Solute–Benzene Interactions: a Nuclear Magnetic Resonance Spectral, Dipole Moment, and Kerr Effect Study

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Benzene-induced ^{1}H n.m.r. shifts reported for a variety of polar solutes are related to the magnitude of the solute dipole moment for groups of structurally similar molecules. N.m.r. and Kerr constant data are interpreted in terms of a time-averaged solvent cluster model; the most favoured stereospecific solute–benzene interactions within the solvation sphere are indicated.

THE solvation of polar molecules in benzene solution has been widely studied in recent years.[1-9] The nature and geometry of the transitory solute–solvent interactions are not completely understood. From an examination of the specific shielding effects of aromatic solvents on the n.m.r. spectra of polar solutes, Ledaal [2] inferred that benzene interacts with a polar solute in such a way that the electric dipole axis of the solute molecule is located along the six-fold symmetry axis of the benzene nucleus, with the positive end of the dipole closest to the benzene π electron system. A similar orientation was proposed for fluoroform– and chloroform–benzene associations by Le Fèvre *et al.*[10] who attributed this geometry primarily to hydrogen bond formation between the relatively acidic halogenoform hydrogen and the benzene π cloud. Brown and Stark,[5] however, do not regard this as a major cause of benzene-induced upfield shifts. They favour a model in which the orientation of aromatic solvent molecules with reference to a polar solute is governed mainly through dipole-induced dipole interactions (as first suggested by Schneider [4] in 1962) and they interpret their data in terms of a time-averaged orientation of solvent molecules with the benzene C_6 planes parallel to the solute molecular dipole vector. Ronayne and Williams [3] have generalised this concept in proposing, on the basis of ^{1}H n.m.r. evidence, that benzene solvent molecules will solvate electron deficient sites of *local* dipoles in solute molecules; the stereospecific approach of the benzene rings is directed through local dipole-induced dipole interaction of the solute with benzene, the π electron system of the latter tending to lie away from the negative end of the local dipole. More recently, Bertrand *et al.*[7] showed that for dipolar polycyclic molecules such as $\overset{\delta-}{\mathrm{H}}\mathrm{C[OCH_2]_3}\overset{\delta+}{\mathrm{C}}\mathrm{CH_3}$, the sensor protons located at the negative end of the molecular dipole experience strong benzene-induced downfield shifts while those at the positive end exhibit the expected large upfield shifts. They proposed a solvent clustering in which the π clouds of benzene molecules are attracted towards positive sites in the solute and, in addition, *other* benzene molecules tend to orient with their relatively positively charged peripheries directed towards negative sites within the solute. Engler and Laszlo [9] have stressed the short lived nature of the binary encounters involved (on the n.m.r. time scale) and they emphasise the notion of a time-averaged cluster of solvent molecules about the solute. In the present work we explore further such interactions from studies of the ^{1}H n.m.r. spectra, electric dipole moments, and Kerr constants of solutes.

EXPERIMENTAL

The solutes, obtained commercially or synthesised, were purified immediately before use. Solvents were dried and purified by standard procedures.[11,12] The ^{1}H n.m.r. spectra were measured on a Varian A60 n.m.r. spectrometer using tetramethylsilane as internal reference. The benzene-induced solvent shifts $\Delta\tau$, defined as $\tau_{\mathrm{benzene}} - \tau_{\mathrm{dioxan}}$, were derived from measurements of the chemical shifts in benzene and in dioxan at infinite dilution. Initially *ca.* 5% solutions were made up (or, alternatively, saturated solutions were used where the solubility is low) and these were successively diluted until no further changes in τ could be observed. The results are summarised in the Table together with solute dipole moments μ and molar Kerr constants (where they exist) quoted from the literature. The term $_{\infty}(_{\mathrm{m}}K_2)$ refers to the molar Kerr constant of the solute at infinite dilution.

DISCUSSION

Comparison of the chemical shift data of columns 3 and 4 of the Table shows clearly that, apart from the halogenoforms, the τ values in dioxan are very close to those in carbon tetrachloride. Since the substances examined are all soluble in dioxan we have, for consistency, derived benzene-induced shifts $\Delta\tau$ relative to dioxan. Solubility limitations precluded the use of cyclohexane as a general inert reference solvent though the corresponding τ values

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[3] J. Ronayne and D. H. Williams, *Chem. Comm.*, 1966, 712; *J. Chem. Soc.* (*B*), 1967, 540; J. Ronayne and D. H. Williams in 'Annual Review of Nuclear Magnetic Resonance Spectroscopy,' ed. E. F. Mooney, Academic Press, New York, 1969, vol. 2, p. 83.

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Chemical shifts (τ), dipole moments, and molar Kerr constants

	τ				Δτ ($\tau_{C_6H_6} - \tau_{C_4H_8O_2}$)	μ/D	$10^{12}\infty({}_mK_2)$ (' Inert ' solvent)	$10^{12}\infty({}_mK_2)$ (Benzene)
Solute	Cyclohexane	Carbon tetrachloride	Dioxan	Benzene				
$(CH_3)_3Y$								
$(CH_3)_3CCl$	8·45	8·40	8·42	8·65	0·23	2·14 [a]	72 [a]	
$(CH_3)_3CBr$	8·27	8·21	8·24	8·50	0·26	2·19 [b]	146 [b]	
$(CH_3)_3CI$	8·11	8·06	8·09	8·37	0·28	2·14 [c]	215 [c]	
$(CH_3)_3N$			7·89	7·94	0·05	0·77 [d]	−1·7 [d]	1·6 [d]
$(CH_3)_3NBH_3$			7·43	7·97	0·54	4·62 [e]	22·7 [e]	−217 [e]
$(CH_3)_3NBH_3$			8·33	7·70	−0·63	4·62 [e]	22·7 [e]	−217 [e]
$(CH_3)_3NBCl_3$			7·07	7·97	0·90	6·33 [e]	−126 [e]	−565 [e]
$(CH_3)_3NBBr_3$			6·90	7·85	0·95	6·61 [e]	−472 [e]	−849 [e]
$(CH_3)_3P$			9·04 [f]	9·16 [f]	0·12	1·19 [f]	−10·1 [f]	
$(CH_3)_3PO$		8·59 [f]	8·65 [f]	9·10 [f]	0·45	4·39 [f]	−39·5 [f]	−387 [f]
$(CH_3)_3PS$		8·29 [f]	8·34 [f]	8·95	0·61	4·87 [f]	634 [f]	1·1 [f]
$(CH_3)_3As$		9·06 [f]	9·08 [f]	9·20 [f]	0·12	1·10 [f]	−9·4 [f]	
$(CH_3)_3AsO$		8·46 [f]	8·54 [f]	9·16	0·62	5·11 [f]	−17·1 [f]	−554 [f]
$(CH_3)_3AsS$		8·29	8·33	9·02	0·69	5·35 [f]	722 [f]	346 [f]
CH_3X								
CH_3Br	7·52	7·38	7·36	8·09	0·73	1·70 [b]	51·6 [b]	
CH_3I	8·00	7·85	7·85	8·56	0·71	1·48 [c]	48·5 [c]	
CH_3NO_2		5·72	5·72	7·00	1·28	3·14 [b]		89·0 [b]
CH_3CN		8·05	8·07	9·35	1·28	3·38 [b]	217 [g]	244 [h]
HCX_3								
$HCCl_3$	2·88	2·74	2·31	3·77	1·46	1·10 [i]	−24·2 [g]	−40·9 [g]
$HCBr_3$	3·22	3·15	2·78	4·11	1·33	1·02 [j]		−33·8 [j]
HCI_3	5·17	5·09	4·84	6·01	1·17	0·86 [j]		−14·0 [j]
NNN′N′-Tetramethylethylenediaminezinc(II) chloride								
CH_2			7·36	8·53	1·17	8·7 [k]	−6 [k]	−2200 [k]
CH_3			7·48	8·12	0·64			

[a] R. J. W. Le Fèvre and B. J. Orr, *J. Chem. Soc.* (*B*), 1966, 37. [b] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1954, 1577. [c] R. J. W. Le Fèvre and B. J. Orr, *J. Chem. Soc.*, 1965, 5349. [d] K. R. Skamp, personal communication. [e] R. S. Armstrong, G. J. Peacock, K. R. Skamp, and R. J. W. Le Fèvre, *J.C.S. Dalton*, 1973, 1123. [f] R. S. Armstrong, M. J. Aroney, R .J. W. Le Fèvre, R. K. Pierens, J. D. Saxby, and C. J. Wilkins, *J. Chem. Soc.* (*A*), 1969, 2735. [g] R. J. W. Le Fèvre, D. V. Radford, G. L. D. Ritchie, and P. J. Stiles, *J. Chem. Soc.* (*B*), 1968, 148. [h] R. J. W. Le Fèvre, G. L. D. Ritchie, and P. J. Stiles, *J. Chem. Soc.* (*B*), 1967, 819. [i] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1953, 4041. [j] R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 1963, 4933. [k] M. J. Aroney, R. J. W. Le Fèvre, and H. J. Vaughan, *J. Chem. Soc.* (*A*), 1970, 2224.

are included (in column 2) where it was possible to make measurements in this solvent. In all cases, except that of the BH_3 protons in trimethylamine–borane, upfield shifts were experienced in benzene indicating effective shielding of the sensor protons through stereospecific interactions between the solute and the solvating benzene molecules. Following Schneider [4] and Brown and Stark,[5] we explore possible correlations between the magnitude of the benzene-induced shifts Δτ and the solute dipole moments μ. Accordingly, we have plotted the upfield shifts Δτ of the Table against μ and also against μ^2 (since the induction force arising from dipole-induced dipole interactions would be proportional to μ^2) for structurally related groups of solutes (Figure 1). The relationships thus obtained, though not strictly regular, suggest that dipolar interactions between the solute and the solvent molecules within the solvation sphere are *one* important factor in the solvation process. We do not pursue this further in terms of dipolar interaction energies since a meaningful analysis could be effected only if the assumption is made of a solute–solvent complex of fixed geometry.

The halogenoforms differ from the other solutes examined in that the proton shifts in dioxan are appreciably downfield from those in carbon tetrachloride or cyclohexane; this is reasonably ascribed to hydrogen-bonding of the HCX_3 proton with the oxygen atoms of dioxan. Smith and Ihrig [13] have reported proton shifts for fluoroform which correspond to τ values of 3·75

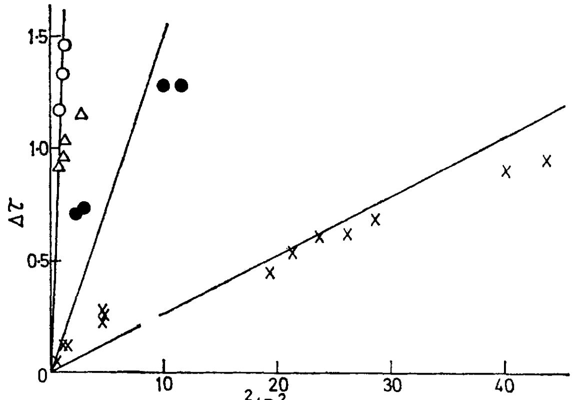

FIGURE 1 Plot of Δτ against μ^2 for various solutes: ○, HCX_3; ●, CH_3X; ×, $(CH_3)_3Y$; △, $\tau_{C_6H_6} - \tau_{CCl_4}$ for HCX_3

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[13] W. B. Smith and A. M. Ihrig, *J. Phys. Chem.*, 1971, **75**, 497.

(C_6H_{12}), 3·54 (CCl_4), and 4·69 (C_6H_6). Thus for the series HCX_3 we have τ (C_6H_6) − τ (CCl_4) values of 1·15, 1·03, 0·96, and 0·92 respectively for X = F, Cl, Br, and I, and these, when plotted against $\mu^2(HCX_3)$, lead to the triangles in Figure 1. An approximately regular gradation is apparent. It has been suggested[8,10,13] that halogenoform molecules form hydrogen bonds between the acidic HCX_3 proton and the π electron cloud of benzene solvent molecules and this tends to stabilise a weakly associated species HCX_3,C_6H_6 in which the solute dipole axis is collinear with the six-fold symmetry axis of benzene and the positive end of the HCX_3 dipole is closest to the benzene π electrons. We do not regard such associations as exclusive but merely energetically favoured over other binary encounters which also occur.

With the molecules CH_3X (X = Br, I, NO_2, or CN) $\Delta\tau$ exhibits a very approximate dependence on the magnitude of μ^2 despite the fact that the stereospecificity of the *preferred* solute–benzene interactions is probably not the same throughout. The Kerr effect evidence of Le Fèvre *et al.*[8] can be interpreted to indicate that methyl chloride is stereospecifically solvated in benzene such that, within the solvation sphere, encounters in which the methyl chloride dipole axis is perpendicular to the benzene ring plane *outweigh* those which have the solute dipole parallel to that plane. The reverse is the case with methyl cyanide. N.m.r. data for CH_3Cl in dioxan are not available but Abraham[14] has reported that benzene-induced proton shifts for methyl chloride and methyl bromide (relatively to a cyclohexane environment) are almost identical. Since the dipole moments of the two solutes are closely similar,[15] it is reasonable to expect that $\Delta\tau$ for methyl chloride would, like that of methyl bromide, lie close to the CH_3X plot of Figure 1.

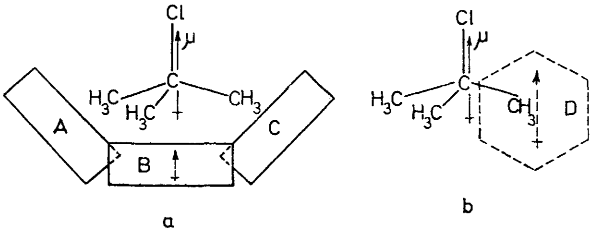

FIGURE 2 Benzene–$(CH_3)_3Y$ interactions

The thirteen compounds designated $(CH_3)_3Y$ in the Table also exhibit an internally consistent, though not very regular, variation of $\Delta\tau$ with μ^2, however, the slope is appreciably lower than for the substances HCX_3 or CH_3X. This could indicate that the solute–benzene interactions occurring in proximity to the protons are even weaker in $(CH_3)_3Y$ because of the steric effect of the methyl groups, *e.g.* for encounters of the types shown as A, B, C, and D in Figure 2 the benzene π cloud is not able to approach as closely to the positive end of the solute dipole as it could with the methyl halides. By contrast, with the halogenoforms, the benzene–proton interactions occur at that end of the halogenoform molecule which is sterically least affected by the halogen atoms. Brown and Stark[5] have proposed that molecules of the type CH_3X and $(CH_3)_3Y$ are solvated by benzene to give a time-averaged orientation of benzene molecules having their C_6-ring planes parallel to the solute molecular dipole moment; refer to Figure 2 of ref. 5. Though models of this type may be compatible with a dipole-induced dipole mechanism of interaction, they do not explain the large *negative* $\Delta_m K$ increments observed for the compounds $(CH_3)_3Y$. Rather, they would result from the Langevin–Born expressions[8] in predicted large positive $\Delta_m K$ values since the solute dipole vectors would be directed parallel or near parallel to the planes of maximum polarisability of the associated benzene molecules (Figure 2b). A variety of stereospecific solute–benzene interactions undoubtedly occurs but the negative $\Delta_m K$ values indicate clearly that the overall effect is to increase the polarisability in the plane perpendicular to the solute dipole axis more so than in a direction parallel to that axis. It is tempting to interpret these observations in terms of a model in which perpendicular or near-perpendicular encounters (*e.g.* B in Figure 2a) *predominate* over the parallel interactions proposed by Brown and Stark.[5] Irrespective of the mode of solvent orientation one important component of the interaction energy would be that due to dipole-induced interactions so it is not surprising to observe rough correlations between μ^2 (solute) and the observed $\Delta\tau$ values. The polarisability of benzene in the aromatic plane is greater than that normal to the plane ($b_1 = b_2 = 11{\cdot}15$ Å^3; $b_3 = 7{\cdot}44$ Å^3)[16] so that the moments induced for perpendicular solute–benzene interactions would be smaller than for parallel interactions for comparable distances between the benzene molecules and μ (solute). It may be, however, that the perpendicular dispositions are stabilised through closer approach of benzene to the positive end of the polarising solute dipole (and in the case of the halogenoforms, through hydrogen bonding). Benzene molecules having parallel orientations would tend to be deflected by the negative Y group in $(CH_3)_3Y$ and adopt angular approaches such as A or C in Figure 2a. We favour a dynamic model in which benzene molecules in the vicinity of the positive end of the solute dipole undergo a directive influence which causes slight deviations from randomness; *e.g.* some benzene molecules would be guided into occupying a number of available positions equivalent to A about the $(CH_3)_3$ group before either being deflected away from the solute or alternatively moving into position B and then to C before leaving the solvation sphere. It should be emphasised that on a time-averaged basis, all orientations of benzene occur but dispositions such as those described above are favoured.

Other factors besides dipole-induced dipole interactions, hydrogen bonding, and steric repulsions may also be important in determining the orientations of

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[14] R. J. Abraham, *Mol. Phys.*, 1961, **4**, 369.

[15] C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, 1954, 1577.

[16] R. J. W. Le Fèvre and L. Radom, *J. Chem. Soc.* (*B*), 1967, 1295.

solvating benzene molecules, *e.g.* repulsions between the benzene π cloud and electron rich centres at the negative end of the solute dipole [17] and attraction of the relatively positive peripheries of benzene molecules to centres of high electron charge within the solute.[7] Evidence for interactions of this nature is provided by the benzene-induced *downfield* shifts reported for the BH_3 protons in trimethylamine-borane. This strongly suggests that edge-on collisions between benzene molecules and B–H groups (*e.g.* D in Figure 3) are responsible for the deshielding. The benzene-induced shifts Δτ and the negative Δ_mK for trimethylamine–borane are best explained by a model in which the solute is enclosed in a cage of benzene molecules the distribution of which at any instant is not completely random but is affected by the factors outlined above. All orientations are possible but configurations corresponding to dispositions such as A, B, or D of Figure 3 should be marginally favoured energetically. Configurations E in which the same benzene molecules simultaneously shield the methyl groups and deshield the BH_3 protons, are also possible but the statistical weighting of such forms cannot be great since they do not contribute in a negative sense to the Δ_mK.

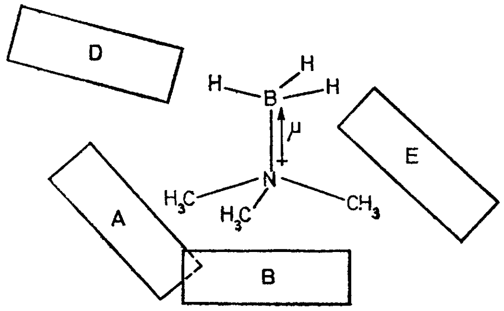

FIGURE 3 Benzene–$(CH_3)_3NBH_3$ interactions

A solvation cage model may also be described for the complex *NNN'N'*-tetramethylethylenediaminezinc(II) chloride in benzene (see Figure 4). The most probable mode of association within the cage is that designated G in which the aromatic π cloud is close to the electrophilic end of the solute dipole. This accounts for the Δτ values found (1·17 for the methylene protons and 0·64 for those of the methyl groups) and for the very large Δ_mK of *ca.* -2200×10^{-12}. H and F represent other favoured approaches which, however, from the n.m.r. shifts are much less likely than G. Interactions between the chlorine atoms and solvent molecules are more difficult to specify. Intuitively one would expect edge-on approaches of benzene molecules in which peripheral hydrogen atoms are directed towards the chlorine lone pairs. Such encounters would most likely involve an infinitude of benzene orientations within a conical region of high electron density about each chlorine atom and could result effectively in time averaged, non-stereospecific solvation.

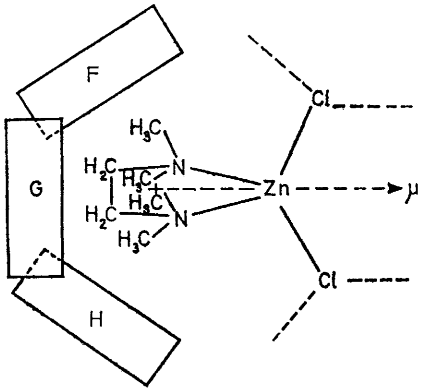

FIGURE 4 Benzene–*NNN'N'*-tetramethylethylenediamine-zinc(II) chloride interactions

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[17] T. Yonezawa, I. Morishima, and K. Fukuta, *Bull. Chem. Soc. Japan*, 1968, **41**, 2297.