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Nitrogen NMR shieldings of nitroalkanes as a structural and conformational probe†

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ABSTRACT: Nitrogen NMR shieldings ($\Delta\sigma = -\delta$ on the frequency scale of chemical shifts), measured by high-precision ^{14}N NMR and bulk susceptibility corrected, of 20 nitroalkanes in dilute solutions in cyclohexane and in acetone are reported, including *vic*-dinitro, *gem*-dinitro and trinitro structures and tetranitromethane. The data obtained for cyclohexane solutions yield an excellent linear correlation with theoretical shieldings calculated for the corresponding isolated molecules by the semi-empirical TNDO/2 method. The NO_2 nitrogen shieldings of nitroalkanes are shown to depend linearly on the net charges of the corresponding nitro groups, each taken as a whole, but there is no correlation with the atomic charges of the nitrogen atoms concerned. Thus, the nitrogen shieldings seem to provide a measure of electron-acceptor or electron-donor strength of the substituted alkyl system bound directly to the nitro group. Solvent polarity effects on the shieldings are discussed. The nitro group nitrogen shieldings are shown to be generally sensitive to conformational effects, particularly in sterically hindered molecules, and to provide insight into conformational or rotamer equilibria in nitroalkane systems. *Ab initio* calculations of the shieldings of some simple nitroalkanes, using the Hartree–Fock/GIAO approach, are reported. They indicate that the semi-empirical method employed, combined with the experimental data, yields results which are comparable to those obtained by the *ab initio* method, as far as relative shieldings are concerned.

KEYWORDS: NMR; ^{14}N NMR; nitroalkanes; nitrogen shieldings; nitrogen chemical shifts; conformation; atomic charges

INTRODUCTION

Just at the twilight of practical applications of nitrogen NMR to structure determination in organic chemistry, it was discovered[1] that nitrogen magnetic shielding increases significantly in the sequence $R_3CNO_2 < R_2CHNO_2 < RCH_2NO_2 < CH_3NO_2 < C(NO_2)_4$, where R is an alkyl group. The variation of the shielding spans a range of about 70 ppm for neat liquid samples. It was disclosed later[2] that the foregoing relationship represents a general trend, called the β-effect, as far as alkyl substituent effects are concerned, on the nitrogen shieldings of a wide range of nitrogenous moieties, not only the nitro group. The question arises of whether the enhancement in the shielding arises from the decreasing electron donation by the alkyls in the sequence above, and whether the effect of aggregation of nitro groups at the same carbon comes from the same origin, that is, the withdrawal of some electron charge from a given nitro group by its neighbors. If this is so, the effect is evidently paramagnetic, since the NO_2 shielding *increases* with the *increasing* electron-withdrawing power of the moiety which is bound directly to the NO_2 group concerned. So far, there have been no conclusive indications[2] about the underlying mechanism of electron migration which is reflected in the nitrogen shielding variation for nitro groups in saturated systems. Thus, one of the aims of the present work was to explain the problem by comparison of theoretical calculations of nitrogen shieldings and charge densities with a set of suitable experimental data on the shieldings. Since quantum-mechanical calculations usually relate to isolated molecules, the experimental data concerned should ideally be those for low-pressure gaseous samples. We have already demonstrated[3] that the NO_2 nitrogen shieldings in simple nitroalkanes are significantly affected by solvent effects, spanning a range of 6–10 ppm for a given molecule. Such effects of molecular interactions in solution on the shieldings, which amount to about 10% of the entire range of the occurrence of nitrogen NMR signals of aliphatic NO_2 groups, can adversely affect any attempt at rationalizing experimental data in terms of theoretical calculations. We therefore used dilute solutions in cyclohexane of a large set of nitroalkanes, including those containing two or three nitro groups, also at geminal positions, as well as tetranitromethane (see Table 1). The saturated hydrocarbon solvent employed is likely to enter into only weak molecular interactions with the solutes, and such experimental data should be suitable for a comparison with theoretical values of the nuclear magnetic shieldings calculated for isolated molecules. Measurements of the shieldings were also made for the same set of compounds in dilute solutions in acetone as a polar solvent, in order to reveal possible consequences of solvent polarity effects.

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† Dedicated to Professor John D. Roberts on the occasion of his 80th birthday.

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We have already shown that the latter are most significant from the point of view of NO_2 nitrogen shieldings whereas the effects of hydrogen bonding are negligible.[2,3] So far, there have been virtually no data reported on dilute solutions of nitroalkanes in cyclohexane, and no data at all for compounds **11**–**19**.[2]

As far as the calculations are concerned, we employed the semi-empirical TNDO/2 method (see Experimental) for the shieldings and electron charge distribution, combined with the PM3 method for geometry optimizations. This combination, in our experience, has already yielded fairly good results for the nitrogen shieldings of oxazole[4] and thiazole[5] ring systems and also nitrosoalkanes.[6] In order to assess the potential merits or demerits of such semi-empirical schemes, we also carried out *ab initio* quantum-mechanical calculations of the nitrogen shieldings of some simple nitroalkanes (see Experimental) using the Hartree–Fock approach combined with a fairly large basis set of wavefunctions.

Another topic that we want to pursue concerns the possible effects on NO_2 nitrogen shieldings of dynamic equilibria between rotamers in the compounds studied. The latter include sterically hindered molecules where such effects are likely to be significant, and a comparison of the relevant experimental data with theoretical calculations should, hopefully, cast some light on the applicability of nitrogen NMR shieldings to conformational problems.

A word of comment is necessary here on the sign convention employed regarding the nitrogen shieldings (chemical shifts). We use here differences, $\Delta\sigma$, between the nuclear magnetic shielding constants of the compounds examined and that of the external reference, neat liquid nitromethane, with corrections for bulk magnetic susceptibility differences. Therefore, we use the term 'nitrogen shielding' for $\Delta\sigma$, since a plus sign is attributed to an *increase* in the magnetic shielding concerned. $\Delta\sigma = -\delta$, where the latter is the chemical shift expressed on the frequency scale, and the only difference between 'nitrogen shieldings' and 'nitrogen chemical shifts' is in the sign. It should also be noted that we employ ^{14}N NMR while we use the general term 'nitrogen shielding' which encompasses both ^{14}N and ^{15}N nuclei; this is because there are no differences of any practical significance between the two isotopes from the point of view of nitrogen shieldings or chemical shifts.[2]

RESULTS AND DISCUSSION

The results of high-precision ^{14}N NMR measurements for **1**–**20** are reported in Table 1 together with TNDO/2-calculated nitrogen shieldings and net charges at the nitro groups involved, taken as algebraic sums of net charges at the relevant nitrogen and oxygen atoms. The reason behind reporting the total net charge at a nitro group rather than the atomic net charge of the nitrogen involved will be explained later. As far as the calculated shieldings are concerned, they were obtained as weighted averages over the rotamer populations concerned, where the latter were derived from the corresponding energies obtained in PM3 optimizations of their structures. However, for symmetry reasons, some of the shieldings reported are not affected by rotamer equilibria (Table 1, data corresponding to footnote a). The problem of conformational or rotamer equilibria and their significance from the point of view of nitrogen shieldings will be discussed later, and we turn now to the general relationship between the experimental data and the calculations. If we take the NO_2 nitrogen shieldings obtained for dilute solutions of **1**–**20** in cyclohexane and compare them with the values calculated for isolated molecules, an excellent linear correlation is obtained (Fig. 1), expressed by the following equation:

$$\Delta\sigma_{\text{exp.}} = 0.8893\Delta\sigma_{\text{calc.}} + 11.25 \quad (1)$$

with a standard deviation of 1.22 ppm and a linear correlation coefficient $r = 0.997$. The standard deviation amounts to less than 2% of the range of variation of nitrogen shieldings throughout **1**–**20**. The slope of 0.8893 means simply that the calculated $\Delta\sigma$ values are exaggerated in magnitude, by about 10%, with respect to the experimental shielding differences. The constant term in the right-hand side of Eqn (1) is reasonably close to the value of $+9.05$ ppm for 0.005 M nitromethane in cyclohexane with respect to neat liquid nitromethane as a reference. The calculated shieldings were referenced to that of an isolated molecule of nitromethane, and thus the linear correlation provides strong support for the initial assumption that solvent effects, in the case of cyclohexane as a solvent, do not affect significantly the nitrogen shieldings of the nitroalkanes

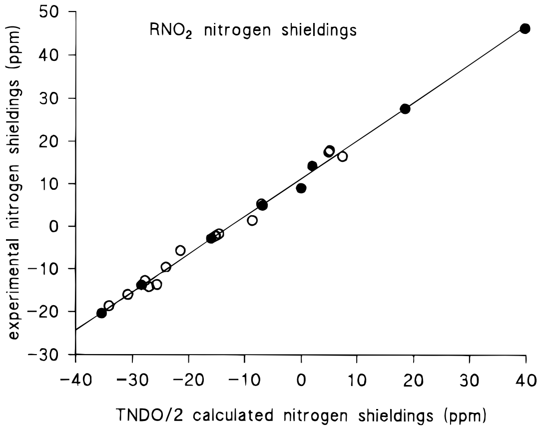

Figure 1. Experimental nitrogen shieldings of cyclohexane solutions of the nitroalkanes **1**–**19**, referenced with respect to neat liquid nitromethane (bulk susceptibility corrected), plotted against TNDO/2-calculated values, the latter with respect to nitromethane. The linear fit concerned is expressed by Eqn (1). (●) Compounds where rotamer equilibria concerned do not affect the nitrogen shieldings (see Table 1, footnote *a*); (○) datapoints where the calculated shielding values were averaged over the relevant populations of rotamer species involved (see Table 1).

Table 1. Experimental bulk susceptibility-corrected and TNDO/2-calculated nitrogen NMR shieldings of nitroalkanes

		Nitrogen shielding in ppm with respect to nitromethane (neat liquid nitromethane for experimental values, 35 °C)				
No.	Compound	Experimental, 0.01 M in cyclohexane	Experimental, 0.01 M in acetone	TNDO/2 calculated	TNDO/2-calculated net charge at NO_2	Footnote
1	CH_3NO_2	+9.05 (0.001 M)	+0.77	0	−0.1474	a
2	$CH_3CH_2NO_2$	−2.84	−9.62	−15.9	−0.2084	a
3	$CH_3CH_2CH_2NO_2$	−1.70	−8.26	−14.5	−0.2092	b
4	$CH_3CH_2CH_2CH_2NO_2$	−2.22	−8.57	−15.2	−0.2117	b
5	$CH_3CH_2CH_2CH_2CH_2NO_2$	−2.19	−8.57	−15.1	−0.2117	b
6	$CH_3CH_2CH_2CH_2CH_2CH_2NO_2$	−2.28	−8.63	−15.1	−0.2116	b
7	$(CH_3)_2CHNO_2$	−13.82	−20.06	−28.4	−0.2545	a
8	Nitrocyclopentane	−13.65	−19.33	−25.7	−0.2480	c
9	Nitrocyclohexane	−12.74	−18.44	−27.8	−0.2595	d
10	$(CH_3)_3CNO_2$	−20.36	−26.15	−35.4	−0.2886	a
11	1-Methylnitrocyclohexane	−18.64	−24.30	−34.1	−0.2891	e
12	$(CH_3)_2(NO_2)CCH_2CH_2NO_2$					b
	CH_2NO_2	+1.45	−4.38	−8.6	−0.1840	
	Me_2CNO_2	−16.00	−21.43	−30.8	−0.2632	
13	$(CH_3)_2(NO_2)CC(NO_2)(CH_3)_2$	−9.57	−12.46	−24.1	0.2418	f
14	$CH_3COOCH_2CH_2NO_2$	+5.36	−1.16	−7.0	−0.1701	b
15	$CH_3CH(NO_2)_2$	+14.28	+9.13	+2.0	−0.1201	a
16	$(CH_3)_2C(NO_2)_2$	+4.94	+1.80	−6.8	−0.1689	a
17	$(CH_3)_2(NO_2)CCH_2CH(NO_2)_2$					g
	NO_2	−14.16	−18.80	−27.1	−0.2457	
	$(NO_2)_2$	+16.56	+12.18	+7.5	−0.1080	
18	$(CH_3)(NO_2)CHCH_2CH(NO_2)_2$					h
	NO_2	−5.67	−11.37	−21.5	−0.2107	
	$(NO_2)_2$	+17.57; +17.93	+12.93	+4.4; +6.0	−0.1081 −0.1091	
19	$CH_3C(NO_2)_3$	+27.71	+25.59	+18.5	−0.0646	a
20	$C(NO_2)_4$	+46.25 (0.005 M)	+46.45 (0.005 M)	+39.8	+0.0448	a

[a] The nitrogen shieldings are not affected, for symmetry reasons, by the rotamer equilibria involved.

[b] Calculated values are averaged over the *trans* and *gauche* rotamer populations (about 36% and 64%, respectively, PM3 energies, 35 °C) where the former show (TNDO/2) less shielding, by about −3 ppm, with respect to the latter.

[c] Calculated values are averaged over puckered cyclopentane ring conformations, with a pseudo-equatorial position of the nitro group; there is only slight variation of the shielding throughout the conformations concerned.

[d] The calculated value is essentially that of the equatorial nitro group, 96% according to PM3 energies, while the shielding of the axial group is smaller by about 0.2 ppm.

[e] The calculations, in combination with experimental data, show clearly that the prevailing conformation is that of a chair with an axial nitro group and an equatorial methyl substituent, as shown in Fig. 6. This is in accord with calculated PM3 energies, which suggest that at 35 °C the latter conformer's population should amount to about 70%.

[f] PM3 calculations show that the population of the *gauche* rotamers is at least 99% and TNDO/2 shows that their nitrogen shielding is higher by about 5 ppm with respect to that of the *trans* form; the least-squares fit (Fig. 1) of the experimental and calculated shieldings is in accord with the foregoing.

[g] The dominant conformation of NO_2 *vs.* $CH(NO_2)_2$ moieties is *gauche* (87%) according to PM3 energies; this is in accord with the least-squares fit of the shieldings, particularly for the latter moiety, where the TNDO/2-calculated *gauche* shielding is higher by 6 ppm with respect to the *trans* rotamer.

[h] For rotamer equilibria concerned, see Table 3 and Fig. 4.

concerned, and are virtually negligible from the point of view of *differences* in the shieldings. An important point in the linear correlation depicted in Fig. 1 is that the compounds where rotamer equilibria do not affect their nitrogen shieldings (denoted by black circles in Fig. 1 and by footnote a in Table 1) follow exactly the correlation. This puts confidence in the results of estimating the rotamer equilibria where they count, and the subsequent calculations of averaged shieldings.

The quality of the correlation between the experimental and computed nitrogen shieldings for nitroalkanes made us look for some factors, possibly close to chemical intuition, that govern the variation of NO_2 nitrogen shieldings in nitroalkane structures. First, we examined the corresponding atomic net charges that were calculated in the TNDO/2 procedures involved in the computation of the shieldings. There was no evident correlation between the latter and any of the atomic charges, including those of the nitrogen atoms, in the molecules concerned. However, close inspection of the data revealed that there is an excellent linear correlation between the total net charges at the nitro groups (sums of the nitrogen and oxygen net charges) and the calculated shieldings. The least-squares fit is shown in Fig. 2, and is expressed by the following equation:

$$\text{NO}_2 \text{ net charge} = 0.04290\Delta\sigma_{\text{calc.}} - 0.1389 \quad (2)$$

with a standard deviation of 0.0067 eu and a linear correlation coefficient $r = 0.997$. The quality of the correlation is comparable to that obtained for experimental *vs.* calculated nitrogen shieldings [Eqn (1)]. An important conclusion follows that the nitrogen shieldings in nitroalkanes seem to provide an attractive tool for the observation of electron charge migration in the direction of the nitro group as an electron sink. According to the correlation [Eqn (2)], the shielding increases linearly with decreasing electron charge density in the nitro group as a whole. It explains the problem of the β-effect discussed in the Introduction, since it indicates that the increasing shielding of the nitrogen nuclei in the NO_2 groups concerned is a result of the decreasing electron-donation ability of the alkyls attached, in the order $R_3C < R_2CH < RCH_2 < CH_3$. If there are any additional nitro groups at carbon C_α, this effect is enhanced, and results in a further increase in the magnetic shielding of nitrogen. A similar, but weaker, effect is observed if an additional nitro group is placed at C_β, as indicated by the data for **10** and **13** (Table 1).

Since Eqn (2) clearly indicates that the shielding of the nitrogen nucleus in a nitro group increases with decreasing electron density at the nitro group as a whole, one can conclude that it is the paramagnetic term, σ_{para}, which is responsible for the variation in the shielding. In the approximation which divides the magnetic shielding constant σ into the diamagnetic term, σ_{dia}, representing the contribution from the spherical part of the electron charge distribution involved, and the paramagnetic term σ_{para}, which accounts for any deviations from the spherical symmetry, the former term should essentially lead to an increase in the shielding with increasing charge density; however, the increasing charge means more electron repulsion, which in turn increases the average orbital radii, and the latter effect largely compensates for the shielding increase owing to the increasing electron density as such.[2] Hence the diamagnetic term is large, positive and fairly insensitive to structural effects in a molecule. The paramagnetic term is essentially negative, and usually larger in magnitude than σ_{dia}. The direction of shielding variation upon changes in the electron density, that expressed by Eqn (2), shows that σ_{para} is responsible for the correlation.

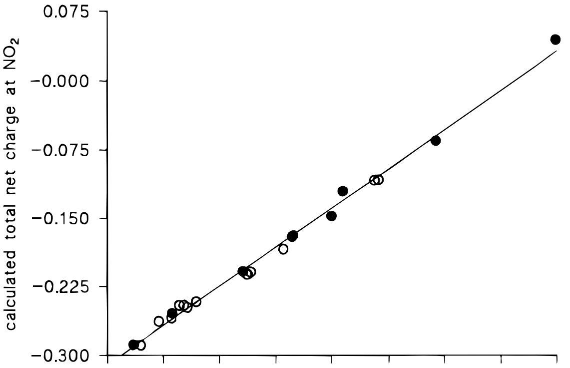

Figure 2. Plot of TNDO/2 calculated net charges at the nitro groups in **1–19** against corresponding TNDO/2 calculated nitrogen shieldings; the linear fit is given by Eqn (2).

The correlation represented by Eqn (1) and Fig. 1 relates to experimental data for dilute solutions of nitroalkanes in cyclohexane and theoretical results obtained for the corresponding isolated molecules. We turn now to assessing possible consequences for such relationships of solvent polarity effects. As was indicated earlier,[3] solvent effects on the NO_2 nitrogen shielding are attributed largely to solvent polarity. If we compare the experimental data (Table 1) obtained for dilute solutions in cyclohexane and acetone, the corresponding differences in the shielding vary significantly throughout the series of compounds **1**–**20**. For tetranitromethane (**20**), the difference is barely significant, + 0.2 ppm for acetone as a solvent with respect to cyclohexane. However, the other nitroalkanes (**1**–**19**) reveal generally a deshielding effect of acetone as a solvent. The latter effect varies from − 8.3 ppm for nitromethane (**1**) to about − 6 ± 1 ppm for other mononitroalkanes, about −3 ppm for **13** and about −2 to −4 ppm for geminal dinitro and trinitro moieties. The effects are not related in any way to the corresponding nitrogen shieldings as such, and there is an obvious inference that they must lead to a deterioration of the overall linear correlation between experimental and calculated shieldings where the latter are obtained for isolated molecules. The result is that the standard deviation increases twofold, with respect to that in Eqn (1), and the correlation coefficient drops to 0.993; this is still a reasonable correlation, but it includes some systematic errors resulting from some incompatibility between the experimental dataset, related to solutions in a polar solvent, and the calculations for isolated molecules.

In view of the excellent correlation [Eqn (1)] between the experimental shieldings for solutions in cyclohexane and the TNDO/2-calculated values, we were interested in a comparison of TNDO/2 with *ab initio* methods. We elected the coupled Hartree–Fock (CHF) approach (no electron correlation effects) combined with the GIAO method of calculation of absolute nuclear magnetic shielding, and a fairly large basis set (see Experimental), with geometry optimization using the same set of wavefunctions. We carried out the calculations for some simple nitroalkanes (Table 2), and a comparison of the

Table 2. *Ab initio* calculations of the absolute nitrogen shieldings of some simple nitroalkanes

Compound	Hartree–Fock/6-31++G**/GIAO calculated nitrogen shieldings (ppm)[a]
1	−159.9
2	−172.4
7	−181.5
10	−186.2
15	−149.3

[a] The geometries concerned were optimized using the same basis set.

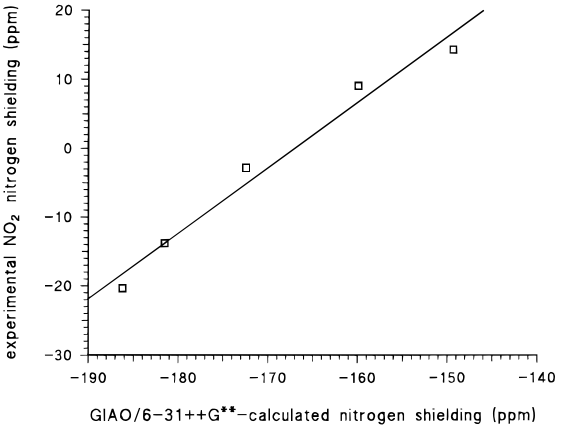

Figure 3. Experimental nitrogen shieldings of dilute solutions in cyclohexane of **1**, **2**, **7**, **10** and **15** plotted against *ab initio*-calculated absolute shieldings (Table 2), the latter with respect to a bare nitrogen nucleus, the linear fit is described by Eqn (3).

results with the corresponding experimental data (Table 1) yielded the following linear correlation:

$$\Delta\sigma_{\text{exp.}} = 0.9502\sigma_{\text{calc.}} + 158.66 \qquad (3)$$

with a standard deviation of 2.67 ppm and a linear correlation coefficient $r = 0.987$ (Fig. 3). Attention is drawn to the fact that in this case the calculated shieldings are absolute, with respect to a bare nitrogen nucleus. While the slope coefficient (0.9502) is closer to the ideal value of unity, as compared with that in Eqn (1), the standard deviation is significantly larger and the correlation coefficient is smaller. Considering the fact that Eqn (3) is based on data for five compounds only, one can conclude that TNDO/2, in the case of nitrogen shieldings of nitroalkanes, is at least as good as the *ab initio* methods which do not account for electron correlation. Obviously, this does not mean that semi-empirical methods like TNDO/2 are generally comparable with *ab initio* methods; the former have usually practical applications only within groups of related structures and, by their nature, can deal only with *relative* shieldings within such groups, but in the present case the success of TNDO/2 is clear.

The overall correlation between experimental and TNDO/2-calculated nitrogen shieldings allows one to have a closer look at the question of differences between individual rotamer species from the point of view of the corresponding shieldings and populations, and of possible effects of the latter on the averaged shielding values (Table 1). The footnotes in Table 1 provide some information on the subject, but we turn now to some details of the most interesting cases. We begin with the

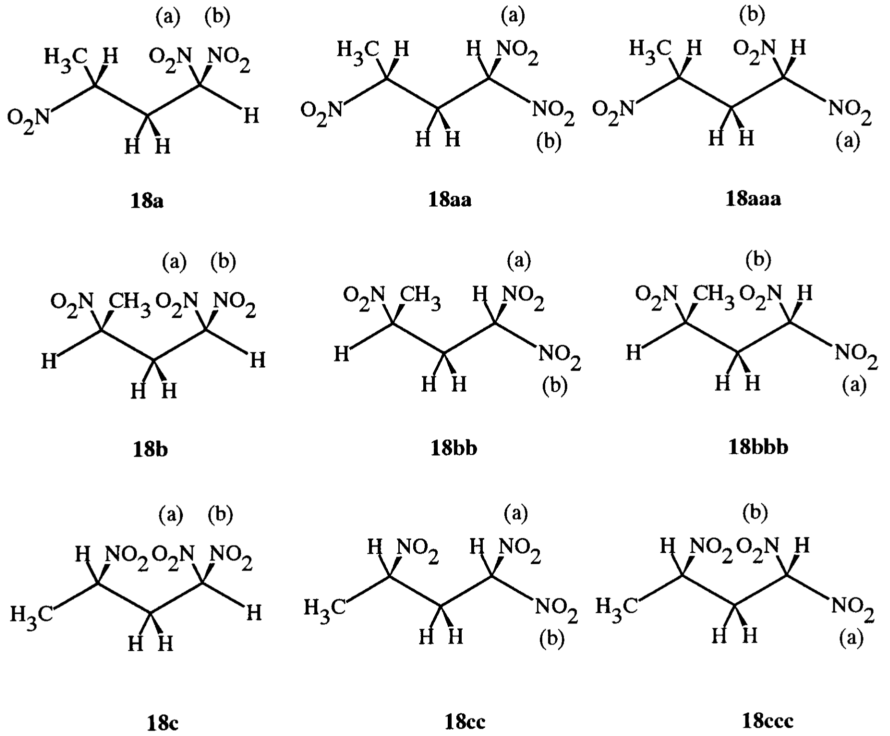

Figure 4. Idealized structures of rotamer species of **18**. They were used as starting points for PM3 geometry optimizations and energy calculations. Since the molecule contains a chiral center, only one enantiomer is shown.

Table 3. TNDO/2 and PM3 calculations for 1,1,3-trinitrobutane (18)

Rotamer[a]	Content at 35 °C (%)	NO_2 shielding (ppm)	NO_2 (a) shielding (ppm)	N_2 (b) shielding (ppm)	Total net charge at NO_2
18a	0	—	—	—	—
18aa	21	−13.7	+4.3	+7.4	−0.1993, −0.1023, −0.0967
18aaa	1	−18.1	+10.1	+1.6	−0.2092, −0.0961, −0.1067
18b	0	—	—	—	—
18bb	8	−27.1	−2.5	+8.8	−0.2098, −0.1234, −0.1081
18bbb	21	−19.9	+4.5	+13.9	−0.2097, −0.1165, −0.0873
18c	0	—	—	—	—
18cc	10	−20.2	+7.3	+1.0	−0.2193, −0.0991, −0.1161
18ccc	39	−25.8	+6.4	+0.6	−0.2154, −0.1063, −0.1259
18 (total)	100	−21.5	+4.4	+6.0	−0.2107, −0.1081, −0.1091

[a] See Fig. 4; PM3 optimized geometries, TNDO/2-calculated shieldings and atomic net charges.

most complicated one, that of **18**, where the rotamer equilibrium concerned can comprise nine distinguishable species (Fig. 4). The relevant populations, according to PM3 energies for individually optimized geometries, are reported in Table 3, together with the corresponding nitrogen shieldings and NO_2 net charges calculated by TNDO/2. Of nine possible conformations, only seven seem to contribute significantly to the equilibrium, and they reveal considerable intrinsic differences in the predicted shieldings among the rotamers involved. The variation of the shielding, for any of the three nitro groups in **18**, spans a range of about 12 ppm according to the direct calculations (Table 3), and of about 11 ppm after rescaling by means of Eqn (1). This is a fairly large value in comparison with the overall range of NO_2 nitrogen shieldings of about 70 ppm. The corresponding weighted averages (Table 3), after a recalculation according to Eqn (1), −7.8, +16.6 and +17.0, respectively, are close to the relevant experimental values for solutions in cyclohexane (Table 1), within less than twice the standard deviation of the overall linear fit [Eqn (1) and Fig. 1] for **1**–**20**. The case of **18** provides an important piece of information on the significance of conformational effects on the nitrogen shielding of aliphatic nitro groups.

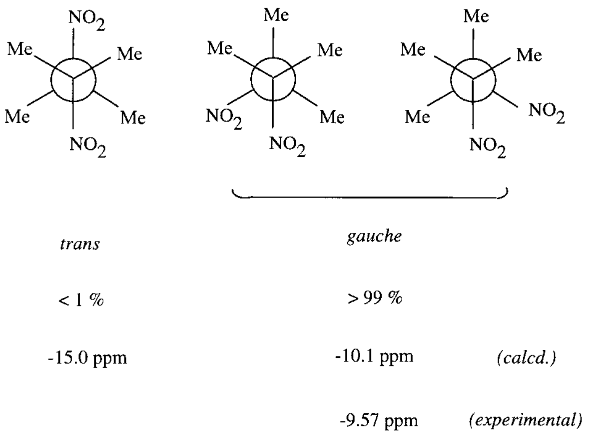

Figure 5. Possible rotamers of **13** and the corresponding nitrogen shieldings calculated by TNDO/2 and modified using Eqn (1). A comparison of the latter with the experimental value suggests about 100% of the *gauche* form, in accord with the relevant populations at 35 °C computed from PM3 energies.

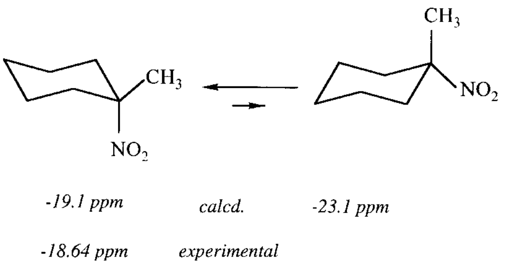

Figure 6. Possible conformations of 1-methylnitrocylohexane (**11**) and the relevant nitrogen shieldings. The calculated values are those obtained from TNDO/2, rescaled by means of Eqn (1).

As far as **13** is concerned, the nitrogen shielding data and PM3 energies suggest that the dominant conformation should be *gauche* (Table 1 and Fig. 5). It is interesting that in the analogous case of 1,2-dinitroethane in solution, the *gauche* form was shown to dominate (more than 90%) the rotamer equilibrium concerned.[7] Hence there seems to be a general tendency of vicinal nitro groups to assume the *gauche* conformation, in view of the fact that there should be a good deal of steric hindrance in **13** as compared with 1,2-dinitroethane.

For nitrocyclopentane (**8**; see Table 1, footnote c), the calculated value of the shielding is averaged over puckered ring conformations, but the intrinsic differences in the shielding are fairly small. As far as nitrocyclohexane (**9**) is concerned, it is known that the preferred conformation of the nitro group is equatorial.[8] The nitrogen shielding data (Table 1, footnote d) are not informative about the conformational equilibrium, since the difference in the shielding between axial and equatorial nitro groups is insignificant, according to TNDO/2 calculations. One can obtain an impression from the foregoing that NO_2 nitrogen shieldings are almost useless in tracing conformations of nitrocycloalkane systems, but this is not exactly so, as indicated by the data on 1-methylnitrocyclohexane (**11**; see Table 1, footnote e). In theory, there should be an equilibrium between two chair forms of the ring, with either an equatorial methyl and an axial nitro group or vice versa (Fig. 6). The calculated shieldings show a large difference between the conformers, and a comparison with the experimental value suggests strongly that the nitro group is largely axial, in accord with PM3 energy calculations.

EXPERIMENTAL

Materials

Some of the compounds studied were commercially available c.p.-grade products (**1**–**10** and **20**); the other were prepared by published procedures: **11**,[8] **12**,[9] **13**,[10] **14**,[11] **15**,[12] **16**,[10] **17**,[13] **18**[13] and **19**.[13] Particular care was taken in the NMR measurements to use very pure and dry solvents, as reported previously.[4–6] The NMR samples concerned were prepared and handled under a dry argon atmosphere in glove-bags.

Spectra

The ^{14}N NMR shielding measurements were made on a Bruker AM500 spectrometer (11.7 T) at 35 ± 0.2 °C, as maintained by a VT unit, at a frequency of 36.14 MHz. Random and systematic errors were reduced to below 0.1 ppm for the solute nitrogen shieldings in different solvents. External neat liquid nitromethane was employed as a reference by means of 10 mm × 4 mm o.d. coaxial tubes. The inner tube contained 0.3 M nitromethane in acetone-d_6 as a reference and a source of deuterium lock; the nitrogen shielding of this solution was +0.77 ppm with respect to that of neat liquid nitromethane.[2] The latter value was obtained from measurements using concentric spherical sample/reference containers in order to eliminate bulk susceptibility effects. The value of +0.77 ppm was used as a correction upon a conversion to the neat nitromethane reference scale of nitrogen NMR shieldings. Bulk susceptibility corrections for the shieldings measured with respect to the actual reference employed (0.3 M nitromethane in acetone-d_6) were made as described previously[2] and, since dilute solutions were used, their magnetic volume susceptibilities are assumed to be equal to those of the corresponding solvents at 35 °C. In our measurements, the exact resonance frequency of the ^{14}N signal of neat nitromethane was 36.141 524 MHz, from which a value of 36.136 826 MHz was obtained for the bare nitrogen nucleus.[2] The latter value was used in conjunction with the relevant resonance frequency differences to calculate the nitrogen shieldings relative to that of neat nitromethane. Lorentzian lineshape fitting of the ^{14}N signals was used to produce values for the precise resonance frequencies of both the samples used and of the external standard as well as the relevant standard deviations of the variables fitted. The latter included not only the resonance frequencies concerned, but also the phases of the signals, their linewidths and intensities and the linear baseline drift. The standard deviations of the resonance frequencies concerned were, in all cases, below 2 Hz, which corresponds to an error of less than 0.05 ppm for the nitrogen shieldings; the latter are reported such that the last digit is uncertain. Typically, the ^{14}N resonance half-height widths of the nitroalkanes concerned were within a range 1–60 Hz.

Calculations

Quantum-mechanical calculations of the nitrogen shieldings concerned were carried out on a Pentium-S (200 MHz)-based system with 64 MB RAM. As far as semi-empirical methods are concerned, the molecular geometries were optimized using the PM3 method, which is known to yield reliable results for polar molecules, and the nitrogen shieldings were calculated by the TNDO/2 method devised as Hypercube (Waterloo, ON, Canada); it is a modification of the INDO method, by introducing parametrizations which are not unique for a given element, but are subdivided into a number of 'types,' depending on the type of bonding involved. The method is implemented and described in their HyperNMR software package which we employed in our computations of the shieldings, in conjunction with the HyperChem 4.0 package for geometry calculations. *Ab initio* calculations of some of the nitrogen shieldings were made using the Hartree–Fock approach and the 6–31 + + G** basis set which places both polar and diffuse functions on both hydrogens and heavy atoms; the latter set seems suitable for molecular systems where lone pair electrons are present. The Gaussian 94 (Revision D.3) software suite[14] was employed for the computations. The nitrogen shieldings were calculated by the GIAO (gauge-included atomic orbitals) method, for geometries which were optimized using the same basis set.

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