MAGNETIC RESONANCE IN CHEMISTRY, VOL. 28, 988–993 (1990)

Study of Solvent Effects on the Nitrogen NMR Shieldings of Some Indolizines

M. Witanowski, W. Sicińska and Z. Grabowski
Institute of Organic Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

G. A. Webb*
Department of Chemistry, University of Surrey, Guildford, Surrey, UK

Solvent effects on the nitrogen NMR shieldings of indolizine and three azaindolizines are presented for a range of thirteen solvents. The results are discussed in terms of hydrogen-bonding an solvent polarity effects. 'Pyridine-type' nitrogen atoms show a much larger range of solvent effects than do 'pyrrole-type' nitrogens; solvent to solute hydrogen bonding is the dominant contribution to the changes in shielding for the 'pyridine-type' nitrogen atoms as the solvent is varied. Solvent polarity effects are important for both types of nitrogen atom in azaindolizines and can be attributed to a solvent-induced electronic charge separation between the nitrogen atoms concerned.

Quantum chemical calculations involving the solvaton model are used to provide supporting evidence for the importance of solvent polarity effects on nitrogen shieldings in azaindolizines.

KEY WORDS Solvent effects Nitrogen shieldings Indolizines

INTRODUCTION

It has been clearly established that nitrogen NMR shieldings, for a variety of molecular environments, provide a very sensitive method for investigating solute–solvent interactions.[1–6] In order to interpret the solvent effects on nitrogen shieldings, a relatively simple scheme, including hydrogen-bonding and solvent polarity polarizability[7–17] properties, may be employed. In these investigations the additivity scheme used is based on that proposed for a generalized account of solvent properties.[18–20]

In *N*-heteroaromatic chemistry there exist, basically, two different types of nitrogen atoms, which can be referred to as the 'pyridine type' and the 'pyrrole type'. Both types involve sp^2 hybridization of the nitrogen atom and the difference lies in the disposition of the lone-pair electrons. In the 'pyridine type' these occur in a localized sp^2 hybrid orbital of σ symmetry, whereas in the 'pyrrole type' the lone pair is found in a non-hybridized p atomic orbital whereby they become delocalized into the molecular π network. A result of this difference in electronic environment is a large difference in the resulting nitrogen shieldings.[1–5,21] Previous studies of solvent effects on nitrogen shieldings have shown that these are large in the case of pyridine.[9,13,16]

Currently we are interested in establishing whether a similar solvent sensitivity exists for 'pyridine-type' nitrogen shieldings when the nitrogen atom in question resides in a five- rather than a six-membered aromatic ring. It is also of interest to consider the extent of the solvent sensitivity of the shieldings of 'pyrrole-type' nitrogen atoms.

To further these aims we report here the results of a study of solvent effects on the nitrogen shieldings of indolizine and some aza analogues as shown in Fig. 1.

All of the molecules represented in Fig. 1 contain a 'pyrrole-type' nitrogen atom at a bridgehead position (N-4). In addition, the azaindolizines studied have a 'pyridine-type' atom in the five-membered ring at various positions with respect to N-4. A study of nitrogen shielding in a series of azaindolizines, in dimethyl sulphoxide (DMSO), containing one or more 'pyridine-type' nitrogen atoms in the five-membered ring moiety showed that the algebraic difference between the 'pyridine-type' and 'pyrrole-type' nitrogen shieldings correlates linearly with an algebraic difference in the net electronic charges on the atoms concerned.[21] In general, an increase in charge splitting results in a smaller nitrogen shielding difference between the two types of nitrogen atom in the series of molecules studied in the same solvent, DMSO.

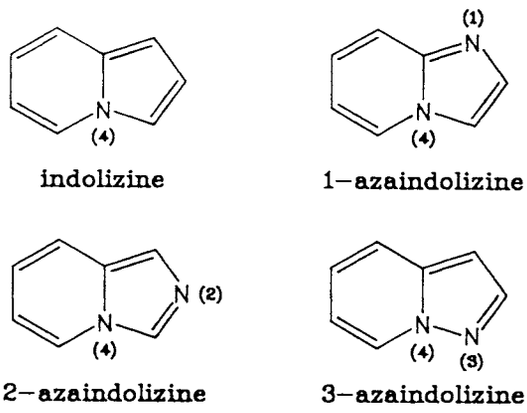

Figure 1. Structures of the molecules studied.

* Author to whom correspondence should be addressed.

0749–1581/90/110988–06 $05.00

Received 11 May 1990
Accepted 7 August 1990

An important aspect of this work was to consider whether, for a given azaindolizine, an increase in solvent polarity can induce similar nitrogen shielding changes. In principle, one may expect that, owing to solute–solvent polarity interactions, an increase in solvent polarity should induce a solute electron redistribution resulting in an increased charge splitting between the nitrogen atoms concerned.

If protic solvents are to be included in the investigation, i.e. those capable of hydrogen bonding to 'pyridine-type' nitrogen atoms, then it is necessary to separate the nitrogen shielding variations arising from hydrogen bonding and those due to solute–solvent polarity effects. It is also of interest to demonstrate whether quantum chemical calculations based on the solvaton model[22,23] are able to account for solvent polarity effects on the nitrogen shieldings of the two types of nitrogen atoms studied.

RESULTS AND DISCUSSION

The procedure employed to estimate the various contributions to the nitrogen shielding due to hydrogen-bonding and polarity–polarization effects requires the use of the four parameter master equation[18–20]

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

where XYZ is a given 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. cyclohexane solution; π^* is the polarity–polarizability term for the solvent, α corresponds to its hydrogen-bond donor strength, β is 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 relevant solute molecular property to the appropriate solvent property. The solvent parameters employed in this work are given in Table 1; the justification for choosing this set of parameters is presented in the footnotes. The set of solvents used represent a wide range of hydrogen-bonding and polarity properties.

This work is based on high-precision ^{14}N NMR measurements which are made using a high magnetic field, a line-shape fitting procedure and a rigorous calibration technique, the relevant details of which are presented under Experimental. Tables 2–5 give the experimental results and those of a least-squares fitting of the observed nitrogen shieldings of the molecules studied in a range of solvents to those predicted by Eqn. (1).

A survey of the data in Tables 2–5 shows that for the 'pyrrole-type' nitrogen atom, N-4, the observed solvent effects on its shielding are small and within about 2 ppm for all of the molecules studied. For the 'pyridine-type' nitrogen atoms, Tables 3–5 show that a contrasting situation arises in that the solvent effects on the nitrogen shielding are *ca* 30 ppm in all cases. This range compares reasonably with that found for pyridine,[9,13,16] which is about 38 ppm for a similar series of solvents. This observation demonstrates a similar degree of sensitivity to solvent effects of the shielding of 'pyridine-type' nitrogen atoms in both five- and six-membered rings. It is noteworthy that the range of solvent-induced shielding changes does not depend drastically on the relevant positions of the two nitrogen atoms in the three azaindolizines studied.

It is noteworthy that for 'pyridine-type' nitrogen atoms, where the effects of solvent on nitrogen shielding are fairly large, the sequence of solvents according to an induced increase in shielding is essentially the same for all of the azaindolizines studied. The solutions in cyclo-

Table 1. Solvent parameters employed[a]

Solvent	α	β	π^*	δ
Cyclohexane	0	0	0	0
Benzene	0	0.1	0.59	1.0
Carbon tetrachloride	0	0	0.29	0.5
Chloroform	0.34	0	0.76	0.5
Dichloromethane	0.22	0	0.80	0.5
Diethyl ether	0	0.47	0.27	0
Dioxane	0	0.37	0.55	0
Acetone	0.07	0.48	0.72	0
Dimethyl sulphoxide	0	0.76	1.00	0
Ethanol	0.86	0.77	0.54	0
Methanol	0.98	0.62	0.60	0
2,2,2-Trifluoroethanol	1.51	0	1.02	0
Water	(1.13)[b]	(0.18)[b]	(1.09)[b]	0

[a] The parameters are essentially those recommended in Ref. 18, and employed in our earlier work;[8–12] later modifications thereof[19,20] seem to deteriorate the least-squares fitting results in our case.
[b] These values are uncertain, but in the present case they seem to fit well into the set of experimenta data.

Table 2. Solvent effects on nitrogen NMR of indolizine

Solvent[a]	Nitrogen shielding in ppm referred to neat CH_3NO_2 Exp.[b]	Calc.	^{14}N resonance half-height width (Hz)
Cyclohexane	190.90	191.08	68
Diethyl ether	190.69	190.69	45
Carbon tetrachloride	191.04	190.92	81
Benzene	190.74	190.71	53
Dioxane	189.92	190.01	97
Acetone	189.93	189.70	51
Dimethyl sulphoxide	189.04	189.12	162
Dichloromethane	190.02	190.05	63
Chloroform	189.99	190.14	85
Ethanol	190.07	190.10	72
Methanol	189.93	190.05	52
Water (0.01 M)	189.19	189.31	100
2,2,2-Trifluoroethanol	189.75	189.12	187

Calculated responses of nitrogen shielding to solvent properties according to Eqn (1)

Parameter	Value (±s.d.)
XYZ_0 (ppm)	+191.08 ± 0.14
a (ppm/unit scale of α)	+0.19 ± 0.13
b (ppm/unit scale of β)	−0.24 ± 0.21
s (ppm/unit scale of π^*)	−1.78 ± 0.20
d (per unit scale of δ)	−0.39 ± 0.12
Correlation coefficient	0.9709
S.d. (ppm)	0.18

[a] Solute concentration, 0.25 M unless stated otherwise; temperature, 35 ± 0.3 °C.
[b] Bulk susceptibility corrected.

Table 3. Solvent effects on nitrogen NMR of 1-azaindolizine

	N-1			N-4		
Solvent[a]	Nitrogen shielding (ppm)[b] Exp.	Calc.	^{14}N signal half-height width (Hz)	Nitrogen shielding (ppm)[b] Exp.	Calc.	^{14}N signal half-height width (Hz)
Cyclohexane	132.85	133.16	190	180.06	180.25	53
Diethyl ether	134.97	135.43	160	179.77	179.46	39
Carbon tetrachloride	135.44	135.89	166	180.21	180.18	70
Benzene	136.03	136.89	170	180.14	179.95	40
Dioxane	136.74	136.43	275	179.00	179.07	68
Acetone	138.42	138.72	172	179.00	178.77	37
Dimethyl sulphoxide	139.19	139.31	394	178.04	178.04	104
Dichloromethane	141.60	141.16	201	179.41	179.54	44
Chloroform	143.92	143.18	277	179.59	179.72	58
Ethanol	153.03	153.04	573	179.54	179.57	98
Methanol	155.85	155.15	323	179.46	179.69	57
Water	159.03	159.04	321	178.92	179.34	87
2,2,2-Trifluoroethanol	164.60	165.27	855	180.45	179.94	170

Calculated responses of nitrogen shielding to solvent properties according to Eqn (1)

Parameter	Value (±s.d.) N-1	N-4
XYZ_0 (ppm)	+133.16 ± 0.14	+180.26 ± 0.24
a (ppm/unit scale of α)	+18.29 ± 0.45	+0.91 ± 0.22
b (ppm/unit scale of β)	+2.30 ± 0.74	−0.74 ± 0.35
s (ppm/unit scale of π^*)	+4.40 ± 0.70	−1.65 ± 0.34
d (per unit scale of δ)	+0.21 ± 0.18	−0.49 ± 0.22
Correlation coefficient	0.9988	0.9268
S.d (ppm)	0.63	0.30

[a] Solute concentration, 0.25 M; temperature, 35 °C.
[b] Referred to neat nitromethane, bulk susceptibility corrected.

Table 4. Solvent effects on nitrogen NMR of 2-azaindolizine

	N-2			N-4		
Solvent[a]	Nitrogen shielding (ppm)[b] Exp.	Calc.	^{14} signal half-height width (Hz)	Nitrogen shielding (ppm)[b] Exp.	Calc.	^{14}N signal half-height width (Hz)
Cyclohexane	102.07	102.66	367	187.47	187.66	66
Diethyl ether	104.14	104.26	274	187.07	186.74	44
Carbon tetrachloride	104.49	103.99	540	187.44	187.37	86
Benzene	104.85	105.48	391	187.17	186.97	53
Dioxane	105.88	105.14	617	186.42	186.37	92
Acetone	106.58	107.07	303	186.03	185.99	48
Dimethyl sulphoxide	107.32	107.28	832	185.27	185.22	147
Dichloromethane	109.54	109.53	373	186.31	186.56	55
Chloroform	112.16	111.40	549	186.43	186.65	72
Ethanol	119.50	120.10	1350	186.09	186.17	138
Methanol	123.17	122.13	748	186.00	186.24	73
Water	125.16	125.83	703	185.64	185.88	126
2,2,2-Trifluoroethanol	132.8	131.73	1930	186.73	186.26	229

Calculated responses of nitrogen shielding to solvent properties according to Eqn (1)

Parameter	Value (±s.d.) N-2	N-4
XYZ_0 (ppm)	+102.66 ± 0.57	+187.65 ± 0.22
a (ppm/unit scale of α)	+16.82 ± 0.52	+0.21 ± 0.20
b (ppm/unit scale of β)	+1.35 ± 0.85	−0.98 ● 0.33
s (ppm/unit scale of π^*)	+3.61 ± 0.81	−1.68 ± 0.32
d (per unit scale of δ)	+0.16 ± 0.25	−0.24 ± 0.20
Correlation coefficient	0.9981	0.9398
S.d. (ppm)	0.73	0.28

[a] Solute concentration, 0.25 M; temperature, 35 °C.
[b] Referred to neat nitromethane, bulk susceptibility corrected.

Table 5. Solvent effects on nitrogen NMR of 3-azaindolizine

	N-3			N-4		
	Nitrogen shielding (ppm)[b]		^{14}N signal half-height	Nitrogen shielding (ppm)[b]		^{14}N signal half-height
Solvent[a]	Exp.	Calc.	width (Hz)	Exp.	Calc.	width (Hz)
Cyclohexane	89.54	90.06	269	144.33	144.41	92
Diethyl ether	90.98	90.64	250	144.24	144.30	63
Carbon tetrachloride	91.65	91.06	373	144.78	144.42	128
Benzene	92.24	92.08	303	144.66	144.44	79
Dioxane	92.05	91.72	501	144.07	144.12	139
Acetone	93.15	93.29	287	144.40	144.19	71
Dimethyl sulphoxide	93.23	93.08	647	144.09	144.90	216
Dichloromethane	95.51	96.12	362	144.25	144.63	89
Chloroform	97.43	97.73	538	144.50	144.92	120
Ethanol	103.68	104.00	631	145.96	146.05	168
Methanol	105.98	106.08	450	146.08	146.28	113
Water (0.1 M)	110.18	110.35	491	146.08	146.33	181
2,2,2-Trifluoroethanol	116.3	115.79	1630	147.71	147.20	462

Calculated responses of nitrogen shielding to solvent properties according to Eqn (1)

	Value (±s.d.)	
Parameter	N-3	N-4
XYZ_0 (ppm)	+89.97 ± 0.36	+144.40 ± 0.27
a (ppm/unit scale of α)	+14.64 ± 0.33	+2.22 ● 0.25
b (ppm/unit scale of β)	−0.70 ± 0.55	+0.04 ± 0.41
s (ppm/unit scale of π^*)	+3.61 ± 0.52	−0.54 ± 0.38
d (per unit scale of δ)	0.00 ± 0.16	−0.64 ± 0.78
Correlation coefficient	0.9990	0.9664
S.d. (ppm)	0.47	0.35

[a] Solute concentration, 0.25 M; temperature, 35 °C.
[b] Referred to neat nitromethane, bulk susceptibility corrected.

hexane, which are considered to be the reference states (Table 1), produce the smallest nitrogen shieldings for a given molecule in all cases.

For pyridine, solvent to solute hydrogen-bonding effects account for most of the observed range of nitrogen shielding variations.[9] The analysis of the shielding data for 'pyridine-type' nitrogen atoms in Tables 3–5 reveals that the a term representing the response of the nitrogen shielding to solvent hydrogen-bond donor strength is dominant. The value of a is about 17 ppm per unit scale of α. By considering the range of α values in Table 1, it is apparent that hydrogen-bonding effects can contribute up to about 26 ppm to the nitrogen shielding in all cases considered. This is comparable to the situation observed for pyridine where the a term is about 21 ppm per unit scale of α,[9] and the corresponding shielding contribution due to hydrogen bonding is about 30 ppm. Consequently, this work shows that 'pyridine-type' nitrogen atoms in both five- and six-membered rings have nitrogen shieldings which are amongst the most sensitive of all nitrogen-bonding environments to solvent hydrogen-bonding effects.[1–17]

With respect to the 'pyrrole-type' nitrogen atoms (N-4) considered in Tables 2–5, solvent to solute hydrogen-bonding effects on the nitrogen shielding are essentially insignificant, with the exception of 3-azaindolizine (Table 5), where $a = 2.22 \pm 0.25$ ppm per unit scale of α. In this molecule the fact that the two nitrogen atoms are in adjacent positions suggests that this observed value for a may arise from a proximity effect due to hydrogen bonding to the 'pyridine-type' nitrogen atom in position 3.

Interesting conclusions can be drawn from consideration of the effects of solvent polarity–polarizability on the nitrogen shieldings of the molecules studied, as witnessed by the parameter s. For the 'pyrrole type' of nitrogen atoms, N-4, s appears to be the only parameter with a significant value as shown in Tables 2–5, being in the range from about -1 to -2 ppm per unit scale of π^*. For the 'pyridine-type' nitrogen atoms in the molecules studied it has a value of about $+4$ ppm per unit scale of π^*. Hence the responses of the shieldings for the two types of nitrogen atom to changes in the solvent polarity–polarizability are of opposite sign. Consequently, the shielding difference for these two types of nitrogen atom within a given molecule is reduced as the solvent polarity is increased. This observation corresponds closely with our earlier results obtained for a series of azaindolizines in a single solvent, DMSO.[21] In this earlier work we demonstrated from quantum chemical calculations and experimental data that the shielding difference for the two types of nitrogen atom considered decreased as the relevant charge separation increased. This result implies that in the present case, where a simple solute in a range of solvents of different polarities is considered, the s values obtained can be interpreted in terms of an increase in nitrogen charge separation with increasing polarity of the solvent.

With a view to substantiating this conclusion, we performed some INDO/S–SOS nitrogen shielding calcu-

Table 6. Solvaton calculations of solvent polarity effects on nitrogen NMR shieldings in indolizines

Solute	Nitrogen atom	Nitrogen NMR shielding (ppm) induced by increasing dielectric constant of solvent: $\varepsilon=2$	$\varepsilon=4$	$\varepsilon=10$	$\varepsilon=20$	$\varepsilon=40$
Indolizine	N-4	0[a]	−0.41	−0.60	−0.71	−0.77
1-Azaindolizine	N-1	0[a]	+1.43	+2.27	+2.54	+2.67
	N-4	0[a]	−0.38	−0.58	−0.67	−0.74
2-Azaindolizine	N-2	0[a]	+0.83	+1.22	+1.49	+1.62
	N-4	0[a]	−0.39	−0.57	−0.68	−0.75
3-Azaindolizine	N-3	0[a]	+0.84	+1.31	+1.55	+1.67
	N-4	0[a]	−0.39	−0.58	−0.67	−0.74

[a] Arbitrary reference corresponding to solutions in alkane solvents.

lations using the solvaton model,[22,23] the results of which are reported in Table 6.

As noted in Table 6, the solvaton calculations predict a decrease in shielding for N-4 and an increase in shielding for the 'pyridine-type' nitrogen atoms considered as the dielectric constant (ε) of the solvent increases. This is the same trend as noted above for the s terms. A comparison of the two sets of results is shown in Fig. 2. The values of s are given in terms of ppm per unit scale of π^*; this corresponds to a change of solvent from cyclohexane to DMSO (Table 1). The corresponding change in the dielectric constant is from about 2 to about 40; a solvaton-predicted difference in nitrogen shieldings, within this range of values of the dielectric constant, is therefore used in the plot given in Fig. 2. The plot obtained suggests a reasonably linear relationship which is described by $s = 1.907(\sigma_{\varepsilon=40} - \sigma_{\varepsilon=2}) - 0.011$ for the best-fitting line shown in Fig. 2.

As shown in Tables 2–5, the remaining parameters used in Eqn (1) are sufficiently small to be ignored.

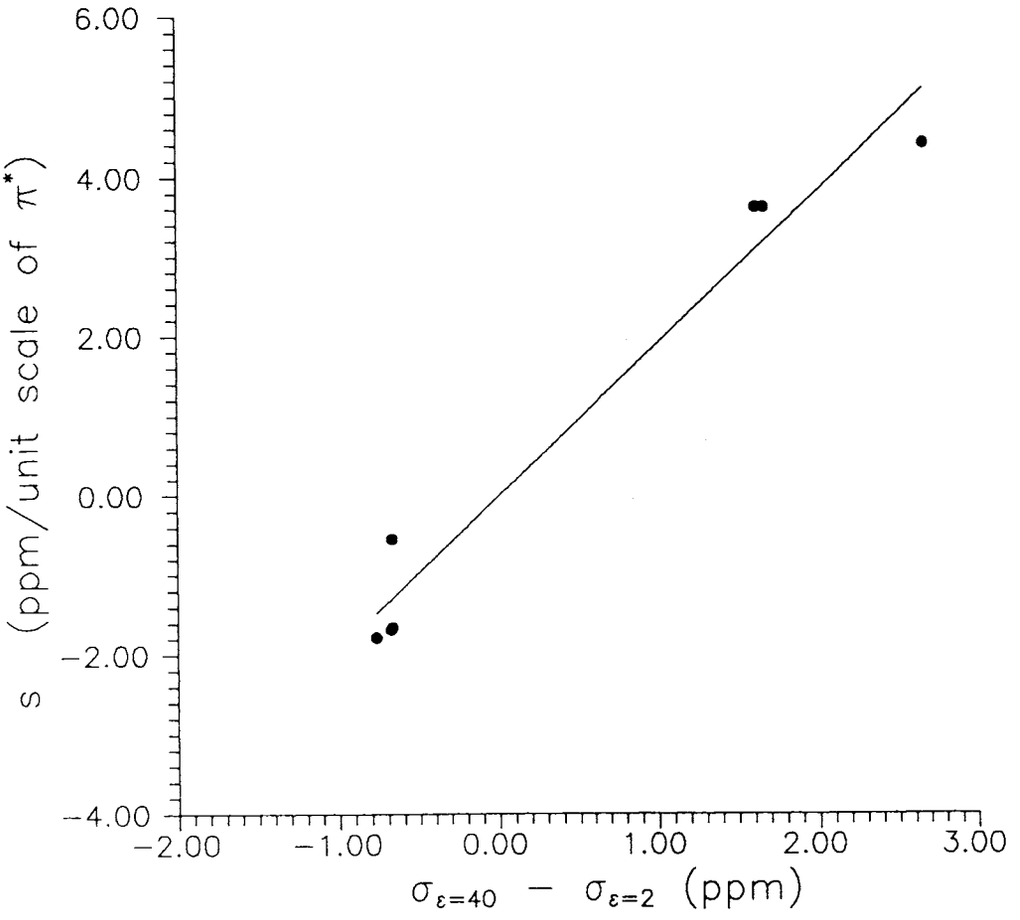

Figure 2. Plot of experimentally determined and INDO/S–SOS-calculated solvent polarity effects on the nitrogen shieldings of azaindolizines. The s term corresponds to the response of the experimental nitrogen shielding to solvent polarity–polarizability according to Eqn (1) and Tables 2–5. The term $\sigma_{\varepsilon=40} - \sigma_{\varepsilon=2}$ is the solvaton-calculated change in the nitrogen shielding as the dielectric constant (ε) of the solvent changes from 2 to 40.

CONCLUSIONS

We conclude that 'pyridine-type' nitrogen atoms in five-membered rings have shieldings which are very sensitive to solvent effects, similarly to those of their counterparts in six-membered aromatic rings. In contrast, the 'pyrrole-type' nitrogen atoms in indolizine ring systems show only a weak shielding response to a change in solvent.

For 'pyrdine-type' nitrogen atoms in azaindolizines, the dominant contribution to the variation of shielding produced by a change in solvent arises from hydrogen bonding from solvent to solute. In addition, solvent polarity effects also play a significant role and operate in the same direction as the hydrogen-bonding effects, thus producing a large range of nitrogen shieldings with change in solvent. This arises from the fact that strong hydrogen-bond donors are usually polar molecules. For 'pyrrole-type' nitrogen atoms the only significant solvent-induced nitrogen shielding variation comes from the solvent polarity effect, the direction of which is opposite to that observed for 'pyridine-type' nitrogen atoms. The resulting effect of solvent polarity is therefore to reduce the shielding difference between 'pyrrole-type' and 'pyridine-type' nitrogen atoms in azaindolizines.

Convincing evidence is presented to this contribution of solvent polarity to nitrogen shielding variations in azaindolizines is a measure of electronic charge separation between the two types of nitrogen atom within a given molecule.

EXPERIMENTAL

The compounds examined were prepared according to published procedures: indolizine (pyrrocoline)[24] 1-azaindolizine (imidazolo[1,2-*a*]pyridine),[25] 2-azaindolizine (imidazolo[1,5-*a*]pyridine)[26] and 3-azaindolizine (pyrazolo[1,5-*a*]pyridine.[27] They were purified by conventional methods and stored under dry argon. Where applicable the solvents were dried. The alcohols used were distilled over magnesium and the chlorinated solvents were passed through a column of basic alumina directly before use. DMSO was distilled over calcium hydride, benzene was distilled over P_2O_5 and diethyl ether was distilled over sodium. All NMR samples were prepared under an atmosphere of dry argon.

High-precision ^{14}N NMR measurements were performed on a Bruker AM 500 spectrometer as described elsewhere,[11,12] the overall precision of the shieldings being better than 0.1 ppm. The measurements were taken at a field corresponding to 36.141524 MHz for the ^{14}N reasonance of neat nitromethane. This field corresponds to the resonance of a bare nitrogen nucleus at 36.136826 MHz.[1,12] The experimental reference standard was a 0.3 M solution of nitromethane in acetone-d_6. The results were recalculated with respect to neat nitromethane as standard and corrected for bulk susceptibility effects.[11] All measurements were taken at 35.0 ± 0.2 °C, which was maintained by a VT unit. All shieldings are reported with respect to nitromethane such that an increase in shielding corresponds to a positive increment. Coaxial sample and reference tubes were employed in the locked mode, using the acetone-d_6 deuterium signal.

Standard geometries[28] were used in the INDO/S–SOS solvaton shielding calculations, which were performed on the University of Surrey Primenet system using procedures given elsewhere.[22]

Acknowledgement

We are pleased to acknowledge support from Project CPBP 01.13.1.25 of the Polish Academy of Sciences.

REFERENCES

1. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, edited by G. A. Webb, Academic Press, New York, **18**, 1 (1986).
2. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, edited by G. A. Webb, Academic Press, New York, **11B**, 35 (1981).
3. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, edited by G. A. Webb, Academic Press, New York, **7**, 118 (1977).
4. M. Witanowski, L. Stefaniak and G. A. Webb, *Annu. Rep. NMR Spectrosc.*, edited by E. F. Mooney, Academic Press, New York, **5A**, 395 (1972).
5. M. Witanowski, L. Stefaniak and H. Januszewski, in *Nitrogen NMR*, edited by M. Witanowski and G. A. Webb, p. 163. Plenum Press, New York (1973).
6. G. A. Webb and M. Witanowski, in *Topics in Molecular Interactions*, edited by W. J. Orville Thomas, p. 240. Elsevier, Amsterdam (1986).
7. M. Witanowski, L. Stefaniak, S. Szymanski and H. Januszewski, *J. Magn. Reson.* **28**, 217 (1977).
8. M. Witanowski, L. Stefaniak, B. Na Lamphun and G. A. Webb, *Org. Magn. Reson.* **16**, 57 (1981).
9. M. Witanowski, J. Sitkowski, S. Biernat, B. Kamienski, B. T. Hamdi and G. A. Webb, *Magn. Reson. Chem.* **23**, 748 (1985).
10. M. Witanowski, J. Sitkowski, S. Biernat, L. V. Sudna and G. A. Webb, *Magn. Reson. Chem.*, **25**, 725 (1987).
11. M. Witanowski, W. Sicińska and G. A. Webb, *Magn. Reson. Chem.* **27**, 380 (1989).
12. M. Witanowski, W. Sicińska, S. Biernat and G. A. Webb, *J. Magn. Reson.* **83**, 351 (1989).
13. O. W. Kolling, *Anal. Chem.* **51**, 1324 (1979).
14. O. W. Kolling, *Anal. Chem.* **56**, 430 (1984).
15. M. J. Kamlet and C. Dickinson, *J. Chem. Soc., Perkin Trans. 2* 353 (1981).
16. R. Duthaler and J. D. Roberts, *J. Am. Chem. Soc.* **100**, 4969 (1978).
17. G. J. Martin, T. Bertrand, D. le Botlan and J.-M. Letournaux, *J. Chem. Res. (S)* 408 (1979).
18. M. J. Kamlet, J. L. M. Abboud and R. W. Taft, *Prog. Phys. Org. Chem.* **13**, 485 (1980).
19. M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.* **48**, 2877 (1983).
20. R. W. Taft, J. L. M. Abboud, M. J. Kamlet and M. H. Abraham, *J. Solution Chem.* **14**, 153 (1985).
21. M. Witanowski, J. Sitkowski, W. Sicińska, S. Biernat and G. A. Webb, *Magn. Reson. Chem.* **27**, 88 (1989).
22. I. Ando and G. A. Webb, *Theory of NMR Parameters*. Academic Press, London (1983).
23. G. Klopman, *Chem. Phys. Lett.* **1**, 200 (1967).
24. O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, **498**, 44 (1932).
25. J. G. Lombardino, *J. Org. Chem.* **30**, 2403 (1967).
26. L. C. Craig and R. M. Hixon, *J. Am. Chem. Soc.* **53**, 4367 (1931).
27. V. Boekelheide and N. A. Fedoruk, *J. Org. Chem.* **33**, 2062 (1968).
28. J. A. Pople and M. S. Gordon, *J. Am. Chem. Soc.* **89**, 4233 (1967).