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Solvent-Induced Effects on the Nitrogen NMR Shieldings of Some Nitrosobenzene Systems

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High-precision ^{14}N NMR measurements of solvent-induced shielding variations are reported for some nitrosobenzene systems. These variations are shown to result from a combination of three major factors, solvent to solute hydrogen bonding where the solute nitrogen lone pair electrons are involved, solvent polarity and interactions between the electron-deficient benzene ring of the nitrosobenzenes and basic centres in the solvent molecules. The last of these three factors produces nitrogen deshielding of the nitroso group, and in the present work this interaction was found to be the largest of its type so far observed. Consequently, this implies that, in nitroso aromatic compounds, the benzene ring shows a remarkable deficit of electronic charge. The former two factors produce an increase in nitroso nitrogen shielding, thus indicating a strong electron-withdrawing effect of the nitroso group which is consistent with previous observations. INDO/S parameterized molecular orbital calculations of solute nitrogen shieldings, incorporating the Solvaton model of non-specific solute–solvent interactions, predict that the nitrogen shielding will increase as the polarity of the medium increases. This is in very good agreement with the observation that the nitroso nitrogen shielding analysis yields a large and positive value for the *s* term which describes the influence of solvent polarity/polarizability on the shielding variation as a function of solvent. For the 0.2 M solutions studied at 35 °C, a significant amount of the dimeric isodioxy form is only observed for *o*-nitrosotoluene.

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INTRODUCTION

Our previous studies on nitrogen NMR shieldings, $\Delta\sigma$ (which is equivalent to $-\Delta\delta$ on the frequency scale of chemical shifts), of the N=O group in nitroso alkane systems, show that the shieldings provide a sensitive probe for substituent-induced perturbations of electronic charge distributions, steric effects and molecular interactions in solutions.[1,2] In addition, nitrogen NMR can provide useful information on the dimerization equilibria, between the nitroso monomer and the azodioxy dimer forms, of nitroso compounds,[1–4] as shown in Fig. 1. For nitrosobenzene the dimer is essentially in the *cis* form; however, in concentrated $CDCl_3$ solutions the ^{15}N NMR spectrum shows that about 6% of the *trans* form is present and exchange is slow on the NMR time-scale.[4]

In the case of aliphatic nitroso compounds,[2] solvent-induced nitrogen shielding variations are mainly due to solvent polarity effects. An increase in solvent polarity results in a deshielding of the nitrogen nucleus. The mechanism for this has been ascribed to the withdrawing of electrons from the nitrogen to the oxygen atom when the solvent polarity increases. The direction of this effect on the solute nitrogen shielding has been shown to be opposite to that observed for N=C systems, such as imines and their analogues.[2]

The present study is concerned with comparable effects for aromatic nitroso compounds where the conjugation of the π-electron systems of the nitroso group and the aromatic ring can enhance the removal of electronic charge from the ring to the nitroso group. This is in addition to the so-called inductive effect of the

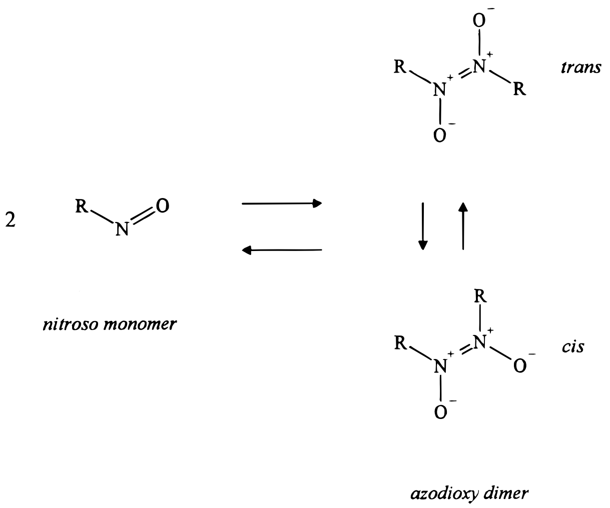

Figure 1. Schematic representation of the reversible dimerization of nitroso compounds to the corresponding azodioxy dimers.

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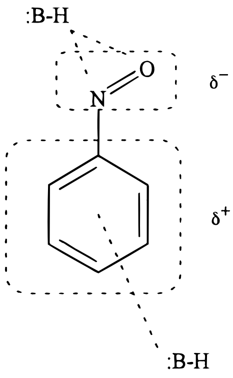


Figure 2. Schematic representation of possible interactions in solutions of nitrosobenzene.

nitroso group. There are indications[5,6] that the nitroso group in aromatic compounds exerts a remarkable electron-withdrawing influence on the aromatic ring. This effect is so large that in *para*-disubstituted compounds other substituents are found to be electron deficient even if they are potential electron acceptors. This is entirely due to the presence of the N=O group.

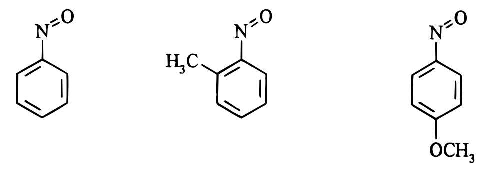
In principle, an increase in the polarity of the surrounding medium should enhance the electron-withdrawing ability of the nitroso group. A comparable effect should occur upon the formation of hydrogen bonds where the solvent is the donor and the acceptor is either the nitrogen or oxygen atoms of the nitroso moiety. If both of these effects are operative then the accumulation of electron charge at the nitroso group can result in the aromatic ring becoming electron deficient. Under these conditions the ring could interact with electron-rich basic centres in solvent molecules, as shown in Fig. 2.

The question arises as to whether, and how, the nitrogen NMR shielding of the nitroso group would respond to such a possible situation.

In our work we employ the sign convention such that a plus sign corresponds to an increase in nuclear shielding. Thus we use the term 'nitrogen shielding,' $\Delta\sigma$, rather than 'nitrogen chemical shift,' $\Delta\delta$. The two terms are equivalent in magnitude but are of opposite sign.[7]

RESULTS AND DISCUSSION

The compounds studied in the present work are shown in Fig. 3. These include the simplest aromatic nitroso compound, nitrosobenzene (**1**), 2-nitrosotoluene (**2**), where steric interactions may occur between the methyl and nitroso groups and *p*-nitrosoanisole (**3**) where the OCH_3 group is known to supply electrons to the π-conjugated system of the aromatic ring.



1 *nitrosobenzene* **2** *2-nitrosotoluene* **3** *4-nitrosoanisole*

Figure 3. Structures of the compounds studied.

Table 1 shows the results of some high-precision ^{14}N NMR measurements on compounds **1**, **2** and **3** in a variety of solvents. The solvents chosen represent a large range of hydrogen bonding properties and polarities. In some cases, for the 0.2 M solutions used, we observe ^{14}N signals from both the nitroso monomer and the corresponding dimer. At equilibrium the amount of the dimer is obtained from integral intensities of the corresponding resonance signals, produced by lineshape fitting as described in the Experimental section. We have not chosen to pursue the question of dimerization in great detail but some observations are in order. A significant amount of dimer is observed only for **2** in most solvents. However, in a CF_3CH_2OH (TFE) solution both **1** and **2** exist, to the extent of almost 75%, in the dimeric form. Thus in TFE solutions the dimer content appears to be enhanced. Steric strain between the nitroso and methyl groups of **2** may be relieved by dimerization. A similar conclusion was reached in our earlier work on aliphatic nitroso compounds.[1]

A general survey of the nitrogen shielding data presented in Table 1 shows that, if solutions in TFE are excluded from consideration, the range of nitrogen shielding variations as a function of solvent is modest, about 8 ppm. For **3** the range is slightly larger, about 15 ppm. This is understandable on account of the occurrence of conjugation between the electron donor group, OCH_3, and the nitroso group in the *para* position. However, there appears to be no obvious relationship between solvent-induced changes in nitrogen

Table 1. Solvent effects on the nitrogen NMR shieldings of some nitrosobenzene systems[a]

	Nitrogen NMR shielding (ppm) referred to neat liquid nitromethane[b]		
Solvent	1	2	3
Cyclohexane	−532.46	−543.42	−499.69
Et_2O	−532.68	−544.26	−497.98
CCl_4	−529.85	−542.53 (+72.58, <1%)	−495.52
Benzene	−530.85	−543.13	−494.88
Dioxane	−530.90	−543.31 (+72.4, 4%)	−494.02
Acetone	−531.52	−543.29	−492.34
DMSO	−528.71	−538.25 (+72.50, 17%)	−491.46
CH_2Cl_2	−526.26	−538.78 (+72.52 +, 4%)	−486.94
$CHCl_3$	−524.54	−537.16 (+72.65, 5%)	−485.38
EtOH	−528.43	−540.61 (+73.22, 4%)	−486.55
MeOH	−527.57	−539.81 (+72.51, 13%)	−484.48
CF_3CH_2OH	−500.6 (+73.6, 27%)	−515.2 (+72.82, 76%)	−447.2

[a] Shieldings of the corresponding dimeric species are given in parentheses together with the content of the latter (%, w/w).

[b] All data are corrected for bulk susceptibility effects and related to 0.2 M solutions at 35 ± 0.2 °C

shielding and hydrogen bonding or polarity properties of the solvents used. TFE solutions of all three compounds studied show large shielding effects which extend the range of shielding variations to about 30 ppm for **1** and **2** and to 52 ppm for **3**.

Thus it is possible that the overall nitrogen shielding variation, as a function of solvent, arises from the partial cancellation of large effects of opposite sign, with exception of solutions in TFE. As can be seen from the data in Table 1, TFE as a solvent appears to enhance the dimer content of **1** and **2**.

The assumption of a partial cancellation of effects of opposite sign is fully corroborated by using a full analysis of the various specific and non-specific contributions to the solvent-induced nitrogen shielding variations by means of the empirical scheme based on the following master equation:[8,9]

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

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, β represents the hydrogen bond acceptor strength of the solvent or, possibly, the ability of electron-rich sites in solvent molecules to interact with electron deficient sites in the solute, 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 given by the solute terms, *a*, *b*, *s* and *d*. The nitrogen shielding in the reference state, cyclohexane solution, is given by σ_0.

Table 2 lists the relevant solvent parameter set employed in the present study. A scrutiny of these bulk medium properties shows that the data for TFE are different from those of the other solvents employed. TFE is the most potent hydrogen bond donor of the solvents considered, $\alpha = 1.51$, and a very polar one, $\pi^* = 0.73$, while $\beta = 0$, which is unusual for a good hydrogen bonding and very polar solvent.

Table 2 also includes the least-squares fitted estimates of the solute nitrogen shielding responses and the linear correlation coefficients for the experimental shieldings with respect to those produced by means of Eqn (1) in the present work. The values of the *d* term given in Table 2 are insignificant, whereas the *a*, *b* and *s* terms are not only fairly large but also the negative *b* term is opposite in sign to the values of both the *a* and *s* terms. This provides an explanation for the apparently unusual effect of TFE as a solvent, noticed in the present work. Since TFE has a β value of zero (Table 2), the product expression $\beta(i)b(j)$ drops out of Eqn (1) for the compounds studied.

The magnitudes of the *b* values given in Table 2 are the largest so far reported from studies on nitrogen shielding variations as a function of solvent. The large negative *b* values reflect strong interactions between electron-deficient centres in the solutes and basic, electron-rich, centres in the solvent molecules. Consequently, the benzene ring of the nitroso compounds is electron deficient and thus becomes the source of such interactions, as depicted in Fig. 2.

A more detailed insight into the electron charge distribution throughout the nitrosobenzene molecule (**1**) can be obtained from *ab initio* molecular orbital calculations. We employed a $6\text{–}31^{++}G^{**}$ basis set at the Hartree–Fock level to optimize the geometry of **1** and to calculate the electron charge distribution as shown in Fig. 4. This basis set places both diffuse and polar functions on all of the atoms in the molecule which appears to be a reasonable choice to describe the lone pair electrons located on both the oxygen and nitrogen atoms. The results in Fig. 4 predict a general shift of electron charge towards the nitroso group and simultaneously

Table 2. Solvent parameters used and least-squares fitted solute parameters for a set of master equations [Eqn (1)]

Solvent	α	β	π^*	δ	Dielectric constant, ε[a]
Cyclohexane	0	0	0	0	1.87
Et_2O	0	0.47	0.27	0	3.89
CCl_4	0	0	0.29	0.5	2.21
Benzene	0	0.10	0.59	1	2.25
Dioxane	0	0.37	0.55	0	2.19
Acetone	0.07	0.48	0.72	0	19.75
DMSO	0	0.76	1.00	0	45.80
CH_2Cl_2	0.22	0	0.80	0.5	8.54
$CHCl_3$	0.34	0	0.76	0.5	4.55
EtOH	0.86	0.77	0.54	0	24.20
MeOH	0.98	0.62	0.60	0	30.71
CF_3CH_2OH	1.51	0	0.73	0	—

Compound	σ_0 (ppm)	*a* (ppm/unit scale)	*b* (ppm/unit scale)	*s* (ppm/unit scale)	*d*	Correlation coefficient, *r*
1	−531 ± 3	+11 ± 2	−17 ± 5	+12 ± 5	−0.6 ± 0.3	0.95
2	−543 ± 3	+10 ± 2	−15 ± 5	+12 ± 5	−0.7 ± 0.4	0.93
3	−497 ± 3	+20 ± 3	−21 ± 6	+19 ± 6	−0.5 ± 0.3	0.97

[a] The constants were recalculated for a temperature of 35 °C from the data available in Ref. 10.

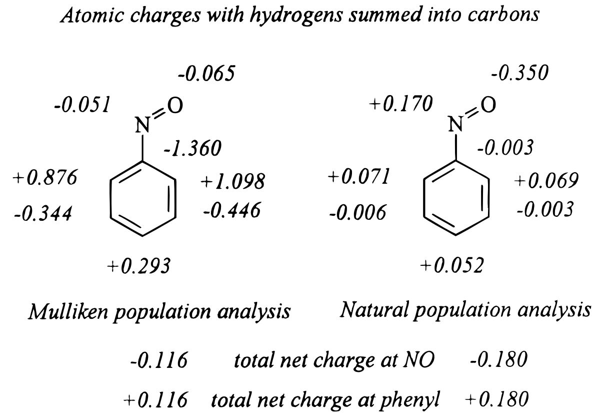


Figure 4. Calculated atomic charges for nitrosobenzene obtained from Hartree–Fock calculations using a 6–31^{++}G** basis set. The same basis set was employed to optimize the geometry used in the calculation of the charges. The results of both Mulliken and natural[11] population analyses are given.

an extreme differentiation of electron density throughout the benzene ring. From these results obtained using Mulliken populations the benzene ring atoms appear as an aggregate of carbonium ions (C-2, C-4 and C-6) and carbanions (C-1, C-3 and C-5). In contrast, the nitroso moiety bears an overall negative net charge, but there is little differentiation between N and O. In addition, the nitroso group is attached to C-1, which is the most negatively charged atom in the molecule. However, Mulliken population analyses are known to be basis set dependent, thus we also include in Fig. 4 the results from a natural population analysis.[11] These data show a less drastic, but still a substantial separation of the charges at the various carbon atoms of the phenyl ring. Both sets of population analyses predict a considerable net negative charge at the NO moiety as a whole.

These results provide the basis of an explanation of the change in direction of the solvent polarity effects on the nitrogen shielding of the nitroso group in nitrosobenzenes compared with that in nitrosoalkanes.[2] In addition, an explanation is available for the unexpected sensitivity of the nitrogen shielding to solute interactions with basic centres in the solvents concerned. It seems very likely that the CH groups at ring positions 2, 4 and 6 are responsible for such interactions.

The large and positive *a* terms reported in Table 2 suggest that strong hydrogen bonds are formed where the nitrogen atom of the nitroso group acts as hydrogen bond acceptor. The values of the *s* terms, which represent the response of the solute nitrogen shielding to an increase in solvent polarity, are also large and positive. This implies that the whole nitroso group becomes more electron rich as the solvent polarity increases. Support for this viewpoint is provided by the results of some INDO/S parameterized molecular orbital calculations of nitrogen nuclear shieldings for **1**, **2** and **3** using the Solvaton model.[11,12] Within this model the solute and solvent molecules interact non-specifically by means of their dipoles, thus the solute nuclear shielding is dependent on the dielectric constant, ε, of the bulk solvent. The results of the Solvaton calculations for **1**, **2** and **3** are given in Table 3. The large calculated increases in the nitrogen shieldings of the three solutes considered, as the value of ε for the solvent medium increases, is entirely consistent with the large and positive values of *s* found for the nitrosobenzene systems studied.

Table 3. Nitrogen shielding increments induced by varying the dielectric constant (ε) of the medium as calculated by the Solvaton model

	Nitrogen shielding increment (ppm) with respect to that for $\varepsilon = 2$		
ε	1	2	3
4	+5.49	+5.23	+8.22
8	+7.65	+7.38	+11.47
10	+8.73	+8.45	+13.10
20	+9.80	+8.51	+14.80
40	+9.90	+8.52	+14.82

For aliphatic nitroso compounds, the value of the *s* term is smaller in magnitude and negative in sign.[2] This implies that the nitrogen atom becomes electron deficient in this case as the solvent polarity increases. Thus for aliphatic nitroso compounds the major electronic rearrangement is charge transfer from the nitrogen to the oxygen atom of the nitroso group.

EXPERIMENTAL

The compounds studied were either obtained commercially (**1** and **2**) or prepared by a previously published procedure (**3**).[13]

Very pure and dry solvents were used in the NMR measurements, as reported previously.[1–3] The solutions were prepared and handled under a dry argon atmosphere in glove-bags. The ^{14}N shielding measurements were made on a Bruker AM500 spectrometer 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 used 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 ; the nitrogen shielding of this solution is +0.77 ppm from that of neat liquid nitromethane.[7] This 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 conversion constant. Thus the contents of the inner tube act both as a reference, with respect to neat nitromethane as standard, and as a deuterium lock for the NMR spectrometer. The exact resonance frequency of the ^{14}N signal of neat nitromethane is 36.141 524 MHz, from which a value of 36.136 826 MHz is obtained for the bare nitrogen nucleus.[7] This 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. Dilute solutions were used in the present study, hence their susceptibilities are assumed to be equal to those of the corresponding solvent at 35 °C.

The *ab initio* molecular orbital calculations were performed at the Institute of Organic Chemistry in Warsaw using a Pentium 120 MHz-based ESCOM system and the Gaussian 94 (Revision D.3) software package.[14] The INDO/S Solvaton calculations of nitrogen shieldings as a function of solvent dielectric constant[12,15] were performed on the University of Surrey HP central system using INDO optimized geometries.

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