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THE EFFECT OF AROMATIC SOLVENTS IN NMR SPECTROSCOPY.

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As pointed out by Bothner-By and Click (1) and independently by Reeves and Schneider (2), aromatic solvents show a specific shielding affect upon protons in the NMR spectra of polar solutes. This effect and some interesting aspects of it have been further investigated by Schaefer, Schneider and Buckingham (3,4,5,6,7). More recently Bhacca and Williams (8,9,10,11,12) and other workers (13,14,15,16,17,18) have made use of the effect in structure elucidation and conformational analysis. Bertelli and Golino (19) correlated solvent shifts with π-electron delocalisation, and Brown and Stark (20) found a correlation between the dipole moments of various solutes and $\Delta\tau$. Steric factors and benzene solvent effect were studied in some detail by Anderson (21).

The present author encountered solvent shifts in connection with NMR measurements on certain ketone peroxides and felt it of interest to test the effect under practical conditions on more simple compounds.

The preliminary results of these tests are presented here. The solvent shielding effect of benzene on 25 solutes are given in Table I below as $\Delta\delta = \delta(CCl_4) - \delta(C_6H_6)$ i.e. as the difference in observed maximum chemical shifts of the solute protons expressed in ppm when carbon tetrachloride and benzene respectively were used as solvents.

TABLE I

Solvent shielding effect of benzene on various solutes.

Solute	Δδ solute	Solute	Δδ solute
phenol	ca 1.20	α-trichlorotoluene	0.39
chloroform	0.82	nitrobenzene	0.39
bromoform	0.77	1,4-cyclohexandione	0.38
acetonitrile	0.72	aniline	0.35
acrylonitrile	0.70	chlorobenzene	0.31
p-benzoquinone	0.69	dimethyl sulfoxide	0.30
methylene chloride	0.67	ethyl methyl ketone	0.30
cyclohexanol	0.61	benzyl chloride	0.30
methyl iodide	0.52	acetic acid	0.29
nitromethane	0.50	benzonitrile	0.28
γ-butyrolacetone	0.50	1,4-dioxane	0.26
pyrrole	0.45	tetrahydrofurane	0.25
benzal chloride	0.44		

The shielding seems to parallell the acidic and electrophilic character of the solute protons concerned, while no simple correlation with dipole moments can be seen.

According to the "carbonyl plane rule" (11,13) very little shielding would be expected for p-benzoquinone and 1,4-cyclohexanedione. Despite this and their small dipole moments, large solvent shifts are observed for the two compounds.

In Table II the shielding effects of 20 aromatic compounds used as solvents upon the same solute, i.e. acetonitrile are given.

TABLE II

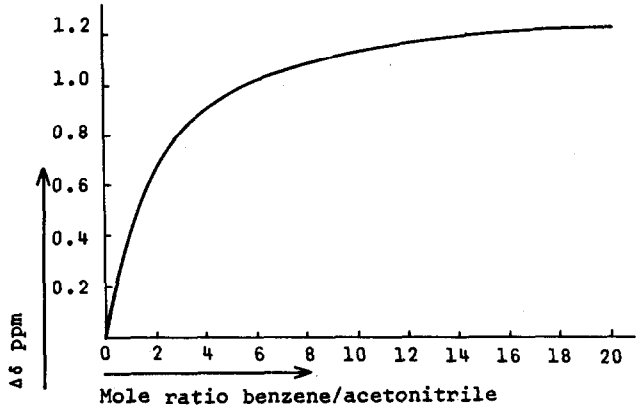
Solvent shielding of various solvents on acetonitrile.

Solvent	Δδ acetonitrile	Solvent	Δδ acetonitrile
toluene	0.75	furan	0.41
pyrrole	0.73	chlorobenzene	0.37
benzene	0.72	α-trichlorotoluene	0.34
thiophene	0.62	hexafluorobenzene/ benzene 1:1	0.33
aniline	0.55	bromobenzene	0.31
m-xylene	0.51	iodobenzene	0.30
benzal chloride	0.48	benzonitrile	0.03
mesitylene	0.47	p-nitroaniline	0.01
anisole	0.45	pyridine	0.00
benzyl chloride	0.42	nitrobenzene	+ 0.04

For the more polar solvents nitrobenzene, pyridine and benzonitrile the shielding is seen to be absent.

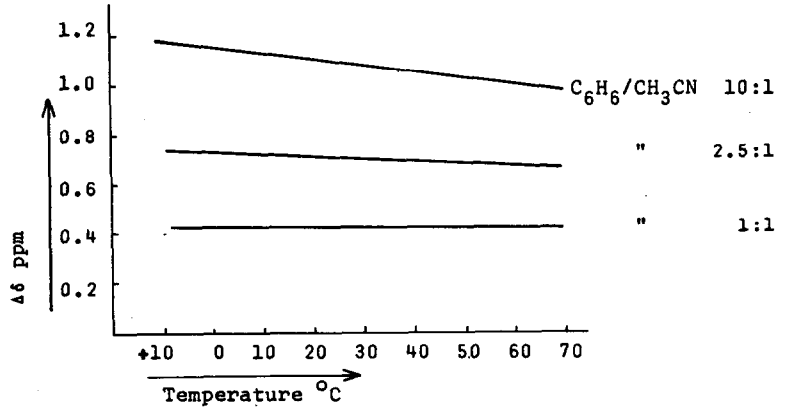
Fig. 1 shows shielding effect of benzene on acetonitrile as a function of the mole ratio benzene/acetonitrile.

FIG 1



The effect is seen to increase strongly with increasing dilution, which also was found to be the case with other solutes. This demands special caution in interpretation of NMR data, especially when a computer measuring technique is employed.

FIG 2



Shielding effects as a function of temperature for 3 different mole ratios benzene/acetonitrile are given in Fig. 2. The influence of temperature is seen to be more pronounced at the higher dilution, while it is absent at the mole ratio 1:1. This fact may indicate a competition between solute/solute- and solvent/solute- association.

EXPERIMENTAL

The chemicals used were ordinary analytical grade, concentrations ca 15 per cent w.w. and the temperature during measurements 20°C unless otherwise stated. The NMR apparatus was a Varian Associate Dual Purpose Spectrometer operating at 60 Mc/sec. Tetramethylsilane was used as an internal standard.

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