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A study of solvent polarity and hydrogen bonding effects on the nitrogen NMR shieldings of N-nitramines and ab initio calculations of the nitrogen shieldings of C-nitro, N-nitro and O-nitro systems ☆

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Abstract

High-precision nitrogen NMR shieldings, bulk susceptibility corrected, are reported for dimethylnitramine (**1**) and diethylnitramine (**2**) in a variety of solvents which represent a wide range of solvent properties from the point of view of polarity as well as hydrogen bond donor and acceptor strength. The observed range of solvent-induced nitrogen shielding variations of **1** and **2** is significant for the amino-type nitrogens, up to about 10 ppm, and originates essentially from the deshielding effect of the increasing polarity of solvent. On the other side, the nitro nitrogens reveal a very weak and rather chaotic response to solvent effects, within about 2 ppm. This is in a sharp contrast with the behavior of the nitrogen shieldings of C-nitro and O-nitro groups where solvent effects induce variations within at least 6 ppm which follow a regular pattern of enhanced magnetic deshielding with increasing polarity involved. This apparent insensitivity of the N-nitro group shielding to solvent effects seems to stem from the cancellation of opposite effects, the shielding effect of the electron charge migration to the nitro group upon increasing solvent polarity, and the deshielding effect produced by the flattening of the pyramidal arrangement of bonds at the amino nitrogen with the increasing polarity of the medium. Ab initio quantum-mechanical calculations using the GIAO/B3PW91/6-311 + +G** approach and geometry optimizations employing the same basis set and density functionals show an excellent linear correlation with the experimental data and reproduce not only major changes but also most of the subtle variations in the experimental nitrogen shieldings of the nitro systems as a whole.

Keywords: Nitrogen NMR shieldings; Solvent effects; Hydrogen bonding; Ab initio calculations; N-nitramines

1. Introduction

We have already presented the results of our extensive studies of solvent induced effects on the nitrogen NMR shieldings (chemical shifts) of C-nitro groups in nitroalkanes [1–5] and nitrobenzenes [6], and the O-nitro group in methyl nitrate [7], in a wide range of solvents encompassing a broad spectrum of polarity and hydrogen-bonding properties. It was shown there that the solvent effects concerned are quite significant and span a range of about 6–12 ppm for the nitro group nitrogen atoms. They can be rationalized in terms of non-specific interactions of the solutes with the medium polarity/polarizability.

The aim of the present work is to extend our studies

☆ Dedicated to Professor Graham A. Webb on the occasion of his 65th birthday.

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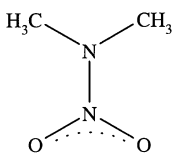
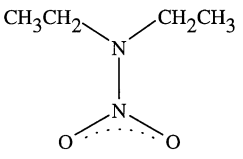


Dimethylnitramine

1



Diethylnitramine

2

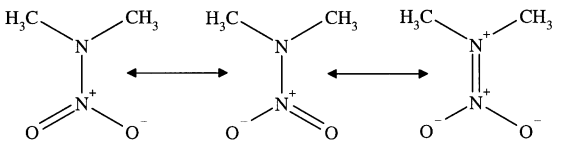
Fig. 1. Structures of compounds **1** and **2** studied experimentally in the present work.

over the N-intro groups in nitramines with due attention paid to the relevant amino moieties. We have selected for this purpose two simple nitramines, dimethylnitramine (**1**) and diethylnitramine (**2**) (Fig. 1) whose amino nitrogens bear two alkyl groups as substituents, in order to avoid complications that may arise from the possibility of solute-to-solvent hydrogen bond effects on the nitrogen shieldings in the case of the parent nitramine NH_2NO_2 or $NH(R)NO_2$ nitramines. The NH-containing nitramines can also be involved in tautomeric equilibria where the NH hydrogens migrate to the corresponding nitro oxygen atoms [8], and can also form quite stable associates [9] via hydrogen bonding between the amino NH moieties as donors and the nitro oxygen atoms of another nitramine molecule as acceptors. Thus we also want to avoid any effects on the nitrogen shieldings of such equilibria which are likely to be solvent dependent. The compounds studied presently, **1** and **2**, have sufficient solubility in the wide range of solvents, including cyclohexane, employed in our previous work on other nitro systems [1–7].

Finally, the present work combined with our earlier studies on nitro systems provide a large set of nitrogen shieldings for dilute solutions of the molecules concerned in cyclohexane where molecular interaction effects on the nitrogen shieldings are likely to be weak. This seems to be a suitable experimental basis for a comparison with ab initio calculations of the shieldings of isolated molecules. As far as the calculations are concerned, we have chosen the density functional approach in order to account for electron correlation effects, and the large 6-311++G** basis set of wavefunctions which places both polar and diffuse functions on hydrogens as well as on heavy atoms (see Section 3). This seems to be a reasonable choice for polar molecules which include nitrogen atoms bearing lone pair electrons and direct nitrogen–oxygen and nitrogen–nitrogen bonds.

Table 1
Nitrogen NMR shieldings of dimethylnitramine and diethylnitramine in 0.1 M solutions

Solvent	Nitrogen shielding in ppm ref. to neat liquid nitromethane corrected for bulk susceptibility			
	$(CH_3)_2N–NO_2$		$(CH_3CH_2)_2N–NO_2$	
	Me_2N	NO_2	Et_2N	NO_2
Cyclohexane (0.005 M)	+221.06	+24.98	+197.81	+28.72
CCl_4 (0.03 M)	+220.05	+25.67	+196.45	+29.24
Et_2O (0.01 M)	+219.58	+24.43	+195.84	+28.40
Benzene	+219.43	+25.37	+195.09	+28.52
Dioxane	+217.20	+24.30	+194.88	+28.03
Acetone	+216.47	+24.00	+192.81	+27.69
DMSO	+212.75	+24.25	+192.20	+27.62
CH_2Cl_2	+216.90	+24.85	+192.52	+28.12
$CHCl_3$	+217.52	+24.99	+193.00	+28.07
EtOH	+216.89	+24.42	+191.54	+27.42
MeOH	+216.24	+24.27	+191.87	+27.61
CF_3CH_2OH	+214.33	+25.58	+186.5	+28.46
H_2O	+210.20	+26.16	+187.12	+28.86



1a **1b** **1c**

Fig. 2. Conventional representation of the electronic structure of **1** in terms of resonance structures **1a**, **1b**, and **1c**. The fairly significant barrier (ca. 10 kcal/mol) to rotation about the N–N bond suggests some contribution of **1c** to the actual structure.

As in our earlier reports [1–7], we present our results in terms of $\Delta\sigma$ which represents the differences in the nitrogen nuclear shielding constants σ of the compounds studied and that of neat liquid nitromethane used as external reference, with due corrections for bulk magnetic susceptibility differences. Thus we use the expression 'nitrogen shielding' for $\Delta\sigma$, since a positive sign corresponds to an increase in magnetic shielding. Hence $\Delta\sigma = -\delta$, where the latter is commonly termed as the chemical shift. Consequently, 'nitrogen shieldings' and 'nitrogen chemical shifts' differ only in their sign.

2. Results and discussion

Table 1 reports the high-precision ^{14}N NMR shieldings measured for **1** and **2** (Fig. 1), respectively, in 13 solvents which represent a wide range of solvent properties from the point of view of hydrogen bonding and polarity effects. The nitrogen shieldings of the amino moieties of the nitramines **1** and **2**, as a function of solvents effects, span a considerable range of about 12 ppm within the set of solvents employed. At first glance, the shielding variation seems to follow the polarity of solvent in the sense of enhanced deshielding with the increasing polarity, and this point will be discussed in detail in conjunction with Eq. (1). This behavior of nitrogen shieldings is typical of amino moieties whose lone pairs of electrons are engaged in a delocalized π-electron system, and the delocalization of the lone pair is augmented by solvent polarity or any other effects [1]. Thus, in the present case of nitramines, the latter process would involve a gradual shift of the actual structure from **1a/1b** to that represented by **1c** (Fig. 2), with a possible change in the geometry concerned, from non-planar to planar, as a result of the increasing polarity of the medium. The significant difference between the amino nitrogen shieldings of **1** and **2** in a given solvent, about 22 ppm, is an example of the so called β-effect of alkyl groups. It has already been established [1] that nitrogen magnetic shielding decreases significantly in the following sequence of alkyl substitution at a nitrogen atom for a given X residue.

$$CH_3N(X) \rightarrow RCH_2N(X) \rightarrow R_2CHN(X) \rightarrow R_3CN(X)$$

where R is an alkyl group, and X represents any atom or group of atoms. This is called the β-effect [1] as each step involves the introduction of a carbon atom to the β-position with respect to the nitrogen atom concerned, and produces a deshielding effect $\Delta\sigma = -6$ to -12 ppm. In the present case, the replacement of the two methyl groups in **1** with two ethyl groups, which yields the structure of **2**, produces a double β-effect and a concomitant deshielding of the amino nitrogen, $\Delta\sigma =$ about -22 ppm, just within the range expected. Needless to say, such comparisons make sense only in the case of solutions in the same solvent.

The N-nitro groups in nitramines **1** and **2**, however, give rather surprising results, from the point of view of solvent effects on their nitrogen shieldings (Table 1), if compared with analogous observations for C-nitro and O-nitro moieties [1–7] where the effects span a considerable range and are governed primarily by solvent polarity. The N-nitro nitrogen shieldings of **1** and **2** show only little variation, within about 2 ppm, as a function of solvent, and this weak response is fairly chaotic from the point of view of solvent bulk properties. In view of the significant and regular changes in the nitrogen shieldings of other nitro groups as a function of solvent polarity, there is something peculiar in the case of the N-nitro group examined, and the weak and chaotic response to solvent of their nitrogen shieldings seems to arise from a cancellation of opposite effects. If one assumes that the nitrogen magnetic shielding of the N-nitro groups decreases with the increasing solvent polarity as does for other nitro moieties, there must be another effect of the same order of magnitude, which increases

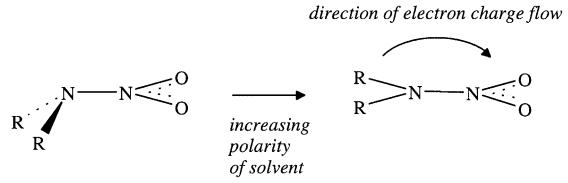


Fig. 3. A plausible explanation of the observed solvent effects on the nitrogen shieldings of nitramines **1** and **2** in terms of electron charge migration toward the nitro moiety and concomitant changes in the molecular geometry in the direction of a planar structure as a result of the increasing polarity of solvent.

the shielding. A plausible explanation for the latter comes from the bond geometry of the atom which is bound directly to the nitro group. For nitroalkanes, nitroarenes, and covalent nitrates, the bond configuration of C_α, tetragonal in nitroalkanes and planer in nitroarenes, is not likely to be affected by solvent to any significant degree. On the other side, the three bonds of the amino nitrogen in intramines can assume a planar or non-planar configuration, and the latter can be affected by the surrounding medium. If the configuration in non-polar media is slightly pyramidal, and if polar solvents induce changes in the direction of a planar structure, as depicted in Fig. 3, the flattening of the structure should produce an increase in the nitrogen shielding of the nitro group as can be reckoned, by analogy, from the corresponding data on nitroalkanes and nitrobenzene in cyclohexane solutions (Table 3). In the latter case, the shielding is augmented by about 4 ppm upon passing from nitromethane to nitrobenzene as solutes, and the effect is even more pronounced if other mono-nitroalkanes are considered. Thus the opposite effects on the N-nitro nitrogen shielding of electron charge migration and the concomitant changes in geometry of the amino moiety, as a function of solvent polarity, can produce the apparent weak response of the shielding to solvent effects, in contrast with the evident sensitivity of nitroalkane and nitrobenzene nitrogen shieldings to solvent polarity.

Table 3
Ab initio calculations of nitrogen NMR shieldings of C-nitro, N-nitro and O-nitro systems

Compound	Experimental values of nitrogen shielding (ppm, dilute solutions in cyclohexane, ref. to neat nitromethane)	B3PW91/6-311++G** calculated nitrogen NMR shielding (ppm, referred to a bare nucleus)
CH_3–NO_2	+9.50[a]	−138.90
CH_3CH_2–NO_2	−2.84[a]	−147.95
$(CH_3)_2CH$–NO_2	−13.82[a]	−164.11
$(CH_3)_3C$–NO_2	−20.36[a]	−168.64
Nitrobenzene	+12.21[b]	−129.50
$(CH_3)_2N$–NO_2		
(NO_2)	+24.98	−112.69
(Me_2N)	+221.06	+76.27
$(CH_3CH_2)_2N$–NO_2		
(NO_2)	+28.72	−104.76
(Et_2N)	+197.81	+58.02
CH_3–O–NO_2	+42.21[c]	−100.56

[a] Experimental data from our earlier work [5] obtained under the same experimental conditions as those employed in the present study.
[b] As above, Ref. [6].
[c] As above, Ref. [7].

A more detailed insight into the various site-specific and non-specific contributions to the solvent induced variations of the amino nitrogen shieldings of **1** and **2** can be obtained by making use of the empirical scheme represented by the master equation (1) [10,11]

$$\sigma(i,j) = \sigma_0(i) + a(i)\alpha(j) + b(i)\beta(j) + s(i)[\pi^*(j) + d(i)\delta(j)] \quad (1)$$

where i and j denote the solute and solvent, respectively, σ is the nitrogen shielding, α represents the hydrogen bond donor strength of the solvent as a bulk medium, β gives its hydrogen bond acceptor strength, π^* is its polarity/polarizability, and δ is a correction for polychlorinated solvents ($\delta = 0.5$) and aromatic solvents ($\delta = 1$). The corresponding response of the solute nitrogen shielding to a given solvent property is represented by the solute terms *a, b, s,* and *d*, respectively. The nitrogen shielding in the reference state, cyclohexane solution, is given by σ_0; the latter is a least-squares fit of the data obtained for all of the solvents employed rather than the experimental value concerned.

Table 2 shows the solvent parameter sets employed in the present work [10,11] as well as the results of a

Table 2
Solvent parameters used and least-squares fitted solute parameters for a set of master master equation (1)

Solvent	α	β	π^*	δ		
Cyclohexane	0	0	0	0		
Et_2O	0	0.47	0.27	0		
CCl_4	0	0	0.29	0.5		
Benzene	0	0.10	0.59	1		
Dioxane	0	0.37	0.55	0		
Acetone	0.07	0.48	0.72	0		
DMSO	0	0.76	1.00	0		
CH_2Cl_2	0.22	0	0.80	0.5		
$CHCl_3$	0.34	0	0.76	0.5		
EtOH	0.86	0.77	0.54	0		
MeOH	0.98	0.62	0.60	0		
H_2O	1.13	0.18	1.09	0		
CF_3CH_2OH	1.51	0	0.73	0		
Compound/nitrogen atom	σ_0 (ppm)	a (ppm/unit scale)	b (ppm/unit scale)	s (ppm/unit scale)	d (dimension less)	Correlation coefficient r
I/NMe_2	$+221.49 \pm 0.63$	-0.78 ± 0.55	$+0.66 \pm 0.99$	-8.54 ± 0.92	-0.40 ± 0.12	0.98
II/NEt_2	$+197.48 \pm 0.50$	-3.79 ± 0.43	$+1.06 \pm 0.79$	-6.01 ± 0.73	-0.23 ± 0.13	0.99

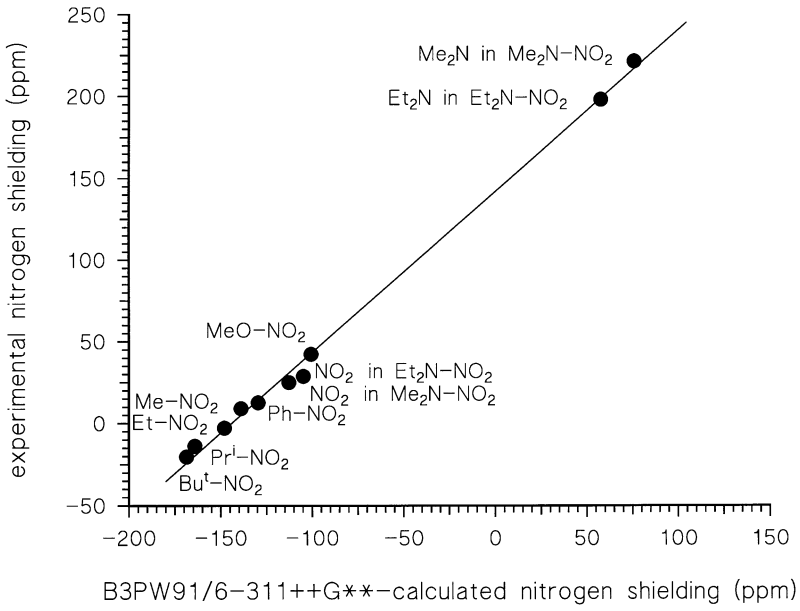


Fig. 4. A plot of experimental nitrogen shieldings, referenced to neat liquid nitromethane, against B3PW91/6-311 + +G**-calculated absolute nitrogen shieldings for the nitramines **1** and **2** as well as for some examples of C-nitro ond O-nitro groups. The relevant values of the shieldings are reported in Table 3, and the linear regression concerned is represented by Eq. (2). The experimental shieldings, bulk susceptibilty corrected, are taken on dilute solutions in cyclohexane.

multiple regression analysis performed over the corresponding sets of master equation (1) for the compounds and amino nitrogen atoms involved. The least-squares fitted values of the relevant solute/atom terms σ_0, a, b, s, and d are reported together with their standard deviations. The terms b and d are not significant, but the s term (nitrogen shielding response to solvent polarity) is highly significant for both **1** and **2** and shows that the increasing polarity results in an appreciable, deshielding of the amino nitrogen nuclei. It is the only term that counts in the case of **1**, but for **2** there is some contribution of the term a (nitrogen shielding response to solvent-to-solute hydrogen bonding) which reveals that the increasing hydrogen bond donor strength of solvent produces a moderate deshielding effect on the amino nitrogen.

This is in accord with the picture of the increasing delocalization of the lone pair electrons of the amino nitrogen with the increasing polarity of the medium, and also with analogous observations for pyrrole-type nitrogen atoms in azole ring systems [12–16]. Generally, in view of the fact that the values of π^* for the set of solvents employed span a range from 0 (cyclohexane) to 1.09 (water), the effects of solvent polarity on the nitrogen shielding of the amino nitrogen can reach −10 ppm for compound **1** thus accounting for the entire range of the solvent effects observed. The solvent polarity effect on the shielding of the amino nitrogen in **2** is less pronounced, up to about −7 ppm, while the maximum effect of solvent to solute hydrogen bonding amounts to about −4 ppm. The two values taken together account for the whole of the range of solvent effects on the shielding concerned. Thus the hydrogen bondings seems to hamper the delocalization of the lone pair electrons of the amino moiety, and the inference is that the primary acceptor site for the hydrogen bonds is the amino nitrogen in **2**. The magnitude and sign of the hydrogen bonding effect is typical of other amino moieties [1].

Now, since the present work combined with our earlier studies on nitro systems [1–7] provides a comprehensive set of nitrogen shielding data which includes measurements for dilute solutions of the solutes concerned in cyclohexane, we endeavored to calculate the relevant absolute nitrogen shieldings

Table 4
B3PW91/6-311++G** optimized geometry of dimethylnitramine (**1**)

Bond lengths (in pm)[a]		Bond angles (°)[a]	
CN	145.22	∠CNC	120.01
NN	137.50	∠CNN	116.02
NO	122.14	∠NNO	117.08
		∠ONO	125.81

[a] In picometers (100 pm = 1 Å); the geometry was fully optimized, including hydrogen atoms, but results reported in the table relate only to the heavy atoms concerned. The sum of ∠CNC + ∠CNN + ∠CNN amounts to 352.09° which is short of the full angle value by 7.91°, and this shows a slightly pyramidal configuration of the bonds of the amino moiety.

using ab initio methods (Table 3). The saturated hydrocarbon solvent employed is likely to enter into rather weak molecular interactions with the solutes, and therefore the experimental data are suitable for a comparison with theoretical values of the nuclear shieldings calculated for isolated molecules. Attention is drawn to the fact that the calculations of the shieldings were based on optimized geometries using the same basis set, 6-31++G**, for both the optimization and nitrogen shieldings. There is an excellent linear relationship between the experimental data and the theoretical shieldings (Fig. 4), as expressed by the following equation which includes the relevant standard deviations of the linear fit.

$$\sigma_{\text{exp.}} = [0.9828(\pm 0.0200)\sigma_{\text{calcd}} + 141.62(\pm 2.50)] \pm 5.27 \text{ ppm} \quad (2)$$

with a linear correlation coefficient $r = 0.998$. The slope coefficient of 0.9828 shows that the calculations slightly overestimate the magnitudes of the absolute shieldings, by less than 2%, and the free term yields an estimate of the absolute shielding of the references employed, neat liquid nitromethane, as about −142 ppm. Actually, if one considers the standard deviation of ±0.02 for the slope coefficient, the latter does not differ significantly from the ideal value of unity. The experimental nitrogen shieldings of the nitro systems concerned in dilute solutions in cyclohexane (Table 3) cover a range of about 241 ppm, from −20 ppm for Bu^t–NO_2 through +221 ppm for the amino moiety in nitramine **1** with respect to neat liquid nitromethane; thus, the standard deviation of the linear fit, ±5.27 ppm, amounts to only about 2% of the range of the shieldings concerned. Needless to say, we compare here calculations relating to isolated molecules with experimental data obtained for solutions in cyclohexane rather than with those for low-pressure gas phase, and thus we neglect any gas-to-solution shifts of the shieldings involved or, more precisely, any differentiation therein throughout the set of the nitrogen shieldings considered. In view of the good linear relationship obtained, Eq. (2), such a differentiation for solutions in cyclohexane seems to be small, particularly if we take into account the limitations effected by a finite basis set of wavefunctions and by the density functional theory (DFT) in accounting for electron correlation effects. Moreover, many subtle points of experimentally observed differences in the nitrogen shieldings are reproduced precisely by the computations. These include the increasing magnetic shielding in the following sequence. C-nitro < N-nitro < O-nitro groups, the augmented shielding of nitrobenzene with respect to nitromethane, the deshielding of the nitrogen nuclei in nitroalkanes, R–NO_2, following the order R = $CH_3 \rightarrow CH_2CH_3 \rightarrow CH(CH_3)_2 \rightarrow C(CH_3)_3$ which is a manifestation of the so-called β-effect of alkyl branching on nitrogen shieldings, and an analogous effect on the shielding of the amino moiety of **2** with respect to **1**. As far as nitramines **1** and **2** are concerned, the computations reproduce not only the large differences in the nitrogen shieldings between the nitro and amino groups, but also the subtle difference between the nitro groups in **1** and **2**.

Generally, it seems that the density functional approach at the level of sophistication employed in the present work yields good results in confrontation with experimental nitrogen shieldings; this is corroborated by our earlier results [17] obtained for *N*-methylsydnone and all isomeric oxazoles and oxadiazoles. Attention is drawn to the fact that the experimental and theoretical datasets compared in the present work are internally consistent. All of the experimental values of the nitrogen shieldings were obtained under the same conditions and relate to dilute solutions in cyclohexane; measurements for such solutions are likely to provide the closest approximation to gas-phase nitrogen shieldings, and even more so with respect to relative shieldings. On the other side, the ab initio theoretical values of the

shieldings were obtained using a large basis set, for molecular geometries which were optimized using the same set, so that there is no arbitrariness involved like that when one employs 'experimental' geometries of various and often dubious quality or when the optimization is carried out using a different, usually much smaller basis set.

A word of comment about the geometries of nitramines **1** and **2** is necessary here. Our calculations (Table 4) show a slightly pyramidal structure of the amino moieties in **1** and **2** (the latter is not reported in the table). This is in accord with the most recent report [18] on ab initio calculations for **1**, on a similar level of sophistication, and gas-phase electron diffraction by **1**. The latter [18] also shows a slightly pyramidal structure of the amino moiety, but indicates that the electron diffraction assessed sum of the bond angles at the amino nitrogen is rather inaccurate in view of strong correlations that exist between various geometrical parameters involved in the analysis. On the other side, X-ray and neutron diffraction data suggest a planar structure of **1** in the solid state [19]. All of this is in accordance with our conclusion, drawn from the analysis of the nitrogen shieldings of **1** and **2** as a function of solvent, that the geometry of the nitramines can vary from a pyramidal structure in nonpolar media to a planar structure in a polar environment.

3. Experimental

The compounds studied experimentally, **1** and **2**, were prepared by a published procedure [20]. Particular care was taken in the NMR measurements to use very pure and dry solvents as reported previously [2–7]. The NMR samples concerned were prepared and handled under a dry argon atmosphere in glove bags. The ^{14}N NMR shielding measurements were taken on a Bruker Avance DXR-500 system (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 is +0.77 ppm with respect to that of neat liquid nitromethane [1]. The latter value is obtained from measurements using concentric spherical sample/reference containers in order to eliminate bulk susceptibility effects. The value of +0.77 ppm is 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 [1], 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 36.141524 MHz, from which a value of 36.136826 MHz is obtained for the bare nitrogen nucleus [1]. The latter value is 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, and this 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.

The ab initio calculations were carried out using the GAUSSIAN 94 software package [21]. Both the full geometry optimization and nitrogen shielding calculations were performed with a 6-311++G** basis set of wavefunctions using DFT with the hybrid B3PW31 functionals and the GIAO method (gauge included atomic orbitals) for computing the magnetic shieldings concerned. The large set of wavefunctions employed uses both diffuse and polar functions on hydrogen and the heavy atoms concerned and appears to be a satisfactory choice for polar molecules containing lone pairs of electrons, and particularly those containing direct nitrogen–oxygen and nitrogen–nitrogen bonds.

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