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Solvent-Induced Variations in Nitrogen NMR Shieldings of *tert*-Butyl Isocyanide as a Probe for Solvent Polarizability–Polarity

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The nitrogen NMR shielding of *tert*-butyl isocyanide (1) is shown to be a sensitive probe of solvent polarizability–polarity, since the shielding is demonstrated to be unresponsive to hydrogen bonding effects between 1 and the solvent. The direction of solvent effects observed is explained in terms of the solvaton model, used within the INDO/S–SOS framework. A comparison is made with solvent-induced nitrogen shielding variations of the corresponding isomeric covalent cyanides.

KEY WORDS Nitrogen NMR shielding *tert*-Butyl isocyanide Solvent-induced variations Solvent polarizability–polarity

INTRODUCTION

Nitrogen nuclear shieldings have been demonstrated to be very sensitive probes to solution intermolecular interactions.[1–6] These consist of both non-specific interactions relating to solvent polarizability–polarity[1–9] and specific interactions where solvent molecules may act as either hydrogen bond donors or acceptors. An important aspect of these observations is that nitrogen NMR can be employed in order to assess the validity of various empirical and semi-empirical scales of bulk solvent properties. Consequently, the behaviour of the solvent as a bulk medium towards solutes can be investigated by nitrogen NMR studies of the solutes.

With respect to the various proposed scales of solvent properties, it has been shown that only that reported by Kamlet and co-workers[7–9] is satisfactory for the interpretation of the very sensitive data provided by nitrogen NMR studies.

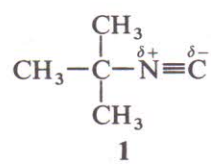
This approach uses four parameters to describe the solvent properties and the same number to represent the corresponding responses of a given solute property, which in the present case is nitrogen NMR shielding. The relevant equation is

$$XYZ = XYZ_0 + s(\pi^* + d\delta) + a\alpha + b\beta \qquad (1)$$

where XYZ represents the nitrogen shielding for a solute molecule in a given solvent; XYZ_0 is the nitrogen shielding in a reference state which is a cyclohexane solution; π^* is the polarizability–polarity term for the solvent; α represents its hydrogen bond donor strength; β represents its hydrogen bond acceptor strength; δ is a correction for polychlorinated solvents ($\delta = 0.5$) and aromatic solvents ($\delta = 1.0$); and s, d, a and b are the corresponding response of the appropriate solute molecular property to the relevant solvent property.

Normally, nitrogen NMR shieldings are found to be sensitive to all four of the solvent parameters π^*, α, β and δ. In principle, nitrogen NMR can be used to place solvents on the corresponding four scales of solvent properties. However, for most solutes at least two of the solvent properties are involved in making significant contributions to solvent-induced nitrogen shielding variations of the solute. Our aim is to identify solutes which will react significantly to only one of the set of four solvent properties. Such solutes could then be used as reliable probes for classifying solvents with respect to a particular property.

The results of the present study indicate that such a probe for solvent polarizability–polarity has been found, and this is the nitrogen shielding of *tert*-butyl isocyanide (**1**).



1

As shown this is a polar molecule, and as such is expected to interact with the polarity of its environment. However, the nitrogen atom is likely to be shielded from direct specific solvent interactions such as hydrogen bonding, thus rendering **1** a suitable probe for the investigation of the non-specific polarizability–polarity properties of solvents.

RESULTS AND DISCUSSION

The results of high-precision ^{14}N NMR measurements obtained on **1** are given in Table 1. Truly high-

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Table 1. Solvent effects on nitrogen NMR of *tert*-butyl isocyanide

Solvent[a]	Nitrogen NMR shielding (ppm, ref. to neat $MeNO_2$)[b]	^3J (^{14}N, H) coupling (Hz)	Corresponding ^3J (^{15}N, H) (Hz)
Cylohexane	188.07	1.89	2.65
CCl_4	187.33	1.92	2.70
Et_2O	186.90	1.93	2.71
CF_3CH_2OH	186.03	—	—
Benzene	185.80	1.96	2.75
EtOH	185.40	1.91	2.68
MeOH	184.79	1.97	2.76
Dioxane	184.75	1.96	2.75
$CHCl_3$	184.44	1.95	2.74
Acetone	184.25	1.98	2.77
CH_2Cl_2	184.21	1.97	2.76
H_2O (satd)	182.27	—	—
DMSO	182.20	1.98	2.77

[a] Solute concentration 0.2 M; saturated aqueous solution which is less than 0.2 M.
[b] Corrected for bulk susceptibility, temperature 35 °C.

Table 2. Results of a least-squares fitting[a] of the nitrogen shielding of *tert*-butyl isocyanide in a variety of solvents to Eqn (1) and the solvent parameters employed

Solvent	Experimental shielding	Shielding predicted by Eqn (1)	Solvent parameters used[b] α	β	π^*	δ
Cyclohexane	188.07	188.26	0.0	0.0	0.0	0.0
CCl_4	187.33	187.12	0.0	0.0	0.29	0.50
Et_2O	186.90	186.64	0.0	0.47	0.27	0.00
Benzene	185.80	185.91	0.0	0.10	0.59	1.00
EtOH	185.40	185.30	0.86	0.77	0.54	0.00
MeOH	184.79	184.99	0.98	0.62	0.60	0.00
Dioxane	184.75	185.00	0.00	0.37	0.55	0.00
$CHCl_3$	184.44	184.46	0.34	0.00	0.76	0.50
Acetone	184.25	184.02	0.07	0.48	0.72	0.00
CH_2Cl_2	183.21	184.19	0.22	0.00	0.80	0.50
H_2O (satd)	182.27	182.20	1.13	0.18	1.09	0.00
DMSO	182.20	182.33	0.00	0.76	1.00	0.00

$XYZ_0 = 188.26 \pm 0.17$ ppm.
$a = 0.31 \pm 0.18$ ppm per unit value of α.
$b = -0.07 \pm 0.29$ ppm per unit value of β
$s = -5.88 \pm 0.25$ ppm per unit value of π^*.
$d = -0.19 \pm 0.05$ (dimensionless).

[a] In the fitting procedure the standard deviation is 0.22 ppm and the correlation coefficient is 0.9951.
[b] The solvent parameters used are based on the sets reported in Refs 1–9.

resolution ^{14}N NMR data were obtained for **1**, where ^3J (^{14}N, ^1H) splittings appear in the spectra. This situation sometimes arises for nitrogen atoms which bear a formal positive charge producing a small electric field gradient at the nucleus and, thus, a relatively slow ^{14}N quadrupolar relaxation rate. The observed ^3J coupling data given in Table 1 do not show any significant variation with change of solvent. In contrast, the ^{14}N shieldings span a range of about 6 ppm for the solvent studied. The shielding results given in Table 1 are corrected for bulk susceptibility effects and are sufficiently accurate that only the last figure given contains some uncertainty. Thus the ^{14}N shieldings are suitably accurate for the investigation of nitrogen shielding variations within the observed range.

An evaluation of the various possible solvent properties, expressed by Eqn (1), to the observed ^{14}N shielding range is given in Table 2, from which we note that the least-squares fit of the experimental and predicted nitrogen shieldings is very good, with a correlation coefficient of 0.9951. The results indicate that the only really significant contribution to the solvent-induced ^{14}N shielding arises from the term s, which represents the relevant response to solvent polarizability–polarity. A smaller contribution arises from the term d, which is the response to the hyperpolarizability of chlorinated and aromatic solvents. Trifluoroethanol as a solvent is excluded from the data given in Table 2 since its relevant parameters are uncertain.[3] The terms a and b, which represent solute–solvent hydrogen bonding interactions, are shown to be relatively insignificant in Table 2.

In view of the evaluation of the various solvent property contributions to the ^{14}N shielding variations of **1**, which show the overriding importance of the term s, the combined polarizability–polarity term $(\pi^* + \delta d)$ is plotted against the observed corresponding nitrogen shieldings of **1** in Fig. 1. A very good linear correlation is obtained expressed by the equation

$$(\pi^* + \delta d) = 31.5556 - 0.16752\sigma_N \qquad (2)$$

where σ_N is the nitrogen shielding with respect to neat nitromethane. The correlation coefficient found from the use of Eqn (2) is 0.9920 and the corresponding standard deviation is 0.038.

The combined term $(\pi^* + \delta d)$ contains the product δd, which includes the solute property d, but this has been evaluated with high accuracy (Table 2) for **1**. Consequently, π^* for a given solvent can be determined accurately from Eqn (2) if the nitrogen shielding of **1** is known in that solvent. Hence **1** is a convenient probe, via its nitrogen shielding, for the assessment of the solvent polarizability–polarity.

We now consider the solvent-induced nitrogen shielding variation of an isocyanide group with respect to that of an isomeric alkyl cyanide. Compounds of the latter type have been thoroughly investigated previously.[5] A comparison of the present results with those for covalent cyanides can be summarized as follows:

Solvent property	Effect on nitrogen NMR shielding of solute	
	t-Bu—$\overset{\delta+}{N}\equiv\overset{\delta-}{C}$	R—C≡N (R = Me, Et, i-Pr, t-Bu)
Solvent to solute hydrogen bonding	Insignificant	Large increase
Solvent polarity	Significant decrease	Significant increase

An alkyl cyanide has a lone pair of electrons on its nitrogen atom and this produces a large response of its shielding to hydrogen bonding effects. This is typical of a nitrogen atom which has both a lone pair of electrons and which is involved in a multiple bonded system.[10] In contrast, the isocyanide has no lone pair of electrons on the nitrogen atom and does not exhibit such effects. It is noteworthy that solvent polarity effects on covalent

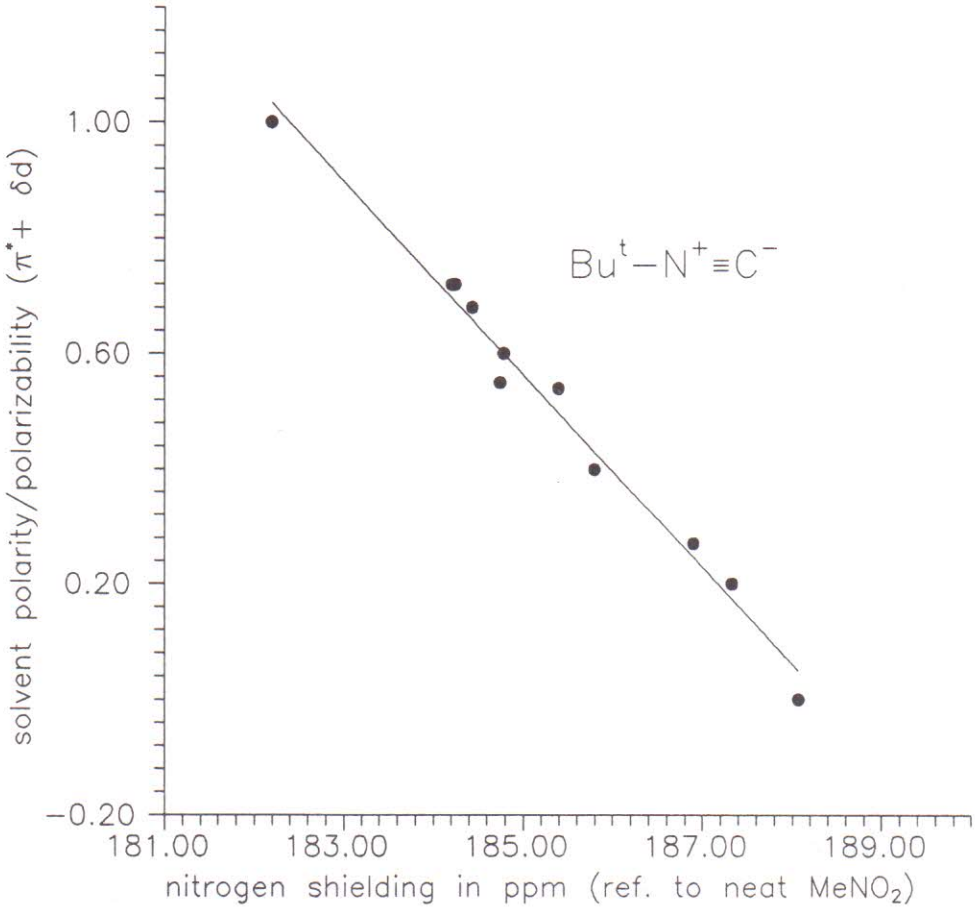

Figure 1. Plot of solvent polarizability–polarity against the nitrogen shielding of **1** in a series of solutions.

cyanide and isocyanide structures are similar in magnitude but opposite in sign. This demonstrates that the directions of the C—N dipoles in these structures are opposite to each other.

The direction of the solvent polarity effects on the nitrogen shieldings of alkyl cyanides has been accounted for[5] in terms of semi-empirical MO calculations combined with the solvaton model of solute–solvent interactions.[11,12] Analogous calculations were performed in this study for **1**, the results of which are given in Fig. 2. The calculations indicate that the nitrogen shielding of **1** should decrease with an increase in polarity of the solvent, as expressed by the dielectric constant, ε, in accord with our observed results in Table 1. The solvaton calculatons underestimate the magnitude of the change in nitrogen shielding of **1** as the solvent is changed. However, the predicted change within the range of dielectric constants concerned, about 2 ppm in the deshielding direction, is of the same order of magnitude as the experimental results. The absolute nitrogen shieldings calculated by the solvaton model do not depart significantly from those found experimentally and which can be obtained from the observed shieldings and that for nitromethane, whose absolute shielding is believed to be about −120 ppm.[13]

EXPERIMENTAL

A commercial sample of **1** was used following purification by fractional distillation under an argon atmosphere; its purity was verified by means of ^{1}H NMR. Carefully purified solvents were used. Where applicable, the solvents were dried. The chlorinated solvents were passed through a column of basic alumina directly before use, dimethyl sulphoxide (DMSO) was distilled over calcium hydride, the alcohols were distilled over magnesium, benzene was distilled over P_2O_5 and diethyl ether was distilled over sodium. All sample preparations were performed in an atmosphere of dry argon. Solutions of **1** of 0.2 M were employed; the results obtained were not found to be affected by further dilution.

The nitrogen shielding results[14] were obtained by high-precision ^{14}N PFT NMR measurements at a magnetic field which gives the signal of neat nitromethane at a frequency of 36.141 524 MHz. As reported elsewhere,[14] this field produces the resonance of a bare nitrogen nucleus at 36.136 826 MHz. This frequency, is used to obtain the reported nitrogen shieldings with respect to neat nitromethane. All measurements were taken at 35.0 ± 0.2 °C, which is maintained by a VT unit on a Bruker AM500 spectrometer. Concentric tubes, 10/4 mm, were used and a 0.3 M solution of nitromethane in acetone-d_6 was placed in the inner tube; this acts both as a secondary standard and as a deuterium lock. The solutions of **1** were placed in the outer tube. The nitrogen shielding of the 0.3 M solution of nitromethane was measured, by means of spherical concentric containers, in order to remove bulk susceptibility effects on nitrogen shielding, and was found to be 0.77 ppm[15] with respect to that of neat nitromethane. The

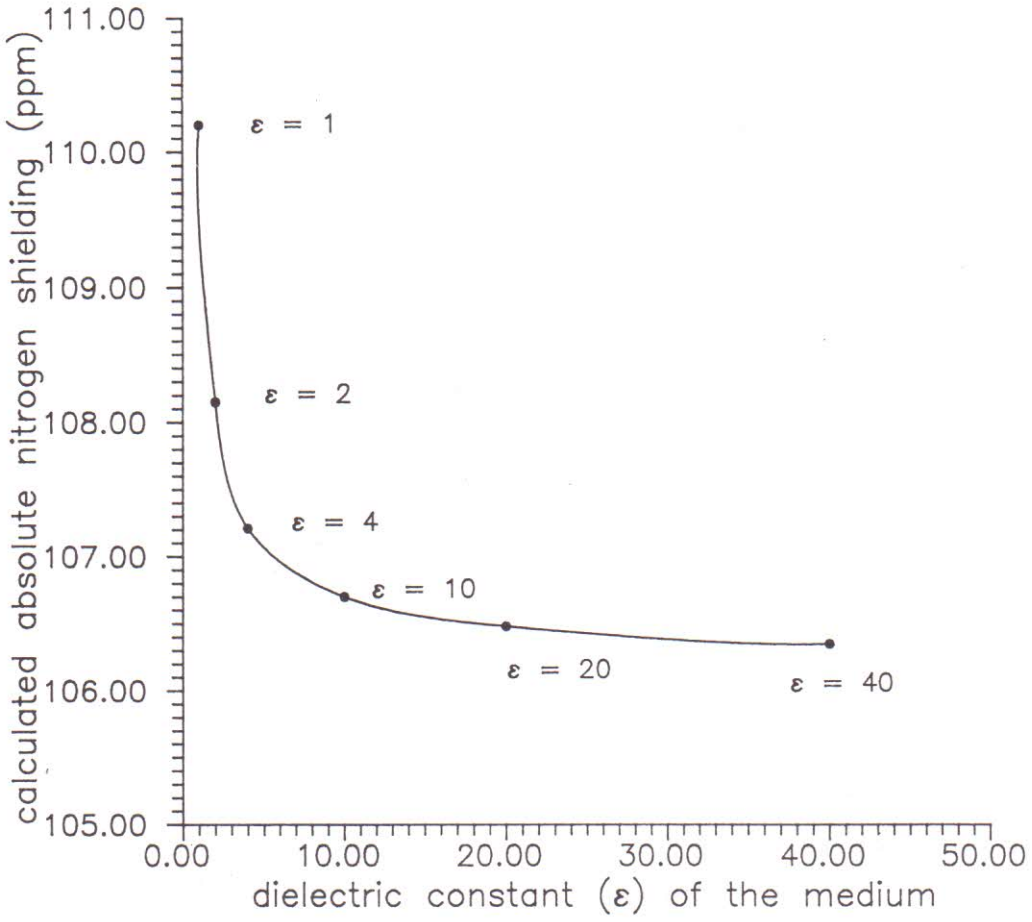

Figure 2. Plot of the INDO/S–SOS solvaton calculated absolute nitrogen shielding of **1** as a function of the dielectric constant (ε) of the surrounding medium.

shieldings presented in Table 1 are given with respect to that of neat nitromethane after including bulk susceptibility corrections and 0.77 ppm for the standard used, as described by

$$\sigma_N \text{ (ref. I)} = \sigma_N \text{ (ref. II)} + 0.77 - \tfrac{1}{3}(\chi_{\text{ref. II}} - \chi_{\text{sample}}) \quad (3)$$

where ref. I is neat liquid nitromethane, ref. II is a 0.3 M solution of nitromethane in acetone-d_6 and χ is the volume magnetic susceptibility in SI units.[14] The measurements were taken with the sample and reference tubes parallel to the applied magnetic field. The following parameters were commonly used in the ^{14}N measurement: 90° pulse corresponding to 40 μs, spectral width of about 8 kHz with quadrature detection, acquisition time *ca.* 0.13 s, zero relaxation delay and *ca.* 2000 accumulated scans per spectrum. The ^{14}N peak positions were obtained by means of a Lorentzian lineshape fitting procedure applied independently to the nitromethane signal and to that of **1**.

The MO solvaton shielding calculations were performed within the framework of the INDO/S–SOS procedure on the University of Surrey Primenet System using a standard geometry[16] and procedures given elsewhere.[12]

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