Calculations of the Solvent Effects on Some Nitrogen Chemical Shifts

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Nitrogen screening constants are calculated by the sum-over-states method using INDO/S parameters and by the finite perturbation procedure employing INDO parameters. The solvaton model is employed to describe changes in nuclear screening as a function of the dielectric constant of the medium. The calculated variations of nitrogen screening are in reasonable agreement with the available experimental data. The effects on screening of hydrogen bonding are included in the sum-over-states calculations by means of dimer models.

In order to obtain a close comparison between theoretical and experimental estimates of nuclear screening some allowance should be made for medium effects. Contributions from the bulk magnetisation and the diamagnetic anisotropy of the solvent to the total screening can be effectively removed by a suitable choice of solvent and the use of an internal standard. Account should also be taken of van der Waals interactions between solute and solvent, which usually deshield the nucleus of interest,[1,2] polar effects due to the charge distribution in neighbouring solvent molecules and specific solute solvent interactions such as hydrogen bonding and complex formation.

The influence of van der Waals interactions are likely to be most pronounced in the case of relatively nonpolar systems. For polar molecules it seems reasonable to suppose that effects due to solvent-charge distribution and specific solute-solvent interactions will dominate.

The polar effects of solvents on nuclear screening may be accounted for by means of the solvaton model.[3] This has been successfully employed in the calculation of solvent effects on ^{13}C chemical shifts in a number of molecules.[4,5]

In the present study these investigations are extended to nitrogen chemical shifts. Since these are more sensitive to medium effects than ^{13}C chemical shifts,[6] it is anticipated that they may provide a closer insight into the effects of solute-solvent interactions on chemical shifts.

As discussed elsewhere[7] Pople's model[8,9] appears to provide the most acceptable basis for satisfactory discussions of nuclear screening. Calculations using semi-empirical MO parameter sets are often inadequate due to the difficulties involved in accurately determining the contributions to the paramagnetic component of the screening tensor from the excited states. Two approaches to this problem are currently available. The sum-over-states method incorporating parameter sets which provide a realistic description of the excited states. In addition, there is the finite perturbation procedure which does not explicitly involve the estimation of excited state eigenfunctions.

Both of these approaches are employed in the present work. The sum-over-states calculations use INDO/S parameters which have been demonstrated to provide a satisfactory account of nitrogen chemical shifts[10] and the finite perturbation method employs INDO parameters within a revised formulation.[11] In the latter case, the values of the bonding parameters β_H° and β_C°, for the hydrogen and carbon atoms respectively, are taken to be -13 eV and -15 eV. The correction factor K for π-π interactions takes the value of 0.85. Calculations incorporating these values provide a reasonable account of some ^{13}C chemical shifts.[11]

Results and Discussion

The results of the calculations of the total charge density on the nitrogen atom, q, the averaged value of its screening tensor, σ, and the relative chemical shift, δ, as a function of the dielectric constant of the medium, ε, for both the sum-over-states (SOS) and finite perturbation (FPT) calculations are presented in Table 1.

The decrease in screening of the nitrogen nucleus in nitromethane as ε increases is almost entirely due to changes in the paramagnetic contribution to the screening tensor. As ε increases from 1 to 80 the diamagnetic term reduces by 1.83 ppm in the sum-over-states calculations and 0.95 ppm in the finite perturbation results. This follows a reduction in the nitrogen charge density. In general, it is found that the calculated changes in the diamagnetic term, as a function of ε, are very small when compared with those in the paramagnetic contribution. Consequently only changes in the total nuclear screening are reported in Table 1.

The data reported in Table 1 imply that changes in q, as a function of ε, do not always follow in the same direction as variations in σ. This is most probably due to the fact that differences in σ are controlled by changes in the paramagnetic contribution which, in general, are not expected to depend linearly on charge density differences.[7]

Both sets of calculations qualitatively follow the trend of changes in nitrogen screening with ε for nitromethane reported experimentally.[6] More quantitative data would reveal whether the large change in σ, predicted by the sum-over-states calculations, or the smaller change indicated by the finite perturbation results is the more accurate.

The finite perturbation results reported in Table 1 do not contain the contribution to the diamagnetic term arising from the 1s electrons. Thus the values of σ reported are smaller than those obtained from the sum-over-states calculations. However, this should not influence the calculated changes in σ as a function of ε.

The sum-over-states results indicate a value of about -141 ppm for the nitrogen screening of neat nitromethane which is in reasonable agreement with the estimated

Table 1. Some sum-over-states (SOS) and finite perturbation (FPT) calculations of the dependence of some nitrogen charge densities (q), screening constants (σ) in ppm and chemical shifts (δ) in ppm upon dielectric constant

Species	Method	Data	Dielectric constant						
			1	2	6	10	20	40	80
CH_3NO_2	SOS	q	4.519	4.438	4.383	4.372	4.363	4.359	4.357
		σ	−112.46	−126.26	−136.93	−138.94	−140.45	−141.20	−141.57
		δ	0.0	13.80	24.97	26.48	27.99	28.74	29.11
	FPT	q	4.448	4.406	4.378	4.372	4.368	4.366	4.365
		σ	−444.46	−446.91	−448.41	−448.70	−448.92	−448.96	−449.07
		δ	0.0	2.45	3.95	4.24	4.46	4.50	4.61
NH_3	SOS	q	5.282	5.337	5.373	5.381	5.386	5.389	5.390
		σ	112.12	120.62	125.78	126.88	127.80	128.20	128.40
		δ	0.0	−8.50	−13.66	−14.76	−15.68	−16.08	−16.28
	FPT	q	5.276	5.286	5.293	5.295	5.296	5.296	5.297
		σ	−127.24	−126.04	−125.24	−125.07	−124.96	−124.91	−124.86
		δ	0.0	−1.20	−2.00	−2.17	−2.28	−2.33	−2.38
Pyridine	SOS	q	5.297	5.308	5.316	5.317	5.318	5.319	5.319
		σ	−20.40	−20.27	−20.17	−20.14	−20.12	−20.11	−20.11
		δ	0.0	−0.13	−0.23	−0.26	−0.28	−0.29	−0.29
	FPT	q	5.206	5.221	5.227	5.231	5.231	5.231	5.232
		σ	−465.82	−451.63	−444.33	−442.88	−441.80	−441.24	−441.11
		δ	0.0	−14.19	−21.49	−22.94	−24.02	−24.58	−24.71
CH_3CN	SOS	q	5.294	5.304	5.311	5.313	5.314	5.315	5.315
		σ	35.51	35.47	35.23	35.12	35.08	35.06	35.04
		δ	0.0	0.04	0.28	0.39	0.43	0.45	0.47
	FPT	q	5.202	5.235	5.250	5.255	5.258	5.260	5.261
		σ	−349.77	−337.41	−329.59	−327.99	−326.81	−326.18	−325.92
		δ	0.0	−12.36	−20.18	−21.78	−22.96	−23.59	−23.85
CH_3NC	SOS	q	5.118	5.124	5.131	5.132	5.133	5.134	5.134
		σ	91.50	93.79	94.10	94.09	94.16	94.13	94.11
		δ	0.0	−2.29	−2.60	−2.59	−2.66	−2.63	−2.61
	FPT	q	5.029	5.004	4.987	4.984	4.981	4.980	4.979
		σ	−144.05	−149.37	−153.06	−153.80	−154.37	−154.65	−154.79
		δ	0.0	5.32	9.01	9.75	10.32	10.60	10.74
NO_3^-	SOS	q	4.477	4.359	4.281	4.263	4.250	4.235	4.231
		σ	−94.98	−192.14	−237.36	−291.83	−306.17	−316.26	−320.03
		δ	0.0	97.16	178.38	196.85	211.19	221.28	225.05
	FPT	q	4.323	4.260	4.219	4.211	4.206	4.203	4.201
		σ	−537.91	−465.39	−413.88	−406.70	−401.43	−398.83	−397.54
		δ	0.0	−72.52	−124.03	−131.21	−136.48	−139.08	−140.37
NH_4^+	SOS	q	4.822	4.817	4.814	4.814	4.813	4.813	4.813
		σ	137.56	175.30	192.42	195.47	197.54	199.47	199.99
		δ	0.0	−37.74	−54.86	−57.91	−59.98	−61.91	−62.43
	FPT	q	4.965	4.986	5.002	5.005	5.008	5.009	5.010
		σ	−66.32	−88.19	−107.22	−111.44	−114.72	−116.38	−117.24
		δ	0.0	21.87	40.90	45.12	48.40	50.06	50.92

a) The chemical shifts are reported with respect to the isolated molecule, $\varepsilon=1$, shifts to higher frequency being positive.

value of −130 ppm.⁶⁾

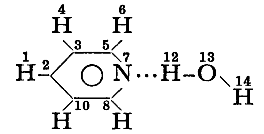
In the case of ammonia both sets of calculations predict an increase in nitrogen screening as ε increases. This appears to be in contradiction to the available experimental data which show a nitrogen screening decrease by up to 21 ppm when gaseous ammonia is dissolved in various solvents.[6)] However, the nitrogen screening of the ammonium ion can be 40 to 50 ppm less then in ammonia[6)] and since the available experimental solution data on ammonia involves media conductive to protonation and/or hydrogen-bonding the comparison with the theoretical results in Table 1 may not be a valid one.

The small increase in the nitrogen screening of pyridine as ε increases, from the sum-over-states calculations, follows the trend of the available experimental data for non-hydrogen bonding media.[6,12)] In hydrogen-bonding solvents large increases in the nitrogen screening are reported which are dominated by changes in the paramagnetic term.[12)] To investigate this we have calculated the nitrogen screening constant for the hydrogen-bonded pyridine–water dimer in a minimum

TABLE 2. SUM-OVER-STATES CALCULATED VALUES OF THE CHARGE AND CONTRIBUTIONS TO THE NUCLEAR SCREENING TENSOR (ppm) OF SOME NITROGEN NUCLEI IN CASES WHERE HYDROGEN BONDING IS SIGNIFICANT

Compound	q	Average weighted value of transition energies (eV)	σ^d	σ^p (loc)	σ^p (nonloc)	σ	δ
NO_3^- (isolated)	4.4770	14.08	318.48	−416.29	2.83	−94.98	0.0
Hydrated NO_3^- [14]	4.4879	14.33	318.62	−408.35	2.34	−87.39	−7.59
Pyridine (isolated)	5.2973	11.82	327.11	−349.80	2.30	−20.40	0.0
Pyridine/Water[a]	5.2775	12.37	326.93	−334.04	2.50	−4.61	−15.79
CH_3CN (isolated)	5.2944	11.510	327.15	−289.45	−5.19	35.51	0.0
CH_3CN/CH_3OH[b]	5.2593	13.075	326.82	−256.14	−1.13	69.56	−34.05

a)



$C_2H_1 = C_3H_4 = C_{10}H_{11} = 1.105$ Å

$C_5H_6 = C_8H_9 = 1.114$ Å

$C_2C_3 = C_3C_5 = C_8C_{10} = C_2C_{10} = 1.407$ Å

$C_5N_7 = C_8N_7 = 1.334$ Å

$N_7H_{12} = 4.626$ Å

$H_{12}O_{13} = H_{14}O_{13} = 0.949$ Å

$H_1\hat{C}_2C_3 = H_4\hat{C}_3C_2 = 120.3°$

$C_2\hat{C}_3C_5 = C_2\hat{C}_{10}C_8 = 118.1°$

$C_3\hat{C}_5N_7 = C_{10}\hat{C}_8N_7 = 121.8°$

$C_3\hat{C}_5H_6 = 121.7°$

$C_5\hat{N}_7C_8 = 120.7°$

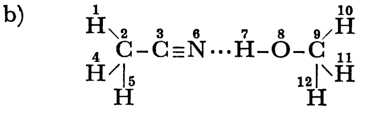
$N_7\hat{C}_8H_9 = 116.6°$

$C_5\hat{N}_7H_{12} = 118.0°$

$N_7H_{12}O_{13} = 180.6°$

$H_{12}\hat{O}_{13}H_{14} = 103.7°$

b)



$H_1C_2 = H_4C_2 = H_5C_2 = 1.121$ Å

$C_2C_3 = 1.424$ Å

$C_3N_6 = 1.196$ Å

$N_6H_7 = 1.406$ Å

$H_7O_8 = 1.072$ Å

$O_8C_9 = 1.362$ Å

$C_9H_{10} = C_9H_{11} = C_9H_{12} = 1.126$ Å

$H_1\hat{C}_2C_3 = 110.9°$

$C_2\hat{C}_3N_6 = 179.5°$

$H_7\hat{N}_6C_3 = 175.0°$

$O_8\hat{H}_7N_6 = 174.6°$

$C_9\hat{O}_8H_7 = 111.6°$

$H_{10}\hat{C}_9O_8 = 111.6°$

energy conformation obtained from an INDO geometry optimization procedure.

The results given in Table 2 reveal an increase in nitrogen screening of 15.79 ppm due to hydrogen-bond formation. This compares with a measured increase of about 25 ppm.[12] The increase arises from a reduction in the paramagnetic contribution to the screening as a result of increases of energy denominators weighted by transition elements in various transitions.[10] The major transition changes result from the effective removal of the nitrogen lone pair due to hydrogen-bond formation.

The finite perturbation results (Table 1) show a much larger increase in the nitrogen screening of pyridine, with an increase in ε, without specifically incorporating the formation of a hydrogen bond.

A similar situation arises in the case of acetonitrile. The observed increase in the nitrogen screening in methanol appears to be accounted for by the finite perturbation calculations on the solvaton model, whereas the sum-over-states method requires the acetonitrile-methanol dimer as a model (Table 2) to reproduce the experimental trend. The structure used in this calculation again corresponds to a minimum energy conformation as obtained from INDO calculations.

The available experimental data on the nitrogen resonance of methyl isocyanide[13] indicate that it is far less sensitive to changes in solvent than is its counterpart for acetonitrile. The calculations reported here support this conclusion. However, the opposing trends predicted by the two sets of calculations are probably indicative of medium effects which are not specifically incorporated in the solvaton model.

The sum-over-states calculations for the nitrate ion indicate that the nitrogen atom in the free ion suffers a large decrease in screening as ε increases. However, in the presence of water a hydrogen-bonded structure has been reported.[14] Calculations on this structure (Table 2) reveal an increase of nitrogen screening. The increase in nitrogen screening, as a function of ε, is predicted by the finite perturbation calculation without invoking hydrogen-bonding.

Since nitrate ion is usually used in aqueous media the opposing screening trends due to the solvaton and hydrogen-bonding interactions renders its nitrogen resonance position very susceptible to changes in concentration and pH. Taken together these effects make nitrate ion unsatisfactory as a reference standard for nitrogen NMR.[6]

The trend obtained (Table 1) by the sum-over-states calculations for the nitrogen screening of the ammonium ion, as a function of ε, is in reasonable agreement with the available experimental data.[6] The opposing trend suggested by the finite perturbation calculations implies that interactions other than those described by the solvaton model are operative.

For use as a nitrogen NMR reference material the position of a nitrogen signal should be relatively insensitive to solvent changes in order to compare results between different laboratories. The calculations reported here indicate that the ammonium ion is not to be recommended as a nitrogen standard.[6]

At present it is not clear why the sum-over-states calculations for pyridine, acetonitrile and nitrate ion require both solvaton and hydrogen bonding effects to reproduce experimental trends, whereas only solvaton interactions are necessary in the finite perturbation approach. However, in general, the effects of the medium on nitrogen chemical shifts appear to be reasonably well accounted for by the calculations reported here involving both the solvaton model and specified hydrogen-bonding interactions. To examine these data more searchingly further experimental results of changes in nitrogen screening as a function of ε are required.

Experimental

The sum-over-states calculations were performed on the CDC 7600 systems of the Universities of London and Manchester using a modified version of QCPE 174. Standard geometries$^{15)}$ were used in the calculations. The finite perturbation calculations were performed on the HITAC M180 system of the Tokyo Institute of Technology.

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