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Effects of Solute–Solvent Interactions on the Nitrogen Nuclear Shieldings of Some Alkyl Cyanides

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It was found that the range of solvent effects on the nitrogen NMR shielding of the cyano group appears to be almost independent of the nature of the attached alkyl group and to be in excess of 20 ppm. Effects due to both the polarity of the medium and hydrogen bonding are observed to contribute almost equally to the nitrogen shielding ranges measured for four alkyl cyanides. These contributions are determined from the shielding in nitrogen variations with the solvent by means of a four-parameter model and are supported by molecular orbital calculations employing the solvaton description of non-specific solute–solvent interactions. The observed responses of the nitrogen shieldings to solvent effects are found to be significantly different from those reported for sp^2-type nitrogen atoms.

KEY WORDS Nitrogen nuclear shieldings Alkyl cyanides Solute–solvent interactions

INTRODUCTION

It is well known that solute–solvent interactions can have a significant effect on nitrogen nuclear shieldings,[1–6] and nitrogen NMR therefore suggests itself as a suitable means of investigating the nature of solute–solvent interactions. The interactions in question may arise from specific cases, such as protonation or hydrogen bonding, and also from non-specific sources such as the dipole–dipole case. Previously we have demonstrated that the solvaton model[4–8] adequately accounts for non-specific solvent effects on nitrogen nuclear shieldings. In addition, we have employed a linear model[9] which incorporates solvent properties such as hydrogen bond donor and acceptor strengths and polarizability–polarity interactions in order to consider individually the specific and non-specific influences on nitrogen nuclear shielding.

To date our studies have involved only nitrogen atoms whose bonding environment may be characterized as being of the sp^2 type. We now report an extension of this work to include cases of nitrogen involved in sp-type bonding situations where the lone-pair electrons are contained in an sp hybrid orbital. Alkyl cyanides ($RC \equiv N$) represent a good model for this bonding arrangement; in this work R is CH_3, CH_3CH_2, $(CH_3)_2CH$ or $(CH_3)_3C$.

The major aims of this study were to discover both the sign and magnitude of solvent polarity effects on the electronic structure and the nitrogen nuclear shieldings of alkyl cyanides. In addition we used the solvaton model to provide a comparison between observed and predicted effects of solute–solvent interactions on nitrogen nuclear shieldings. We have previously noted that for sp^2-type nitrogen structures large shielding effects were observed when hydrogen bonding occurs to the nitrogen lone pair electrons. It is of interest to compare that situation with the linear sp-type structure of the cyano group.

Another aim was to investigate the effects of possible weak interactions between the hydrogen atoms of the alkyl groups of the cyanides and the acceptor centres of the chosen solvents, such as those already noted for sp^2-type nitrogen structures.[4–6] Finally, we were interested in the possible effects of the increasing size of the alkyl groups on the observable solute–solvent interactions.

RESULTS AND DISCUSSION

In Table 1 we report the nitrogen NMR shieldings of some alkyl cyanides observed by means of high-precision ^{14}N measurements using a high magnetic field, a line shape fitting procedure and rigorous calibration as described under Experimental. Thirteen solvents covering a range of hydrogen bonding properties and differences in polarity were employed.

In general, ^{14}N NMR line widths tend to be controlled by quadrupolar interactions dependent on local electric field gradients at the nitrogen nucleus. Thus the broadest ^{14}N signals reported in Table 1 arise from solutions of the alkyl cyanides in those solvents which are the strongest hydrogen bond donors, such as trifluoroethanol.

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Table 1. NMR data for some alkyl cyanides in various solvents (0.25 M solutions at 35 ± 0.2 °C)

Compound	Solvent	^{14}N shielding[a] (ppm)	Peak width at half-height of ^{14}N signal[b] (Hz)
CH_3CN	Cyclohexane[c]	125.81	69.1
	CCl_4	127.22	107.6
	Benzene	129.66	84.3
	Et_2O[d]	129.75	68.1
	Dioxane	132.21	137.7
	Acetone	133.52	73.2
	DMSO	133.99	210.0
	$CHCl_3$	134.53	136.9
	CH_2Cl_2	134.58	94.0
	MeCN[e]	135.29	73.9
	EtOH	138.34	213.5
	MeOH	139.62	116.9
	H_2O	145.47	102.7
	CF_3CH_2OH	148.82	439.5
CH_3CH_2CN	Cyclohexane	128.22	102.9
	CCl_4	129.25	156.4
	Et_2O[d]	131.03	89.6
	Benzene	131.28	119.3
	Dioxane	133.66	175.8
	Acetone	134.54	93.9
	DMSO	134.89	248.6
	CH_2Cl_2	136.46	127.9
	$CHCl_3$	136.58	189.0
	EtOH	138.59	230.6
	MeOH	140.63	148.6
	H_2O	146.98	136.9
	CF_3CH_2OH	151.40	568.5
$(CH_3)_2CHCN$	Cyclohexane	129.80	138.7
	CCl_4	131.03	210.3
	Et_2O[d]	132.23	109.8
	Benzene	132.78	155.7
	Dioxane	134.76	223.8
	Acetone	135.81	118.3
	DMSO	136.05	306.4
	CH_2Cl_2	137.78	167.2
	$CHCl_3$	138.39	245.7
	EtOH	139.58	264.5
	MeOH	141.74	175.6
	H_2O	148.36	181.5
	CF_3CH_2OH	151.83	671.5
$(CH_3)_3CCN$	Cyclohexane	131.51	155.5
	CCl_4	132.70	237.0
	Et_2O[d]	134.02	123.9
	Benzene	134.46	171.4
	Dioxane	136.30	256.9
	Acetone	137.33	136.5
	DMSO	137.51	364.6
	CH_2Cl_2	139.78	194.5
	$CHCl_3$	140.56	281.4
	EtOH	140.84	285.5
	MeOH	143.07	193.3
	H_2O[c]	149.89	196.2
	CF_3CH_2OH	153.87	726.5

[a] All shieldings are reported with respect to neat nitromethane, such that an increase in shielding corresponds to a positive increment. The data given are corrected for solvent magnetic susceptibility effects and are accurate to within 0.1 ppm.

[b] Line width data are accurate to between 1.0 and 0.3 Hz as described under Experimental.

[c] Saturated solution used, which is less than 0.25 M.

[d] Spectra recorded at 30 °C.

[e] Neat liquid was measured.

Table 2. Solvent parameters employed

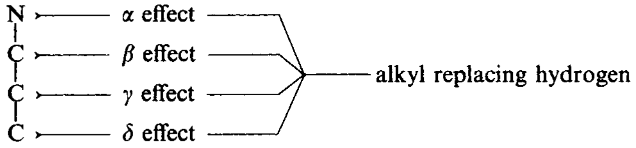
Solvent	Parameters used in Eqn (1) α	β	π*	δ[a]	Dielectric constant[b]
Cyclohexane	0.0	0.0	0.0	0.0	1.87
CCl_4	0.0	0.0	0.29	0.5	2.21
Benzene	0.0	0.0	0.59	1.0	2.25
Et_2O	0.0	0.47	0.27	0.0	3.89
Dioxane	0.0	0.37	0.55	0.0	2.19
Acetone	0.07	0.48	0.72	0.0	19.75
DMSO	0.0	0.76	1.00	0.0	45.80
$CHCl_3$	0.34	0.0	0.76	0.5	4.55
CH_2Cl_2	0.22	0.0	0.80	0.5	8.54
MeCN	0.07	0.48	0.72	0.0	36.60
EtOH	0.86	0.77	0.54	0.0	24.20
MeOH	0.98	0.62	0.60	0.0	30.71
H_2O	1.13	0.18	1.09	0.0	76.70
CF_3CH_2OH	1.51	0.0	1.02	0.0	—

[a] A value of 0.0 or 0.1 may be used for this parameter. On using both we found that better results were obtained when 0.0 was used in all cases considered here.

[b] The dielectric constants are reported for a temperature of 35 °C as calculated from the data given in Ref. 10.

As shown in Table 1, the cyanide nitrogen shielding variation, as a function of solvent, is approximately 22 ppm; this range is independent of the bulkiness of the alkyl group attached to the cyano function. Hence it seems that the *tert*-butyl group does not shield the cyanide group from the possible solute–solvent interactions observed in the molecules studied. In general, it is shown that the increases in cyanide nitrogen shielding with change of solvent follow a comparable solvent order in each case.

It is known that the replacement of hydrogen atoms with alkyl groups can influence nitrogen shieldings. The various effects, α, β, γ, δ, etc., depend on the position of substitution as shown:



In this study only γ effects are possible in passing from methyl to *tert*-butyl cyanide. In general, the γ effect is thought to produce an increase of about 1 ppm in the nitrogen shielding for each methyl group introduced. However, since solvent effects on shielding are usually larger than this, so far there has been no rigorous demonstration of the existence of γ effects. The data in Table 1 show clearly, from a comparison of the nitrogen shieldings of the four cyanides studied in a given solvent, that the γ effect is preserved independently of the solvent considered. In addition, the γ effect is fairly constant at about 2 ppm per methyl group.

Separation of the contributions to the nitrogen shielding arising from hydrogen bonding effects on the one hand, and non-specific polarization–polarity effects on the other, is sought from the four-parameter master equation:[9]

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

Table 3. Results of least-squares fitting[a] of the nitrogen shielding of methyl cyanide in a variety of solvents to Eqn (1)[b]

Solvent	Experimental shielding	Shielding predicted by Eqn (1)
Cyclohexane	125.81	126.60
CCl_4	127.22	127.90
Benzene	129.66	129.30
Et_2O	129.75	128.73
Dioxane	132.21	131.22
Acetone	133.52	133.25
DMSO	133.99	134.96
$CHCl_3$	134.53	134.91
CH_2Cl_2	134.58	134.23
EtOH	138.34	134.32
MeOH	139.62	139.94
H_2O	145.47	145.70
CF_3CH_2OH	148.82	148.43

[a] In the fitting procedure the standard deviation is 0.77 ppm and the correlation coefficient is 0.99.

[b] $XYZ_0 = 126.60 \pm 0.60$ ppm; $a = 8.57 \pm 0.55$ ppm per unit value of α; $b = -0.46 \pm 0.93$ ppm per unit value of β; $s = 8.81 \pm 0.86$ ppm per unit value of π^*; $d = -0.28 \pm 0.11$ (dimensionless).

Table 5. Results of least-squares fitting[a] of the nitrogen shielding of isopropyl cyanide in a variety of solvents to Eqn (1)[b]

Solvent	Experimental shielding	Shielding predicted by Eqn (1)
Cyclohexane	129.80	130.46
CCl_4	131.03	131.50
Et_2O	132.23	131.34
Benzene	132.78	132.62
Dioxane	134.76	134.05
Acetone	135.81	135.75
DMSO	136.05	136.72
CH_2Cl_2	137.78	137.68
$CHCl_3$	138.39	138.32
EtOH	139.58	139.79
MeOH	141.74	141.75
H_2O	148.36	148.54
CF_3CH_2OH	151.83	151.60

[a] In the fitting procedure the standard deviation is 0.57 ppm and the correlation coefficient is 0.99.

[b] $XYZ_0 = 130.46 \pm 0.45$ ppm; $a = 8.20 \pm 0.41$ ppm per unit value of α; $b = -3.07 \pm 0.68$ ppm per unit value of β; $s = 8.59 \pm 0.63$ ppm per unit value of π^*; $d = -0.34 \pm 0.08$ (dimensionless).

where XYZ refers to a particular molecular property such as nitrogen shielding for a solute molecule in a chosen solvent, XYZ_0 is the same molecular property in a given reference state, e.g., a cyclohexane solution, π^* is the polarizability–polarity term for the solvent, where α represents its hydrogen bond donor strength and β 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 responses of the appropriate solute molecular property to the relevant solvent property. The solvent parameters used in this work are given in Table 2. The values employed are based on our earlier work in this area,[5,6] which has given a successful analysis of the various effects of solvents on nitrogen nuclear shielding. As can be seen from Table 2, the

Table 4. Results of least-squares fitting[a] of the nitrogen shielding of ethyl cyanide in a variety of solvents to Eqn (1)[b]

Solvent	Experimental shielding	Shielding predicted by Eqn (1)
Cyclohexane	128.22	128.96
CCl_4	129.25	129.89
Et_2O	131.03	130.00
Benzene	131.28	130.92
Dioxane	133.66	132.72
Acetone	134.54	134.50
DMSO	134.89	135.55
CH_2Cl_2	136.46	136.23
$CHCl_3$	136.58	136.90
EtOH	138.59	138.80
MeOH	140.63	140.77
H_2O	146.98	147.58
CF_3CH_2OH	151.40	150.71

[a] In the fitting procedure the standard deviation is 0.76 ppm and the correlation coefficient is 0.99.

[b] $XYZ_0 = 128.96 \pm 0.59$ ppm; $a = 8.49 \pm 0.54$ ppm per unit value of α; $b = -2.84 \pm 0.91$ ppm per unit value of β; $s = 8.75 \pm 0.84$ ppm per unit value of π^*; $d = -0.37 \pm 0.11$ (dimensionless).

Table 6. Results of least-squares fitting[a] of the nitrogen shielding of *tert*-butyl cyanide in a variety of solvents to Eqn (1)

Solvent	Experimental shielding	Shielding predicted by Eqn (1)
Cyclohexane	131.51	132.27
CCl_4	132.70	133.32
Et_2O	134.02	132.84
Benzene	134.46	134.44
Dioxane	136.30	135.67
Acetone	137.33	137.31
DMSO	137.51	138.11
CH_2Cl_2	139.78	139.57
$CHCl_3$	140.56	140.20
EtOH	140.86	141.04
MeOH	143.07	143.12
H_2O	149.89	150.32
CF_3CH_2OH	153.87	153.49

[a] In the fitting procedure the standard deviation is 0.69 ppm and the correlation coefficient is 0.99.

[b] $XYZ_0 = 132.23 \pm 0.54$ ppm; $a = 8.16 \pm 0.50$ ppm per unit value of α; $b = -3.73 \pm 0.82$ ppm per unit value of β; $s = 8.72 \pm 0.78$ ppm per unit value of π^*; $d = -0.31 \pm 0.99$ (dimensionless).

Table 7. Comparison of parameters describing the nitrogen nuclear shielding response to a number of solvent properties for various molecules, obtained from Eqn (1)

	Solute parameter				
Solute	*a*	*b*	*s*	*d*	Reference
Pyridine	21.50 ± 0.97	−0.35 ± 1.33	4.8 ± 1.48	0.002 ± 0.23	5
Bu^tONO	20.51 ± 0.99	6.70 ± 1.77	−9.88 ± 1.46	−0.29 ± 0.15	5
CH_3NCS	1.52 ± 0.88	−0.91 ± 1.53	−7.36 ± 1.12	−0.08 ± 0.15	6
$Bu^tN{=}NBu^t$	∼0	∼0	∼0	∼0	5
CH_3NO_2	1.34 ± 0.48	−3.3 ± 0.87	−7.22 ± 0.73	−0.26 ± 0.11	5
CH_3ONO_2	−0.16 ± 0.31	−0.85 ± 0.57	−3.75 ± 0.46	−0.26 ± 0.11	6
RCN	∼8.5	∼3[a]	∼8.7	∼ −0.3	This work

[a] With the exception of CH_3CN where *b* is not significantly different from zero (Table 3).

choice of solvents employed provides a wide range of hydrogen bonding and polarizability–polarity properties. Dielectric constant data for the solvents are also included in Table 2.

The results of least-squares fitting of the observed nitrogen shieldings in a range of solvents, and those predicted by Eqn (1), are given for the four alkyl cyanides studied in Tables 3–6. In all cases good agreement between the two sets of data is achieved, as noted by the correlation coefficients of 0.99.

It is noteworthy that the values of *a*, *s* and *d* are approximately constant for the four compounds investigated. A comparison of the values of these parameters for cyanides (RCN) and a variety of other molecules is presented in Table 7. From a consideration of the parameter *a*, which describes the response of the nitrogen shielding to the hydrogen bond donor strength of the solvent, a range of values are observed. The value of *a* is large and positive (*ca.* +20 ppm per unit value of α) when the nitrogen lone pair is involved in sp^2-type hybridization and is readily available to receive a hydrogen bonding source (e.g. pyridine and Bu^tONO). If competition for hydrogen bonding occurs (S atom in CH_5NCS) or there are steric effects ($Bu^tN{=}NBu^t$), or if the lone pair is involved in a π electron system (CH_3NO_2 and CH_3ONO_2), then the value of *a* decreases towards zero. From the present work, where the nitrogen atom is involved in sp hybridization, the *a* term is significant and positive and less than half of that observed for sp^2-hybridized cases, where the lone pair is readily available for hydrogen bonding.

The results in Table 7 show that the parameter *d* is insignificant in all cases considered. However, the parameter *s*, which represents the response of the nitrogen shielding to solvent polarizability–polarity effects, is of interest in that it provides a comparison with the results of solvaton calculations of nitrogen nuclear shieldings.[7] In all our previous work[5,6] (Table 7) the signs and approximate magnitudes of the effects of solvent polarizability–polarity on nitrogen nuclear shielding were correctly predicted by the calculations based on the solvaton model. Consequently, we performed INDO/S-SOS nitrogen shielding calculations[7] for the four cyanides considered in this work, the results of which are given in Table 8. These data show that the nitrogen nuclear shielding is expected to increase as the solvent polarity, measured in terms of the dielectric constant, increases. This is in good agreement with the experimental results for the alkyl cyanides as shown in Tables 3–7, hence the solvaton calculations appear to be fairly reliable as a means of discussing the medium polarity effects on the nitrogen nuclear shielding of the alkyl cyanides investigated.

The fact that solvaton calculations appear to predict a smaller nitrogen shielding range than that given by the corresponding value of *s* can be accounted for by the fact that there is no simple relationship between dielectric constant and the polarizability–polarity parameters, π^*, used in Eqn (1). However, the solvaton calculations predict that the nitrogen shielding range, resulting from a change in polarity of the medium, is expected to be fairly constant for the four cyanides considered. This is in accord with the values of the *s* parameters given in Tables 3–6 from the experimental data.

For the four cyanides, the results in Tables 3–6 show that the effects of solvent polarizability–polarity and hydrogen bonding from solvent to solute produce increases in nitrogen nuclear shielding of comparable magnitudes. Hence these two effects contribute about 50% each of the total nitrogen shielding variation of the cyano group with a change in solvent. From previous work,[5,6] the only case we have observed where both *a* and *s* parameters are significant and positive is that of pyridine. However, in this case the *a* parameter is significantly larger than the *s* term (Table 7), whereas the two parameters are of similar magnitude for the cyanides.

We now turn to a consideration of parameter *b* in Eqn (1), which represents the response of the nitrogen nuclear shielding to solvent hydrogen bond acceptor

Table 8. INDO/S-SOS shieldings[a] calculated using the solvaton model for some alkyl cyanides, expressed with respect to that of the compound in a solution with a dielectric constant of 2[b]

	Variation of shielding for the four compounds			
Dielectric constant, ϵ	CH_3CN	CH_3CH_2CN	$(CH_3)_2CHCN$	$(CH_3)_3CCN$
2	0.0[c]	0.0[c]	0.0[c]	0.0[c]
4	1.68	1.76	1.79	2.06
10	2.46	2.69	2.77	3.14
20	2.57	2.83	3.05	3.49
40	2.63	2.85	3.10	3.53

[a] All shieldings are in ppm.

[b] The value of $\varepsilon = 2$ is arbitrarily chosen as the origin to correspond to values of ε for a number of hydrocarbon solvents.

[c] Taken as arbitrary zero.

strength, the β parameter. From our earlier work[5,6] the values of b indicate the presence of some weak interactions between the H atoms of solute alkyl groups with solvent hydrogen bond acceptor sites. With the exception of CH_3CN, this term appears to be significant (Tables 4–6) for the alkyl cyanides, suggesting some possible hydrogen bond formation between the alkyl groups of the cyanides and the solvent acceptor centres. The values of b reported in Tables 4–6 suggest that the extent of this hydrogen bonding increases with increase in the number of methyl groups on the alkyl cyanide.

In the case of CH_3CN (Table 3), the b value is not significantly different from zero, which is consistent with the presence of intermolecular association between the methyl hydrogen atoms and the nitrogen lone-pair electrons. Such an association would tend to increase the nitrogen nuclear shielding in opposition to the possible effect of solute–solvent hydrogen bonding as indicated by the parameter b. Hence the resulting small value of b for methyl cyanide is probably the result of possible competition between self-association and solute–solvent interactions.

We conclude that the nitrogen nuclear shielding of alkyl cyanides is fairly sensitive to solvent interactions of both the hydrogen bond and polarity types, and the contributions to the total shielding variation of about 22 ppm from these two effects are approximately equal. This is in contrast to the results observed for nitrogen atoms of the sp^2 type. The total nitrogen shielding ranges for the four cyanides appear to be independent of the nature of the alkyl group present, which indicates that the cyano group is equally exposed to solvent interactions even when it is attached to a bulky *tert*-butyl group. This extension of our previous work to include sp-type nitrogen atoms reveals the suitability of the models involved in interpreting solute–solvent interactions on nitrogen nuclear shielding and the use of the shielding variations to study the nature and extent of the interactions.

EXPERIMENTAL

High-precision ^{14}N PFT NMR measurements were carried out to give the nitrogen shielding data. The field used corresponds to a frequency of 36.141524 MHz for the ^{14}N signal of our primary standard, neat nitromethane. As discussed elsewhere,[11] this field produces the resonance of a bare nitrogen nucleus at 36.136826 MHz. We use this information to obtain the reported shieldings referred to neat liquid nitromethane in Table 1. All measurements were taken on a Bruker AM500 spectrometer at $35.0 \pm 0.2\,^{\circ}C$, this temperature being maintained by a VT unit. Concentric tubes, 10/4 mm, were used for the measurements. In the inner tube was a 0.3 M solute of nitromethane in acetone-d_6, which acts as both a secondary standard and a deuterium lock. The outer tube contained the sample to be measured.

As measured by means of spherical concentric containers, to remove possible bulk susceptibility effects on nitrogen shielding, the shielding of the 0.3 M solution of nitromethane is 0.77 ppm.[4] The data given in Table 1 are referred to neat liquid nitromethane after including bulk susceptibility corrections, for the concentric tube arrangement used, and 0.77 ppm for the 0.3 M nitromethane solution, according to the equation

$$\sigma_{N(\mathrm{Ref.\ I})} = \sigma_{N(\mathrm{Ref.\ II})} + 0.77 - \tfrac{1}{3}(\chi_{\mathrm{Ref.\ II}} - \chi_{\mathrm{sample}}) \quad (2)$$

where Ref. I is neat liquid nitromethane, Ref. II is a 0.3 M solution of CH_3NO_2 in acetone-d_6 and χ is the volume magnetic susceptibility in the SI system.[11] The experimental arrangement employed the sample and reference tubes in a parallel direction with respect to that of the applied magnetic field. The following parameters were commonly used for measuring the ^{14}N spectra: a 90° pulse corresponding to 50 μs; spectral width, *ca.* 8 kHz with quadrature detection; acquisition time, *ca.* 0.13 s; zero relaxation delay; and *ca.* 2000 accumulated scans per spectrum. No exponential multiplication of the FID was employed before the FT. The ^{14}N peak positions were evaluated using a Lorentzian line shape fitting procedure. This procedure is applied independently to the signal of nitromethane and to that of the sample concerned. The frequency obtained for the sample is subtracted from that of nitromethane and the result divided by the frequency of a bare nitrogen nucleus to give the relative nitrogen shielding of the sample. The ^{14}N line widths were obtained simultaneously from the fitting procedure.

The samples used were obtained commercially and purified and dried by conventional methods. Particular attention was paid to drying the solvents used. All sample preparations were performed in an atmosphere of dry argon. The alcohols used as solvents were distilled over magnesium. The chlorinated solvents were passed through a column of basic alumina directly before use. DMSO was distilled over calcium hydride, benzene over P_2O_5 and diethyl ether over sodium. The INDO/S-SOS solvaton shielding calculations were performed using modified versions of QCPE 174 and QCPE 312 on the University of London CDC 7600 system. Standard molecular geometries were used in the calculations.[12]

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