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SOLVENT EFFECTS IN NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

SOLVENT SHIFTS INDUCED BY BENZENE IN AMINES

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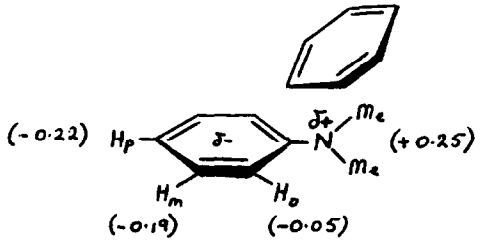
It is now well known[1] that benzene causes considerable solvent shifts of proton resonances ($\Delta = \tau_{C_6D_6} - \tau_{CCl_4}$) with respect to an 'inert' solvent in NMR spectra. The origin of such solvent shifts is believed to lie in the ability of benzene to solvate an aromatic or aliphatic solute molecule at electron deficient sites of local dipoles in a sterospecific manner, the shifts arising due to the magnetic anisotropy of the benzene ring. It has been suggested by Williams and co-workers[1] that nonplanar collision complexes are formed, in which the π-electron system of benzene interacts in such a way that the benzene ring lies as far as possible from the negative end of the dipole. Thus, in the case of dimethylaniline the methyl groups are shifted upfield and the aromatic protons downfield in benzene relative to carbon tetrachloride, and Williams has accounted for this by the schematic representation:



In connection with other work we have had occasion to determine the NMR spectra of N-methylaniline and the toluidines in various solvents at 100 Mc. The results obtained, by a first-order analysis of the spectra, are summarised in Table I. In the case of m- and p-toluidine the position of the methyl resonance has not been shifted to any significant extent, whereas in the case of o-toluidine and N-methylaniline the methyl groups are strongly shielded in benzene. In the latter cases both methyl groups must lie under the

TABLE I

Solute	Solvent Shifts (Δ)						
	CH_3	NH	H_2	H_3	H_4	H_5	H_6
N-Methylaniline	+0.48	+0.98	+0.06	-0.11	-0.16	-0.11	+0.06
o-Toluidine	+0.28	+0.65	-	-0.08	-0.13	-0.19	+0.10
m-Toluidine	+0.09	+0.76	+0.11	-	-0.13	-0.11	+0.09
p-Toluidine	+0.05	+0.76	+0.09	-0.07	-	-0.07	+0.09
Toluene[2]	+0.23	-	-	-	-	-	-

shielding cone of the associated benzene solvent molecule. The fact that the methyl groups in m- and p-toluidine are moved upfield slightly in benzene, not downfield as in the case of the corresponding ring protons in dimethylaniline, suggests that the methyl groups are secondary sites for solvation by the benzene solvent molecules, the interaction being weaker, however, than the solvent-solute interaction associated with the amino group. The fact that these methyl groups are not shielded to the same extent as in toluene can be attributed to their lying in the deshielding region of the benzene solvent molecule associated with the amino group.

The other apparent anomaly is that all the ortho protons are shielded slightly, whereas in the case of dimethylaniline all the ring protons are deshielded. We believe that this may be explained in terms of the angle between the planes of the solvent and solute molecules. As the amino group becomes more substituted, so the plane of the solvent molecule becomes more steeply inclined to that of the solute. Consequently, the solute aromatic protons would be brought progressively further into the deshielding zone of the solvent. When the amino group is unsubstituted or mono-substituted the solvating molecule can lie closer to the electron deficient site and can be inclined less steeply to the plane of the solute molecule. To test these conclusions we have examined a further series of primary (Table 2), secondary (Table 3) and tertiary aromatic amines (Table 4).

The ortho protons of the primary amines are all shielded as expected, except that ortho to both an amino and methoxyl group, but it has recently been shown[2] that an ortho-methoxyl group makes the solvent shift of an adjacent substituent more negative compared

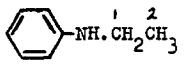
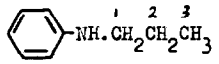
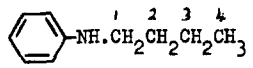
TABLE 2

Solute	Solvent Shift (△)						
	CH_3	NH	H_2	H_3	H_4	H_5	H_6
Aniline	-	+0.71	+0.17	-0.04	-0.09	-0.04	+0.17
*o-Anisidine[‡]	+0.47	+0.39	-	-	-	-	-
*m-Anisidine	+0.31	+0.72	-0.03	-	-0.11	-0.10	+0.04
*p-Anisidine	+0.27	-	+0.13	-0.16	-	-0.16	+0.13

* At 60 Mc

‡ Aromatic region too complex for a first-order analysis

TABLE 3

Solute	Solvent Shift (△)						
	C_1	C_2	C_3	C_4	o	m	p
	+0.35	+0.41	-	-	0.00	-0.13	-0.19
	+0.31	+0.36	+0.28	-	0.00	-0.14	-0.20
	+0.32	+0.35		+0.17	+0.12	-0.03	-0.08

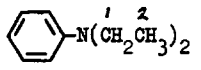
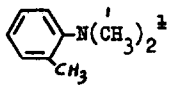
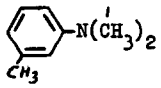
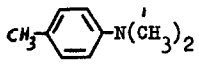
with the unsubstituted isomer, or m- and p- isomers.

In the case of secondary amines (Table 3) the ortho protons are not deshielded in benzene with respect to carbon tetrachloride, whereas the m- and p- protons are significantly deshielded. It is of interest to note that the shielding of the side chain is at a maximum for approximately C_2, as compared with the purely aliphatic analogue, n-butylamine, where the shielding decreases in a uniform manner:

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}NH_2$$

+0.09 +0.17 +0.22

TABLE 4

Solute	Solvent Shift (△)							
	C_1	C_2	C-CH_3	H_2	H_3	H_4	H_5	H_6
* 	+0.30	+0.24	-	-0.06	-0.17	-0.20	-0.17	-0.06
	+0.20	-	-0.02	-	-	-	-	-
	+0.33	-	+0.03	-0.12	-	-0.22	-0.14	-0.10
	+0.31	-	0.00	-0.13	-0.16	-	-0.16	-0.13

* At 60 Mc

‡ Aromatic region complex

With tertiary amines, however, the ortho protons are deshielded, in agreement with the above mentioned conclusions concerning the degree of inclination of the solvent to solute planes. Even the ortho-methyl group shows a slight downfield shift, whereas there is a considerable upfield shift in the case of o-toluidine. The N-methyl groups are not as strongly shielded in the ortho-isomer as with the m- and p- isomers or N-methylaniline, but this is probably best rationalised in terms of greater steric inhibition of resonance resulting in a weaker solvent-solute interaction (although the angle between the solvent and solute planes would be expected to affect the shielding of the alkyl, as well as the aromatic, protons). Further investigations of solvent shifts in amines are in progress.

REFERENCES

1. J. Ronayne and D. H. Williams, J. Chem. Soc. (B), 540 (1967), and references therein.

2. J. H. Bowie, J. Ronayne and D. H. Williams, J. Chem. Soc. (B), 535 (1967).