂H₅, *n*-C₃H₇, *n*-C₄H₉
 ΔG[‡] = 80–85 (379)

TABLE 40 (cont.)

CH ₃ ON=O	N—O	N—Pd	N—Sb	(386)
	gas (at several pressures) liquid $E_a \approx 43.9$	(380)	[(CH ₃) ₃ C] ₂ Sb—N[Si(CH ₃) ₃] ₂	
		 $R^1 = R^2 = R^3 = \text{CH}_3, R^4 = \text{Ph}; \Delta G^\ddagger = 67$		(382)
(CH ₃) ₂ N—As(Cl)C ₆ H ₅ in CH ₂ Cl ₂ , $T_c = 166 \text{ K}, \Delta G^\ddagger = 33.9$	N—As	(358)		

^a $\Delta G^\ddagger$ is in kJ mol⁻¹. See also reference 104 for barriers to conformational changes in hydroxylamines C₆H₅CH₂N(R¹)OR² (nitrogen inversion); 450 for dynamic processes in R₂NSOCl; 492 for enantiomerization in bis(diisopropylamino)amino boranes; 528 and 508 for B—N rotational barriers in aminoboranes containing *N*-trimethylsilyl-, -germyl, or -stannyl substituents; 500 for calculation of the barrier to internal rotation in (CH₃)₂NSiH₃; 529 and 523 for activation parameters concerning the B—N bond of R₂P(S)NR'B(CH₃)₂ and XC₃H₄B(Cl)N(CH₃)CH₂C₆H₅, respectively; 507 for stereoisomerism in compounds ArN(CH₃)B(R)Ar; 514 for the origin of the rotational barriers around the N—Si bonds in aminosilanes and the importance of steric effects.

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Multiple Resonance

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I. INTRODUCTION

In 1971 Waugh wrote¹ that his instrumentation had been developed to such an extent that he could devise and implement a new pulse sequence every week. Advances in microprocessor technology and their adoption by the main instrument manufacturers have now placed most NMR spectroscopists in this happy position. This is reflected by much of the work reported in this article, which is intended to cover the period from mid-1978 (when the last report² on multiple resource appeared in this series) to mid-1983. In addition to annual coverage³ in the *NMR Specialist Periodical Reports* published by the Chemical Society, aspects of the subject have been reviewed in various other places. These include some excellent expositions⁴⁻²⁶ of various facets of multiple resonance, and worthy of especial mention are a book on the subject of 2D NMR¹⁶ and an article¹⁸ which also describes the most important new pulse sequences. Multiple quantum methods and their potential uses have

been reviewed,²⁷ as have various special pulse sequences.²⁸⁻³³ There have also been more general reviews,³⁴⁻⁴² and the nuclear Overhauser effect (NOE) has received attention in this respect.^{34,35,39}

Following the realisation that, in addition to providing improved sensitivity, pulsed Fourier transform (FT) methods give the experimenter considerable control over the spin dynamics, there has been a spate of "new" pulse sequences intended to aid assignments of ^{13}C spectra in particular and to give different types of 2D spectra. Indeed, this latter aspect of multiple resonance is one of the most important developments, and there are now a growing number of real chemical problems that have been solved with the aid of this technique. In this connection it may be noted that the availability of high-field spectrometers has produced much excellent work on large, biologically important molecules such as proteins, wherein 2D methods can permit the resolution of signals from individual proton sites, and NOE experiments can provide details of molecular geometry that were previously available only from full X-ray diffraction studies.

Very many NMR experiments nowadays incorporate some form of double resonance and so we have exercised considerable selectivity in choosing the material for this review. In general, we have emphasised new methods and ideas, rather than routine applications, and expressed preference for the most recent work. In view of the importance of pulse methods it is now better to define a multiple resonance experiment as "one in which the sample is affected by several radiofrequency (rf) fields," thus removing the requirement of simultaneity in their application.

II. THEORETICAL ASPECTS

Although the basic theory of selective and off-resonance decoupling was satisfactorily worked out some time ago there have been a number of treatments of particular aspects. For example, results are now available⁴³ for the X-offset dependence in experiments upon $\text{AB}_m\text{C}_n\text{X}$ systems (X irradiated), and graphs have been provided⁴⁴ which simplify the prediction of effects in ABX systems (A,B irradiated). In many experiments with fairly weak rf fields it is necessary to allow for simultaneous line-splitting and spin-population transfer effects. This has been done⁴⁵ using the usual spin-tickling equations together with the Bloch equivalent circuit model, and also by combining them⁴⁶ with Bain's⁴⁷ equations. The problem can be simplified if the experiment is arranged to avoid line-splitting effects by suitable gating of the decoupler, and the NOEs of individual transitions can be calculated⁴⁸ using a theory based upon effective magnetic fields rather than saturation. The superspin formalism correctly predicts line positions and intensities in gated irradiation experiments on AX systems,⁴⁹ and this approach has also been

used to study the behaviour of pulse sequences designed to detect multiple quantum transitions.⁵⁰

For pulsed experiments it is necessary to take into account the flip angle and the repetition interval,^{51,52} and in general the density matrix treatment is the best one in this area.⁵³⁻⁵⁹ However, this does not necessarily provide a very clear physical picture of what is going on, and it can be useful to view a nonselective pulse as a cascade of pulses, each affecting only certain transitions at any time,⁶⁰ a method which has been applied in detail to an AX system and which can be readily extended. The converse of this is a density matrix treatment⁶¹ of composite pulse sequences which can be used to give good spin-population inversion. The Heisenberg vector model has also been used^{62,63} to avoid the rigours of the density matrix, and has been applied^{64,65} to the analysis of polarization transfer sequences such as DEPT and INEPT for which a correspondence has been demonstrated.⁶⁶ A Heisenberg *picture* description of the DEPT sequence can be applied to AX_n systems with A of spin $\frac{1}{2}$ and X of any spin.⁶⁷

The problems of the selective excitation of forbidden transitions have been examined and sequences have been devised which can achieve this.⁶⁸

$$90_x^\circ - \tau - (-\theta_\alpha^\circ - t_s -)_n$$

This is of course just part of the more general area of multiple (including zero) quantum NMR on which a good deal of theoretical effort has been expended. Pulse sequences have been described which use repeated $2\pi/n$ phase shifts to build up chosen coherences and cancel all others, and they have been analysed in detail.^{69,70} The whole problem of achieving selectivity in multiple quantum experiments has been attacked⁷¹⁻⁷⁴ and methods are available⁷⁵ for optimising the experimental conditions used. Multiple quantum NMR is especially valuable for the identification of networks of coupled spins, and the results which arise from 15 different systems of up to six spins have been surveyed,⁷⁶ as have the ways in which zero quantum NMR can aid the analysis of complicated first-order spectra such as occur in carbohydrates.⁷⁷ Pure double quantum coherence can be produced by a $90_x^\circ - \tau - 90_x^\circ$ sequence.⁷⁸ The other major area of application of multiple quantum NMR is to molecules oriented in liquid crystals, where even quite small molecules can give very complex single-quantum spectra. However, the higher quantum spectra are much simpler and correspondingly easy to analyse, while at the same time they can provide just as much information. Thus, in partially oriented 2,3-dimethylmaleic anhydride the four-, five-, and six-quantum proton transitions had frequencies which demonstrated independent internal rotation of the two methyl groups,⁷⁹ and n -quantum transitions for $n = 1-8$ have been selected in oriented molecules such as benzene,⁸⁰ 1-bromobutane,⁸⁰ and acetaldehyde.⁸¹ It has been noted⁸² that this type of experiment can provide a useful alternative to isotopic labeling. It has been further pointed out that

multiple quantum transitions cannot occur between energy levels of different symmetry classes,⁸³ so that if multiple quantum coherence between the highest and lowest levels of a system (which must always be of *A* symmetry) is converted by means of a 90° pulse into single-quantum coherence the resulting spectrum will contain transitions of *A* symmetry only.

The above multiple quantum work embodies many of the concepts used in 2D NMR, although in most cases 2D manipulation of the data is not required. The superspin method has been used⁵⁵ to analyse the 2D experiment, and the 2D spectra obtained from partially oriented molecules have also been analysed.^{84,85} A program based on LAOCN3 is available and analytical expressions have been devised for the AB₂ and AB spin systems. A much more general approach to two- and multidimensional NMR is to use stochastic excitation, which has been shown⁸⁶ by perturbation theory to have the same basis as 2D correlated and double resonance experiments in that all depend upon nonlinear responses. The stochastic experiment can give a 3D data matrix⁸⁷ from which 1D and 2D cross-sections can be extracted given sufficient computing power.^{88,89} The 2D spectrum has been calculated⁹⁰ for a weakly coupled AX spin $\frac{1}{2}$ system undergoing chemical exchange. The spin saturation transfer behaviour of systems involved in three-site chemical exchange has been examined⁹¹ and it is interesting that the presence of only very small (0.1%) amounts of one of the components can markedly affect the results. Other treatments of exchange are available,⁹²⁻⁹⁴ including some which consider⁹⁵⁻⁹⁸ the effects of double irradiation upon relaxation in large molecules such as lysozyme and AMP, and calculations have been made of the NOE in exchanging systems and those involving internal rotations which lead to changes of internuclear distances.^{99,100} Increased precision in the measurement of slow exchange rates can be attained in saturation transfer experiments if a modulated rf field is used. This leads to additional responses with intensities which depend upon the exchange rate; this can therefore be measured with considerable precision.¹⁰¹

Other theoretical treatments of various aspects of multiple resonance relate to *J*-cross-polarisation (JCP) in AX_{*n*} systems,¹⁰² pulsed field gradient spin-echo spectra,¹⁰³ the effects of transient excitation in homonuclear experiments,¹⁰⁴ stochastic excitation in inversion-recovery measurements of spin-lattice relaxation times,¹⁰⁵ and the use of multiple quantum NMR to simplify chemically induced dynamic nuclear polarisation (CIDNP) spectra.¹⁰⁶

Two important papers by Waugh^{107,108} demonstrate, with the aid of average Hamiltonian theory, that present methods of broadband decoupling have little sound basis, and that previous theoretical treatments have serious inadequacies. The best possibility appears to be to use a sequence of phase-shifted 90° pulses with negligible time delay between each pulse (i.e., the

decoupler is permanently on and its phase is repeatedly altered at intervals of nt_{90° , where t_{90° is the 90° pulse length). Such sequences can be designed systematically and the following 66-step set of values of n (a bar indicates the phase reversal) is very effective:

883143531483143535831435314831435883143531483143535831435314831435

Despite appearances to the contrary this is not just a form of random noise decoupling, and for $J = 200$ Hz, $\gamma B_2/2\pi = 5000$ Hz, the residual splittings are less than 0.1 Hz over a 7000-Hz range. Even better results can be achieved by changing the pulse lengths by a few percent. Examples of various approaches to effective broadband decoupling are presented in Section III.

III. EXPERIMENTAL METHODS AND INSTRUMENTATION

"Complete" decoupling does not mean that there is no longer any interaction between the observed and irradiated spins. Rather there is an oscillatory exchange of magnetisation via multiple quantum coherence which is induced by the decoupler field.¹⁰⁹ This leads to observable effects in various types of gated decoupler experiment and in particular can produce anomalous intensities for the components of multiplets in INEPT and 2D J spectra according to the exact timing used.¹⁰⁹ Equation (1) has been used to define¹¹⁰ Ξ as a proton decoupler figure of merit. $2\Delta B_{\max}$ is the total range of proton

$$\Xi = 2\Delta B_{\max}/(B_2 d^{1/2}) \quad (1)$$

decoupler offsets over which the observed signal has at least 80% of its full height, B_2 is the decoupler power, and d is its duty cycle.

The growing availability of high-field instruments with wide spectral ranges has generated ideas for improving decoupler efficiency beyond what could be achieved with noise modulation. Initially, sequences of 180° proton flips applied in the times between the data points during the ^{13}C acquisition period were used. This can be very effective and also leads to low ($\sim 20\%$) decoupler duty cycles so that undue sample heating is avoided.¹¹¹ Better approaches are to use sequences such as (2), where $R = 90_x^\circ 270_y^\circ 90_x^\circ$ and $\bar{R} = 90_{-x}^\circ 270_{-y}^\circ 90_{-x}^\circ$,

$$RR\bar{R}\bar{R} \bar{R}RR\bar{R} \bar{R}\bar{R}RR R\bar{R}\bar{R}R \quad (2)$$

and various permutations and combinations of this which are termed cycles and supercycles MLEV-4, MLEV-16, etc.¹¹²⁻¹¹⁴ These schemes can be improved somewhat by varying the timings,¹¹⁵ and unwanted sidebands can be eliminated by ensuring that the decoupler phase cycling and data acquisition are asynchronous.¹¹⁶ The need for both 90° and 180° phase shifts can be avoided by using the spin inversion sequences $S = 90_x^\circ 180_{-x}^\circ 270_x^\circ$

(= $\bar{1}\bar{2}\bar{3}$ in the notation of page 297) and $\bar{S} = \bar{1}\bar{2}\bar{3}$, which then leads to sequences (3) and (4), which are known as WALTZ-4 and WALTZ-16, respectively.¹¹⁷

$$SS\bar{S}\bar{S} = \bar{1}\bar{2}\bar{3}\bar{1}\bar{2}\bar{3}\bar{1}\bar{2}\bar{3} \quad (3)$$

$$\bar{3}\bar{4}\bar{2}\bar{3}\bar{1}\bar{2}\bar{4}\bar{2}\bar{3} \quad \bar{3}\bar{4}\bar{2}\bar{3}\bar{1}\bar{2}\bar{4}\bar{2}\bar{3} \quad \bar{3}\bar{4}\bar{2}\bar{3}\bar{1}\bar{2}\bar{4}\bar{2}\bar{3} \quad \bar{3}\bar{4}\bar{2}\bar{3}\bar{1}\bar{2}\bar{4}\bar{2}\bar{3} \quad (4)$$

WALTZ-16 has been tested experimentally and gave excellent performance; details have been published of its implementation by TTL circuitry.¹¹⁸ These sequences have been analysed by Waugh's procedure¹⁰⁷ and of course come quite close to his own theoretical proposals.

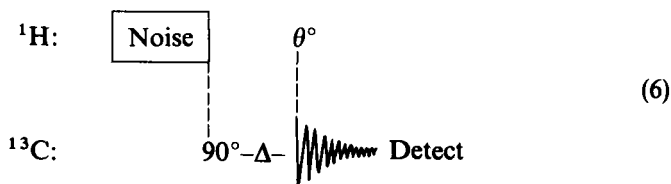
Circuits are also available for the implementation of MLEV-16¹¹⁹ and for various multiple modulation schemes which can be used to improve substantially the efficiency of heteronuclear decoupling.¹²⁰⁻¹²³ Studies¹²⁴⁻¹²⁷ of rf sample-heating effects have shown that they are worst for electrolytes and can be minimised by using low ionic strengths,¹²⁵ placing beryllium oxide plugs in the sample,¹²⁶ using proper decoupler coil design,¹²⁷ and using a liquid as thermostating fluid.¹²⁸ Most forms of heteronuclear decoupling other than of protons are nonstandard and circuits are available¹²⁹⁻¹³⁵ for modifying decoupler coils to accommodate a variety of nuclear combinations. These include $^1\text{H}-\{^{14}\text{N}, ^{59}\text{Co}\}$,¹²⁹ $\text{X}-\{^{103}\text{Rh}\}$,¹³⁰ $^{13}\text{C}-\{^1\text{H}, ^{14}\text{N}\}$,¹³¹ and $^{13}\text{C}-\{^1\text{H}, ^2\text{H}\}$.^{132,133} Various circuits have been described for homonuclear decoupling.¹³⁵⁻¹³⁸ An interesting method which uses bilinear rotations (BIRD) has been described for broadband homonuclear proton decoupling.¹³⁹ ^{13}C satellites are observed so as to isolate a particular proton, and ^{13}C pulses permit the local ^{13}C field to act as a decoupling field which eliminates all $^{13}\text{C}-\text{H}$ and $\text{H}-\text{H}$ couplings.

Deuterium decoupling is becoming relatively common¹⁴⁰ and by alternate addition and subtraction of ^{13}C spectra obtained with and without ^2H irradiation it is possible to eliminate signals from carbons not coupled to deuterium.¹⁴¹ In oriented samples such experiments may be difficult to perform owing to the deuterium quadrupole moment which leads to splittings of tens of kilohertz, and a viable alternative is to use spin-echo spectra which can give effective deuterium decoupling.^{142,143}

Modern spectrometers are usually already equipped with very versatile pulse generators, but some of the designs currently described in the literature are also of value,¹⁴⁴⁻¹⁴⁹ and of special interest are those for digital phase shifters needed for multiple quantum work which can provide increments of 90° ,¹⁵⁰ 22.5° ,¹⁵¹ and 15° .^{152,153} Computer control of a frequency synthesizer has been described.¹⁵⁴ Low-frequency and quadrupolar nuclei still give problems as a result of acoustic ringing and/or pulse breakthrough and sequence (5) is reported to suppress these very effectively.^{155,156} Delay should

$$\text{Delay}-\theta^\circ-\text{Acquire}(+)-\text{Delay}-180^\circ-\tau-\theta^\circ\text{Acquire}(-)-\dots \quad (5)$$

be considerably longer than T_1 and θ can be set to the Ernst angle. The sequence (6) with $\Delta = 1/(2J_{AX})$ can be used to calibrate the decoupler field strength in A-{X} experiments, since when $\theta(X) = 90^\circ$ the A signal is nulled.¹⁵⁷



Methods of solvent (usually HDO) suppression continue to attract attention. Although instrumental methods have been used¹⁵⁸ the usual approach¹⁵⁹⁻¹⁶⁵ is based upon a suitable pulse sequence—commonly Redfield 2-1-4—and under suitable conditions it is possible to decouple signals almost degenerate with the water resonance (“underwater decoupling”).¹⁵⁹ Similar methods permit the elimination of ^{13}C signals from deuterated carbons in the solvent,¹⁶⁵⁻¹⁶⁷ and from protonated carbons¹⁶⁸ although doubts have been expressed¹⁶⁹ about the efficacy of the last of these.

INDOR spectra given by AX_n systems¹⁷⁰ and by monosaccharides¹⁷¹ have been studied, and time saving in the production of FT pseudo-INDOR has been achieved by subtracting spectra obtained with irradiation of different transitions rather than by using an unperturbed master spectrum.¹⁷² Some triple resonance INDOR spectra have also been reported.¹⁷³ Spectral subtraction is often allied to double resonance to eliminate unwanted signals, for example, in work on NH proton resonances. In this work, 180° pulses on ^{15}N on alternate scans, together with addition and subtraction of successive spectra, eliminated signals from ^{14}N -containing species.¹⁷⁴ Similar results were obtained using ^{13}C .¹⁷⁵ In homonuclear experiments differential Bloch-Siegert shifts can give imperfect subtraction, and useful computer routines are now available which can correct for these effects.¹⁷⁶

Selective population transfer and inversion methods for the enhancement of signals from insensitive nuclei are now being replaced by INEPT and similar pulse sequences discussed in the next section, but a few interesting examples of their use have been reported. These include ^{15}N -{ ^1H } experiments on pyrrole,¹⁷⁷ fluoropyridine,¹⁷⁷ *N*-alkylformamides,¹⁷⁸ and substituted pyridines¹⁷⁹; ^{29}Si -{ ^1H } experiments on $(\text{CH}_3)_3\text{SiMn}(\text{CO})_5$,¹⁸⁰ and dimethylsilyl ethers derived from coal¹⁸¹; and ^2H -{ ^1H } experiments on oriented CDHCl_2 .¹⁸² The selectivity of the method was utilised in the measurement¹⁸³⁻¹⁸⁵ of couplings involving ^{15}N and/or ^{13}C and ^{29}Si , and double-selective transfer experiments can yield results equivalent to those obtained from INEPT.^{186,187}

IV. SPECIAL PULSE SEQUENCES

Modern spectrometers are equipped with extremely versatile pulse programmers so that a range of pulse sequences are now available that can effect quite remarkable improvements in sensitivity and that can facilitate spectral assignments in a way unthought of only a few years ago. In many cases the experimenter may be let down by his hardware, which can have serious defects in terms of pulse length and rf inhomogeneity. Freeman and Levitt¹⁸⁸ therefore developed the idea of the "composite pulse" whereby a nominally 90° or 180° pulse is built up from a number of other pulses in such a way as to eliminate many of these defects. Initially a series of short minipulses was used,¹⁸⁸ but it has since become apparent that combinations of phase-shifted multiples of 90° pulses are more effective.¹⁸⁹⁻¹⁹¹ Consider the case of rf spatial inhomogeneity and a region of sample where the nominally 90° pulse is only 85° , and the nominally 180° pulse is 170° , so that poor spin inversion would be obtained. Figure 1 illustrates in a simple way the effect of the sequence $90_x^\circ 180^\circ 90_x^\circ$. In the region of sample under consideration the first pulse (actually of say 85_x°) rotates the magnetisation vector to a position just above the xy plane, the second to a position correspondingly below this plane, and the third pulse (again actually only 85_x°) rotates the magnetization to align almost exactly along the $-z$ axis, so that accurate spin inversion is obtained. Similar considerations apply to other deviations of either sign from the nominal pulse lengths (i.e., to other regions of the sample) so that the effects of rf spatial inhomogeneity and, of course, incorrectly set pulse lengths are virtually eliminated. This sequence can bring about dramatic improvements in many spin-echo and other experiments that require accurate 180° pulses¹⁸⁹ and can substantially reduce artifacts in 2D spectra¹⁹² even when pulse lengths deviate

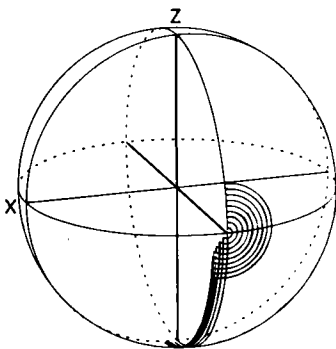


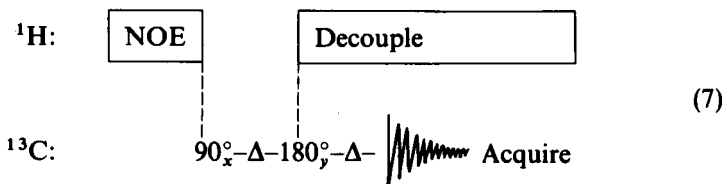
FIG. 1. Paths of the ends of the magnetisation vectors when the sequence $90_x^\circ 180^\circ 90_x^\circ$ is used to convert $+z$ into $-z$ magnetisation, for a range of incorrect settings of the nominal pulse lengths.

by up to 30% from optimum. The sequence can also be useful for broadband decoupling,¹¹⁴ but the other techniques described in Section III are even better.

Off-resonance effects are another problem in experiments requiring 180° pulses on nuclei with large chemical shift ranges, since the magnetization vector can then become rotated out of the yz plane, even though the pulses are nominally along the x axis and the sequence $90_x^\circ 240_y^\circ 90_x^\circ$ can provide good compensation in this case.¹⁸⁸⁻¹⁹⁰ Detailed analysis and computer-aided optimisation has shown that the sequence $90_x^\circ 200_y^\circ 80_y^\circ 200_y^\circ 90_x^\circ$ is even more effective¹⁹¹ and can provide 90% spin inversion at offsets of up to $0.95\gamma B_2/2\pi$ although compensation is not provided for rf spatial inhomogeneity.

A disadvantage of using off-resonance decoupling for the determination of the ^{13}C multiplicity associated with one-bond coupling to protons is that anomalous intensity patterns can arise, and there is also interference from longer range couplings. These difficulties are avoided by the technique of “ J -scaling” whereby short decoupler pulses of alternating phase are applied during the acquisition period so as to reduce all ^{13}C –H splittings by a constant factor.¹⁹³ Various modifications and improvements to the original experiment have been proposed^{194,195} and a detailed examination of the whole problem^{196,197} has led to some impressive spectra together with instructions for the optimisation of parameters. However, it should be pointed out that this method is now superseded by the other simpler methods of multiplicity determination discussed below.

One of the simplest of these methods¹⁹⁸ is to use the spin-echo gated decoupler sequence (7) which is that originally proposed¹⁹⁹ for obtaining 2D- J spectra. The present use is a purely one-dimensional one [Eq. (7)].



The behaviour of the ^{13}C magnetization vectors is illustrated in Fig. 2, and it can be seen that with Δ set to $[^1J(^{13}\text{CH})]^{-1}$ CH and CH_3 groups will give inverted signals, while C and CH_2 groups will give normal ones, as shown by cholesterol in Fig. 3. This experiment is of high sensitivity since fully decoupled ^{13}C signals are detected, and is, of course, reminiscent of early homonuclear experiments.²⁰⁰ Often such an establishment of parity of the multiplicity will be all that is needed for assignment purposes. However, it is possible to proceed further if necessary, and one of the most effective

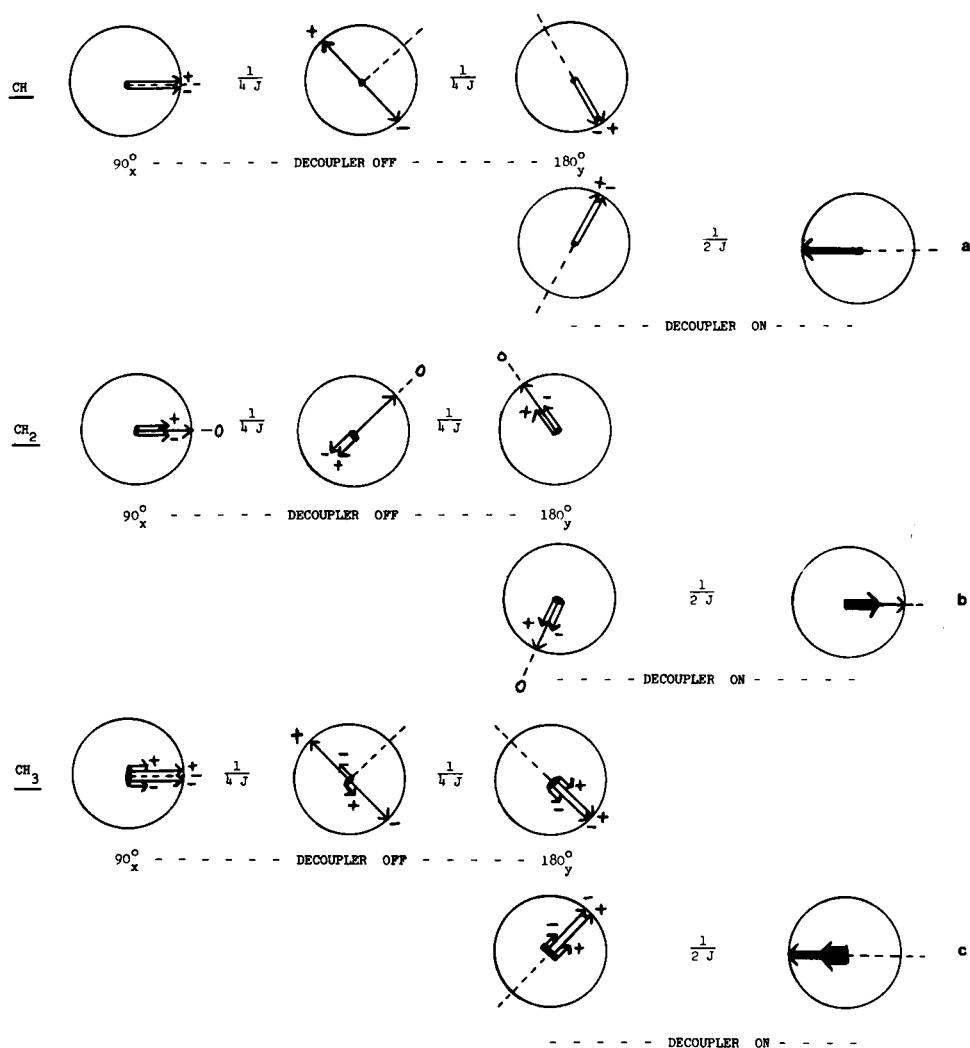


FIG. 2. ^{13}C magnetisation vectors in the xy plane for sequence (7). The full and broken arrows refer to ^{13}C spins associated with different proton spin states, and in the first part of the sequence each precesses in the rotating frame at its own rate. After the application of the refocusing pulse the vectors precess under proton-decoupled conditions at their mean frequency. (a) Components of doublet from a CH group. (b) Outer components of triplet from a CH_2 group; the central component is also refocused along the x axis. (c) Outer components of quartet from CH_3 group; the inner components behave as in (a).

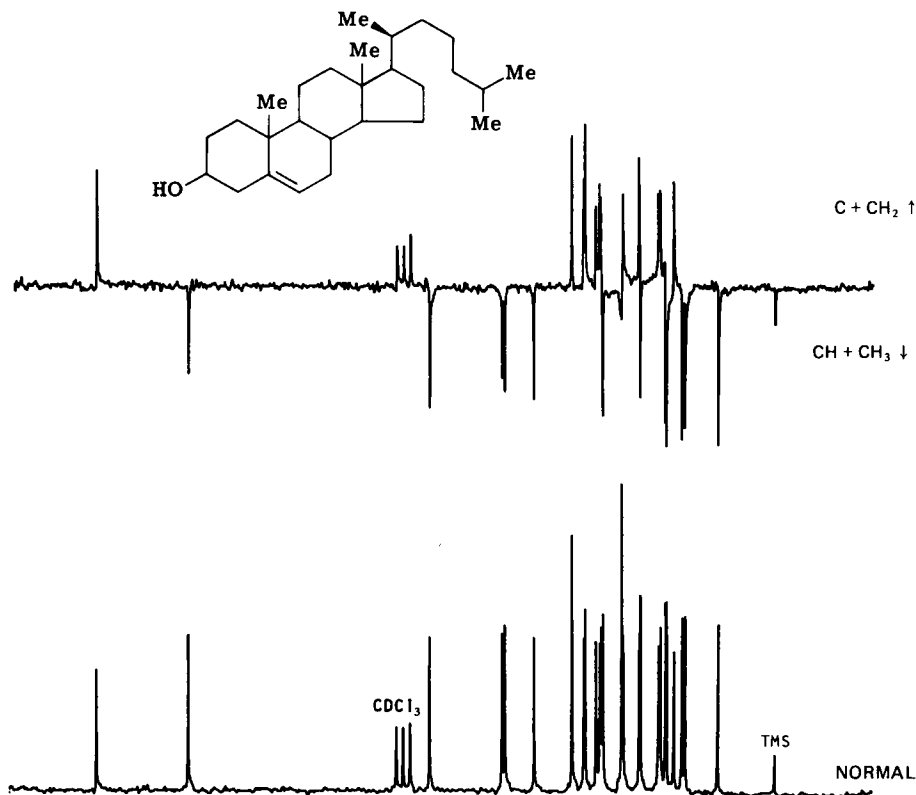
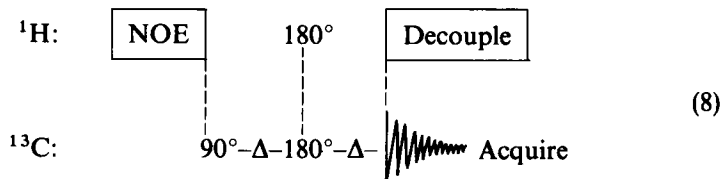


FIG. 3. The application of sequence (7) to the ^{13}C spectrum of cholesterol. Only the aliphatic portion of the spectrum is shown, and resonances from CH and CH_3 groups are inverted, while those from C and CH_2 are of normal phase. Spectra were obtained at 22.5 MHz.

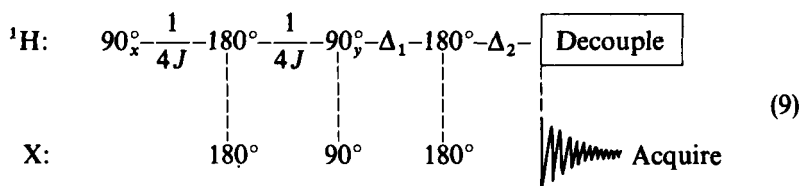
solutions is to use sequence (8) in a "proton-flip" version²⁰¹ of the foregoing experiment. With $\Delta = [4^1J(^{13}\text{CH})]^{-1}$, nonprotonated carbons give a strong



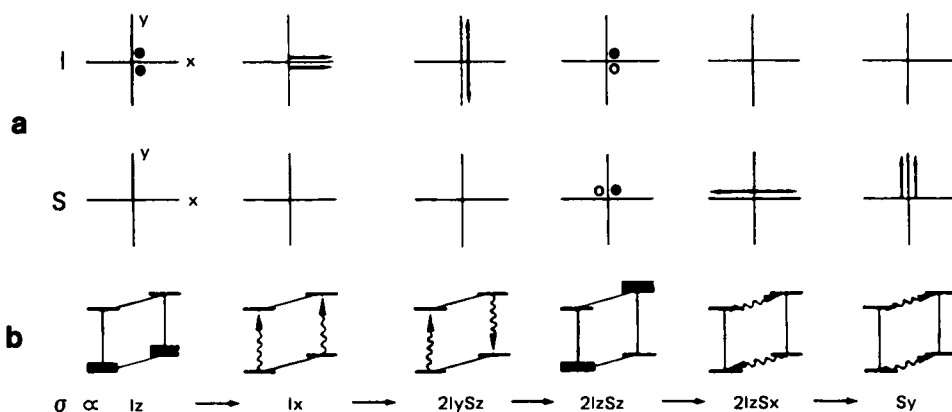
signal while others give a null signal. For incorrect settings of Δ of about 10% the nulling of the signals from CH_2 and CH_3 groups is still good, but CH signals are much more sensitive to any deviations and this can be used to distinguish them from CH_3 groups. Thus the two preceding types of

experiment can identify all four kinds of carbon. Indeed it is possible to go further and to determine whether the CH group has an sp^2 ($J \sim 165$ Hz) or an sp^3 ($J \sim 125$ Hz) hybridized carbon, since if Δ is set to 1.76 msec ($\equiv J = 145$ Hz) the former will give *weak inverted* lines and the latter *weak normal* ones. Similar results have also been achieved²⁰² using sequence (7) with $\Delta = 0.304[{}^1J({}^{13}\text{CH})]^{-1}$ when CH_3 and CH experience 19% and 58% intensity reductions, respectively. Experiments of this type have been subject to theoretical analysis^{203,204} and a variety of similar sequences have been described and applied to a range of chemical problems^{167,205-215} including homonuclear ${}^{31}\text{P}$ multiplicity determination in nucleotides,²⁰⁴ and distinguishing between CD, CD_2 , and CD_3 groups.^{212,213} Some of these experiments have involved short bursts of noise decoupling to give randomization of the spins,^{107,108} and a 2D approach to this problem has been described.²¹⁶

When allied to addition and subtraction routines the foregoing experiments can be used for spectral subediting to produce individual spectral traces from each kind of carbon, but the most usual approach to this is via the INEPT and DEPT sequences. INEPT²¹⁷ (insensitive nuclei enhancement by polarization transfer) is essentially a form of heteronuclear selective population inversion which uses refocusing pulses to eliminate any dependence upon the chemical shifts of the protons from which spin polarization is transferred. Sequence (9)

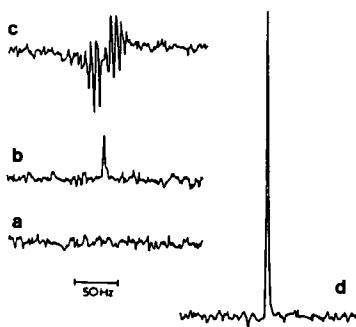


shows the experiment as modified by Burum and Ernst,²¹⁸ and Fig. 4 illustrates the behaviour of the magnetization vectors for a simple HX system. The initial 90° proton pulse aligns the two proton vectors (corresponding to opposite spin states of X) along the y axis in the rotating frame and they precess for a time $(4J)^{-1}$ (where J is the XH coupling) when they will have diverged by 90° . The 180° proton pulse then generates an echo at time $(2J)^{-1}$ when all proton chemical shifts are refocused, but since the 180° X pulse has reversed the labelings of the proton spin states the two vectors have continued to diverge during the second precessional period, and as a result at time $(2J)^{-1}$ they are 180° apart and are aligned along the $+x$ and $-x$ axes, respectively. The 90° proton pulse along the y axis then rotates one of these vectors back to its original position along the z axis, while the other becomes aligned along $-z$, that is, selective inversion of one of the two proton transitions has been achieved. This is just what is done in a normal SPI experiment,²¹⁹ and a 90° X-read pulse applied at this time will give a spectrum in which the X lines exceed



their normal intensities by a factor of $(\gamma_H/\gamma_X) \pm 1$ as a result of polarization transfer from protons. If desired these intensity factors can be equalised at $\pm \gamma_H/\gamma_X$ by a saturating X pulse applied immediately prior to the experiment.

For nuclei with small magnetogyric ratios even this simple form of the experiment leads to worthwhile gains in sensitivity, as illustrated in Fig. 5 for ^{29}Si . In common with SPI a negative γ poses no disadvantage (in contrast to the situation with the nuclear Overhauser enhancement) and the repetition rate for the experiment is governed by $T_1(\text{H})$ rather than $T_1(\text{X})$, which may be unduly large. The main advantage over SPI is that the experiment is independent of the proton chemical shifts, and, indeed, an error of up to 20% in the chosen value of $J(\text{XH})$ can be tolerated with little loss of intensity.



If proton decoupling is desired it is necessary to incorporate additional time delays and refocusing pulses as shown in the right-hand half of sequence (9), where for an XH (X of spin $\frac{1}{2}$) system, Δ_1 should be made equal to $(4J)^{-1}$. For XH_n systems, Δ_2 should be shorter,²¹⁸ e.g., $(2J)^{-1}$ for $n = 2$, $(4J/3)^{-1}$ for $n = 3$, and, as n gets larger, greater enhancements become possible. Table 1 lists²²⁰ optimum settings of Δ and theoretical enhancements for values of n up to 18.

Although the INEPT sequence is most effective when $J(\text{XH})$ is fairly large so that T_2 relaxation during the periods of free precession is minimised, normally that is when there is a direct X–H bond, good results can also be achieved for $J(\text{XH})$ of only 1 Hz or so. This is illustrated in Fig. 6, which shows the natural abundance (0.35%) ^{15}N spectrum of CH_3CN . In this molecule $J(^{15}\text{NH})$ is 2.2 Hz and $T_1(^{15}\text{N}) > 160$ sec. In cases where several different X–H couplings are available to effect the polarization transfer, it is generally best to set the times so as to use the largest. Even so, when there are several values of $J(\text{XH})$, anomalous intensity patterns can occur in proton-coupled spectra as a result of some magnetization vectors completing several circuits in the rotating frame.

INEPT has now been used to get spectra at high sensitivity for a number of nuclei including ^{15}N in benzyloxycarboxylglycylglycine methyl ester,²²¹ in enamines, pyrimidines, and pyridines,²²² in 1-methyl- N^4 -methoxycytosine,²²³ and in peptides²²⁴; ^{13}C in peptides,²²⁵ in 6*H*-pyrido-[4,3-*b*]-5,11-dimethylcarbazole,²²⁶ in lipoteichoic acid,²²⁷ in paramagnetic transition metal complexes where the normal NOE is ineffective,²²⁸ and in

TABLE 1

Optimum settings of Δ_1 and maximum theoretical enhancements in the INEPT sequence (9) for different numbers (n) of equivalent coupled protons

n	$\Delta_1 (J^{-1})$	Enhancement ($\gamma_{\text{H}}/\gamma_{\text{X}}$)
1	0.5	1
2	0.25	1
3	0.196	1.155
4	0.167	1.1299
6	0.134	1.553
8	0.115	1.772
9	0.108	1.873
12	0.093	2.147
15	0.083	2.389
18	0.076	2.610

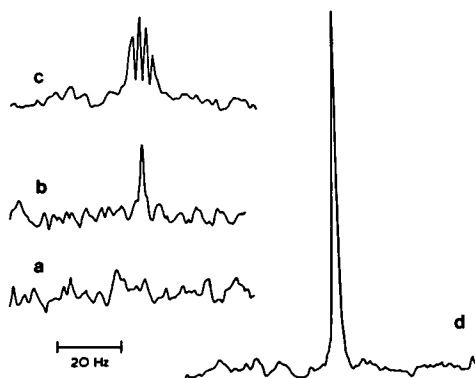


FIG. 6. Natural abundance ^{15}N spectra at 9.0 MHz of neat MeCN in a 10-mm tube. (a) Normal spectrum without proton decoupling from four transients. (b) INEPT spectrum with proton decoupling, single transient. (c) INEPT spectrum without proton decoupling, 80 transients in 400 seconds (d) INEPT spectrum with proton decoupling in 400 seconds.

amino acids and nucleotides, although in the latter there are difficulties associated with short values of T_2 for high-molecular-weight molecules²²⁹; ^{103}Rh , ^{109}Ag , and ^{183}W in some complexes^{230,231}; and ^{29}Si and ^{119}Sn which have negative γ .^{220,232} Polarization transfer has also been achieved to quadrupolar nuclei including ^{10}B , ^{11}B , and ^{14}N , although here the advantage is questionable since the pulsing rate is governed by $T_1(\text{H})$ whereas it could be much faster for straight observation of the quadrupolar nucleus.²³³ Transfer from nuclei other than protons has also been used, as in $^{13}\text{C}\{-^2\text{H}\}$ experiments²³⁴ used for the detection of C-D bonds [$^1J(^{13}\text{C}^2\text{H})$ is ~ 25 Hz] and in phosphine complexes of transition metals where the existence of $^1J(\text{M}^{31}\text{P})$ permitted substantial enhancements to be obtained²³⁰ for ^{57}Fe , ^{103}Rh , and ^{183}W , which all are of poor sensitivity.

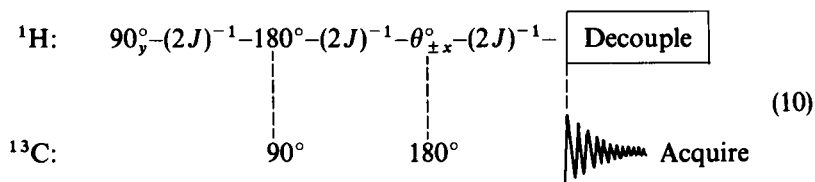
INEPT can also be used in reverse to transfer spin polarization from another nucleus X to protons and thus give selective detection of protons attached to (strictly coupled to by the chosen value of J) X, which can be important if X is of low natural abundance. An early example of this approach was by Bodenhausen and Ruben²³⁵ who used a sequence of 10 pulses to transfer polarization from protons to ^{15}N and then back again to protons whose superior sensitivity to detection was thereby utilised. A variable delay between the two transfers and double Fourier transformation is used to probe the ^{15}N chemical shifts. Reverse INEPT allied to spectral subtraction²³⁶ is used to record ^{13}C satellites in the proton spectrum of acetaldehyde at suppression ratios in excess of 800:1. Comparable results can be attained using spin echoes and simultaneous ^{13}C 180° pulses.^{236,237} This ability of the INEPT sequence to select particular protons has also been used

to measure proton longitudinal relaxation times in cholesteryl acetate.²³⁸ An initial 180° proton pulse is applied to the system and then after a delay τ , a ^{13}C INEPT sequence yields ^{13}C lines with intensities that reflect the proton populations; by varying τ the proton relaxation times can be determined in the usual way. Since the dispersion in ^{13}C spectra is usually much greater than for protons this method is useful for complex molecules, and some problems associated with second-order effects may also be avoided. Similar experiments together with ^{13}C decoupling during acquisition of the proton free induction decay (FID) were used to get proton signals from individual carbon sites in sparteine.²³⁹

Direct measurements of relaxation times can be aided by using an INEPT sequence to generate enhanced non-Boltzmann X populations and then studying their decay in the normal way,²⁴⁰ and the method promises to be especially valuable for ^{15}N and ^{29}Si . If proton decoupling is used during data acquisition there may be difficulties of interpretation associated with the rate of build-up of the NOE, but these are avoided in ^{15}N experiments on linear peptides²⁴¹ where proton-coupled spectra are recorded. INEPT has also been used selectively to transfer polarization from chosen protons only,²⁴² and a set of spectra can then be obtained which when presented as a stacked plot yield a visualization of, for example, $^{13}\text{C}/^1\text{H}$ chemical shift correlations. In a rather similar vein the chemical shift of M has been determined in connection with A- $\{X\}$ INEPT experiments on an AMX system where A and M are of the same nuclear species.²⁴³ In the case where $J(\text{MX}) = 0$ selective decoupling of M is necessary if the full INEPT effect is to be achieved, and the frequency needed for this gives $\delta(\text{M})$. Versions of INEPT have also been used to get 2D J correlated spectra.²⁴⁴

It is also possible to use INEPT to determine proton-coupled ^{13}C multiplicities by omitting the final 180° proton and ^{13}C refocusing pulses, but including a delay Δ prior to data acquisition and simultaneous decoupling.²⁴⁵ Using this sequence quaternary carbons are always suppressed, while with $\Delta = (2J)^{-1}$ only CH carbons appear. With $\Delta = 3(4J)^{-1}$, CH_2 carbons give inverted signals and those from CH and CH_3 groups are normal, so when these spectra are combined with a normal one in a suitable subtraction routine it is possible to obtain traces containing decoupled responses from carbons of chosen multiplicity only.²⁴⁵

Unfortunately the preceding use of INEPT leads to serious phasing anomalies across the spectrum which cannot normally be corrected by using the zero- and first-order phase parameters. This difficulty is avoided²⁴⁶ in the distortionless enhancement by polarization transfer (DEPT) sequence (10), which uses variable pulse angles instead of variable delays to achieve the desired discrimination among the different types of carbon according to their multiplicity. A simple description in terms of magnetization vectors is not



easy but this sequence has been fully analysed²⁴⁷ for the CH , CH_2 , and CH_3 cases, and experimental examples have been given for XH_n system with n as large as 12. For work on ^{13}C it is necessary to perform three experiments with θ (which is applied alternately along the plus and minus x axes) set to 45° , 90° , and 135° and store the results in computer memory. Linear combinations of these spectra in proportions which are usually determined empirically then yield subspectra containing responses from CH , CH_2 , and CH_3 groups only, with remarkably little distortion, as illustrated in Fig. 7. Problems that do

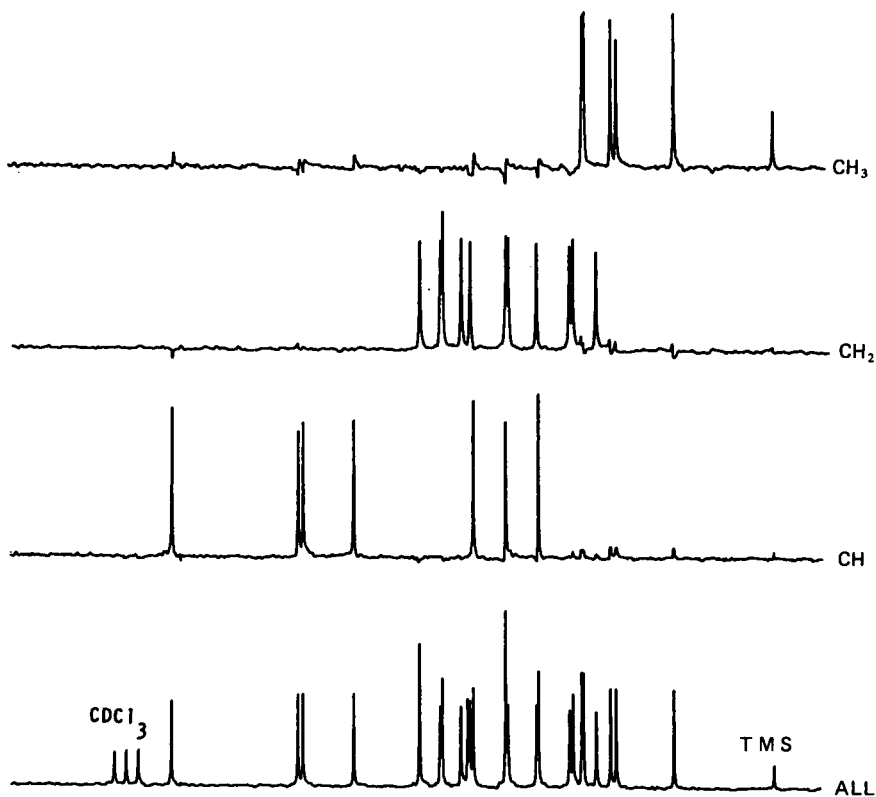


FIG. 7. ^{13}C DEPT spectra at 22.5 MHz of cholesterol. Decoupled spectra from proton-bearing carbons of chosen multiplicity can be selected at will.

arise with DEPT are generally due to inadequate pulse power, which can be avoided by applying phase-alternated 90° ^{13}C pulses prior to acquisition of the data,²⁴⁸ or to a wide spread of values of $J(\text{CH})$, which can also be avoided.²⁴⁹ In fact DEPT and INEPT have the same basis,⁶⁶ so it is not surprising to find that inverse DEPT for identifying CH , CH_2 , and CH_3 groups in proton spectra²⁵⁰ and a $^{13}\text{C}-\{^2\text{H}\}$ version of DEPT^{251,252} have been described. Unusual relaxation behaviour in large molecules can also lead to abnormal intensities in DEPT spectra, but these can be of use for the identification of isolated, freely rotating methyl groups.²⁵³

More generally, a full analysis²⁵⁴ of INEPT and DEPT has led to INEPT⁺ [sequence (11)], DEPT⁺ [sequence (12)], and DEPT⁺⁺ [sequence (13)], which have greater freedom from distortions than their predecessors. It should be noted that although INEPT has more pulses than DEPT the total time required is less, and this may be important for minimising T_2 relaxation when J is small. The sequence (14) also uses a variable angle rather than a delay to achieve multiplet selection.²⁵⁵

It is sometimes difficult to implement INEPT and DEPT on older spectrometers because of the need for a 90° phase shift in the decoupler channel. This is avoided in the sequence (15) for enhancing the resonance of X by polarization transfer, although there is a dependence upon transmitter offset which could give problems in multiline spectra.²⁵⁶ The Exclusive Polarization Transfer (EPT) sequence can give spectra from CH groups only.²⁵⁷

In solid-state NMR, cross-polarization methods using the dipole-dipole couplings are commonly used to enhance ^{13}C and other spectra via magnetization transfer from protons. In liquids it is possible to use $J(^{13}\text{CH})$ [or more generally $J(\text{XH})$] in a similar way²⁵⁸ by using spin-locking experiments and satisfying the Hartmann-Hahn matching condition $\gamma(^1\text{H})B_2 = \gamma(^{13}\text{C})B_1$. The method is termed J cross polarization (JCP) and has the same advantages as INEPT in terms of sensitivity and dependence of repetition rate upon $T_1(^1\text{H})$ and has been used to enhance the spectra of ^{13}C , ^{15}N , and ^{29}Si .²⁵⁸⁻²⁶⁴ A difficulty with JCP is its undue sensitivity to the exactness of the Hartmann-Hahn match and the value of $J(\text{XH})$, and this and various phase anomalies are avoided in refocused-JCP (RJCP)²⁶⁵ and phase-corrected JCP (PCJCP).²⁶⁶ Other related experiments have also been described.^{267,268}

The sequence (16) can be used to give signals from nonprotonated carbons only for a wide range of values of $^1J(^{13}\text{CH})$ such as may be found when both aliphatic and aromatic carbons are present.²⁶⁹ Many earlier sequences are unable to handle such situations in a satisfactory manner.

As a result of the low natural abundance of ^{13}C , molecules containing two such nuclei are very rare, but nonetheless can be detected on modern

$$\begin{array}{lcl}
 {}^1\text{H}: & 90^\circ_x - (4J)^{-1} - 180^\circ_y - (4J)^{-1} - 90^\circ_{\pm y} - \Delta - 180^\circ_y - \Delta - 90^\circ_x & \\
 {}^{13}\text{C}: & \begin{array}{c} \text{---} 180^\circ_y \quad \quad \quad 90^\circ_x \quad \quad \quad 180^\circ_y \end{array} & \begin{array}{c} \text{---} \text{Acquire } \pm \end{array}
 \end{array} \quad (11)$$

$$\begin{array}{lcl}
 {}^1\text{H}: & 90^\circ_x - (2J)^{-1} - 180^\circ_y - (2J)^{-1} - \theta^\circ_{\pm y} - (2J)^{-1} - 180^\circ_y & \\
 {}^{13}\text{C}: & \begin{array}{c} \text{---} 90^\circ_y \quad \quad \quad 180^\circ_y \end{array} & \begin{array}{c} \text{---} \text{Acquire } \pm \end{array}
 \end{array} \quad (12)$$

$$\begin{array}{lcl}
 {}^1\text{H}: & 90^\circ_x - (2J)^{-1} - 180^\circ_y - (2J)^{-1} - \theta^\circ_{\pm y} - (4J)^{-1} - 180^\circ_y - (4J)^{-1} - 90^\circ_x - (4J)^{-1} - 180^\circ_y - (4J)^{-1} - & \\
 {}^{13}\text{C}: & \begin{array}{c} \text{---} 90^\circ_x \quad \quad \quad 180^\circ_y \end{array} & \begin{array}{c} \text{---} \text{Acquire } \pm \end{array}
 \end{array} \quad (13)$$

$$\begin{array}{lcl}
 {}^1\text{H}: & \begin{array}{c} \boxed{\text{Noise}} \quad \quad \theta^\circ_x \quad \quad \boxed{\text{Decouple}} \end{array} & \\
 {}^{13}\text{C}: & \begin{array}{c} \text{---} 90^\circ - \tau - 180^\circ - \tau - \end{array} & \begin{array}{c} \text{---} \text{Acquire} \end{array}
 \end{array} \quad (14)$$

$$\begin{array}{lcl}
 {}^1\text{H}: & 90^\circ_x - (2J)^{-1} - 90^\circ_x & \\
 \text{X}: & \begin{array}{c} \text{---} 90^\circ \end{array} & \begin{array}{c} \text{---} \text{Acquire} \end{array}
 \end{array} \quad (15)$$

$$\begin{array}{lcl}
 {}^1\text{H}: & & 180^\circ \\
 & \text{---} & \text{---} \\
 {}^{13}\text{C}: & 90^\circ - (2J)^{-1} - 180^\circ_{\pm x, \pm y} - (2J)^{-1} - & \boxed{\text{Decouple}} \\
 & & \text{Acquire}
 \end{array} \quad (16)$$

spectrometers if methods are used to suppress signals from species with only one ^{13}C nucleus. The value of $^1J(^{13}\text{C}^{13}\text{C})$ is usually some tens of hertz, and longer range ^{13}C - ^{13}C couplings are much less, so molecules with *adjacent* ^{13}C nuclei will give AB or AX spectra, while molecules with only one ^{13}C will give single-line spectra. Sequence (17) can be used to detect the former selectively

$$90^\circ_x - \tau - 180^\circ_{\pm y} - \tau - 90^\circ_x - \Delta - 90^\circ_\psi \text{ Acquire}_\psi \quad (17)$$

by creating multiple quantum coherence and then converting it into single quantum coherence which can be detected. The phase ψ is cycled through $+x$, $+y$, $-x$, $-y$, so as to eliminate signals from single- ^{13}C species, and the delay Δ is normally only a few μsec to allow for the resetting of the phase of the final read pulse. The time τ is set so that when the refocusing pulse is applied the components of a ^{13}C -coupled multiplet are 90° out of phase, that is $\tau = (2n + 1)/(4J_{cc})$ where $n = 0, 1, 2, \dots$. This experiment has been dubbed INADEQUATE (*incredible natural abundance double quantum transfer experiment*) by Bax and Freeman,²⁷⁰ and autocorrelation by Turner (in a 2D modification)²⁷¹ since it permits the recognition of adjacent carbons by identifying common values of $^1J(^{13}\text{C}^{13}\text{C})$. Figure 8 shows an example of an INADEQUATE spectrum, and it is worth noting that better suppression of the signals from one- ^{13}C species can be achieved by using more elaborate

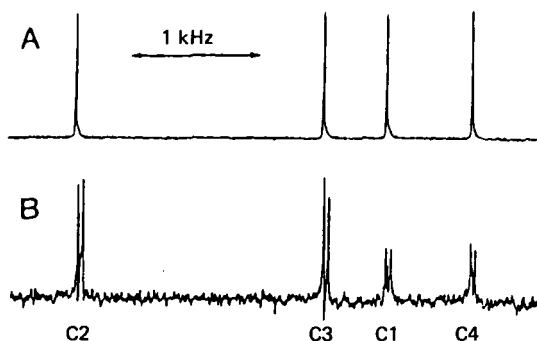


FIG. 8. (A) Normal ^{13}C spectrum of butan-2-ol at 50 MHz. (B) Same spectrum with singlets suppressed by using sequence (17) to give doublets from species with adjacent ^{13}C nuclei. From reference 271.

phase cycling than indicated above. It is of course necessary to set τ correctly, and indeed this parameter can be used as a running time variable in a 2D experiment as described in Section V. However, it is always possible to choose n so that the value of τ is appropriate to several values of $J(^{13}\text{C}^{13}\text{C})$, although there can be problems with strongly coupled spin systems.²⁷² A computer program COSMIC is available²⁷³ that can be used to aid the interpretation of a 1D INADEQUATE spectrum in terms of carbon-carbon connectivities, and other methods have been reported for detecting species containing two ^{13}C nuclei at natural abundance²⁷⁴⁻²⁷⁶ and at high enrichments.^{277,278} By adjusting the delay Δ in sequence (17) it is possible to select a particular frequency of double-quantum coherence and hence aid assignments.^{279,288} The foregoing methods have been used to study $^1J(^{13}\text{C}^{13}\text{C})$ in monosaccharides,²⁸⁰ $^nJ(^{13}\text{C}^{13}\text{C})$ in *n*-octanol,²⁸¹ anthrasteroids,²⁸² sites of ^{13}C enrichment in metabolic studies,²⁸³ the diterpene velloziolide,²⁸⁴ patchoulol,²⁷⁴ and pinane and codeine.²⁷⁵ The sensitivity of INADEQUATE can be improved by prefacing it with an INEPT sequence instead of using the normal proton NOE,²⁸⁵ and the use of 60 or 120° read pulses also brings about improvements.²⁸⁶

It is also possible to apply INADEQUATE to proton systems, and although the results are more complex they can often be regarded as arising from sets of AMX systems and may also give relative signs of coupling constants.²⁸⁷ An application to 9-hydroxytricyclodecan-2,5-one has been reported.²⁸⁷ In a similar vein, the DOUBTFUL (DOUBle quantum Transitions for Finding Unresolved Lines) technique²⁸⁸ has used double-quantum coherence to detect AX and AB systems in cytosines,²⁸⁹ and triple-quantum coherence to detect three-spin systems in the proton spectra of proteins.²⁹⁰

Multiple- (including zero-) quantum experiments are growing in importance and are the subject of a valuable review.²⁷ Many of them involve the use of 2D methods even though a 2D plot may not always be produced. They are discussed in Section V; however, it is appropriate to discuss a number of aspects here. Many methods for exciting multiple-quantum coherences require phase shifts that are not multiples of 90°; it has been shown²⁹¹ that it is possible to achieve these by using composite pulse sequences if the appropriate hardware is not available. For example, the sequence (18) is equivalent to (19) and generates a rotation of Θ° about the z axis at the beginning of the evolution period.

$$90_x^\circ - \tau - \Theta_y^\circ 90_x^\circ - t_1 - 90^\circ \text{ Acquire} \quad (18)$$

$$90_x^\circ - \tau - 90_x^\circ \Theta_z^\circ - t_1 - 90_x^\circ \text{ Acquire} \quad (19)$$

Spin-tickling experiments have been used to lift degeneracies in order to get multiple-quantum spectra from quadrupolar nuclei.^{292,293} Wide-band selective excitation of n -quantum transitions for n up to 6 with the aid of small phase shifts has been described²⁹⁴ and other methods for getting similar results have also been reported.^{295–300}

Various kinds of spin-echo experiment have found a range of applications^{301–313} including the indirect detection of ^{199}Hg signals at high sensitivity.^{314,315} Pulse sequences used for special purposes include RELAY³¹⁶ (relayed correlation spectroscopy), for transferring magnetization between uncoupled nuclei; the “1-2-1” sequence³¹⁷; and a combination³¹⁸ of DANTE (Delays Alternating with Notations for Tailored Excitation) selective excitation with WEFT (Water-Eliminated Fourier Transform) for solvent suppression; the sequence (20), which can provide information on cross-correlation spectral densities in macromolecules³¹⁹; and sequences useful in connection with relaxation time and diffusion measurements.^{320–323}

$$\begin{array}{ll}
 {}^1\text{H}: & 180^\circ \\
 & \vdots \\
 {}^{13}\text{C}: & 180^\circ - \tau - 90^\circ \quad \text{Acquire}
 \end{array} \quad (20)$$

V. TWO-DIMENSIONAL NMR

Most of the basic ideas behind two-dimensional NMR (i.e., experiments wherein frequency dispersion is obtained in two dimensions, with the intensity being represented along a third axis) were worked out and demonstrated between 1971 and 1978 and are discussed in reference 2. The period since then has seen much refinement and consolidation of the technique together with numerous examples of its routine application to a wide variety of chemical problems. An excellent guide to most of the 2D techniques of use to chemists is available,¹⁸ and a book has been published on the subject by one of its most active practitioners.¹⁶ Many other reviews have also been published.^{4–10,12,13,27}

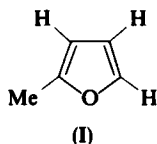
Although displays of 2D NMR spectra as a mountainous landscape have considerable visual appeal, they are time consuming to produce, and for most purposes appropriate cross-sections and projections can be adequately or even more informative.^{324,325} In particular, “skyline” projections, which are obtained by noting the maximum intensity along each slice of the full spectrum,³²⁵ can be superior, in terms of line shapes, to those obtained by summing the signal intensities.³²⁴ Contour plots^{325,326} are also a popular way of presenting 2D spectra, but it should be borne in mind that much can be concealed by (un)suitable choices of plotting threshold. In homonuclear 2D J spectroscopy 45° projections can give spectra displaying only chemical shifts

and heteronuclear couplings,^{327–329} that is, the appearance of broadband homonuclear decoupling can be achieved; cross-sections will have splittings arising from homonuclear coupling only, that is, the effect of heteronuclear decoupling will be obtained.³²⁷ Similar results can be obtained by skewing the whole 2D spectrum through 45° prior to projection, and projections have been used to achieve broadband homonuclear decoupling in complex ^{31}P spectra.³³⁰

Many forms of 2D experiment yield spectra with a “phase-twist” line shape which necessitates the use of an absolute value mode of presentation with its attendant unsatisfactory line shapes. These can be avoided³³¹ by acquiring complete spin echoes (rather than only the second half as is usual) or (at the expense of sensitivity) by shaping the FID prior to transformation so that it resembles a spin echo.³³² More generally, this kind of problem has been tackled by a computer routine which applies phase corrections to remove all twist appearance,³³³ by combining gated-decoupler $^{13}\text{C}/^1\text{H}$ correlated spectra obtained in the decoupler on/off and off/on modes,³³⁴ by confining attention to particular cross-sections so that only two phasing variables are needed,^{335,336} by delaying acquisition in 2D *J*-resolved spectra,³³⁷ by using separate quadrature detection in both dimensions for NOE spectra,³³⁸ and by means of the FOCSSY (fold-over corrected correlated spectroscopy) method.³³⁹ All of the foregoing can provide much needed improvements in resolution for crowded spectra from large molecules.

Other problems associated with experimental 2D NMR that have been studied include effects due to incorrectly set and/or inhomogeneous rf pulses,^{189,192,340} spinning sidebands in both dimensions,³⁴¹ and ways of reducing the size of the data matrix required by applying a mask³⁴² to the FID and by various forms of controlled foldback.³⁴³ The usual way of recording a 2D spectrum is to perform a separate experiment for each value of t_1 , but this is rather time consuming. This can be avoided in *J*-resolved spectroscopy by applying a Carr–Purcell–Meiboom–Gill (CPMG) sequence and acquiring all n echoes and hence all the 2D data in a single experiment with nT (T = time between successive refocusing pulses) as the running t_1 time variable.³³¹ This can place some restrictions on the resolution in the f_2 dimension since the acquisition time cannot exceed $T/2$, but nonetheless a great saving in time overall can be achieved. A powerful alternative approach to the same problem is to use the MUDISM (*Multidimensional stochastic magnetic*) resonance technique,^{344,345} in which a set of 10^6 or more raw data is collected in a time of only a few seconds. Given sufficient computer power it is then possible to obtain many types of 3D, 2D, and 1D spectra (the last two as cross-sections), and no decisions about the nature of the experiment need be made until this stage. Considerable experimental and computational detail has been published on this technique.³⁴⁵

On the whole, workers in 2D NMR tend to avoid spin systems with second-order features, but LAOCOON has been adapted to calculate 2D J spectra,^{84,346} and analytical solutions have been presented for the AB,^{346,347} AB₂,⁸⁴ and other spin systems.^{346,348} Two-dimensional spectra have also been obtained from molecules oriented in a liquid crystal solvent,^{57-59,84,85,178,349,350} and it is clear that multiple-quantum methods will have much to offer in the study of such systems. Notwithstanding the superior resolving power of 2D NMR there are still occasions when there is serious overlapping of resonances, and these often can be alleviated by the application of older double-resonance methods as part of the 2D experiment. Thus selective proton decoupling was used in J -resolved homonuclear proton experiments on the α -proton and methyl resonances of the basic pancreatic trypsin inhibitor³⁵¹ and a detailed examination of this type of experiment has considered off-resonance effects and gated modes of operation which can provide selective decoupling in either the f_1 or f_2 dimension.³⁵² Such experiments were also used to determine proton chemical shifts in the ¹³C/¹H 2D spectrum of (I),³⁵³ and in ³¹P/¹H spectra.³⁵⁴



A variant on this is to produce 2D spectra in a time/frequency (rather than time/time) domain experiment by stepping a weak irradiating field through the resonances of one of the nuclear species together with spin-echo or subtraction methods to eliminate unperturbed signals. One-dimensional Fourier transformation of the individual traces for each value of the irradiating frequency can then yield the 2D spectrum as a stacked plot. This method has been used to produce ¹³C/¹H³⁵⁵ and ³¹P/¹⁰⁷Ag³⁵⁶ chemical shift correlated spectra, and there have been similar applications of selective INEPT experiments.²⁴² The DEPT pulse sequence has been used in conjunction with 2D methods to separate the resonances from CH₃, CH₂, and CH groups^{357,358} and similar results have been obtained by using difference spectroscopy.³⁵⁹

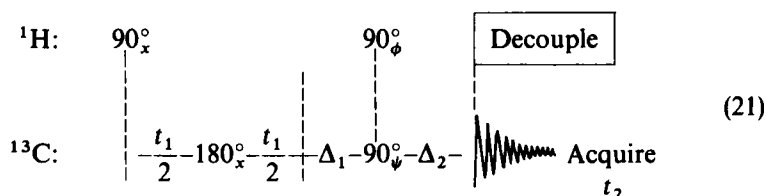
The sequence (21) leads to 2D spectra in which the f_1 axis exhibits proton dispersion and the f_2 exhibits ¹³C dispersion, all ¹³C–H splittings being eliminated in both dimensions. The delays Δ_1 and Δ_2 are set to be $[2^1J(^{13}\text{CH})]^{-1}$ and about half of this, respectively, to avoid mutual cancellation of out-of-phase signals, the latter time being a compromise adopted to cater for CH₃, CH₂, and CH groups.³²⁶ An improvement using phase cycling in accordance with Table 2 permits quadrature in both dimensions, so that the proton pulse can be set at the middle of the f_1 dimension, and makes

TABLE 2

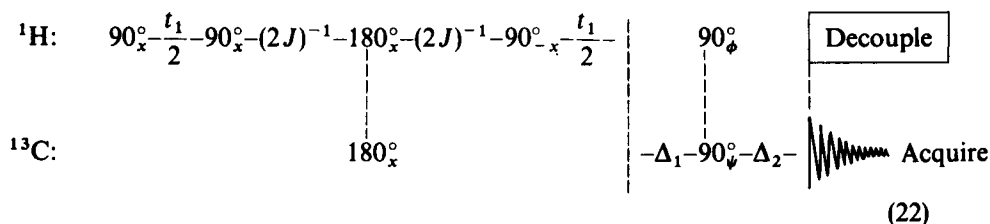
Phases for the final proton (ϕ) and ^{13}C (ψ) pulses for use with sequences (21) and (22) in order to get quadrature in both dimensions

Cycle	ϕ	ψ
1	$+x$	$+x$
2	$+y$	$-y$
3	$-x$	$-x$
4	$-y$	$+y$

better use of the rf power and provides better resolution.³⁶⁰ Figure 9 shows cross-sections from the $^{13}\text{C}/^1\text{H}$ chemical shift correlation spectrum of 1-fluoronaphthalene obtained in this way.



These cross-sections show fine structure due to proton-proton coupling. They indeed can provide a convenient means of measuring such couplings in second-order spectra, but the splittings can be a nuisance if the main objective is to determine proton chemical shifts as accurately as possible. This problem can largely be avoided by using sequence (22), in which a pulse sequence is



applied to the protons at the same time as the ^{13}C refocusing pulse so as to flip selectively only the spins of protons bound to the relevant ^{13}C nucleus. This produces the desired decoupling effect in the t_1 dimension for all protons except inequivalent ones within the same CH_2 group. Thus all the proton signals become either singlets or part of AB or AX patterns,³⁶¹ and there is a considerable improvement in signal-to-noise ratio and effective resolution. Figure 10 demonstrates the value of the technique when applied to raffinose even on a low-field (protons at 90 MHz) spectrometer.

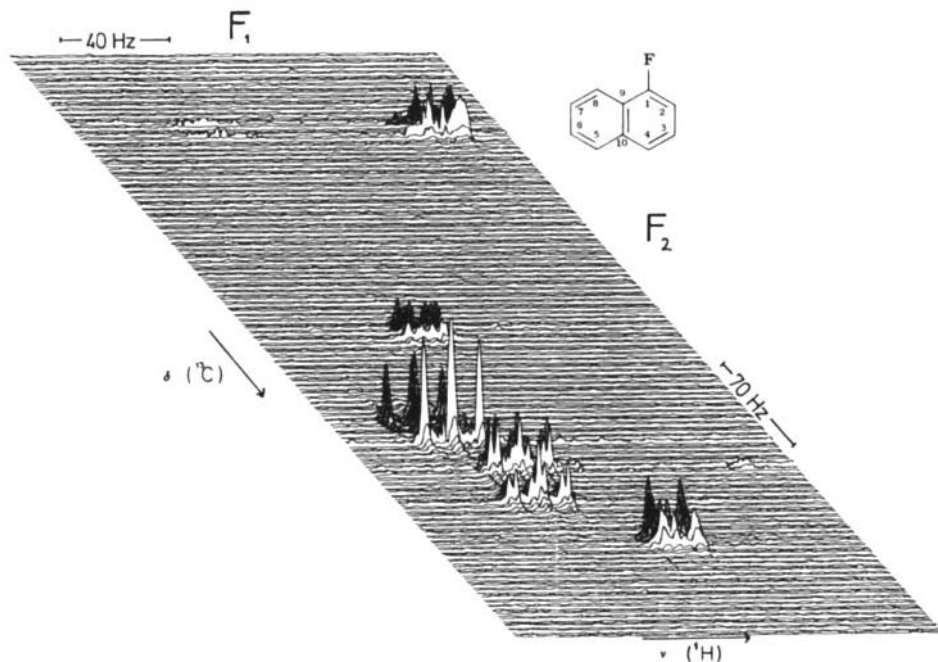
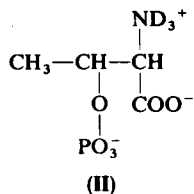


FIG. 9. ^{13}C - ^1H 2D chemical shift correlated spectrum of 1-fluoronaphthalene showing homonuclear proton couplings, together with ^{13}C - ^{19}F and ^1H - ^{19}F couplings in different dimensions. ^{13}C , 22.5 MHz; ^1H , 89.6 MHz; 256×1024 data matrix. $\square$, $^{19}\text{F}_\alpha$; $\blacksquare$, $^{19}\text{F}_\beta$; C_2 not shown.

$^{13}\text{C}/^1\text{H}$ chemical-shift correlated spectra have ^{13}C intensities which reflect the initial proton populations and thus can be used for the measurement of proton relaxation times in complex spectra with many overlapping lines.³⁶² This idea of using a "spy" nucleus can be extended to probing the populations of individual proton (or other nucleus) spin states so as to get details of exchange rates for example.³⁶³ It is also possible to use these kinds of effect in more extended coupling networks, so that the studied nucleus need not be coupled directly to the observed one.³⁶⁴⁻³⁶⁶ Thus in (II), ^{31}P observation was used to detect the CH_3 protons, even though these are not coupled to phosphorus.³⁶⁴



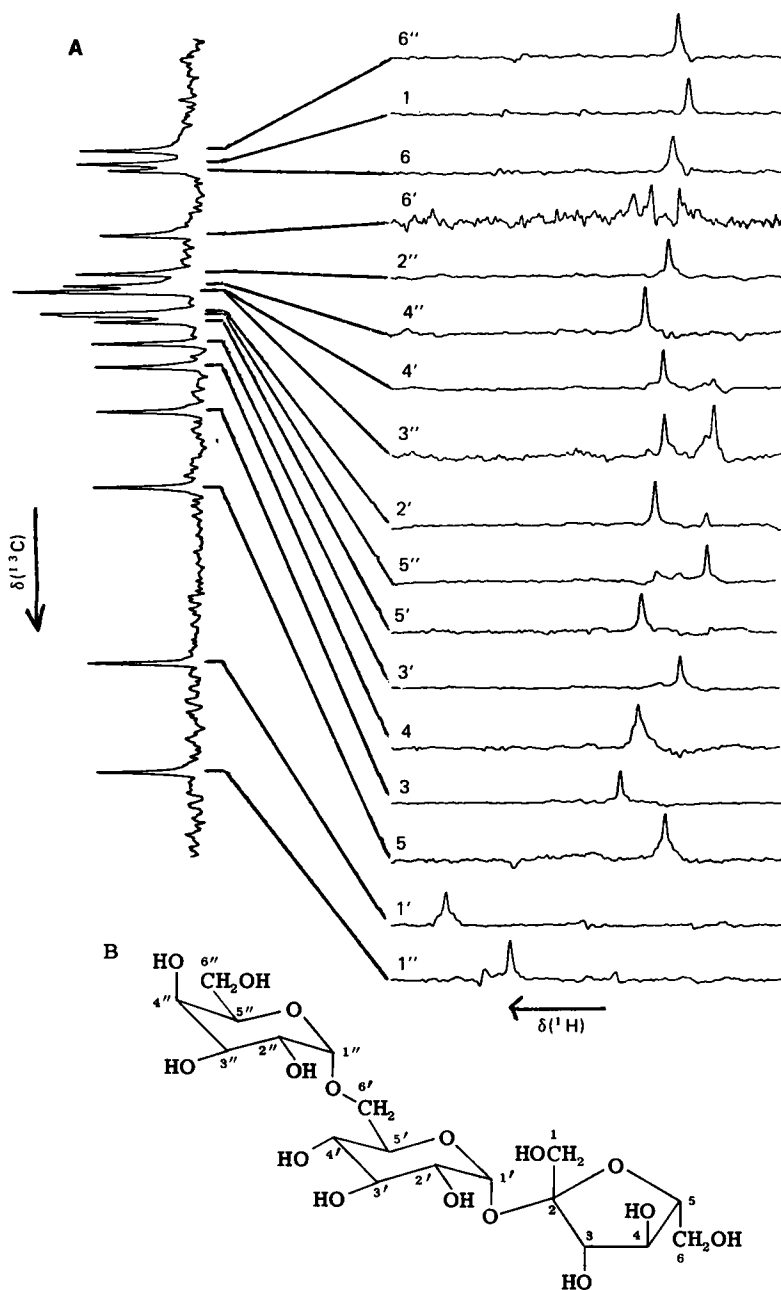
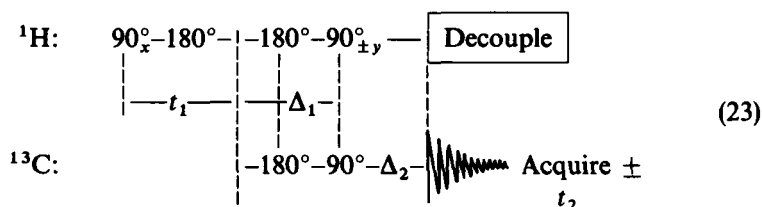


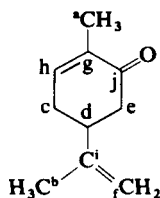
FIG. 10. (A) Slices from the ^{13}C - ^1H 2D chemical shift correlated spectrum of raffinose at 22.5 MHz with homonuclear proton couplings eliminated by using sequence (22). (B) Structure of raffinose.

A further extension of the foregoing ideas is to use sequence (23) to generate indirect 2D J spectra.³⁶⁷ These have ^{13}C chemical shifts in the f_2 dimension

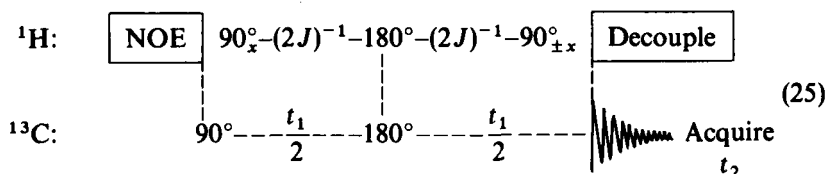
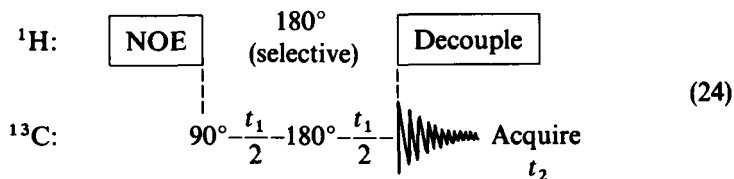


and homonuclear proton couplings in f_1 . The timings are as for sequence (21) and all effects due to proton chemical shifts and ^{13}C - ^1H couplings are eliminated so that the frequency spread in f_1 is quite small and the data matrix needed is not large. Figure 11 illustrates the application of this sequence to sucrose.

In its usual form a ^{13}C - ^1H 2D J spectrum has splittings due to one-bond and longer range ^{13}C - ^1H couplings, which may well be an unnecessary complication. Sequence (24) uses a selective 180° proton pulse to invert proton spin over a range of only 20 Hz or so to give spectra in which the ^{13}C signals are split in the f_1 dimension by a chosen long-range proton coupling only, and is illustrated in Fig. 12 by experiments on (III).³⁶⁸ More generally, sequence (25) will provide 2D ^{13}C - ^1H J spectra in which either the long-range



(III)



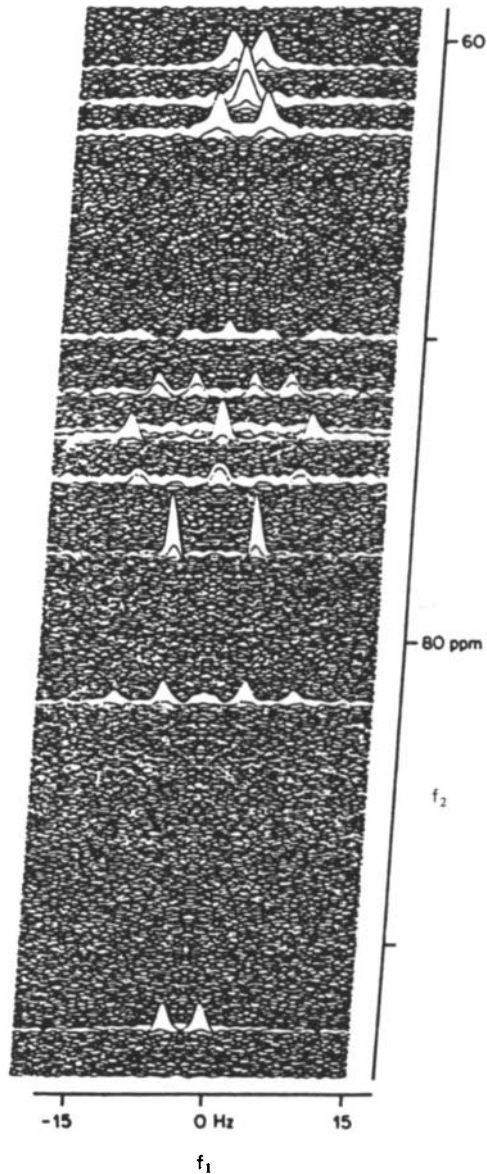


FIG. 11. Indirect 2D J spectrum for aqueous sucrose showing the proton homonuclear multiplet structure in the f_1 dimension correlated with ^{13}C chemical shifts in f_2 . From reference 367.

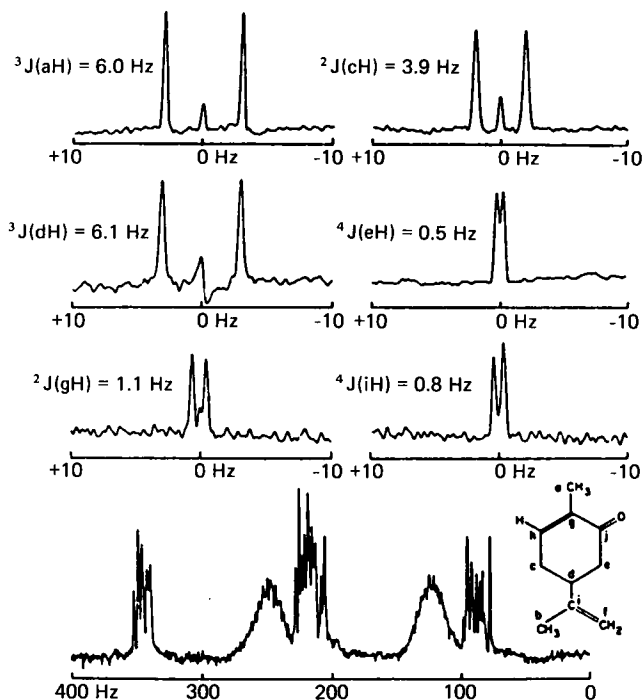


FIG. 12. Selective observation of long-range ^{13}C - ^1H couplings in carvone (III) using sequence (24). From reference 368.

or the one-bond ^{13}C - ^1H splittings in the f_1 dimension can be suppressed at will.³⁶⁹ This uses the same technique as sequence (22) for achieving proton flips selectively according to the size of the relevant coupling. With the final 90° proton pulse along $-x$, only the longer range ^{13}C - ^1H couplings are inverted so that in the f_1 dimension the resonances are *sharp* quartets, triplets, or doublets from CH_3 , CH_2 , or CH groups, respectively. With the final 90° proton pulse along $-x$, only the longer range ^{13}C - ^1H couplings appear in f_1 with a corresponding reduction in the size of the data matrix required.³⁶⁹

It is a useful feature of many of the above experiments that the presence of a single ^{13}C nucleus significantly reduces the degree of second-order character in the proton spectrum, but, even so, accidental degeneracies can lead to residual effects as inspection of the spectra of 1-fluoronaphthalene and sucrose in Figs. 9 and 11 shows. Of course, these effects can be of value for determining otherwise inaccessible interproton coupling constants,³⁷⁰ but usually they are a nuisance and can be reduced substantially by using continuous wave (CW) ^{13}C decoupling instead of a 180° inverting pulse.³⁷¹

In most 2D experiments it is necessary to wait long enough between cycles for most of the proton magnetization to be restored to the z direction, and a number of special sequences have been described for accelerating this process so as to roughly halve the time of the experiment.³⁷²

Some of the most exciting 2D experiments currently being performed are homonuclear proton ones on large molecules conducted on high-field spectrometers. Many of these rely upon the basic pulse sequence proposed by Jeener³⁷³ in 1971, which was somewhat ignored in the early development of the subject. Sequence (26) is a simple modification of the Jeener experiment in

$$90^\circ_x - t_1 - 90^\circ_\phi \text{ --- } \text{Acquire } (t_2) \quad (26)$$

which the phase ϕ of the second 90° pulse is cycled through $+x, +y, -x, -y$ and yields a so-called COSY spectrum³⁷⁴ (*correlated spectroscopy*) in which both axes represent proton (or other nucleus) chemical shifts. The normal 1D spectrum appears along the $f_1 = f_2$ main diagonal and there are off-diagonal cross-peaks with f_1, f_2 coordinates that show which pairs of protons are spin-coupled.³⁷⁵ In principle, this kind of information is available from a series of selective homonuclear decoupling experiments, but the COSY experiment is generally much more satisfactory, especially in crowded spectra. Figure 13 illustrates the application of this experiment to the proton spectrum of viomycin at 200 MHz.

A further advantage of this experiment is that if the second pulse is 45° rather than 90° then magnetization transfer will take place in a selective manner and will involve only *connected* transitions, i.e., those with a common energy level. Thus only half the normal number of cross-peaks will appear, and these will be in positions that depend upon the relative signs of coupling constants which therefore may be determined by inspection of the 2D spectrum.³⁷⁵ Heteronuclear ($^{13}\text{C}/^1\text{H}$) versions of this experiment for getting the relative signs of coupling constants have also been reported,³⁷⁶ and sequence (27) yields a 2D matrix from which a homonuclear broadband

$$90^\circ - \frac{t_1}{2} - 180^\circ - \left(t_d - \frac{t_1}{2}\right) - 45^\circ - \Delta \text{ --- } \text{Acquire } t_2 \quad (27)$$

decoupled spectrum can be obtained by projection onto the f_1 axis. In this sequence, t_d is fixed and Δ is adjusted so that the middle of the t_2 period follows the 45° pulse after a time t_d .

Closely related to COSY is FOCSSY, which uses the same sequence and permits folding in the f_1 dimension to reduce the size of the data matrix.³³⁹ The effects of the foldover are subsequently corrected by computational

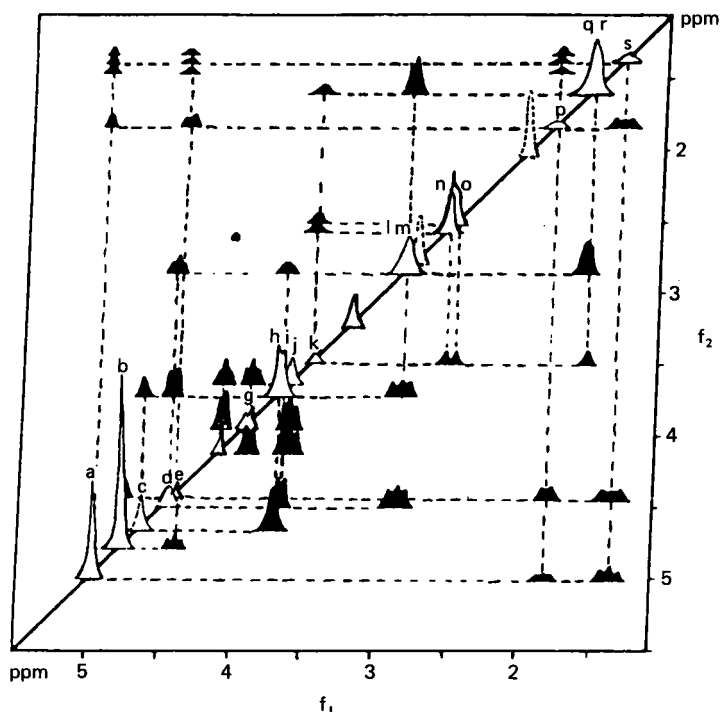


FIG. 13. Two-dimensional proton chemical shift correlation spectrum of viomycin at 200 MHz, with the conventional 1D spectrum running along the main diagonal. From reference 375.

means, and, since absorption spectra without dispersion-mode tails are obtained, the method is especially suitable for large molecules like proteins, which have very crowded proton spectra. Computational foldover correction has also been used in homonuclear 2D J spectra when data acquisition begins immediately following the 180° pulse and provides better resolution and sensitivity,³⁷⁷ and the SECSY (spin-echo correlated spectroscopy) sequence (28)³³⁹ also provides homonuclear chemical shift correlations with economies in the size of the data matrix required.

$$90_x^\circ \frac{t_1}{2} - 90_x^\circ \frac{t_1}{2} - \text{Acquire} \quad (28)$$

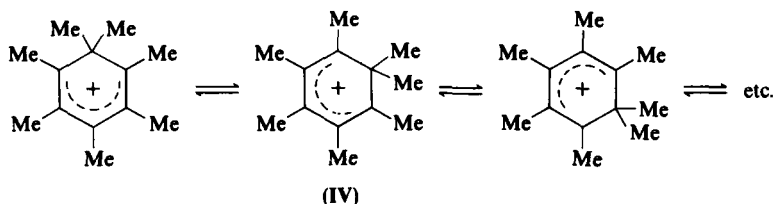
t_2

Sequence (29) can be used to give 2D spectra of chemically exchanging systems and yields a COSY-like plot, with the normal spectrum (typically of

$$90_x^\circ - t_1 - 90_x^\circ - \tau_m - \text{Acquire} \quad (29)$$

t_2

^{13}C) along the main $f_1 = f_2$ diagonal and cross-peaks in positions that connect the sites being interchanged.^{378,379} Its first application was to demonstrate that the exchange indicated in (IV) proceeds via a 1,2 shift mechanism, and the method may well replace Hoffman–Forsén saturation transfer experiments



for mapping out exchange networks. It is desirable to include a magnetic field gradient pulse immediately after the second 90° pulse in order to destroy transverse interference between the evolution and detection periods, and τ_m depends upon the exchange rate. When such experiments are used for abundant nuclei such as protons or ^{31}P , homonuclear coupling will lead in addition to J cross-peaks that may be confused with the ones due to exchange and a range of methods including phase-shifted pulses, field gradients, digital filtering, and zero-quantum techniques is available for removing these J cross-peaks.³⁸⁰ In many cases it is best to acquire two 2D spectra—one with the J cross-peaks to analyze the spin system, and the other without them to elucidate the exchange network.

If it is desired to use sequence (29) to study exchange rates as well as networks then a series of 2D experiments with different values of τ_m must be performed. This is really a 3D experiment and is obviously very time consuming. A way around this difficulty is provided by the “Accordion” experiment³⁸¹ illustrated in Fig. 14 and applied successfully to the study of the inversion of *cis*-decalin via ^{13}C observation. Effectively, t_1 and τ_m are accommodated on one axis, and, provided that they are associated with substantially different line widths, it is possible to separate them by back Fourier transformation allied to window functions designed to extract either a broad or a sharp component.³⁸¹ A similar approach has been adopted to combine results from δ - and J -correlated 2D experiments.³⁸²

Sequence (29) really generates in the 2D spectrum cross-peaks arising from cross-relaxation processes, and these include, in addition to transfer of magnetization via chemical exchange, effects due to the NOE.³⁸³ Consequently, such 2D NOESY experiments provide an extremely powerful way of mapping out spatial relationships from the proton spectra of complex molecules, and it is now fair to say that 2D high-field NMR experiments can provide information on the conformations of molecules like proteins which is comparable to that available from complete X-ray diffraction investigations.

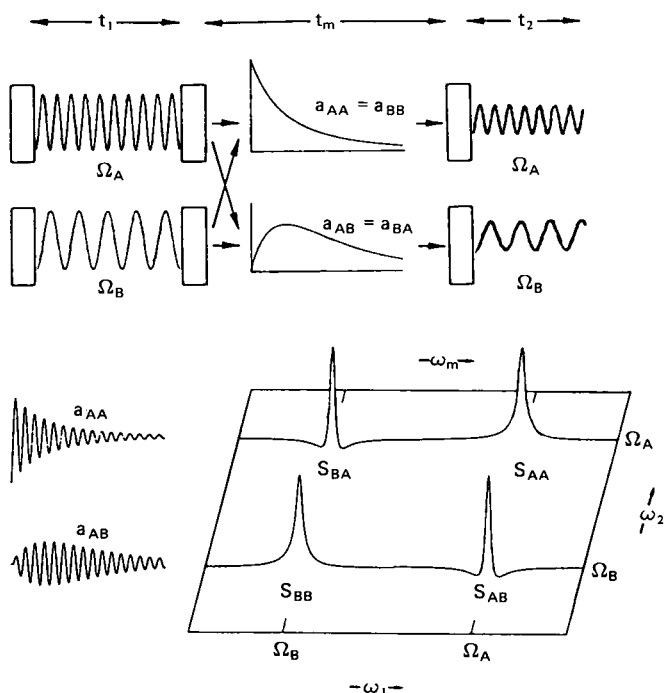


FIG. 14. The ACCORDION experiment as applied to a two-site exchange system. From reference 381.

Normally the 2D NOESY experiment using sequence (29) or a SECSY variant of it will yield a plot with cross-peaks in positions which immediately identify those pairs of protons which are dipolar coupled and which therefore exhibit a NOE. In an interesting comparison of one- and two-dimensional methods, Bösch *et al.* concluded that, for large molecules, the 2D approach could acquire the necessary data much more rapidly than could the requisite large number of 1D NOE experiments.³⁸⁴ It is of course necessary to identify and preferably eliminate J cross-peaks from NOESY spectra, and ways of doing this have been discussed which are also applicable to chemical exchange spectra.³⁸⁵ However, in the latter case, they are not needed if ^{13}C or another rare nucleus is observed, as in studies of bond shifts in bullvalene and *cis*-decalin.³⁸⁶

In many of the above experiments the important cross-peaks often occur in symmetry-related positions, whereas noise and some artifacts are distributed randomly. Various computational routines—symmetrisation and triangular multiplication—are therefore available which make use of this to effect improvements in the appearance of the spectra and to achieve a signal-to-noise ratio better by a factor of $\sqrt{2}$.^{387,388} With the aid of a 45° tilt of the data

matrix similar improvements can be brought about in homonuclear 2D J spectra as demonstrated on the 400-MHz proton spectrum of 6 α -methylprogesterone acetate.³⁸⁹ Problems also arise in the foregoing experiments because of the strong peaks on or near the main diagonal whose tails can distort or hide cross-peaks of interest. These can be reduced or removed by a range of techniques³⁹⁰ including subtraction of a 2D spectrum obtained with a different ("wrong") mixing time^{390,391} and the use of prerelaxing pulse sequences.³⁹¹ An improvement on COSY is TOCSY (total correlation spectroscopy), which uses pulse sequences to give isotropic mixing and hence net magnetization transfer.³⁹² By using a range of mixing times a set of phase-sensitive 2D spectra is obtained which can be combined to yield a map containing, in principle, all the spin correlations present in the system. The potential uses of 2D NOE experiments have been reviewed.³⁹³

Two-dimensional methods are well suited to the production of multiple-quantum spectra,^{27,394,395} and Fig. 15 summarises pulsing possibilities for heteronuclear experiments.³⁹⁶ In addition, a multiple-quantum filter sequence has been described which can remove unwanted signals from 2D spectra and in general can isolate specific spin systems.³⁹⁷ To chemists in general the most valuable multiple-quantum two-dimensional experiment is ^{13}C autocorrelation²⁷¹ or INADEQUATE.²⁷⁰ This uses pulse sequence (17) with Δ as the t_1 variable. It yields a 2D plot with ^{13}C chemical shifts along one axis and double-quantum frequencies along the other such that individual cross sections contain signals from *selected pairs* of directly bound ^{13}C atoms at the appropriate positions, with all signals from single ^{13}C molecules being suppressed.^{398,399} If a 135° read pulse is used it is possible to determine the sign of the double-quantum frequencies and hence to use quadrature detection in the t_1 dimension.⁴⁰⁰ This is important because with ^{13}C shifts along each axis the frequency spread and consequent size of the data matrix required can be very large at the high field strengths needed to get adequate sensitivity to detect the doubly substituted species at natural abundance. Nonetheless, double-quantum methods are often the best technique⁴⁰¹ for ^{13}C autocorrelation even though certain proposed modifications⁴⁰² to INADEQUATE may not always offer the expected advantages.⁴⁰³ If in sequence (17) the interval τ [normally set to $(4J)^{-1}$] is used as the t_1 variable then the 2D spectrum will contain only signals from molecules containing two ^{13}C nuclei, and the various homonuclear ^{13}C splittings will appear along the f_1 axis.⁴⁰⁴

There have been many "routine" applications of two-dimensional methods to the solution of real problems, and these are summarised as follows.

a. ^{13}C - ^1H Chemical Shift Correlation. Spectra from bromobenzene yielded parameters which agreed with earlier values.⁴⁰⁵ Assignments have been obtained for pyridine carboxylic acids,⁴⁰⁶ raffinose,⁴⁰⁷ three forms of

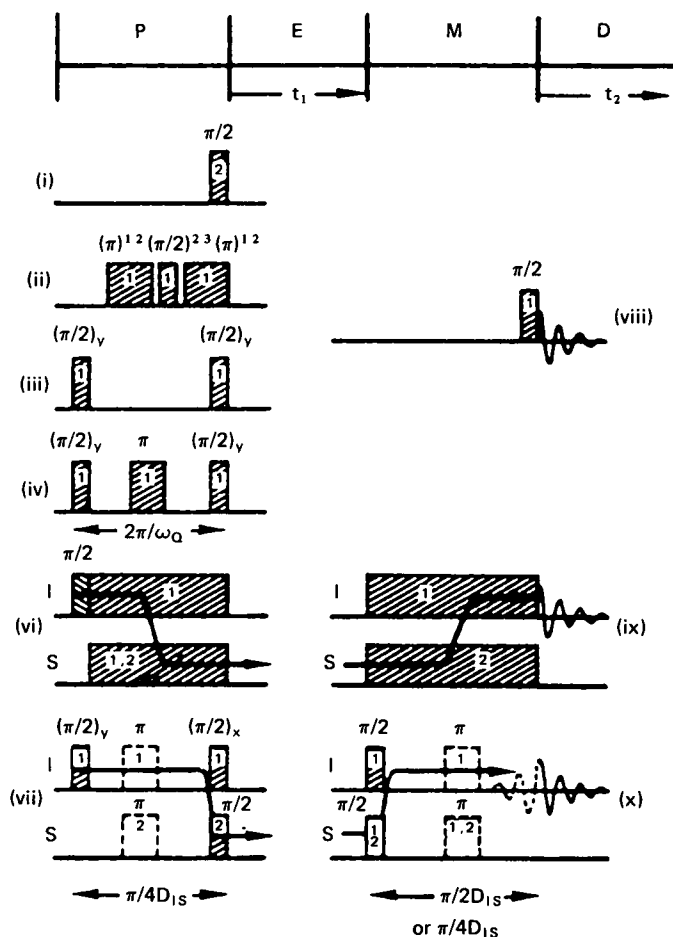
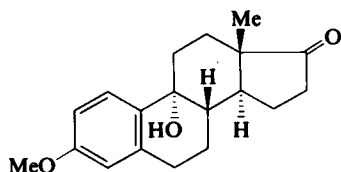
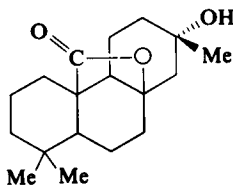


FIG. 15. Preparation and detection schemes for multiple-quantum coherence. P, Preparation period; E, evolution period; M, mixing period; D, detection period. From reference 396.

fructose,⁴⁰⁷ viomycin,⁴⁰⁸ (V),⁴⁰⁹ *d*-biotin,⁴¹⁰ alkaloids,⁴¹¹ 8,11-bisdehydrobenzo[18]annulene,⁴¹² and other materials.⁴¹³⁻⁴²¹



(V)

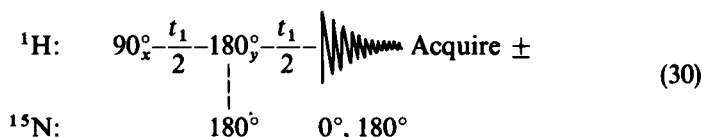


(VI)

b. ^{13}C - ^1H J spectra have been used in the study of ^{13}C multiplicities,⁴²² oligosaccharides,⁴²³ monensin,⁴²⁴ ^{13}C -labeled adamantanes⁴²⁵ and norbornanes,⁴²⁵ and pyrazine derivatives.⁴²⁶

c. ^{13}C autocorrelation was used to study a menthyl phosphine,²⁵⁵ lupane,⁴¹⁶ alkaloids,¹⁶⁴ nonactin,⁴²⁷ erythronolide B,⁴²⁸ a trimer of biacetyl,⁴²⁹ (VI),⁴³⁰ an enedione in superacid medium,⁴³¹ riboflavin,⁴³² mevinoxin,⁴³³ a photodimer of a steroid,⁴³⁴ and monensin.⁴²⁴

d. *Other Heteronuclear Correlations.* ^{11}B - ^1H experiments have been applied to the carbaborane $2,4\text{-C}_2\text{B}_5\text{H}_7$ without decoupling⁴³⁵ and to decaborane with heteronuclear decoupling in both dimensions.⁴³⁶ Sequence (30)



has been reported for generating a 2D proton spectrum in which signals from species not containing ^{15}N are highly suppressed,⁴³⁷ and ^{15}N - ^1H experiments have been used to study transfer RNA⁴³⁸ and isomer conversion in polypeptides.²²⁴ The basis of ^{31}P - ^1H experiments which can give otherwise inaccessible P-H couplings has been described in detail with particular reference to cellular phosphates,⁴³⁹ and the method has been applied to guanosine 2-monophosphate,⁴⁴⁰ uridine 2,3-cyclic monophosphate,⁴⁴¹ phosphothreonine,⁴⁴² phosphoserine,⁴⁴³ cytidine 5-phosphate,⁴⁴³ and sequence assignments in the backbone of the tetranucleotide $d\text{-CpTpAgG}$.⁴⁴⁴ Homonuclear 2D ^{31}P experiments have been used to study transition metal complexes such as $[\text{Re}(\eta^2\text{-CH}_2\text{PMe}_2)(\text{PMe}_3)_4]$,^{445,446} polyphosphine selenides,³²⁹ and mixtures of cellular phosphate metabolites.⁴⁴⁷

Two-dimensional deuterium experiments have been used to avoid difficulties due to the quadrupole moment,^{448,449} and ^{11}B COSY experiments have been used to determine cage connectivities in polyhedral boranes even when $^1J(^{11}\text{B}^1\text{H})$ is comparable with the (quadrupolar broadened) line width.⁴⁵⁰

e. *Proton Experiments.* For large molecules in particular, these are one of the most important uses of 2D NMR, although it has been pointed out that they cannot completely replace the need for high magnetic fields⁴⁵¹ since when second-order features are present it is not possible to obtain a fully decoupled 1D spectrum by projection. Proteins have provided some of the most impressive applications of the technique, as in the identification of 41 aliphatic proton spin systems in the basic pancreatic trypsin inhibitor.^{452,453} It is often desirable to use selective decoupling also in this kind of work,⁴⁵⁴ and a strategy has been described for using a spin-echo sequence to obtain a

data matrix which is subsequently processed to yield various kinds of 1D and 2D NMR spectra.⁴⁵⁵ Other systems studied in this way appear in references 224, 350, 409–411, 413–415, 444, and 452–509.

f. Chemical Exchange Spectra. For simple systems various kinds of 1D saturation-transfer experiments are still probably the most effective way of studying slow exchange rates and establishing exchange networks. However, in more complicated cases, the 2D approach is superior and provides a graphical picture of the network; it is this aspect that has received most attention so far. Such experiments involving protons have been applied to enzyme-catalysed reactions,⁵¹⁰ allyl–palladium complexes,⁵¹¹ amide proton exchange in the basic pancreatic trypsin inhibitor⁵¹² and in glutathione,^{513,514} the conformational behaviour of cyclo-[Pro-NBGly₂],⁴⁷⁴ solid tropolone (with cross-polarization and magic-angle spinning),⁵¹⁵ and solute–solvent interactions.⁵¹⁶ ¹³C experiments have been used to study the rearrangement of allyl–chromium complexes,³⁹¹ and a ³¹P 2D spectrum has been obtained from perfused rat heart which demonstrates exchange involving phosphocreatine and γ -ATP.^{516a}

Another kind of 2D experiment should also be noted here. This technique involves combining 2D methods with imaging techniques to provide a map showing the spatial distribution of substances having different ¹H or ¹³C chemical shifts. It is depicted in Fig. 16 for what is described as a “phantom” object (although it appeared to be real enough) consisting of a pack of capillary tubes containing water, acetone, benzene, and methylene dichloride.⁵¹⁷ This “chemical microscopy” approach⁵¹⁷ uses field gradients applied along the *x*, *y*, and *z* axes, and has also been implemented using ³¹P observation.⁵¹⁸

VI. SATURATION TRANSFER

As mentioned in Section V, this technique¹⁷ for studying relatively slow chemical exchange processes is being superseded by 2D methods, but for many simple systems it still provides the most convenient approach. The area has been reviewed^{17,519} and improvements in technique have been reported. These include ways of studying multisite problems with very few or no zero rate constants with the aid of simultaneous multiple saturation,⁵²⁰ a spin-locking technique for use when the saturated and observed sites give resonances with a small frequency separation,⁵²¹ and the use of FT methods and spin inversion rather than saturation.⁵²²

Experiments involving protons are most common and have been used in a wide range of studies including many on biochemically significant materials.^{523–555} ¹³C spectra are normally simple and saturation transfer experiments using this nucleus are correspondingly easy to interpret; they

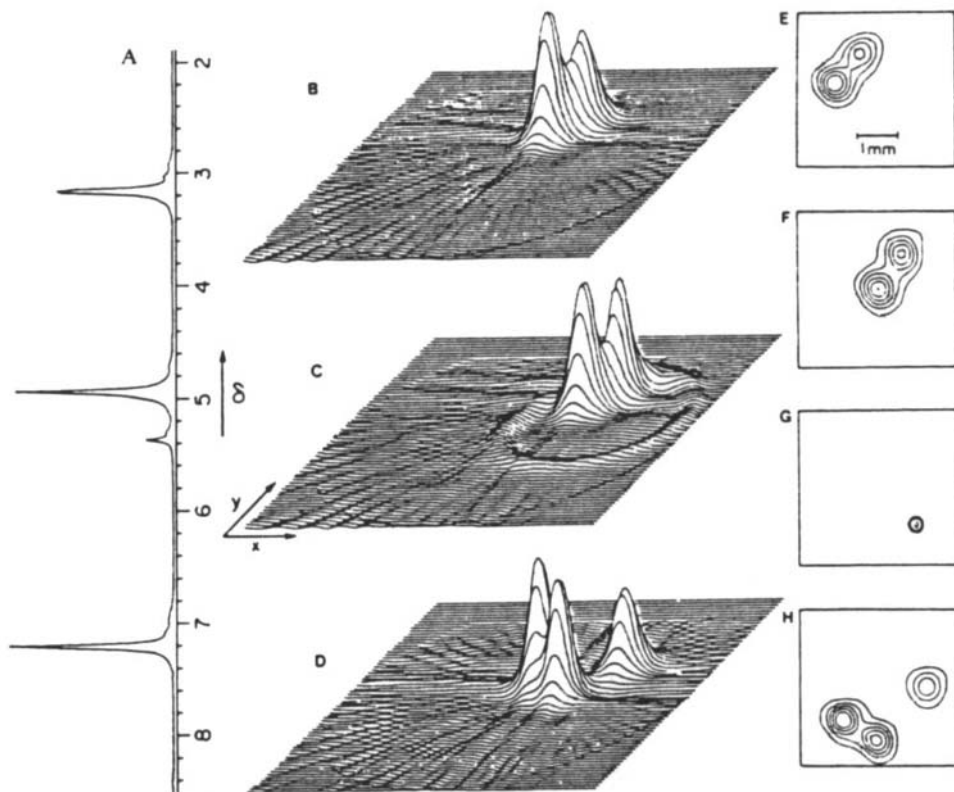


FIG. 16. (A) Proton spectrum at 270 MHz of a set of capillaries containing benzene, water, methylene chloride, and acetone surrounded by D_2O in a 10-mm tube. (B–D) The reconstructed images of acetone, water, and benzene, respectively. (E–H) Contour plots corresponding to the cross-sectional images of acetone, water, methylene chloride, and benzene, respectively. From reference 517.

have often been used in studies of organometallics^{561,562} and are also of use in biological work.^{556–560} The other principal nucleus to be used for this type of work is ^{31}P , again often in a biochemical context,^{563–572} and experiments involving ^{113}Cd have been reported.⁵²¹

VII. THE NUCLEAR OVERHAUSER EFFECT

The NOE is discussed extensively in an excellent review²⁶ of double resonance difference techniques and has also been specifically reviewed by several other authors.^{35,37,39,573} Two-dimensional experiments, which are

usually best for large molecules, were discussed in Section V. It is often necessary to take into account or to suppress the NOE in quantitative measurements⁵⁷⁴⁻⁵⁹³ on nuclei such as ^{13}C , ^{15}N , and ^{31}P , but this has not always been done, even though it is straightforward by gated decoupling (which is time consuming owing to the slow repetition rate needed) and/or by adding a relaxation reagent.

Dynamic methods for measuring the NOE can save a great deal of instrumental time if it is not necessary to reattain equilibrium between cycles⁵⁹⁴ and can also yield values of T_1 according to the following equation:

$$S_t = S_0[\eta + 1 - \eta \exp(-t/T_1)]$$

where S_0 is the signal strength in the absence of any NOE, and S_t is the signal obtained by switching on the decoupler for a time t prior to data acquisition.⁵⁹⁵ Still better are sequences which yield the *initial build-up rate* of the NOE, since this depends upon r^{-6} (r = internuclear distance) even when there is spin diffusion, which may occur in large molecules⁵⁹⁶ for which such TOE (truncated driven nuclear Overhauser effect) spectra are particularly suitable.⁵⁹⁷ So-called time-resolved NOE experiments have also been used to deal with problems of spin diffusion by having the decoupler on for only a short time.⁵⁹⁸ Time saving can also be achieved by adding a diamagnetic shift reagent such as $\text{La}(\text{fod})_3$ to the sample to give reversible complexation which improves the dipole-dipole relaxation efficiency by altering the correlation times.⁵⁹⁹ Effects due to SPT which might be confused with the NOE can be avoided by summing the results of several selective experiments because SPT leads to no *overall* transfer of magnetization,⁶⁰⁰ and detailed theory of the NOE has been developed for a number of specific systems.⁶⁰¹⁻⁶⁰⁵ Various ways have been suggested for increasing the precision of the measurements of intensity which are needed when the NOE is to be used to derive accurate relative distances,^{499,500,606,607} and the ways in which negative interproton NOE values can occur have been discussed.^{598,608-613}

The ^1H - $\{^1\text{H}\}$ NOE. With the ready availability of high-field spectrometers such measurements are now routine and numerous examples are referred to in references 459, 555, 598, and 610-757.

The ^{13}C - $\{^1\text{H}\}$ NOE. The main area of use is in conjunction with carbon T_1 measurements to establish the dipolar contribution for the study of molecular motion in many types of system, and especially in work on macromolecules.⁷⁵⁸ References 759-849 refer to this effect, in almost all cases for systems with C-H bonds, although some work has been done on quaternary carbons and carbonyl groups.^{790,791} The intermolecular ^{13}C - $\{^1\text{H}\}$ NOE has been observed between alkanes and CS_2 and CCl_4 .⁸⁵⁰

The ^{13}C - $\{^{19}\text{F}\}$ NOE has been reported in polyfluoroaromatics.^{783,784,851}

The ^{15}N - $\{^1\text{H}\}$ NOE. Owing to the negative γ of ^{15}N it is often desirable to

suppress this NOE by adding a relaxation reagent to avoid signal cancellation, or to record ^{15}N spectra with the aid of a sequence, such as INEPT, which does not depend upon relaxation effects. This NOE has been reported in compounds with several nitrogen atoms,⁸⁵² polyethylene imine,⁸⁵³ polypeptides and polyamides,⁸⁵⁴ copolymerized amides,⁸⁵⁵ platinum–amine complexes,⁸⁵⁶ the adenine–uracil base pair,⁸⁵⁷ double- and single-stranded DNA,⁸⁵⁸ a cyclohexyl uracil,⁸⁵⁹ extracts from *Staphylococcus aureus* cells,⁸⁴² aldoximes and ketoximes,⁸⁶⁰ peptide hormones,⁸⁶¹ amino acids from *Neurospora crassa*,⁸⁶² and uridine-related bases in tRNA.^{863,864} This NOE has been used to determine the site of spin labeling with $[\text{Gd}(\text{dpm})_3]$ [dpm = bis(diphenylphosphino)methane]⁸⁶⁵ and other materials,⁸⁶⁶ and gave difficulties in quantitative studies of lysine–formaldehyde–urea polymer.⁸⁶⁷

The ^{19}F – $\{^1\text{H}\}$ NOE is especially valuable for motional studies involving relatively small molecules bound to large ones and has been used in experiments on 4-(trifluoromethyl)- α -bromoacetanilide reacting with α -chymotrypsin,⁸⁶⁸ rabbit cyanomethaemoglobin,⁸⁶⁹ trifluoroacetyl dipeptide anilides binding to enzymes,⁸⁷⁰ RNA from 5-fluorouracil,⁸⁷¹ a fluorine-containing complex of agglutinin,⁸⁷² the *m*-fluorotyrosyl gene S protein,⁸⁷³ CH_2FCOONa and 3-fluorotyrosine,⁸⁷⁴ 4-(trifluoromethyl)benzenesulphonylchymotrypsin,⁸⁷⁵ and the interaction of the drug fluoroquinone with DNA and tRNA.⁸⁷⁶

The ^{29}Si – $\{^1\text{H}\}$ NOE can give difficulty owing to the negative γ and is often suppressed with a relaxation reagent.⁸⁷⁷ It has been studied in silyl transition metal complexes,⁸⁷⁸ and in linear and branched silanes.⁸⁷⁹

The ^{31}P – $\{^1\text{H}\}$ NOE is used in biochemical work and has also been studied in smaller molecules where observed values range from $\eta = 1$ to close to the theoretical maximum of 2.24. Results have been reported for cyclic organophosphorus compounds,⁸⁸⁰ trimethyl phosphine over a wide temperature range,⁷⁸⁹ adenosine phosphates,⁸⁸¹ RNA,^{809,882,883} DNA,^{809,884–889} phosphatidylcholine,^{890,891} Ph_4P^+ and other organophosphorus compounds,⁸²⁷ aqueous solutions of nucleotides,^{892–894} phospholipids,^{895,896} the sugar phosphate backbone of poly(inosinic acid),⁸⁹⁷ sonicated phosphatidylcholine liposomes,⁸⁹⁸ and aqueous orthophosphate solutions.⁸⁹⁹

The ^{77}Se – $\{^1\text{H}\}$ NOE is reported to be small in the majority of organoselenium compounds^{900–903} except when there is a direct Se–H bond.⁹⁰⁴ In aqueous Na_2SeO_3 η is 0.4, presumably as a result of intermolecular interactions.⁹⁰⁵

The ^{89}Y – $\{^1\text{H}\}$ NOE. The theoretical maximum of $\eta = -10.2$ (γ is negative) has been reported in cold aqueous yttrium nitrate and in a crown ether complex.⁹⁰⁶

The ^{113}Cd – $\{^1\text{H}\}$ NOE. This negative NOE has been observed in EDTA⁹⁰⁷ and other⁹⁰⁸ complexes, and in cadmium derivatives of bovine superoxide dismutase.⁹⁰⁹

The $^{119}\text{Sn}-\{^1\text{H}\}$ NOE. Although γ is negative the $^{119}\text{Sn}-^1\text{H}$ distance is usually large enough for this effect to be unimportant. However, it has been noticed in certain cases and, in those cases, precautions must be taken to avoid signal cancellation.^{910,911}

The $^{125}\text{Te}-\{^1\text{H}\}$ NOE is usually small or zero,⁹¹² although $\eta = -0.2$ in 2-tellurophene carboxylic acid.⁹¹³

VIII. GENERAL APPLICATIONS OF MULTIPLE RESONANCE

A. Indirect determination of chemical shifts

With the current general availability of multinuclear spectrometers such experiments are now much less important, although they can still offer considerable advantages in terms of sensitivity for low-frequency nuclei such as ^{103}Rh and ^{183}W in suitable compounds. Of course, these suitable compounds (i.e., those with coupling to protons or another high-sensitivity nucleus such as ^{31}P) are also the very ones to which the INEPT sequence can be applied. By contrast, there is growing interest in using 2D NMR methods involving ^{13}C observation (and paying the sensitivity penalty) to get proton parameters in complex spin systems, where the low abundance of ^{13}C and the large values of $^1J(^{13}\text{C}^1\text{H})$ can lead to considerable spectral simplification by reduction of second-order effects. In what follows the experiments are of the type $^1\text{H}-\{\text{X}\}$ unless otherwise stated.

¹⁴N. Nitrogen shielding in isonitrile complexes has been studied.⁹¹⁴

¹⁵N. Shifts have been determined in enriched metalloporphyrins,⁹¹⁵ amides,⁹¹⁶ $\text{PF}_2[\text{N}(\text{SiH}_3)_2]$,⁹¹⁷ silatranes,⁹¹⁸ and germatranes,⁹¹⁹

²⁹Si. Work has been done on cyclic silazanes,⁹²⁰ dimethyl(aryloxy)-silanes,⁹²¹ silatranes,⁹¹⁸ and species with metal-silicon bonds.^{922,923}

³¹P. Lines of low transition moment were detected in a study of $^1J(^{31}\text{P}^{31}\text{P})$ in Me_4P_2 at low temperatures.⁹²⁴

⁵⁷Fe. ^{13}C observation under proton-decoupled conditions has been used to study iron shielding on organoiron compounds.⁹²⁵⁻⁹²⁷

⁷³Ge. Germatranespectra have been measured.⁹¹⁹

⁷⁷Se. Tertiary phosphine selenides have been studied via ^{31}P observation because, although $^1J(^{31}\text{P}^{77}\text{Se})$ is large, $^nJ(^{77}\text{SeH})$ is zero for $n > 2$.^{928,929}

¹⁰³Rh. Rhodium chemical shifts have been obtained using proton observation in complexes of chalcogenide ligands^{930,931} and a hydride,⁹³² by using ^{13}C observation in carbonyl clusters,⁹³³⁻⁹³⁶ and by using ^{31}P observation in a series of complexes *trans*- $[(\text{Ph}_3\text{P})_2\text{Rh}(\text{CO})\text{X}]$.⁹³⁷ A convenient reference for rhodium chemical shifts is $\Xi(^{103}\text{Rh}) = \pi \text{ MHz}$.⁹³⁷

¹⁰⁷Ag. Phosphorus observation gave silver chemical shifts in triethylphosphite complexes and a 2D ³¹P/¹⁰⁷Ag plot was obtained from a time/frequency domain experiment.³⁵⁶

¹¹¹Cd. Cadmium shieldings have been obtained in porphyrin complexes.⁹¹⁵

^{117/119}Sn. Various organotins have been studied,^{938,939} and ¹H, ¹³C, ¹⁹F, and ³¹P observation has been used to demonstrate that any ^{117/119}Sn primary isotope effect upon tin shielding is less than 0.1 ppm.⁹⁴⁰

¹²⁵Te. Organic tellurides⁹⁴¹ and a rhodium complex of Me₂Te⁹³⁶ have been studied.

¹⁸³W. Phosphorus observation was used in studies of diphenylphosphino derivatives⁹⁴² and complexes of tungsten(0).⁹⁴³

¹⁹⁵Pt. Results have been reported in a range of compounds including isocyanide complexes,⁹¹⁴ platinum hydrides,^{944–946,950} and other complexes.^{947–949,951,952} Phosphorus observation has been used in a study of some carbonyl phosphine complexes of platinum(II).⁹⁵³

¹⁹⁹Hg. Halide phosphine complexes,⁹⁵⁴ silyl derivatives,⁹²³ organic carbonyl compounds,⁹⁵⁵ and various simpler species^{949,956,957} have been studied.

²⁰⁷Pb. The dissociation of Me₃PbCl in solution has been studied.⁹⁵⁸

B. Couplings

As with chemical shifts, any advantages in measuring couplings by indirect observation have decreased markedly in recent years. However, multiple resonance experiments are still the most generally applicable way of getting the *signs* of couplings when these are required. References 232, 917, 923, 924, 936–938, 951–954, and 959–1004 describe experiments of this type. Most such experiments are now standard and only a few examples that apply special techniques are mentioned particularly here.

¹H–{¹⁹⁵Pt} INDOR experiments are used to detect weak ¹⁹⁵Pt lines and hence determine ¹J(¹⁹⁵Pt¹⁹⁵Pt) in symmetrical species,⁹⁵¹ and the sign of ²J(¹⁹⁵Pt¹⁹⁵Pt) is found using ³¹P–{¹⁹⁵Pt,¹H} triple resonance in a bridged complex.⁹⁵²

¹⁵N–{¹H} SPT gave sufficient sensitivity for the determination of the sign of ²J(¹⁵N¹⁹F) in 2-fluoropyridine containing ¹⁵N in natural abundance,¹⁰⁰⁰ and the sign of ¹J(¹¹³Cd¹⁵N) in a cadmium porphyrin complex.²³² ¹³C–{³¹P,¹H} experiments are needed to show that the rather small (22 Hz) value of ¹J(³¹P³¹P) in [Me₂P(S)]₂ is negative.¹⁰⁰⁵ A number of groups have used ¹H–{³¹P} experiments to get signs and magnitudes of ⁿJ(³¹P³¹P) in relatively symmetrical bi- and polyphosphorus species,^{929,997,954,974,975} and when the proton spectrum is unduly complex then ¹³C–{³¹P} tickling experiments can often be used instead.^{952,982,1005}

Homonuclear INDOR experiments were used to distinguish the symmetric and antisymmetric sets of transitions in proton AA'XX' spin systems and hence to get signs of long-range couplings.⁹⁶⁶ A wide range of types of double resonance experiment has been used in a comprehensive survey of signs of couplings involving ^1H , ^{13}C , ^{19}F , ^{31}P , and ^{199}Hg in some mercury complexes.⁹⁷¹

C. Miscellaneous applications

Various ^1H - $\{^1\text{H}\}$ and ^{13}C - $\{^1\text{H}\}$ off-resonance and selective decoupling experiments for spectral simplification, spectral assignment, and structural determination are now completely standard and are not discussed here. Furthermore, they are becoming superseded by special pulse techniques and 2D methods, although it should always be remembered that they still may provide the quickest way of solving particular problems. These methods can of course be applied to other nuclei.

Deuterium decoupling has assisted proton conformational studies^{1006,1007} and has also been used to simplify ^{13}C spectra^{141,1008-1011} and in work on liquid crystal samples.¹⁰¹² ^7Li decoupling facilitates the analysis of the ^{31}P spectra of lithiated organophosphorus species.¹⁰¹³ ^{11}B decoupling is quite common and has been applied to $\text{Y}(\text{BH}_4)_3 \cdot 2\text{THF}$ in impressive work that also involved ^{10}B and ^{89}Y quadruple-resonance experiments.¹⁰¹⁴ The technique has also been used in studies of polyhedral platinaboranes,^{1015,1018} $\text{Me}_2\text{BNHBu}'$ (^{13}C spectrum),¹⁰¹⁶ the ^{91}Zr spectrum of $\text{Zr}(\text{BH}_4)_4$,¹⁰¹⁷ various polyhedral boranes¹⁰¹⁹⁻¹⁰²² and carbaboranes,¹⁰²³ and some heteroatom boranes.¹⁰²⁴

^{14}N decoupling has been used¹⁰²⁵ to sharpen the proton spectra of samples enriched in ^{15}N , to simplify the proton spectra of amino compounds,¹⁰²⁶ in the ^{13}C spectra of choline and phosphatidylcholine,¹⁰²⁷ in studies of conformation changes in *N,N*-dimethylpiperidinium iodide,¹⁰²⁸ in a study of isonitrile metal complexes,⁹¹⁴ in the proton spectra of cyclic ammonium salts,¹⁰²⁹ and in some proton inversion recovery experiments.⁹⁴ ^{15}N decoupling is much less common, but difference experiments were used to assign resonances in the proton spectra of uridine-related bases,¹⁰³⁰ and ^{15}N INDOR spectra have been obtained under conditions of ^{14}N decoupling.¹⁰²⁵

The great width of ^{19}F spectra often makes broadband decoupling of this nucleus impracticable, but it was used selectively to simplify ^{13}C spectra in studies of CF_2 groups¹⁰³¹ and of configurational changes in phosphoranes,¹⁰³² and unsuccessfully in attempts to get individual ^{95}Mo signals from an $\text{Mo}(\text{PF}_3)_x(\text{CO})_{6-x}$ mixture.¹⁰³³

^{31}P decoupling has been used in studies of the proton spectra of hydride resonances in germyl and silyl rhodium(III) complexes,¹⁰³⁴ 2,8-

dithia-1,5-dielement-bicyclo[3.3.0]octanes,⁴⁶⁰ the methyl resonances of (MePNMe)₄S₃,¹⁰³⁵ iridium hydrides,¹⁰³⁶ substituted phosphates,¹⁰³⁷ oxazaphospholidines,¹⁰³⁸ a *cyclo*-tetraphosphazene,¹⁰³⁹ and oligonucleotides.¹⁰⁴⁰ Phosphorus decoupling has also been used to simplify and assign ¹³C spectra in work on carbonyl exchange in Rh₄(CO)₈[P(OPh)₃]₄,¹⁰⁴¹ a bridged ruthenium hydride,¹⁰⁴² diphosphazanes,¹⁰⁴³ and the reaction of CS₂ with a dimeric rhodium complex.¹⁰⁴⁴

Other decoupling combinations are much less common but ¹³C-¹⁰³Rh experiments are often used in work on polynuclear carbonyls.¹⁰⁴⁵⁻¹⁰⁴⁸ ¹H-¹⁰⁹Ag experiments demonstrate the presence of two isomers of a silver complex,¹⁰⁴⁹ ¹H-¹¹⁹Sn experiments correlate resonances in proton and tin spectra of a stannatrane,¹⁰⁵⁰ and ¹H-¹⁹⁹Hg spin-echo experiments are used to study mercury shieldings.¹⁰⁵¹

Homonuclear experiments are rare for nuclei other than protons, but have been used in ³¹P studies of a ruthenium hydride,¹⁰⁴¹ and in ¹¹³Cd studies of metallothioneine.¹⁰⁵²⁻¹⁰⁵⁴ A few ¹³C-¹³C experiments have been reported,⁸⁴⁹ and of course the method is used extensively in spin saturation transfer work.¹⁰⁵⁵⁻¹⁰⁵⁷ Similar use is made of homonuclear ¹⁹F experiments in studies of haptene binding.¹⁰⁵⁸

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