Solvent effects on the nitrogen NMR shieldings of cyanamide and *N,N*-dimethyl cyanamide

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Abstract

High precision ^{14}N NMR measurements of solvent induced nitrogen shielding variations in both the NR_2 and cyano moieties of cyanamide and of *N,N*-dimethylcyanamide are reported. The solvent induced shielding changes are much larger for the cyano, than for the NR_2 groups. The NMe_2 group has a nitrogen shielding which is almost invariant to choice of solvent. Solvent effects on the cyano groups of the compounds studied closely match those observed for simple alkyl cyanides. Overall analysis of the nitrogen shielding data favours a highly non-planar geometry for the compounds studied and no significant π electron conjugation between the NR_2 and the cyano groups.

Keywords: NMR spectroscopy; Solvent effects; Cyanamide; N,N-dimethyl cyanamide

1. Introduction

The structures of the cyanamides studied (Fig. 1) are interesting since, in principle, they could be planar with a delocalised system of π electrons including those of the NR_2 and cyano groups. Recent experimental and molecular orbital results indicate a pyramidal bond structure for the NR_2 moiety and a deviation from linearity of the N–C–N system [1,2]. For cyanamide, compound 1, at 13 K in the solid state the deviation from planarity of the NH_2 group is about 14° [1]. Microwave spectroscopy, in the gaseous phase, implies that the out of plane angle is about 45° [2] and the N–C–N spine is non-linear by about 5° [2].

Nitrogen NMR shieldings have previously been

shown to be a sensitive approach to the investigation of molecular interactions in solution [3]. To date this technique has not been applied to investigations of cyanamides. It is of interest to determine the possible effects on the nitrogen shielding of the cyanamide structures due to solvent polarity and more specific interactions such as solvent to solute and solute to solvent hydrogen bonding. In compounds 1 and 2 the potential hydrogen bond centres are the cyano nitrogen atoms and, possibly, the nitrogen atoms in the NR_2 moiety. However, hydrogen bond donor centres exist only in compound 1, namely the hydrogen atoms of the NH_2 moiety.

In our work we use the sign convention such that a plus sign corresponds to an increase in nuclear shielding [3]. Consequently we employ the term "nuclear shielding" rather than "chemical

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1 H_2N—$C\equiv N$
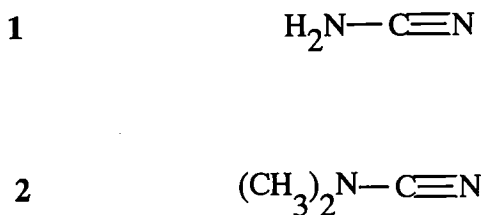
2 $(CH_3)_2N$—$C\equiv N$

Fig. 1. Structures of compounds studied.

shift". These two terms are of opposite sign but are equivalent in magnitude.

2. Experimental

Both cyanamides studied are commercially available. Particular care was taken in the NMR measurements to use only very pure and dry solvents as reported previously [3]. All solutions were prepared and handled under a dry argon atmosphere in glove boxes. The ^{14}N shielding measurements were taken on a Bruker AM500 spectrometer at $35 \pm 0.2°C$ 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 [3]. This value is obtained from measurements using concentric 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 precise 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 36.141524 MHz, from which a value of 36.136826 MHz is obtained for the bare nitrogen nucleus [3]. 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 samples used and of the external standard. Dilute solutions were used, hence their susceptibilities are assumed to be equal to those of the corresponding solvent at 35°C.

Table 1

Nitrogen NMR shieldings of the compounds studied (0.05 M solutions at +35°C, unless specified otherwise)

Solvent	Nitrogen shielding (ppm) referenced to neat liquid nitromethane			
	1		**2**	
	NH₂	CN	NMe₂	CN
cyclohexane	–	–	+369.47	+176.32
Et₂O (+30°C)	+368.93	+184.20	+369.68	+179.10
CCl₄	–	–	+369.16	+178.00
benzene	+370.30	+178.17	+369.72	+179.20
dioxane	+371.78	+184.38	+368.84	+181.32
acetone	+369.63	+185.53	+369.00	+182.46
DMSO	+364.40	+187.59	+367.56	+182.55
CH₂Cl₂	+365.86	+182.88	+368.63	+185.36
CHCl₃	+366.14	+183.50	+368.40	+186.42
ethanol	+367.21	+196.38	+369.07	+189.46
methanol	+371.73	+198.86	+368.90	+191.78
water	+365.41	+198.57	+367.34	+196.64
CF₃CH₂OH	+370.15	+200.63	+369.00	+200.36

DMSO = dimethyl sulphoxide.

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

Solvent	α	β	π^*	δ	Dielectric constant[a]
cyclohexane	0	0	0	0	1.87
Et$_2$O	0	0.47	0.27	0	3.89
CCl$_4$	0	0	0.29	0.5	2.21
benzene	0	0.1	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	45.8
CH$_2$Cl$_2$	0.22	0	0.80	0.5	8.54
CHCl$_3$	0.34	0	0.76	0.5	4.55
ethanol	0.86	0.77	0.54	0	24.2
methanol	0.98	0.62	0.60	0	30.71
water	1.13	0.18	1.09	0	76.7
CF$_3$CH$_2$OH	1.51	0	0.73	0	–

Compound (and group)	σ_0 (ppm)	a (ppm/unit scale)	b (ppm/unit scale)	s (ppm/unit scale)	d (dimensionless)	Correlation coefficient, r
2 (NMe$_2$)	$+369.7 \pm 0.3$	$+3.2 \pm 0.3$	$+0.5 \pm 0.5$	-2.3 ± 0.4	-0.4 ± 0.2	0.885
2 (CN)	$+177.3 \pm 0.6$	$+11.4 \pm 0.5$	-1.8 ± 0.9	$+7.2 \pm 0.9$	-0.2 ± 0.1	0.996

[a] The constants were recalculated for a temperature of 35°C from the data available in Ref. [7].
DMSO = dimethyl sulphoxide.

TNDO/2 shielding calculations and Parametric Method 3 (PM3) geometry optimisations were performed at the Institute of Organic Chemistry, Polish Academy of Sciences, using a Hector 486 DX 50 MHz system and HYPERCHEM release 4.0 and HYPERNMR software packages from Hypercube Inc.

3. Results and discussion

The results of high precision, bulk susceptibility corrected, ^{14}N NMR shielding measurements, made in the present work, are given in Table 1. The variations in solvent induced nitrogen shieldings for compounds 1 and 2 are large for the cyano nitrogen atoms, about 23 ppm, whereas for the NMe$_2$ group the range is about 2 ppm and for the NH$_2$ group about 7 ppm. The difference in the nitrogen shieldings for the NMe$_2$ and NH$_2$ groups indicates that the NR$_2$ moiety is not significantly influenced by solvent polarity and solvent to solute hydrogen bonding effects. The only contribution likely to influence the nitrogen shielding

of the NH$_2$ group in compound 1 is solute to solvent hydrogen bonding. The ranges of the solvent induced nitrogen shieldings of the cyano groups, in compounds 1 and 2, are in extremely good agreement with those found for alkyl cyanides [4]. A more detailed analysis of the solvent induced nitrogen shielding changes can be obtained from an empirical scale of solvent properties as given in Table 2. These can be used together with the master Eq. (1) [5,6]

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

where i and j indicate solute and solvent respectively, σ is the nitrogen shielding, α is the hydrogen bond donor strength of the solvent, β represents its hydrogen bond acceptor strength, π^* is its polarity/polarisability and δ is a correction used for polychlorinated solvents ($\delta = 0.5$) and aromatic solvents ($\delta = 1$). The solute terms a, b, s and d represent the corresponding responses of the solvent employed and σ_0 is the nitrogen shielding in the reference state which is taken to be a

Table 3
Nitrogen shielding increments induced by hydrogen bonding between water molecules and hydrogen bond acceptor sites in N,N-dimethylcyanamide

Nitrogen atom	Acceptor sites involved	TNDO/2-calculated increment (ppm) in nitrogen shielding with respect to an isolated molecule
NMe_2	NMe_2	+12
CN	NMe_2	+2
NMe_2	CN	−1
CN	CN	+19
NMe_2	NMe_2 and CN	+13
CN	NMe_2 and CN	+21

cyclohexane solution. The least squares fitted values of the solute nitrogen shielding responses are also given in Table 2, as well as the linear correlation coefficients for the experimental shielding values with respect to those obtained from Eq. (1). Unfortunately we could only perform this correlation for compound 2 since compound 1 is essentially insoluble in crucially important solvents.

The data given in Table 2 for compound 2 show that the small solvent induced nitrogen shielding range for the NMe_2 group produces very small values for the parameters *a*, *b*, *s* and *d*. The small value for *s* shows that an increase in solvent polarity does not significantly affect the nitrogen shielding of this group. In the case of NR_2 moieties attached to a planar conjugated system a strong nitrogen deshielding effect is observed when lone pair delocalisation from the NR_2 group to the conjugated system occurs [3]. An increase in the polarity of the medium serves to enhance this effect. The present observation is in accord with reports of non-planarity of the NR_2 groups in cyanamide [1,2].

The cyano group of compound 2 appears to interact with solvents in a very similar manner to those of alkyl cyanides [4]. This observation supplies further evidence that there is no π conjugation between the NMe_2 and cyano functions in compound 2. In order to study the structures of compounds 1 and 2 further we have performed calculations of nitrogen shielding differences between the NR_2 and cyano groups using the semi-empirical TNDO/2 procedure. The relevant geometries were optimised by using the semi-empirical PM3 method which is known to provide

reasonable geometries for polar molecules. For both compounds studied the calculated geometries show that the N–C–N system is bent by about 5°. The out of plane angle is calculated to be about 50° for the NR_2 moieties involved, which is in good agreement with experiment [2] and ab initio molecular orbital calculations [8].

The TNDO/2 calculated nitrogen shielding differences between the NR_2 and CN groups show that for compound 1 the NH_2 moiety has a nitrogen shielding of 175 ppm with respect to that of the cyano group. The experimental results (Table 1) show a comparable shielding difference, between 170 ppm and 150 ppm, depending upon solvent. In the case of compound 2 the analogous calculated nitrogen shielding difference is about 140 ppm and the experimental value ranges between 170 ppm and 190 ppm depending upon solvent. Some ab initio multi-configurational SCF calculations on compound 1 show a comparable nitrogen shielding difference which ranges from 128 to 188 ppm depending upon the basis set chosen [9].

Table 3 shows the results of some TNDO/2 calculations of the effects on the nitrogen shieldings of N,N-dimethylcyanamide due to water molecules hydrogen bonded to the two acceptor sites. The geometries of the hydrogen bonded systems concerned were optimised using the PM3 method. Initially the effect of a single water molecule hydrogen bonded to either NMe_2 or CN was considered. The effect of this is found to be a local one in that water hydrogen bonded to the NMe_2 group only shows a significant effect on the nitrogen shielding of this group and not that of the

CN group. The same argument applies when hydrogen bonding to the CN group occurs. Following this we have considered the effect of two water molecules hydrogen bonded to compound **2**. The result shown in Table 3 is that nitrogen shielding increases are found which are essentially the sum of those found when a single water molecule is hydrogen bonded to the two groups considered individually. Consequently we find that the effects of hydrogen bonding on the nitrogen shielding of compound **2** are essentially local ones. This contradicts the view of significant lone pair delocalisation from the NMe_2 to the π system of the cyano group. The results given in Table 3 compare favourably with those for the a term given in Table 2. The sign is correct but the magnitudes are somewhat exaggerated.

We conclude that the nitrogen shielding variations, as a function of solvent, favour a highly non-planar structure for the compounds studied. In addition there appears to be no significant amount of π electron conjugation between the NR_2 and cyano moieties.

Acknowledgements

References

[1] B.H. Torrie, R. von Dreele and A.C. Larson, Mol. Phys., 76 (1992) 405.
[2] R.D. Brown, P.D. Godfrey and K. Kleiboemer, J. Mol. Spectrosc., 114 (1985) 257.
[3] M. Witanowski, L. Stefaniak and G.A. Webb, Annu. Rep. NMR Spectrosc., 25 (1993) 1–480.
[4] M. Witanowski, W. Sicinska and G.A. Webb, Magn. Reson. Chem., 27 (1989) 380.
[5] M.H. Abraham, P.L. Grellier, J.L.M. Abboud, R.M. Doherty and R.W. Taft, Can. J. Chem., 66 (1988) 2673.
[6] Y. Marcus, Chem. Soc. Rev., (1993) 409.
[7] R.C. Weast (ed.), Handbook of Chemistry and Physics, 64th edn. p. E-49, Chemical Rubber Co., Cleveland, OH, 1984.
[8] S.T. Kapellos and A. Mavridis, J. Mol. Struct., 279 (1993) 151.
[9] M. Jaszunski, T. Helgaker, K. Ruud, K.L. Bak and P. Jorgensen, Chem. Phys. Lett., 220 (1994) 154.