

Solute-Hexafluorobenzene Interactions: a Nuclear Magnetic Resonance Spectral, Dipole Moment, and Kerr Effect Study

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¹H N.m.r. are reported for a variety of solutes in hexafluorobenzene and an attempt is made to correlate the solvent-induced shifts with the magnitude of the solute dipole moment. It is confirmed that hexafluorobenzene causes negative shielding of protons near an electrophilic centre in the solute and positive shielding of protons close to a nucleophilic site. Molar Kerr constants of solutes, measured for the first time in hexafluorobenzene, are found to be sensitively affected by hexafluorobenzene solvation. A time-averaged solvent cage model is invoked within which some degree of order is induced through stereospecific solute-solvent interactions.

THE n.m.r. chemical shifts of polar solutes are sometimes sensitively dependent on the nature of the solvent environment. Aromatic solvents, for example, often produce appreciable 'solvent-induced' shifts with reference to absorptions in relatively 'inert' solvents such as cyclohexane or carbon tetrachloride. Such effects have been extensively studied for benzene solvation¹⁻⁵ but little is known about the behaviour of aromatic solvents other than benzene. In 1970, Bertrand *et al.*⁴ examined the ¹H n.m.r. spectra of dipolar, polycyclic molecules such as $\overset{\delta-}{\text{HC}}[\overset{\delta+}{\text{OCH}_2}]_3\overset{\delta+}{\text{CCH}_3}$ as solutes in benzene and in hexafluorobenzene and they found that the latter solvent induces strong *downfield* shifts of protons at the positive solute site and *upfield* shifts of protons in the negative region of the solute, effects which are opposite in sense to those caused by benzene. They suggested a solvent cluster model in which favoured solute-hexafluorobenzene transient associations occur through preferential attraction of the positive end of the solute dipole for the relatively negative peripheral fluorines on the solvent ring. The

purpose of the present work is to investigate further the incidence and stereospecificity of such interactions in hexafluorobenzene from n.m.r. spectral, dipole moment, and Kerr effect data.

EXPERIMENTAL

The solutes, obtained commercially or synthesised, were purified immediately before use. Dioxan was purified by passing through an alumina column then drying over sodium wire before distillation. Hexafluorobenzene, obtained commercially, was fractionated using a 40 cm column packed with glass helices.

The ¹H n.m.r. spectra were measured on a Varian A60 n.m.r. spectrometer using tetramethylsilane as internal reference. 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 τ values so derived in dioxan and in hexafluorobenzene are listed in Table 1 together with the solute dipole moments (which are quoted from ref. 6).

⁴ R. D. Bertrand, R. D. Compton, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 2702.

⁵ E. M. Engler and P. Laszlo, *J. Amer. Chem. Soc.*, 1971, **93**, 1317.

⁶ R. S. Armstrong, M. J. Aroney, R. K. Duffin, H. J. Stootman, and R. J. W. Le Fèvre, preceding paper.

¹ T. Ledaal, *Tetrahedron Letters*, 1968, 1683.

² 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.

³ T. L. Brown and K. Stark, *J. Phys. Chem.*, 1965, **69**, 2679.

The dipole moments and molar Kerr constants of trimethylamine-borane and *NNN'N'*-tetramethylethylenediaminezinc(II) chloride were determined at infinite dilution in hexafluorobenzene (Table 2). The apparatus, techniques, symbols used, and methods of calculation have been described before.⁷⁻¹⁰ The following data¹¹⁻¹³ apply at 25 °C for hexafluorobenzene: $\epsilon_1 = 2.029$; $d_1 = 1.6069$; $(n_1)_D = 1.3798$. The corresponding Kerr constant $(B_1)_D$ was experimentally determined as $0.91(\pm 0.01) \times 10^{-7}$ relatively to benzene for which $(B_1)_D = 0.410 \times 10^{-7}$. The specific Kerr constant for hexafluorobenzene follows as 0.112×10^{-12} from the equation ${}_sK_1 = 6\lambda n_1 B_1 / (n_1^2 + 2)^2 \cdot (\epsilon_1 + 2)^2 d_1$ where λ is the wavelength of the light used to measure B_1 (589.3 nm). The term $\infty(mK_2)$ refers to the molar Kerr constant of the solute at infinite dilution.

DISCUSSION

The $\Delta\tau$ values of column 4 in Table 1 are algebraically negative excepting those for the BH_3 protons in trimethylamine-borane and for the three halogenoforms

TABLE 1
Chemical shifts (τ) and dipole moments of solutes

Solute (CH_3) ₃ Y	τ		$\Delta\tau$ ($\tau_{\text{C}_6\text{F}_6} - \tau_{\text{C}_6\text{H}_6\text{O}_4}$)	μ/D^*
	Dioxan *	Hexafluorobenzene		
(CH_3) ₃ CCl	8.42	8.37	-0.05	2.14
(CH_3) ₃ CBr	8.24	8.17	-0.07	2.19
(CH_3) ₃ CI	8.09	8.00	-0.09	2.14
(CH_3) ₃ NBH ₃	7.43	7.28	-0.15	4.62
(CH_3) ₃ NBH ₃	8.33	8.80	0.47	4.62
(CH_3) ₃ NBCl ₃	7.07	6.78	-0.29	6.33
(CH_3) ₃ NBBR ₃	6.90	6.60	-0.30	6.61
(CH_3) ₃ PS	8.34 †	8.21	-0.13	4.87
(CH_3) ₃ AsS	8.33	8.18	-0.15	5.35
CH₃X				
CH ₃ Br	7.36	7.31	-0.05	1.70
CH ₃ I	7.85	7.77	-0.08	1.48
CH ₃ NO ₂	5.72	5.53	-0.19	3.14
CH ₃ CN	8.07	7.86	-0.21	3.38
H CX₃				
HCCl ₃	2.31	2.67	0.36	1.10
HCF ₃	2.78	3.12	0.34	1.02
HCl ₃	4.84	5.00	0.16	0.86
<i>NNN'N'</i> -Tetramethylethylenediaminezinc(II) chloride				
CH ₂	7.36	7.00	-0.36	8.7
CH ₃	7.48	7.27	-0.21	

* Ref. 6. † $J(^{31}\text{P}-^1\text{H})$ 13.1 Hz.

examined. Dioxan was chosen as a general reference solvent rather than carbon tetrachloride or cyclohexane since many of the solutes studied are insoluble in the latter solvents. It has been shown, moreover, that where comparisons could be made, the τ values in dioxan are very close to those in carbon tetrachloride for all solutes in column 1 except the halogenoforms which,

because of hydrogen bond formation with the oxygen atoms of dioxan, experience a pronounced downfield shift in dioxan. If for the HCX_3 compounds the hexafluorobenzene induced solvent shifts are calculated relatively to a carbon tetrachloride environment⁶ then negative values also result, *i.e.* $\tau_{\text{C}_6\text{F}_6} - \tau_{\text{CCl}_4}$ is -0.07 , -0.03 , and -0.09 for $\text{X} = \text{Cl}$, Br , and I respectively. Comparison of the $\Delta\tau$ estimates of Table 1 with those of ref. 6 shows that aromatic solvent shifts produced by hexafluorobenzene are much smaller than those experienced in benzene. Correlations between the $\Delta\tau$ values and the magnitude of the solute dipole moments (μ) were explored by plotting $\Delta\tau$ against μ and also against μ^2 (since the dipole-induced dipole interaction is a function of μ^2); the latter graphs are represented in Figure 1.

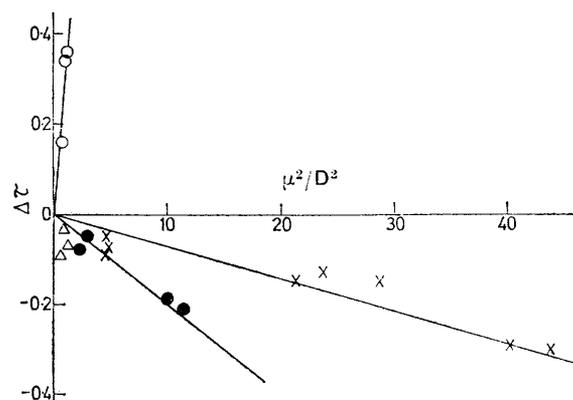


FIGURE 1 Plot of $\Delta\tau$ against μ^2 for various solutes: \circ , HCX_3 ; \bullet , CH_3X ; \times , $(\text{CH}_3)_3\text{Y}$; Δ , $\tau_{\text{C}_6\text{F}_6} - \tau_{\text{CCl}_4}$ for HCX_3

The uncertainty in $\Delta\tau$ is ± 0.03 so that points generally relating to low polarity solutes which have small $\Delta\tau$ values, are not particularly meaningful. Nonetheless there is an approximate dependence of $\Delta\tau$ on the magnitude of the solute dipole moment for structurally related molecules within each group of substances CH_3X , HCX_3 , and $(\text{CH}_3)_3\text{Y}$. The 'corrected' $\Delta\tau$ values for the halogenoforms, shown as triangles, are small and no regular gradation is apparent. In the case of trimethylamine-borane the BH_3 protons experience an *upfield* shift in hexafluorobenzene. We thus confirm and extend the findings of Bertrand *et al.*⁴ that hexafluorobenzene produces aromatic solvent shifts opposite in sense to those of benzene, *i.e.* it causes *downfield* shifts of protons near the positive end of the solute dipole and *upfield* shifts of protons near the negative end. It may be inferred also, from the rough correlations between μ^2 (solute) and $\Delta\tau$, that as for the case of benzene solvation,⁶ one important factor in the solvation process in hexafluorobenzene is that due to dipole-induced dipole interactions and, in addition, the different slopes of the

⁷ C. G. Le Fèvre and R. J. W. Le Fèvre, *Rev. Pure Appl. Chem.*, 1955, **5**, 261.

⁸ R. J. W. Le Fèvre, 'Dipole Moments,' Methuen, London, 3rd edn., 1953.

⁹ C. G. Le Fèvre and R. J. W. Le Fèvre, in 'Physical Methods of Organic Chemistry,' ed. A. Weissberger, Interscience, New York, 3rd edn., vol. I, ch. XXXVI, p. 2459.

¹⁰ R. J. W. Le Fèvre and G. L. D. Ritchie, *J. Chem. Soc.*, 1963, 4933.

¹¹ M. E. Baur, D. A. Horsma, C. M. Knobler, and P. Perez, *J. Phys. Chem.*, 1969, **73**, 641.

¹² F. D. Evans, M. Bogan, and R. Battino, *Analyt. Chem.*, 1968, **40**, 224.

¹³ G. W. Parshall, *J. Org. Chem.*, 1962, **27**, 4649.

lines in Figure 1 underline the influence of the steric factors operating for each particular type of solute.

The magnetic anisotropy of hexafluorobenzene ($10^{30}\Delta\chi = 59$ e.m.u.)¹⁴ determined from measurements of the molar Kerr and molar Cotton-Mouton constants, is qualitatively similar to that of benzene so that the regions of magnetic shielding and deshielding are similarly disposed with reference to the aromatic planes. It

cules. All orientations of C_6F_6 are possible and do occur but specific approaches are favoured in terms of the geometry of the solute and of the solvent, dipole-induced dipole effects, and electrostatic attractions and repulsions between the various nucleophilic and electrophilic centres in both the solute and the solvent molecules.

In order to obtain independent experimental evidence for solvation effects in hexafluorobenzene, dielectric

TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants of solutes (from observations on solutions in hexafluorobenzene at 25 °C)

Solute	Concentration range ($10^3 w_2$)	$\alpha\epsilon_1$ ^a	δ ^a	$\infty P_2/cm^3$	R_D/cm^3 ^b	μ/D ^c	$10^{12}\infty(mK_2)$
Trimethylamine-borane	120–392	51.0	0	440	25.6	4.5	–200
NNN'N'-Tetramethylethylenediaminezinc(II) chloride	46–145	47.6	200	1420	53.0	8.2	5000

^a The quantities $\alpha\epsilon_1$ and δ are defined in turn as $\Sigma\Delta\epsilon/\Sigma w_2$ and $\Sigma 10^7\Delta B/B_1\Sigma w_2$, where $\Delta\epsilon$ and ΔB are the differences found between the dielectric constants and Kerr constants, respectively, of solutions containing weight fractions w_2 of solute, and of the solvent; analogous coefficients β and γ , derived from incremental changes in density and refractive index, respectively, were ignored in calculating μ and mK since, in each case, they were negligibly small in relation to the other terms $\alpha\epsilon_1$ and δ . ^b Ref. 15; ref. 16. ^c Calculated assuming $D_P = 1.06 R_D$.

follows then that the negative shielding of sensor protons at the electrophilic end of the solute dipole by hexafluorobenzene is best attributed to preferred edge-on approaches of C_6F_6 solvent molecules such that the peripheral fluorines are in proximity to $H^{\delta+}$ atoms of the solute (in Figure 2, A and B represent examples of

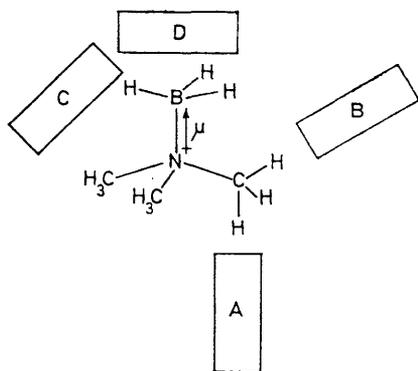


FIGURE 2 Hexafluorobenzene-(CH_3)₃NBH₃ interactions

orientations of this nature). It should be stressed that the occurrence of such dispositions does not preclude solute-solvent interactions of different geometry. For example it seems reasonable to suggest that the low $\Delta\tau$ values found for the halogenoforms may be due to the incidence of both $H \cdots F$ (deshielding) and $H \cdots \pi$ -electron (shielding) associations with the former type predominating. On the other hand the positive $\Delta\tau$ found for the BH_3 protons of trimethylamine-borane indicates that edge-on approaches $B-H \cdots F$ are less important than those in which the hydrogens are in the C_6F_6 shielding region, e.g. C in Figure 2 in which $H^{\delta-}$ is close to $C^{\delta+}$. In common with Verkade *et al.*⁴ we favour a solvent cluster model in which the solute is enclosed in a cage of slightly organised hexafluorobenzene mole-

polarisation and electric birefringence measurements were made on solutions (in C_6F_6) of the highly polar solutes trimethylamine-borane and NNN'N'-tetramethylethylenediaminezinc(II) chloride. The dipole moments so obtained, 4.5 and 8.2 D, respectively, are in reasonable accord with values previously extracted from measurements in dioxan and in benzene.^{15,16} The apparent solute molar Kerr constants (at infinite dilution) are, however, markedly solvent dependent; $\Delta_m K$ [*i.e.* $mK(C_6F_6) - mK$ ('inert' solvent)^{15,16}] is -223×10^{-12} for trimethylamine-borane and $+5000 \times 10^{-12}$ for NNN'N'-tetramethylethylenediaminezinc(II) chloride. For each solute the mK is sensitively affected by solute-aromatic solvent interactions; the corresponding $\Delta_m K$ values in benzene^{15,16} are respectively -240×10^{-12} and -2200×10^{-12} . With trimethylamine-borane the observed molar Kerr constant in hexafluorobenzene can reasonably be explained in terms of the time-averaged solvent cage model, with favoured solute-solvent encounters, proposed from the n.m.r. evidence. The integrated effect of edge-on approaches A, B, *etc.* (in Figure 2) for all the carbon-bonded hydrogen atoms could result in a negative $\Delta_m K$ increment of the magnitude observed. Angular dispositions such as C do not greatly affect the mK value; D is unlikely to be favoured on electrostatic grounds. In the case of NNN'N'-tetramethylethylenediaminezinc(II) chloride, solvation by hexafluorobenzene must result in an overall large effective increase in polarisability in the direction of the solute dipole vector more so than in directions perpendicular to that axis, *i.e.* approaches in which the C_6F_6 aromatic ring planes are parallel or nearly parallel to μ should be relatively favoured. Since μ is very large, dipole-induced dipole interactions may become very important

¹⁵ M. J. Aroney, R. J. W. Le Fèvre, and H. J. Vaughan, *J. Chem. Soc. (A)*, 1970, 2224.

¹⁶ R. S. Armstrong, R. J. W. Le Fèvre, G. J. Peacock, and K. R. Skamp, *J.C.S. Dalton*, 1973, 1132.

¹⁴ C. L. Cheng, D. S. N. Murthy, and G. L. D. Ritchie, *Mol. Phys.*, 1971, 22, 1137.

and could lead to a predominance of encounters E in Figure 3. This would, at least in part, account for the appreciable downfield shifts of the methylene protons as well as the somewhat smaller deshielding of the methyl

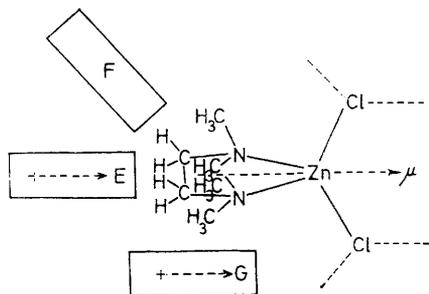


FIGURE 3 Hexafluorobenzene-*NNN'*-tetramethylethylenediaminezinc(II) chloride interactions

hydrogen atoms. Approaches F also would deshield the methylene protons but would not contribute greatly towards $\Delta_m K$; if the angular disposition of these becomes near perpendicular to μ then from the Langevin-

Born equations,⁷ they lead to a negative $\Delta_m K$ value. Parallel orientations such as G increase $\Delta_m K$ but also lead to upfield shifts so they are probably not important. Clear evidence for the inadequacy of the 1:1 complex model is provided by the fact that the greatest (most positive) possible molar Kerr constant calculable for such a complex is 2100×10^{-12} , far short of that observed. We propose that within the solvating cluster of C_6F_6 molecules about this solute, orientations E and probably F are more favoured than other approaches. The Cl atoms near the negative end of the solute dipole also interact with other C_6F_6 molecules through $Cl \cdots F$ and $Cl \cdots \pi$ electron repulsions and possibly also through weak $Cl \cdots C^{\delta+}$ attractions; these effects must lead to time-averaged ordering of solvent molecules such that the aromatic planes are parallel more so than perpendicular to μ (solute) in order to contribute towards the large positive $\Delta_m K$.

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