Unusual Behavior of Hexafluorobenzene and Benzene in the Aromatic Nuclear Magnetic Resonance Shift Effect

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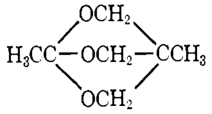
Abstract: In addition to the expected upfield chemical shifts of the protons near the positive end of dipolar polycyclic molecules such as $HC^{\delta-}(OCH_2)_3C^{\delta+}CH_3$ in benzene, strong downfield shifts are observed for the proton at the negative end. Evidence is presented for postulating that the solvent molecules responsible for the upfield shifts are not responsible for the downfield shifts and that separate solvent molecules must be interacting at the negative end of the solute dipole. A solvent clustering model is proposed in which the relatively positive peripheries of more than one benzene molecule are preferentially attracted by the symmetrical oxygen lone-pair electron charge surrounding the deshielded proton. Upfield and downfield shifts (where applicable) in benzene are also recorded for $P(H_3CNCH_2)_3CCH_3$, $Y(OCH_2)_3CCH_3$ (where Y = H_3CC, P, and As), and $Y(OCH)_3(CH_2)_3$ (where Y = HC, H_3C, P, and As) and the results interpreted in terms of a similar model. Temperature dependence studies of these shifts in toluene for several of these derivatives suggest that the interactions are relatively strong ($\Delta H \cong 1.8$ kcal/mol) compared with other such measurements in the literature. Aromatic shifts in nitrobenzene, pyridine, and toluene are also reported for several cases. In hexafluorobenzene a new aromatic shift phenomenon is observed which causes strong downfield shifts of protons at the positive solute site and upfield shifts of the protons in the negative region of the solute. This reversal from the benzene effect is interpreted in terms of a solvent cluster model in which the solute dipole reverses itself in the solvent cage because of preferential attraction of the positive end of the solute dipole for the relatively negative peripheral fluorines on the solvent ring. The possibility of reinforcement of the aromatic solvent shift by an electric field effect from the polar C–F bonds in the solvent is also taken into account. The unusual shift effects are attributed to the unique rigidity and symmetry of the dipolar solutes.

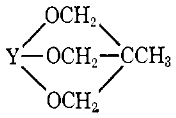
The generally accepted picture of the aromatic shift effect is one in which the aromatic solvent is preferentially oriented with its π electron cloud toward an electron deficient center on a solute molecule in a time-averaged collision complex which involves one or more solvent molecules.[2] Protons in the solute which are close to the center of the ring of the aromatic solvent molecule are shielded while protons near the periphery of the aromatic ring are deshielded. The orientation effect produced by the attraction of aromatic π clouds and positive ends of solute dipoles is enhanced by mutual repulsion of the π cloud and the negative end of the solute dipole although the solute dipole axis need not necessarily be perpendicular to the plane of the solvent molecule.

There appears to be no evidence reported for the orientation of aromatic molecules such as benzene with their relatively positive peripheries toward negative sites on the solute. Protons in the vicinity would then be expected to become deshielded. Although there is no reason to doubt that such orientation events occur, the structural nature of the general solute molecule precludes a sensor proton from being correctly positioned for the expected deshielding. Heretofore, deshielded solute protons were interpreted to arise from their proximity to the periphery of an aromatic nucleus which experiences π cloud orientation from a positive center on the solute.[2] In this paper we report evidence which strongly suggests that protons at the negative ends of dipolar polycyclic molecules of the type shown below are substantially deshielded because of orientation of the relatively electrophilic periphery of aromatic solvents by the nucleophilic end of the solute.

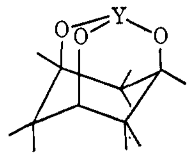


Dipolar polycyclic systems of this type also display a new type of aromatic shift phenomenon in hexafluorobenzene. Protons at the positive end of the dipole are strongly *deshielded* in this solvent while those at the negative end are *shielded*. The reversal of the normal aromatic shift effect is interpreted in terms of preferential orientations of the C_6F_6 molecules in a manner opposite to that of the usual aromatic solvents, provided the diamagnetic anisotropy of the C_6F_6 molecule is in the same sense as in its hydrocarbon parent.

Aromatic shift results for the ten polycycles represented below are reported and compared with the two open-chain analogs $HC(OCH_3)_3$ and $P(OCH_3)_3$. Studies of the temperature dependence of three polycycles



Y = HC, H_3CC, P, As,
$H_3CC(OCH_2)_3P$
$P(H_3CNCH_2)_3CCH_3$



Y = HC, H_3CC, P, As

were carried out in order to obtain a measure of the thermodynamic parameters involved in the interactions. The apparent high degree of influence of these polycycles on aromatic solvents is discussed in terms of their symmetry, rigidity, and unique dipolar nature.

Experimental Section

Proton chemical shifts were measured on a Varian A-60 nmr spectrometer equipped with a variable temperature probe. Chemical shifts were obtained on solutions (~3%) for which further dilution produced no detectable changes. Tetramethylsilane (~5%

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[1] American Chemical Society Petroleum Research Foundation Fellow.

[2] J. Ronayne and D. H. Williams, *Annu. Rev. NMR Spectrosc.*, 2, 83 (1969).

v/v) was used as the internal standard. Frequency calibration was provided by the use of standard side-band techniques employing a Hewlett-Packard Model 200 CD audio frequency oscillator as well as a Hewlett-Packard Model 521 CR frequency counter. Chemical shifts are believed accurate to ±0.1 Hz. Temperature calibration was accomplished by measuring the chemical shift of the hydroxyl proton with respect to either the methyl or methylene resonances for methanol or ethylene glycol, respectively, at each temperature, and obtaining the value of the temperature from the plot of chemical shift *vs.* temperature supplied by Varian in the A-60 operating manual. The temperature stability of this system is reported to be ±1°.

The polycycles $HC(OCH_2)_3CCH_3$,[3] $P(OCH_2)_3CCH_3$,[4] $As(OCH_2)_3CCH_3$,[5] $H_3CC(OCH_2)_3P$,[6] $P(H_3CNCH_2)_3CCH_3$,[7] $HC(OCH)_3(CH_2)_3$,[8] and $P(OCH)_3(CH_2)_3$[4] were prepared as described before.

2,8,9-Trioxa-1-arsaadamantane, $As(OCH)_3(CH_2)_3$. *cis*-1,3,5-Trihydroxycyclohexane (10 g, 75.8 mmol), prepared by the method of Stetter and Steinacker,[9] and 300 ml of dry tetrahydrofuran were placed in a 1-l. three-neck flask equipped with a stirrer, two 125-ml addition funnels, and a nitrogen flushing system. In one addition funnel was placed 18.35 ml (227.4 mmol) of pyridine and 6.35 ml (75.8 mmol) of arsenic trichloride was placed in the other. After the contents of both funnels were diluted to 50 ml with tetrahydrofuran, the solutions were simultaneously added over a period of 30 min while stirring under an atmosphere of nitrogen. The reaction mixture was stirred at room temperature for 2 hr after the addition and then filtered under nitrogen. The filtrate was evaporated to dryness and the residue extracted with anhydrous ether. After evaporation of the ether, the crystalline residue was sublimed at 70° and 0.02 mm yielding 9.1 g (59% yield) of colorless crystals having a melting point of 215–216°. The arsenite is soluble in most organic solvents but immediately hydrolyzed in water.

Anal. Calcd for $C_6H_9O_3As$: C, 35.32; H, 4.45. Found: C, 35.62; H, 4.53.

1,4-Dimethyl-2,6,7-trioxabicyclo[2.2.2]octane. A mixture of 50.0 g (0.42 mmol) of trimethyl orthoacetate and 50.0 g (0.42 mmol) of 2-hydroxymethyl-2-methyl-1,3-propanediol was heated to 100° while stirring under an atmosphere of nitrogen. A few drops of concentrated H_2SO_4 were added and the methanol removed under vacuum while heating at 75°. As soon as crystals began to sublime to the upper regions of the flask, a cold finger was inserted and heating under vacuum continued until 18 g of product (representing a 32% yield) had sublimed onto the cold finger. The product was resublimed before use.

Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.38. Found: C, 58.49; H, 8.45.

Discussion

^1H Nmr Spectra. The nmr spectral features of the bicyclooctane and adamantane systems are straightforward. The CCH_3 ^1H resonances in $HC(OCH_2)_3CCH_3$,[3] $H_3CC(OCH_2)_3CCH_3$ (Figure 1b), $P(OCH_2)_3CCH_3$,[4] $As(OCH_2)_3CCH_3$,[10] $H_3CC(OCH_2)_3P$,[7] $H_3CC(OCH)_3(CH_2)_3$ (Figure 1a), and $P(H_3CNCH_2)_3CCH_3$[7] appear as singlets except for the last compound in which the NCH_3 protons are split by phosphorus ($^3J_{PH}$ = 17 Hz).[7] The methylene protons are not detectably coupled to other nuclei in the arsenite and in $H_3CC(OCH_2)_3CCH_3$, are only slightly coupled to the orthoformyl proton ($^4J_{HH} \sim 0.2$ Hz)[3] in the orthoformate, and are substantially coupled to the phosphorus in the phosphite ($^3J_{PH}$ = 1.8 Hz),[10] phosphine ($^2J_{PH}$ = 8 Hz),[7] and aminophosphine ($^3J_{PH}$ = 3.5 Hz).[7]

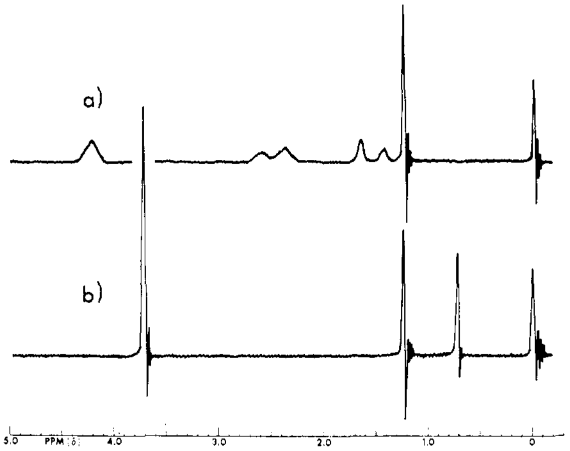

Figure 1. Proton nmr spectra of $H_3CC(OCH)_3(CH_2)_3$ (a) and $H_3CC(OCH_2)_3CCH_3$ (b). Spectral features are discussed in the text.

The methylene protons in $CH_3C(OCH)_3(CH_2)_3$ (Figure 1a), $HC(OCH)_3(CH_2)_3$, $P(OCH)_3(CH_2)_3$, and $As(OCH)_3(CH_2)_3$ give slightly coupled AB patterns arising from their geminal axial and equatorial environments.[10] The AB four-line spectra also contain fine structure arising from coupling to other protons as well as phosphorus in the case of the phosphite.[10] Separation of the two doublets in the spectra is sufficient in all cases to warrant consideration of these systems as essentially AX. Reading the chemical shifts of the axial and equatorial doublets directly from the spectra rather than calculating them in the standard manner results in a 0.03 ppm error which is considered inconsequential in this study. Tentative assignment of the upfield and downfield doublets to the axial and equatorial positions, respectively, stemmed from decoupling experiments, solution dielectric effects, and analogy with other substituted cyclohexanes and acetylated sugars.[10] It was noted, however, that electric field effects due to a solute point dipole and reaction field influences from the solvent were in conflict with this assignment.[10]

The equatorial methine protons in the adamantane molecules appear downfield of the methylenes and they are coupled to the equatorial methylenes ($^3J_{HH}$ = 2.7 Hz) and the axial methylenes ($^3J_{HH}$ = < 1 Hz), as well as to phosphorus ($^3J_{PH}$ = 6.3 Hz) in the phosphite.[10] In the orthoformate, slight coupling with the orthoformyl proton was also observed ($^4J_{HH} \sim 0.2$ Hz) *via* decoupling experiments.[3] Owing to their more acidic nature, the orthoformyl protons in $HC(OCH_2)_3CCH_3$ and $HC(OCH)_3(CH_2)_3$ appear furthest downfield.

Structural Considerations. Because the interpretation of our results depends upon the dipolar nature of the polycyclic molecules, some salient features of their structures are now pointed out. That the configurations of the atoms in these systems are well approximated by the schematic representations below has been shown by X-ray crystallographic studies on $OP(OCH_2)_3CCH_3$,[11] $[Ni[P(OCH)_3(CH_2)_3]_5](ClO_4)_2$,[12] and $SP(OCH)_3(CH_2)_3$.[13] Measured dipole moments of the

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(3) E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Amer. Chem. Soc.*, **88**, 1140 (1966).

(4) J. G. Verkade, T. Huttemann, M. Fung, and R. W. King, *Inorg. Chem.*, **4**, 83 (1965).

(5) J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, **25**, 663 (1960).

(6) E. J. Boros, R. D. Compton, and J. G. Verkade, *Inorg. Chem.*, **7**, 165 (1968).

(7) B. L. Laube, R. D. Bertrand, G. A. Casedy, R. D. Compton, and J. G. Verkade, *ibid.*, **6**, 173 (1967).

(8) H. Stetter, *Chem. Ber.*, **86**, 790 (1953).

(9) H. Stetter and K. Steinacker, *ibid.*, **85**, 451 (1952).

(10) J. G. Verkade, R. W. King, and C. W. Heitsch, *Inorg. Chem.*, **3**, 884 (1964).

(11) D. M. Nimrod, D. R. Fitzwater, and J. G. Verkade, *J. Amer. Chem. Soc.*, **90**, 2780 (1968).

(12) E. F. Riedel and R. A. Jacobson, Abstracts of the Meeting of the American Crystallographic Association, Minneapolis, Minn., 1967, p 10.

(13) B. P. Block, J. Simkin, and L. R. Ocone, *J. Amer. Chem. Soc.*, **84**, 1749 (1962).

Table I. Dipole Moments[a] of Bicyclooctane and Adamantane Molecules in CCl_4 and C_6H_6

Compound	μ (+0.05 D)	
	CCl_4	C_6H_6
$HC(OCH_2)_3CCH_3$	3.21	3.19
$H_3CC(OCH_2)_3CCH_3$	2.76	2.71
$H_3CC(OCH_2)_3P$	1.53	1.54
$P(OCH_2)_3CCH_3$	4.12	4.13
$As(OCH_2)_3CCH_3$	2.64	2.68
$P(H_3CNCH_2)_3CCH_3$	1.62	*b*
$HC(OCH)_3(CH_2)_3$	*b*	3.34
$H_3CC(OCH)_3(CH_2)_3$	*b*	2.94
$P(OCH)_3(CH_2)_3$	4.48	4.42
$As(OCH)_3(CH_2)_3$	2.97	2.89

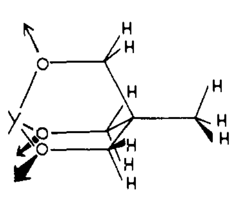
[a] At 25 ± 0.1°. [b] Not measured.

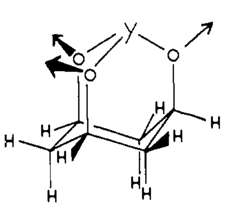
Table II. Proton Chemical Shifts of Bicyclooctane and Adamantane Molecules in CCl_4.

Compound	− end of μ	+ end of μ		
− +	δ H		δ CH_2	δ $(CH_2)_3$-CCH_3
$HC(OCH)_3(CH_2)_3$	5.31[a]		3.79	0.79
$H_3CC(OCH_2)_3CCH_3$	1.28[b]		3.77	0.77
$H_3CC(OCH_2)_3P$	1.23[b]		4.32	
$P(OCH_2)_3CCH_3$			3.86	0.72
$As(OCH_2)_3CCH_3$			3.95	0.63
$P(H_3CNCH_2)_3CCH_3$	2.47[c]		2.49	0.81
		δ OCH	δ CH_{eq}	δ CH_{ax}
$HC(OCH_2)_3CCH_3$	5.28[a]	4.24	2.65	1.65
$H_3CC(OCH)_3(CH_2)_3$	1.25[b]	4.25	2.53	1.57
$P(OCH)_3(CH_2)_3$		4.20	2.99	1.82
$As(OCH)_3(CH_2)_3$		4.24	3.02	1.79

[a] Refers to *H*C(O). [b] Refers to H_3CC(O). [c] Refers to H_3CN.

compounds investigated appear in Table I. The OC bond moments undoubtedly entail a relatively negative charge near oxygen in the covalent bond which in the case of the orthoformates and orthoacetates is expected to vectorially sum to give overall molecular dipoles in the directions shown. The oxygen lone-pair vectors reinforce the molecular dipole because of their components along the C_{3v} axis toward the Y bridgehead group.[14,15] When Y is phosphorus or arsenic, the lone pairs of the latter further add to the dipoles of these molecules. The assignment of the direction of the overall molecular moment is supported by considering some group contributions to the overall moments of a few of the bicyclooctanes. The dipole moment of $H_3CC(OCH_2)_3P$ can be smaller than that of $H_3CC(OCH_2)_3CCH_3$ only if the H_3CCO_3 and $(CH_2)_3P$ contributions in the former are in opposite directions. The $(CH_2)_3P$ contribution is likely to be close to the value measured for $(CH_3)_3P$ (1.19 D),[16] wherein the moment is certainly expected to be toward the phosphorus lone pair. In fact, the differences in the moments of the orthoacetate in CCl_4 and C_6H_6 (Table I) and 1.19 D give values in reasonable accord with the measured moment of $H_3CC(OCH_2)_3P$. Similar arguments based on the moments of $P(OCH_2)_3CCH_3$, $As(OCH_2)_3CCH_3$, and $(CH_3)_3P$ quite reasonably predict the measured moments of $P(OCH_2)_3P$ and $As(OCH_2)_3P$.[17] The validity of this reasoning originates in the fact that the group contributions to the moment are fixed because of the rigid geometrics of these polycycles.





The ^1H chemical shift of the polycyclic solutes in CCl_4 are recorded in Table II and their upfield and downfield shifts in C_6F_6 and C_6H_6 are displayed in Table III. Although the direction of the shifts experienced by protons at the positive end of the dipole in C_6H_6 is not surprising, the magnitudes in the case of the phosphites (~1 ppm) are quite large when compared with the majority of such upfield shifts.[2] It is important to note for two reasons that the $(CH_2)_3CCH_3$ protons are drastically more shielded in C_6H_6 than the CH_2 protons. The first is that this observation tends to confirm our earlier assignments[10] of the equatorial and axial methylene proton chemical shifts in the adamantane molecules. The downfield methylene doublet is affected by C_6H_6 to about the same extent as the methine absorption (Table III) indicating that both types of protons are in the same geometrical environment in the adamantanes. Since the methine proton must be equatorial from geometrical constraints, the downfield doublet can be assigned to the equatorial methylene protons. In contrast, the $(CH_2)_3CCH_3$ protons in the bicyclooctanes are shielded the most in C_6H_6 and are furthest from the waist of the molecular dipole. A similarly large shielding might be expected for the axial protons in the adamantanes. Experimental observation of this predicted effect on the upfield methylene doublet (Figure 1a) leads us to conclude that this absorption must be assigned to the axial protons. The second reason for the importance of the $(CH_2)_3CCH_3$ and CH_{ax} sensitivity to aromatic shifts is brought out in the following discussion.

The shift to lower fields of the protons at the negative end of the dipoles is not easily explained by their proximity to the peripheral deshielding region of the benzene molecule(s) which are also responsible for the shielded protons at the positive site. Although this interpretation has been applied to certain steroidal systems,[2] Dreiding models show that the necessary geometries and distances involved are prohibitive. The untenability of this model for our systems becomes further apparent when it is realized that the π electrons of the aromatic solvent which are attracted by the positive end of the dipole will be repelled by the oxygen lone pairs, thus increasing the angle of attack of the C_6 axis of benzene with respect to the C_{3v} axis of the solute (see Figure 2). The above reason for postulating the necessity for different aromatic molecules in association with each end of these solutes is reinforced by the requirement that the C_6H_6 molecules at the positive end of the solute must be situated well toward the $(CH_2)_3CCH_3$ protons in order to shield them to a greater extent than the CH_2 protons. The slight deshielding of the "waist" protons in several cases suggests that

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(14) A. C. Vandenbroucke, E. J. Boros, and J. G. Verkade, *Inorg. Chem.*, 7, 1469 (1968).

(15) T. L. Brown, J. G. Verkade, and T. S. Piper, *J. Phys. Chem.*, 65, 2051 (1961).

(16) D. R. Lide, *J. Chem. Phys.*, 29, 914 (1958).

(17) J. R. Guyer, J. Rathke, and J. G. Verkade, *J. Org. Chem.*, in press.

Table III. Proton Chemical Shift Increments[a] from CCl_4 to C_6F_6 and C_6H_6 for Bicyclooctane and Adamantane Molecules

– +	C_6F_6	C_6H_6	C_6F_6	C_6H_6	C_6F_6			C_6H_6
	$\Delta\delta$ HC		$\Delta\delta$ CH_2		$\Delta\delta$ $(CH_2)_3CCH_3$			
$HC(OCH_2)_3CCH_3$	→ 0.61[b]	← 0.37[b]	→ 0.02	→ 0.27	← 0.16			→ 0.79
$H_3CC(OCH_2)_3CCH_3$	→ 0.41[c]	← 0.39[c]	← 0.02	→ 0.20	← 0.16			→ 0.72
$H_3CC(OCH_2)_3P$	→ 0.75[c]	← 0.25[c]	→ 0.03	→ 0.32				
$P(OCH_2)_3CCH_3$			← 0.06	→ 0.26	← 0.20			→ 0.90
$As(OCH_2)_3CCH_3$			→ 0.01	→ 0.24	← 0.15			→ 0.70
$P(H_3CNCH_2)_3CCH_3$	→ 0.07[d]	← 0.11[d]	→ 0.01	→ 0.02	← 0.15			→ 0.24
			$\Delta\delta$ OCH		$\Delta\delta$ CH_{eq}		$\Delta\delta$ CH_{ax}	
					C_6F_6	C_6H_6	C_6F_6	C_6H_6
$HC(OCH)_3(CH_2)_3$	→ 0.58[b]	← 0.49[b]	← 0.11	→ 0.29	→ 0.06	→ 0.21	← 0.21	→ 0.64
$H_3CC(OCH)_3(CH_2)_3$	→ 0.41[c]	← 0.41[c]	← 0.12	→ 0.24	→ 0.08	→ 0.25	← 0.22	→ 0.59
$P(OCH)_3(CH_2)_3$			← 0.05	→ 0.37	← 0.05	→ 0.36	← 0.25	→ 0.97
$As(OCH)_3(CH_2)_3$			→ 0.03	→ 0.21	→ 0.03	→ 0.19	← 0.23	→ 0.59

[a] → indicates upfield shift, ← indicates downfield shift. [b] Refers to $HC(O)$. [c] Refers to $H_3CC(O)$. [d] Refers to H_3CN.

these nuclei are in the deshielding region of the C_6H_6 ring associated with the positive region of the solute, although weak deshielding from the periphery of the aromatic rings at the negative end of the solute cannot be entirely ruled out. The larger upfield shifts observed for the bridging CH_2 protons in $P(OCH_2)_3CC_2H_5$ (0.34 ppm) and $P(OCH_2)_3CC_3H_7$ (0.38 ppm) support angular attack of C_6H_6 on the solute C_{3v} axis rather than collinearity of the solvent C_6 axis and the solute C_{3v} axis at the positive end of the solute. The increase in the effect on the CH_2 protons of the ethyl and propyl derivatives probably can be ascribed to a shifting of the clustered solvents to avoid the bulkier bridgehead substituents.

Clustering of the type postulated here for the benzene interaction with positive sites on dipolar solutes has been proposed previously by Stark and Brown[18] for organometallic compounds of the type $(CH_3)_nSnX_{4-n}$ (X = Cl, Br, and I). Fort and Lindstrom[19] also discussed clustering of solvent molecules at the positive region of the dipolar adamantyl halides to account for the weaker shielding of the methylene protons β to the halide compared to those in the γ and δ positions. We presently favor a similar ordering of solvent molecules at the positive sites in our systems and propose that further clustering takes place at the negative end of the dipole in such a manner as to allow orientation of the relatively positively charged peripheries of perhaps two or more solvent molecules toward the negative site while the π clouds of two or more different solvent molecules interact with the positive site. The main driving force for such time-averaged solvent–solute associations at the solute's negative site could be the high concentration of negative charge protruding from the solute molecule in the form of oriented oxygen lone-pair electrons. The centrally located protons on the bridgehead group are then in the best possible position to benefit from the solvent-orienting influence of the three oxygen lone pairs. This unique geometrical arrangement of sensor proton and electrical charge is not found in the vast majority of solutes and could account for the lack of previous observations of this kind.

Hexafluorobenzene does not appear to have been used heretofore in the study of aromatic shifts. The reason it was selected was to test our "solvent cluster" model of benzene (Figure 2) with a solvent which could form a similar cage of solvent molecules but in which the solute dipole could conceivably be reversed because of a negatively charged solvent periphery and a relatively positive charge on the aromatic ring carbons (Figure 3). If the aromatic shift effect persisted in C_6F_6 in the same "sense" as in C_6H_6, shielding could then be expected at the negative end of the solute provided the solvent ring carbons were sufficiently positive to be oriented despite the negatively charged π cloud. In the positive region of the solute, it was possible to expect deshielded protons provided approach of the C_6F_6 periphery was sufficiently close in view of the somewhat larger van der Waals radius of fluorine (1.35 Å) compared with hydrogen (1.2 Å). The directions of the shifts (Table III)

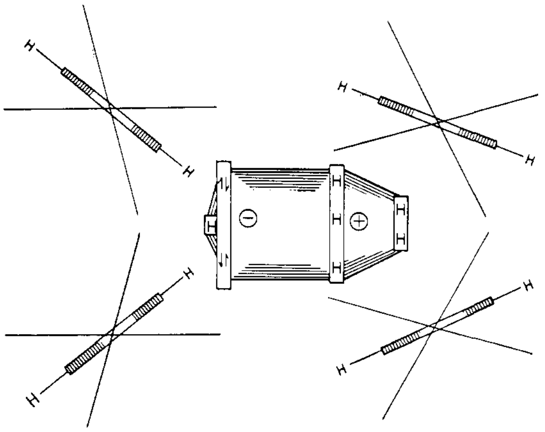

Figure 2. Schematic representation of the interactions of the shielding and deshielding regions of benzene molecules with protons at the charged ends of dipolar bicyclic solutes.

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(18) K. Stark and T. L. Brown, *J. Phys. Chem.*, **69**, 2679 (1965).
(19) R. C. Fort and T. R. Lindstrom, *Tetrahedron*, **23**, 3227 (1967).

Table IV. Proton Chemical Shifts of Bicyclooctane and Adamantane Molecules in Miscellaneous Solvents[a]

Compound	− end of μ	+ end of μ		
− +	δ H	δ CH$_2$	δ CCH_3	Solvent
$HC(OCH_2)_3CCH_3$	$\overleftarrow{5.44^{b}\ (0.13)}$	$\overleftarrow{3.93\ (0.14)}$	$\overleftarrow{0.80\ (0.01)}$	$C_6H_5NO_2$
	$\overleftarrow{5.60^{b}\ (0.29)}$	$\overrightarrow{3.46\ (0.33)}$	$\overrightarrow{0.07\ (0.72)}$	$C_6H_5CH_3$
	$\overleftarrow{5.74^{b}\ (0.43)}$	$\overleftarrow{3.86\ (0.07)}$	$\overrightarrow{0.55\ (0.24)}$	C_5H_5N
	5.31^{b}	3.74	0.76	n-C_6H_{14}
$H_3CC(OCH_2)_3CCH_3$	$\overleftarrow{1.45^{c}\ (0.17)}$	$\overleftarrow{3.92\ (0.15)}$	$\overleftarrow{0.78\ (0.01)}$	$C_6H_5NO_2$
	$\overleftarrow{1.55^{c}\ (0.27)}$	$\overrightarrow{3.52\ (0.25)}$	$\overrightarrow{0.08\ (0.69)}$	$C_6H_5CH_3$
	$\overleftarrow{1.60^{c}\ (0.32)}$	$\overleftarrow{3.86\ (0.09)}$	$\overrightarrow{0.55\ (0.22)}$	C_5H_5N
$P(OCH_2)_3CCH_3$		3.78	0.61	n-C_6H_{14}
		3.78	0.60	C_6H_{12}

[a] Values in parentheses represent shifts from CCl_4 as a solvent. The arrows have the same significance as in Table III. [b] Refers to *H*C(O). [c] Refers to H_3CC(O).

are in good agreement with this model (Figure 3) although as with benzene, small shifts in both directions are observed for protons near the waist of the molecular dipole. While the downfield shifts at the positive end of the dipole in C_6F_6 are decidedly smaller than the upfield shifts in C_6H_6, the upfield shifts in C_6F_6 in the negative region of the solute are up to three times larger than the downfield shifts in C_6H_6. The former phenomenon is not unexpected but the latter is surprising. Changes in the ^{31}P chemical shifts were negligible in benzene and hexafluorobenzene.

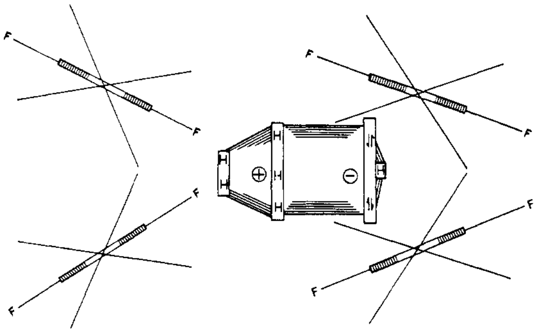
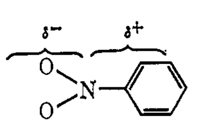
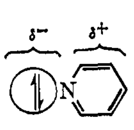


Figure 3. Schematic representation of the interactions of the shielding and deshielding regions of hexafluorobenzene molecules with protons at the charged ends of dipolar bicyclic solutes.

The apparent importance of the solute dipole in our models is highlighted by the aromatic shifts seen in Table IV for some bicyclooctane molecules in $C_6H_5NO_2$ ($\sim$4 D), C_5H_5N ($\sim$2 D), and $C_6H_5CH_3$ (0.4 D)[20] which are also appreciably polar. The interaction of the negative region of the solute dipole with the positive sites of these solvents is likely to be complicated by the localization of this charge on a few of the carbons in the ring near the polar functional group in the cases of nitrobenzene and pyridine. Nevertheless the angle of association appears to be such that substantial deshielding occurs in both cases at the negative end of the dipole. Although there may be some competition between the nitrogen lone pair and the π electrons in pyridine for the positive end of the solute dipole, it appears that the latter is dominant (Figure 4). In $C_6H_5NO_2$ a very different orientation seems to be occurring since both the CH_2 and $(CH_2)_3CCH_3$ protons are *deshielded* with the former even more so than the latter. Here the high concentration of negative charge on the oxygens in this more polar solvent may be more strongly attracted than the π cloud. The greater deshielding of the CH_2 protons could be due to their more acidic nature than the protons in the methyl of the $(CH_2)_3CCH_3$ group. Although the observed deshielding would be expected from the aromatic shift effect, hydrogen bonding may also play an important role in this case (Figure 4).





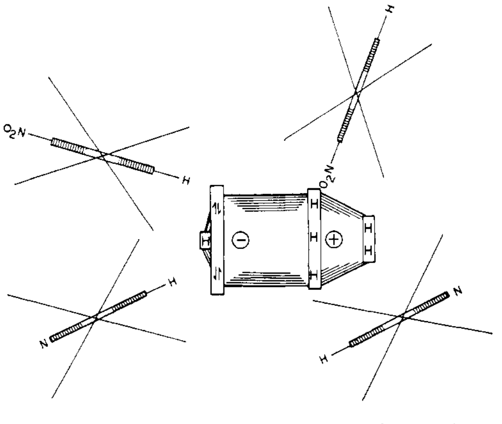


Figure 4. Schematic representation of the interactions of the shielding and deshielding regions of nitrobenzene and pyridine with protons at the charged ends of dipolar bicyclic solutes.

In the slightly polar $C_6H_5CH_3$ (Table IV) the downfield proton shift at the negative end is somewhat smaller than in C_6H_6 which is expected if the time-averaged close approach of the aromatic ring is impeded by the steric requirements of the methyl group. The upfield proton shifts in $C_6H_5CH_3$ in the positive solute region are appreciably smaller for the $(CH_2)_3CCH_3$ protons and substantially larger for the CH_2 protons in contrast

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[20] These are roughly average values estimated from the data given in A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

Table V. Calculated Parameters for Solute–Solvent Complex in Toluene

	$\mathrm{P(OCH_2)_3CCH_3}$	$\mathrm{HC(OCH_2)_3CCH_3}$		$\mathrm{HC(OCH)_3(CH_2)_3}$	
	$\mathrm{C}H_3$	$H\mathrm{C}$	$\mathrm{C}H_3$	$H\mathrm{C(O)}$	$\mathrm{C}H_{\mathrm{ax}}$
ΔH, kcal/mol	-1.76 ± 0.07	-2.44 ± 0.09	-1.70 ± 0.06	-1.85 ± 0.15	-1.41 ± 0.13
ΔS, eu	-4.75 ± 0.14	-6.9 ± 0.2	-4.9 ± 0.1	-5.9 ± 0.2	-4.6 ± 0.1
δ_c[a]	-66.6 ± 1.4	27.9 ± 0.5	-60.2 ± 0.7	37.8 ± 1.6	-61.1 ± 4.8
K at 27.5°	1.78	2.04	1.51	1.14	1.00
ΔG at 27.5°, kcal/mol	0.342	0.423	0.245	0.777	0.000
% complex formation	65	67	60	53	50

[a] δ_c is the chemical shift in toluene with respect to the value measured in *n*-hexane, except for $\mathrm{CH_{ax}}$, where it is with respect to the value measured in $\mathrm{C_6D_{12}}$.

to the situation in $\mathrm{C_6H_6}$ (Table III). This could be due to slight reorientation in the solvent cluster to accommodate the more bulky solvent methyl group.

In addition to accounting for the data, there are three reasons why we feel that polycycles of this sort promote $\mathrm{C_6H_6}$ and $\mathrm{C_6F_6}$ clustering in the manners we have proposed. (a) The polycycles are rigid and do not destabilize collision complexes because of conformational changes and free rotation of large groups. Thus in benzene the aromatic shift effects for $\mathrm{P(OC}H_3)_3$ ($\overrightarrow{0.11}$ ppm) and $\mathrm{HC(OCH_3)_3}$ (HC, 0.0 ppm; CH_3, $\overrightarrow{0.06}$) are negligible by comparison. (b) The polycycles studied are quite comparable in size to the aromatic solvents studied and thus might be expected to require several solvent molecules to surround them. (c) These polycycles behave as dipoles in which the group contributions are fixed geometrically. Thus although $\mathrm{P(OCH_3)_3}$ (1.83 D)[21] is even more polar than the orthoformate and orthoacetate polycycles (Table I), the aromatic shift is small in the phosphite.

That a dipole is necessary for observance of an appreciable aromatic shift is well established.[2] For instance the proton nmr spectra of adamantane in benzene and carbon tetrachloride are practically identical whereas they are not for the adamantyl halides.[19] In some cases the solute dipole moment or the solute dipole moment to molecular volume ratio has been found to be linear with the aromatic shift.[2] We find no linear relationships of this kind but most of the expected trends are quite reasonable. The aromatic shift effects on the $\mathrm{(CH_2)_3CC}H_3$ protons in $\mathrm{C_6H_6}$ and $\mathrm{C_6F_6}$ are seen to progress toward increased shielding and deshielding, respectively, as the dipole moment increases in the series $\mathrm{P(H_3CNCH_2)_3CCH_3} < \mathrm{As(OCH_2)_3CCH_3} < \mathrm{H_3CC(OCH_2)_3CCH_3} < \mathrm{HC(OCH_2)_3CCH_3} < \mathrm{P(OCH_2)_3CCH_3}$. A similar trend is seen for the axial proton in the increasingly dipolar series $\mathrm{As(OCH)_3(CH_2)_3} < \mathrm{H_3CC(OCH)_3(CH_2)_3} < \mathrm{HC(OCH)_3(CH_2)_3} < \mathrm{P(OCH)_3(CH_2)_3}$. These progressions are reasonable since solute shifts are expected to intensify with increased solute–solvent interactions. The erratic behavior of the methylene protons in the bicyclooctane compounds and the equatorial and methine protons in the adamantane systems with increasing polarity is somewhat expected since their locations near the weakly interacting middle region of the dipole probably make them more sensitive to weaker and less specific solvent interactions. In $\mathrm{C_6H_6}$, the increased deshielding of the methyl protons at the negative end of the solute dipole from $\mathrm{H_3C(OCH_2)_3P}$ to $\mathrm{H_3C(OCH_2)_3CCH_3}$ is expected from the polarity increase, but the decreased shielding in $\mathrm{C_6F_6}$ is not. No explanation for the latter observation is presently obvious although a shielding effect from another source may be partially responsible (see later).

A measure of the strength of solvent–solute interactions can be obtained by assuming a specific stoichiometry for the solvent–solute complex, usually 1:1. Although the validity of such an assumption has been criticized many times on the grounds that interaction with only one solvent molecule at a time is questionable, we have calculated the thermodynamic parameters ΔG, ΔH, and ΔS and the equilibrium constants for a number of cases (Table V) based on a 1:1 stoichiometry at each end of the dipole to gain some idea of the magnitudes of the interactions involved compared with other solute systems for which similar values have been obtained. The parameters in Table V were calculated by the method of Abraham[22] using a nonlinear least-squares curve fitting technique[23] to fit the dependent variable $1/\delta$ to the independent variable T and the parameters ΔH, ΔS, and $1/\delta_c$ in the equation

$$1/\delta = 1/\delta_c[e^{\Delta H/RT}e^{-\Delta S/R} + 1]$$

where δ is the observed chemical shift (Table VI) and δ_c is the chemical shift in the complexed form. Because of the expected very small effect of temperature on the chemical shifts of the equatorial and methine protons of $\mathrm{HC(OCH)_3(CH_2)_3}$ and the methylene protons of $\mathrm{P(OCH_2)_3CCH_3}$ and $\mathrm{HC(OCH_2)_3CCH_3}$, no thermodynamic parameters were calculated. Enthalpy values in the literature for upfield shifts range from -0.9 to -1.7 kcal/mol while ΔS ranges from -3.5 to -4.4 eu.[24] It is clear that the analogous shifts occurring at the positive ends of the dipoles in Table V yield ΔH and ΔS values which are on the upper ends of these ranges, suggesting relatively strong interactions. Moreover, the interactions at the negative ends are comparable.

Electric Field Effects. The origin of the shifts has generally been attributed to a ring current effect although the validity of this model has been contested on the basis of errors present in its derivation.[25,26] The rationalization has been put forth that nonlocal atomic anisotropies in an aromatic molecule are not averaged out because of their fixed orientations in the ring system and that this is the origin of the observed effects.[26] Another possible source of shielding and deshielding is the electric field effect of a bond dipole.[27]

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(21) B. A. Arbuzov and T. F. Shavsha, *Dokl. Akad. Nauk SSSR*, **84**, 507 (1952).

(22) R. J. Abraham, *Mol. Phys.*, **4**, 369 (1961).

(23) R. H. Moore and R. K. Ziegler, AEC Report LA-2367, Los Alamos Scientific Laboratory, Los Alamos, N. M., 1960.

(24) T. Ledaal, *Tetrahedron Lett.*, **14**, 1683 (1968).

(25) J. I. Musher, *J. Chem. Phys.*, **46**, 1219 (1967).

(26) J. I. Musher, *Advan. Magn. Resonance*, **2**, 177 (1966).

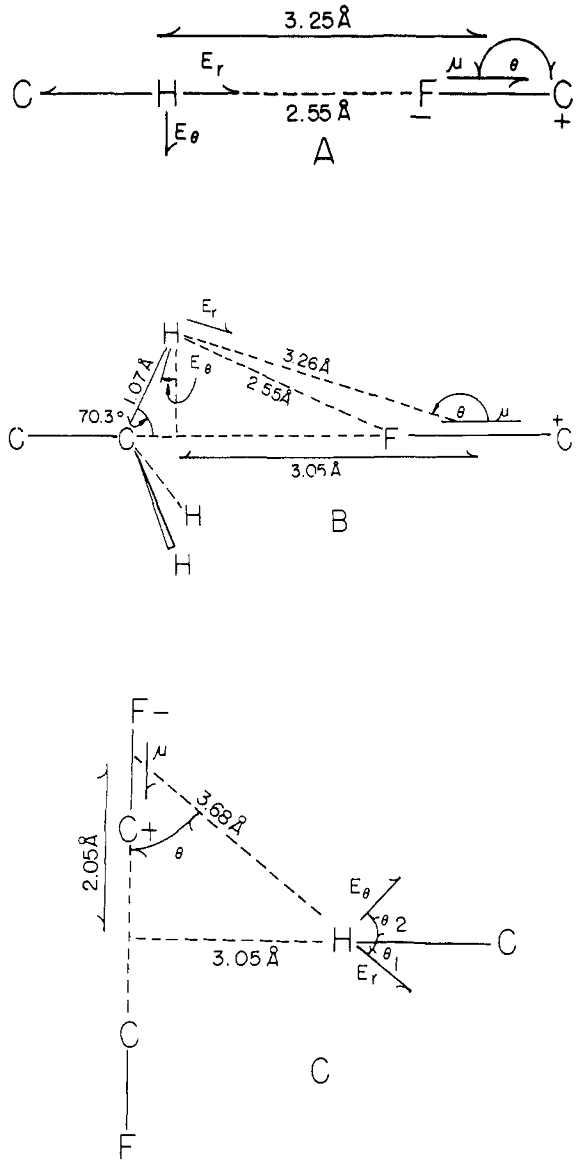

Figure 5. Three possible geometries for the interactions of the point dipolar electric field of a CF bond with a proton attached to carbon.

To examine the possible effect of the C–F and C–H bond dipoles in hexafluorobenzene and benzene on a sensor proton in a solute, three extreme geometric interactions were chosen for calculation and are shown in Figure 5 for hexafluorobenzene.

Buckingham states that the effect of a dipolar electric field on the chemical shift of a proton attached to carbon is essentially given by $|\Delta\sigma| = 2 \times 10^{-12}E_z + 10^{-18}E^2$ where E_z is the component of the electric field along the CH bond. The problem involves determining the component of the electric field along the CH bond (E_z) due to a point dipole assumed to be half way along the CF bond. The radial component of the dipole electric field is given by $E_r = 2\mu \cos \theta/r^3$ and the tangential component is given by $E_\theta = \mu \sin \theta/r^3$, where θ is the angle between the point dipole and the radius vector from the point dipole to the proton.[28] If the component of the dipole electric field is in the C→H direction then the ^{1}H nucleus will be deshielded, while if the component is in the H→C direction, the proton will be shielded.

The distances employed throughout are considered to be the distance of closest approach—the sum of the van der Waals radii for the interacting atoms.[29] Furthermore, the bond dipole for the CF bond (2.0 D) is calculated from the dipole moment of fluorobenzene (1.6 D),[20] in which the negative end is assumed toward fluorine.

Case A represents a geometry in which the CF bond is collinear with the CH bond. Such a situation might occur in the interaction of hexafluorobenzene with one of the methyl protons at the positive end of the molecules under consideration. The association may be due to either a hydrogen bonding mechanism or a dipole–induced dipole interaction. In any event, $E_\theta = 0$, since $\sin 180° = 0$, and $E_z = 1.17 \times 10^5$ esu/cm^3 = E_r. Therefore, $\Delta\sigma = 0.23 \times 10^{-6}$ or 0.23 ppm which is 14 Hz at 60 MHz. Since the component of the dipolar electric field points toward the hydrogen atom, the effect will be to deshield the hydrogen.

Case B is an attempt to determine the effect of the CF bond dipole upon the chemical shift of the protons of a methyl group, assuming the CF bond is collinear with the threefold axis of the methyl group. The angles at carbon were assumed tetrahedral. It can be shown that E_θ makes an angle of only 1° 26′ with the CH bond axis, hence the radial component of the dipolar electric field has a negligible component along the CH bond axis and the component of E_θ along the CH bond axis is essentially E_θ. Since θ is 160° 30′, E_θ is 1.72×10^4 esu/cm^3 toward carbon. This gives a $\Delta\sigma$ of 0.03×10^{-6} that is shielding, and represents 1.8 Hz at 60 MHz.

Model C represents the case of a proton at the negative end of the dipole interacting with the π cloud of the hexafluorobenzene ring such that the CH bond is perpendicular to the plane of the carbon atoms. The half-thickness of the electron cloud is taken to be that for benzene which is thought to be about 1.85 Å. The angle is 56°, $E_r = 4.45 \times 10^4$ esu/cm^3, and E_θ is 3.31×10^4 esu/cm^3. Employing angles θ_1 and θ_2 which are 34° and 56°, respectively, the component of E_r along the CH bond is 3.78×10^4 esu/cm^3 and the component of E_θ along the CH bond is 1.85×10^4 esu/cm^3. This gives a $\Delta\sigma$ of 0.11×10^{-6}. Since there are six such CF bonds symmetrically distributed about the CH bond, the contributions of all six should add to give the total effect. This would result in a shielding of 0.66 ppm which is 39.5 Hz at 60 MHz.

By performing these calculations employing the bond dipole of 0.4 D with negative end at the hydrogen[30] in benzene and a proton–proton interaction distance in cases A and C of 2.4 Å (the sum of the van der Waals radii), it can be shown that for the three cases of Figure 5 the $\Delta\sigma$'s are about one-fifth that for hexafluorobenzene as a consequence of the lower moment of the C–H bond dipole and the slightly different bond distances and van der Waals radii involved. The direction of these effects is the same as that for hexafluorobenzene. It

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[27] A. D. Buckingham, *Can. J. Chem.*, 38, 300 (1960).

[28] E. R. Peck, "Electricity and Magnetism," McGraw-Hill Book Inc., New York, N. Y., 1953.

[29] L. Pauling, "The Nature of the Chemical Bond and the Structure of Molecules and Crystals," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

[30] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, N. Y., 1959.

Table VI. Data for the Chemical Shifts (Hz) from Internal TMS of the Protons in Some Bicyclic Molecules as a Function of Temperature in Toluene[a]

	$P(OCH_2)_3CCH_3$		$HC(OCH_2)_3CCH_3$			$HC(OCH)_3(CH_2)_3$		
Temperature	CH_2	CH_3	H–C	CH_2	CH_3	HC(O)	CH_{ax}	CH_{eq}
−70.0	198.3	22.2	344.3	206.6	10.0	356.5	48.5	150.0
−50.0	199.2	18.3	343.0	206.6	7.1	353.0	53.5	148.8
−31.0		15.2	341.8	207.3	4.6	350.6	56.5	150.5
−17.2	200.8	13.0	340.1	207.0	1.6	348.3	59.0	151.0
+2.5	202.2	9.6	338.2	205.3	+1.7	346.3	61.5	151.0
+14.0	203.1	7.8	337.5	207.3	+3.2	345.4	62.5	150.5
+27.5	203.9	5.8	336.4	210.1	+5.0	343.9	64.0	150.5
+37.0	204.6	4.6		208.2	+6.4	343.4	66.0	152.0
+48.0	205.2	3.1	334.6	210.6	+7.8	342.1	67.0	152.5
+61.0	206.0	1.3	333.6	211.2	+9.1	341.2	68.0	153.0
+75.0	206.4	0.9	332.5	211.8	+11.1	340.5	69.0	152.5
+89.0	206.2	+2.6	331.7	211.4	+12.4	339.0	70.5	152.5
+103.0	207.7	+4.0	330.6	211.5	+13.5	338.6	72.0	153.0

[a] Chemical shifts are negative (downfield) unless indicated otherwise. The concentration of solute was in all cases less than 3% wt/v. Temperatures are °C and are accurate to ±1°.

must be remembered, however, that models A and B involve the negative end of the solute dipole whereas model C involves the positive end when benzene interacts. This reversal is necessary to be consistent with the experimental results discussed above.

From the calculations it is apparent that model A could account for the deshielding in hexafluorobenzene experienced by a proton at a positive site. Moreover, the result for model C is consistent with the magnitude of the shielding in this solvent of a proton at a negative site. Although it is presently not possible to determine the extent of the C–F dipole and ring anisotropy effects in hexafluorobenzene, it is reasonably safe to conclude that the C–H dipole effect is negligible in the case of benzene principally because of the smaller C–H bond moment. That there should be some anisotropy effect in hexafluorobenzene similar to that in benzene is supported by the measured magnetic anisotropy of hexachlorobenzene which[31] is in the same sense as that of benzene. Although the molar Kerr constant of hexafluorobenzene has not been measured, it is highly likely[32] that it will be consistent with that of hexachlorobenzene and benzene.[33]

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(31) K. S. Krishnan and S. Banerjee, *Trans. Roy. Soc. London*, **A234**, 265 (1935).

(32) R. J. W. Le Févre, personal communication.

(33) R. J. W. Le Févre, D. S. N. Murthy, and P. J. Stiles, *Aust. J. Chem.*, **22**, 1421 (1969).