

SOLVENT POLARITY AND HYDROGEN BONDING EFFECTS ON THE NITROGEN NMR SHIELDING OF NITROMETHANE

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ABSTRACT

Solvent effects on the nitrogen NMR shielding in nitromethane are shown to encompass a range of 10 ppm, in the deshielding direction with respect to cyclohexane as a solvent. Solvent polarity-polarizability effects are responsible for about 80% of the range. Hydrogen bonding from solvent to the oxygen atoms in nitromethane does not exert any significant effect on the nitrogen shielding, but nitromethane seems to interact with hydrogen bond acceptor sites in solvent molecules.

INTRODUCTION

It has already been shown that the magnetic shielding of nitrogen nuclei in molecules and ions is quite sensitive to molecular interactions in liquids and solutions (1-6). Solvent effects on the nitrogen shieldings in a variety of organic molecules can be explained in terms of a relatively simple scheme which takes into account solvent polarity-polarizability and its hydrogen bonding properties (7-17). The relevant additive scheme employed in the latter investigations was essentially that proposed by Kamlet, Taft, and co-workers (18-20) in a generalized account of solvent properties.

Nitrogen NMR shieldings provide a rigorous test for the scheme as such as well as for the numerical values of the parameters involved which describe solvent properties. Solvent effects on the nitrogen NMR shielding in nitromethane, which is commonly employed as a reference in nitrogen NMR spectroscopy (1-7), have already been investigated (7, 9), but the relevant data did not comprise solutions in inert solvents such as alkanes, nor did they include 2, 2, 2-trifluoroethanol as an organic solvent which exhibits a remarkable tendency to act as a hydrogen-bond donor.

In the present work, we want to extend the experimental data over the latter solvents and to reassess the solvent effects on the nitrogen shielding, in terms of solvent polarity-polarizability as well as hydrogen bonding properties. The question is interesting from the point of view of how the nitrogen shielding in a solute can be affected by solvent-to-solute hydrogen bonds. There are usually strong shielding effects, up to about 20 ppm, if the nitrogen atom is involved in a conjugated system of electrons and has a lone electron pair which does not participate in the conjugation (1-6).

However, we have found recently that hydrogen bonds between the solvent and the oxygen atom in pyridine N-oxide (12) can also yield similar effects on the nitrogen shielding, comparable to those observed in pyridine (9, 13). The structure of the nitro group is formally that of an N-oxide of the nitroso moiety, where the lone-pair electrons at the nitrogen atom of the latter become engaged in a native bond, that to an additional oxygen atom. However, a preliminary evaluation of various contributions to solvent effects on the nitrogen shielding in nitromethane (9) suggested a rather weak response of the latter to hydrogen bonding, by solvent molecules, of the oxygen atoms in the nitro group.

EXPERIMENTAL

The nitrogen NMR shieldings of nitromethane in cyclohexane (saturated solution, 0.05M) and in $\text{CF}_3\text{CH}_2\text{OH}$ (0.3M) were obtained from the ^{14}N NMR spectra at 36.14 MHz (Bruker AM-500 spectrometer). The spectra were referenced to external neat liquid nitromethane, using a system of 10mm/4mm coaxial tubes, with the standard in the inner tube. The actual standard and lock was 0.3M nitromethane in deuterioacetone whose nitrogen shielding relative to neat nitromethane is +0.77 ppm (1, 7). The latter value was used as a conversion constant to the neat nitromethane scale of nitrogen shieldings. The temperature was maintained at 35°C, by a VT unit. Lorentzian lineshape fitting was performed for the resonance signals of the samples and the reference in order to obtain precise values (better than +0.1 ppm) of the shieldings, which were then corrected for bulk susceptibility effects (see ref. 1, p. 221).

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The remaining experimental data were taken from our earlier work (7). The latter involved ^{14}N NMR measurements at the same temperature, and a direct referencing to neat nitromethane in a system of concentric spherical containers which eliminated bulk susceptibility effects. Attention is drawn to the fact that we use consistently (1-12) the sign convention where the positive direction is ascribed to the increasing magnetic shielding of the nuclei involved and, therefore, we simply use the term "shielding" rather than "chemical shift"; the latter is frequently associated with an opposite sign convention.

RESULTS AND DISCUSSION

The experimental results obtained in the present study for the nitrogen shielding in nitromethane dissolved in cyclohexane and in $\text{CF}_3\text{CH}_2\text{OH}$ are given in Table 1, together with our earlier data (7) for solutions in other solvents. The relevant solvent properties, those in terms of Kamlet-Taft parameters (18-20), are shown and explained in Table 2. The selection of the values quoted in Table 2 is based on the original set recommended at an early stage (18) of development of the scales for solvent polarity-polarizability and for hydrogen-bond acceptor and donor strengths. The set has undergone some modifications since then (19, 20), but we will show that the modifications seem to deteriorate the evaluation of nitrogen shielding responses to the solvent properties concerned in the case of nitromethane. We carried out the evaluation by a least-squares fitting of the whole set of experimental data (Table 1) into equation 1 (Table 3), where XYZ is the nitrogen NMR shielding in nitromethane in a given solvent, while α , β , π^* , and δ are the relevant solvent properties in terms of the coefficients given in Table 2. The variables to be fitted are XYZ_0 (a constant which should come close to the experimental value for solution in cyclohexane) and the terms a , b , s , and d , which represent the responses of the nitrogen shielding to solvent hydrogen-bond donor strength, hydrogen-bond acceptor strength, solvent polarity-polarizability, and superpolarizability, respectively, according to equation 1. The least-squares fitted values and their standard deviations are presented in Table 3.

A scrutiny of the experimental data (Table 1) shows that all of the solvents examined, with respect to cyclohexane, induce magnetic deshielding of the nitrogen nuclei in nitromethane molecules. The effects are quite appreciable, and span a range of about 10.5 ppm. The largest deshielding is found for a solution in DMSO, and this seems to exclude any major contribution of solvent-to-solute hydrogen bonding to the effects observed. This is corroborated by the fact that $\text{CF}_3\text{CH}_2\text{OH}$, the most powerful donor of hydrogen bonds ($\alpha = 1.51$, see Table 2) among the solvents concerned, exerts an effect which is comparable to that of acetone as a solvent. Since $\text{CF}_3\text{CH}_2\text{OH}$ is a poor hydrogen-bond

acceptor ($\beta = ca. 0$), at least as far as its bulk properties with respect to solutes are involved, it is likely that its high polarity ($\pi^* = ca. 1$) is mainly responsible for the effect. On the other side, the experimental values do not follow simply the solvent polarity-polarizability scale π^* (Tables 1 and 2). Nitromethane itself is a weak acid, and one may expect that there should be some interactions of the latter, *via* its hydrogen atoms, with hydrogen-bond acceptor sites in solvent molecules. If the corresponding effects on the nitrogen shielding are significant enough, they may explain the obvious discrepancies between the experimental values and the polarity-polarizability scale of the solvents used.

TABLE 1
Solvent Effects on Nitrogen NMR Shieldings in 0.3M Nitromethane Solutions at 35°C and Corrected for Bulk Susceptibility Effects

Solvent	Nitrogen Shielding (ppm)	
	Experimental	Calculated
cyclohexane (0.05 M)	8.50	8.02
carbon tetrachloride	7.10	6.73
benzene	4.38	5.06
diethyl ether	3.91	4.44
chloroform	3.79	3.22
dichloromethane	3.21	2.78
ethanol	2.70	2.17
methanol	2.01	2.23
dioxane	1.82	2.45
2,2,2-trifluoroethanol	0.88	1.12
acetone	0.77	0.81
acetonitrile	0.20	1.06
N,N-dimethylformamide	-0.69	-1.17
water	-1.98	---
DMSO	-2.01	-2.36

Standard deviation of calculated vs experimental values: 0.59 ppm, correlation coefficient 0.9853.

TABLE 2
Solvent Parameters Employed

Solvent	α	β	π^*	δ
cyclohexane	0.00	0.00	0.00	0.00
carbon tetrachloride	0.00	0.00	0.29	0.50
benzene	0.00	0.10	0.59	1.00
diethyl ether	0.00	0.47	0.27	0.00
chloroform	0.34	0.00	0.76	0.50
dichloromethane	0.22	0.00	0.80	0.50
ethanol	0.86	0.77	0.54	0.00
methanol	0.98	0.62	0.60	0.00
dioxane	0.00	0.37	0.55	0.00
2,2,2-trifluoroethanol	1.51	0.00	1.02	0.00
acetone	0.07	0.48	0.72	0.00
acetonitrile	0.19	0.35	0.75	0.00
N,N-dimethylformamide	0.00	0.69	0.88	0.00
water	(1.13)	(0.18)	(1.09)	0.00
DMSO	0.00	0.76	1.00	0.00

Notes: α represents solvent hydrogen-bond donor strength, β reflects solvent hydrogen-bond acceptor strength, π^* characterizes solvent polarity-polarizability, δ represents superpolarizability of polychlorinated and aromatic solvents; parameters for water are too uncertain to be employed in calculations.

The results of the least-squares fitting (Tables 1 and 3) provide quite a reasonable estimate of the effects on the nitromethane nitrogen shielding of possible molecular interactions between solvent molecules and nitromethane. In accord with the qualitative considerations above, by far the largest contribution to the observed range of solvent effects on the nitrogen shielding of nitromethane comes from solvent polarity-polarizability. The corresponding responses s and d (see Table 3), combined with the π^* and δ values (Table 2), respectively, suggest that solvent polarity-polarizability induces a deshielding effect, up to about 8.2 ppm. The latter value is higher than that based on the early data (7) which did not include cyclohexane and $\text{CF}_3\text{CH}_2\text{OH}$ as solvents. Interactions between nitromethane and hydrogen-bond acceptor centers in solvents seem also to give rise to deshielding effects, but much smaller in magnitude (see the value of b in

Table 3), on the nitrogen nuclei in nitromethane. The contribution can amount to about 2.5 ppm for the strongest acceptors, DMSO and ethanol, where $\beta = ca. 0.8$. Solvent-to-solute hydrogen bonds seem to yield only weak shielding effects, which are barely significant, in view of the calculated response a (Table 3) and the associated standard deviation. The largest shielding effect of this kind should be exerted by CF_3CH_2OH , and it should amount to about 1.5ppm.

TABLE 3
Nitromethane NMR Shielding Response to Solvent properties
(expressed as parameters in equation 1)

Parameter	Its value	Standard deviation
XYZ_0 (ppm)	8.023	0.479
a (ppm/unit scale)	0.937	0.416
b (ppm/unit scale)	-2.933	0.738
s (ppm/unit scale)	-8.153	0.680
d (dimensionless)	-0.263	0.088

$$\text{Equation 1: } XYZ = XYZ_0 + a \alpha + b \beta + s (\pi^* + d \delta)$$

The calculated estimates of the a , b , s , and d terms in equation 1 (Table 3) allow one to explain the apparent lack of correlation between the nitrogen NMR shieldings in nitromethane molecules and any single property of the solvents used. The observed difference between the deshielding effects exerted by DMSO and CF_3CH_2OH , with respect to cyclohexane as a solvent, is simply accounted for by the fact that DMSO is a strong acceptor of hydrogen bonds, and does not exhibit any hydrogen-bond donor properties, while the opposite is true for bulk effects of 2,2,2-trifluoroethanol as a solvent. A similar explanation can be offered for chloroform and CH_2Cl_2 from one side, versus acetone and acetonitrile from the other side. The two groups of solvents are characterized by the same

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polarity-polarizability term, $\pi^* = ca. 0.75$, but their respective influence on the nitrogen shieldings of nitromethane show a significant variation.

The overall agreement between the experimental shieldings and those reproduced by means of equation 1 (Tables 1 and 3) is quite good, with a correlation coefficient of about 0.99. However, the results were obtained using an early version of solvent parameters (18). Some of more recent recommendations (19, 20) suggest modified values for chloroform ($\alpha = 0.44, \pi^* = 0.58$), CH_2Cl_2 ($\alpha = 0.30$), and $\text{CF}_3\text{CH}_2\text{OH}$ ($\pi^* = 0.73$). We tested such modifications, on the set of the nitrogen shieldings presented here. The modifications simply deteriorate the correlation coefficient to about 0.98, and they do not affect significantly the estimated responses of nitromethane nitrogen shieldings to individual solvent properties. It is too early to draw any generalized conclusions about the solvent parameters involved, but it seems that solvent effects on nitrogen NMR shieldings should constitute an interesting probe from the point of view of solvent properties.

CONCLUSION

The data presented here show that solvent effects on the nitrogen NMR shielding of CH_3NO_2 induce variations in the latter, within a range of 10 ppm. About 80% of the range is accounted for by solvent polarity-polarizability effects on nitromethane molecules. The remaining 20% originates mostly from interactions of nitromethane with hydrogen-bond acceptor sites in solvent molecules. The formation of hydrogen bonds between the oxygen atoms of nitromethane and protic solvents does not seem to exert any significant influence on the nitrogen NMR shielding of nitromethane. This is in a sharp contrast with the strong response to such effects observed in the case of pyridine N-oxide (12), where the corresponding variations in the nitrogen shielding amounted to more than 20 ppm. Since the structure of the nitro group is, at least formally, that of an N-oxide of the nitroso group, it seems that hydrogen bonds from solvent molecules to the oxygen atom of an N-oxide structure can yield a wide range of effects on the relevant nitrogen NMR shielding.

The sensitivity of the nitrogen shielding of nitromethane to solvent polarity-polarizability (about 8 ppm per unit scale of π^*) seems to be one of the largest that has ever been observed for nitrogenous molecules. It is comparable to that found in *tert*-butyl nitrite (9), and is higher than those in pyridine (9, 13), pyridine N-oxide (12), alkyl cyanides (11), and other polar molecules (9, 10).

ACKNOWLEDGEMENTS

The authors are grateful for sponsorship by the CPBP 01.13.1.25 and 01.12.10.19 projects of the Polish Academy of Sciences.

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