

Aromatic Solvent-Induced Shift Behavior of Borane Adduct Hydrogen-1 and Fluorine-19 Nuclei in Benzene and Hexafluorobenzene

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Received March 14, 1972

Abstract: Hydridic protons of the borane moiety in H_3BPR_3 and H_3BNMe_3 are shifted 0.6–0.9 ppm downfield in C_6D_6 and 0.3–0.5 ppm upfield in C_6F_6 compared to CCl_4 . These results demonstrate for the first time that the commonly observed ASIS effect (*i.e.*, upfield shifts in benzene) can be reversed when the proton bears a partial negative charge. A collision complex model is proposed to account for these strong shifts and their opposite direction in the two solvents. The negative charge concentration on the fluorines in the series $H_3BPF_x(OMe)_{3-x}$ ($x = 1$ and 2) as well as in $H_3BPF_2(NMe_2)$ is apparently responsible for the downfield shifts (0.3–0.9 ppm) in C_6D_6 and upfield shifts in C_6F_6 (0.2–0.8 ppm) compared to CCl_4 .

A recent publication³ described the discovery of strong downfield shifts in benzene of protons at the negative end of dipolar polycyclic solutes of the type $HC(OCH_2)_3CMe$. In addition to the well-known upfield shift behavior in C_6H_6 of protons at the positive ends of dipoles, sizable downfield shifts were observed in C_6F_6 while protons at negative ends were shifted upfield in this solvent.³ The opposite character of the aromatic solvent-induced shift (ASIS) phenomenon at dipolar *extrema* in benzene was rationalized by invoking solvent–solute collision complexes in which the aromatic solvent tended to orient its shielding negative π -cloud region toward the positive end of the dipole while the deshielding relatively positive peripheral edge of a C_6H_6 molecule tended to be attracted to the negative charge concentration of the dipole. The reversal of these shifts in C_6F_6 was ascribed to opposite solvent orientations at each end of the solute dipole owing to the stronger polarity of CF bonds compared to CH bonds in the aromatic solvents. It was concluded that three factors were involved in promoting clustering of aromatic solvents: (a) the rigidity of the polycyclic solutes, (b) the comparable size of solute and solvent molecules, and (c) the geometrically fixed group contributions to the solute dipole.

The study described herein of the ASIS effects for a series of BH_3 adducts was undertaken for three reasons. First, these compounds afforded the opportunity to study polar solutes which are substantially less geometrically constrained but which are still approximately the same size as the polycyclic systems studied earlier.³ Second, the fluorophosphine adducts made it possible to ascertain the tendency of the ^{19}F nucleus to display the ASIS effect. Third, borane adducts possess relatively hydridic protons compared to $HC(OCH_2)_3CMe$ or $H_3CC(OCH_2)_3CMe$, for example. While borane adduct hydrogens typically appear from 0 to 1.5 ppm, the rather acidic orthoformyl proton absorbs at 5.31 ppm and the orthoacetyl protons absorb at 1.28 ppm in

nonaromatic solvents. Thus the positive regions of aromatic solvents are directed toward the orthoformyl and orthoacetyl protons because of the negative lone-pair density on the oxygens since the acidic protons would tend to repel them. It was important, therefore, to determine if hydridic protons in the borane adducts would attract the positive regions of aromatic solvents, inasmuch as two of the compounds (H_3BPHMe_2 and H_3BNMe_3) have no lone pairs.

Experimental Section

With the exception of Me_3NBH_3 (kindly supplied by Dr. C. W. Heitsch) the compounds were prepared as described earlier.⁴ Nmr samples were prepared by the usual vacuum line techniques or in a nitrogen atmosphere using degassed solvents. Proton magnetic resonance spectra were obtained on either a Varian Associates A-60 or Hitachi Perkin-Elmer R-20B spectrometer operating at 60 MHz. The ^{19}F spectra were obtained on a Varian Associates HR-60 spectrometer operating at 56.4 MHz. The PH and BH_3 proton chemical shifts are believed accurate to ± 0.05 ppm, the ^{19}F shifts to ± 0.1 ppm, and the CH_3 proton shifts to ± 0.01 ppm. Details of the nmr spectra appear in another paper.⁴ Interestingly, the coupling constant $^3J_{FPH}$ is approximately equivalent to $^2J_{FPH}$ (*ca.* 18 Hz) in all the fluorine-containing compounds. The 1H and ^{19}F chemical shifts in CCl_4 are listed in Table I and the ASIS effects

Table I. 1H and ^{19}F Chemical Shifts in CCl_4 ^a

	δCH_3	δF	δBH_3
H_3BPHMe_2 ^b	1.37		0.33
$H_3BP(OMe)_3$	3.68		0.22
$H_3BPF(OMe)_2$	3.80	–69.9	0.33
$H_3BPF_2(OMe)$	3.95	–63.9	0.50
$H_3BPF_2(NMe_2)$	2.80	–73.8	0.53
H_3BNMe_3	2.62		1.42

^a Negative shifts refer to those upfield of the internal references which were TMS for proton and $CFCl_3$ for fluorine spectra. ^b $\delta PH = 4.70$ ppm.

relative to CCl_4 are set forth in Table II. In order to observe the chemical shifts of the broad BH protons, 10% solutions were necessary. Only negligible changes in the spectra occurred on dilution to 3%, the concentration at which the previous studies were carried out.³

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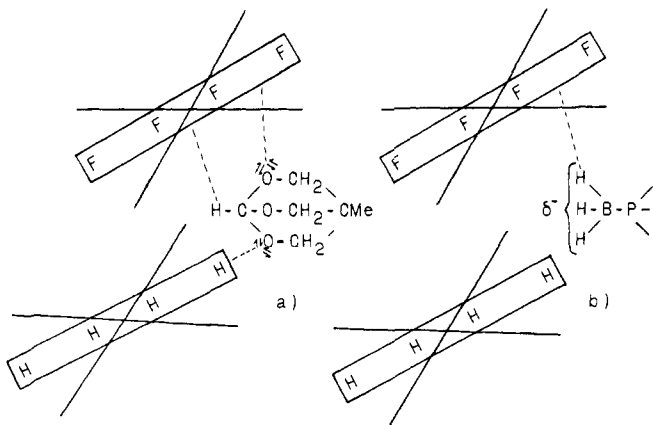


Figure 1. A representation of a favored C₆H₆ and C₆F₆ collisional interaction at the negative end of the dipolar solutes HC(OCH₂)₃-CMe (a) and adducts of the type H₃BPR₃ (b).

Table II. ¹H and ¹⁹F Chemical Shift Increments^a from CCl₄ to C₆F₆ and C₆D₆

	-ΔδCH ₃ -		-ΔδF-		-ΔδBH ₃ -	
	C ₆ F ₆	C ₆ D ₆	C ₆ F ₆	C ₆ D ₆	C ₆ F ₆	C ₆ D ₆
H ₃ BPHMe ₂ ^b	←	→			→	←
H ₃ BP(OMe) ₃	←	→			→	←
H ₃ BPF(OMe) ₂	←	→	→	←	→	←
H ₃ BPF ₂ (OMe)	←	→	→	←	→	←
H ₃ BPF ₂ (NMe ₂)	←	→	→	←	→	←
H ₃ BNMe ₃ ^c	←	→			→	←

^a → indicates upfield shift, ← indicates downfield shift. ^b ΔδPH is 0.03 (←) (C₆F₆) and 0.55 (→) (C₆D₆). ^c Similar shifts from dioxane to C₆H₆ and C₆F₆ were observed by R. J. W. LeFevre (private communication to J. G. V.).

Discussion

The downfield shifts of the BH₃ protons in C₆D₆ (Table II) are *ca.* 2–3 times those experienced by the orthoformyl or orthoacetyl protons in polycyclic compounds³ while the upfield BH₃ proton shifts in C₆F₆ are comparable. The extraordinary deshielding in benzene strongly indicates that, in contrast to the bicyclic ortho esters wherein the oxygen lone pairs are largely responsible for attracting the deshielding positive peripheries of benzene (Figure 1a), the hydridic BH₃ protons must be capable of promoting this interaction (Figure 1b). Borane adducts tend to be more polar than polycyclic ortho esters (H₃BNMe₃, 4.45, 4.62 D;⁵ H₃BP(OMe)₃, 4.07 D;⁶ HC(OCH₂)₃CMe, 3.19 D;³ H₃CC(OCH₂)₃CCH₃, 2.71 D³) and it might be concluded that the larger dipole could be largely responsible for the increased ASIS effect of the BH₃ protons in benzene. Two lines of evidence mitigate against this however. (a) The ASIS effects in C₆D₆ and C₆F₆ on the protons of the group V moiety (the positive end of the dipole) are quite comparable to those observed on the positive extreme of the polycyclic ortho ester dipoles³ even though the adducts are more polar. (b)

Among the polycyclic ortho esters studied, the magnitude of the molecular dipole moment does not appear to be of major importance.³ In fact, systems containing no net molecular dipole and only local polar regions display strong ASIS effects.⁷

In contrast to the unusually large downfield shifts of the BH₃ protons in C₆D₆, their upfield shifts in C₆F₆ are quite comparable to those observed for polycyclic ortho esters.³ The larger steric requirements of C₆F₆ may prevent the more efficient clustering necessary to allow the solvent carbon atoms to face the BH₃ protons (Figure 1b). On the other hand, the upfield shifts of the ortho esters³ due to the attraction of the oxygen lone pairs to the relatively positive carbons of C₆F₆ may be augmented by the simultaneous attraction of the acidic proton by the negative center of the π cloud (Figure 1a).

The present studies permit some elaboration of the factors (*cf.* introduction) which govern clustering of aromatic solvents around dipolar solutes. Although the ASIS effects of the adducts demonstrate that solute rigidity is not essential, it is of some importance, however, since open-chain analogs of polycyclic ortho esters generally show only negligible ASIS effects.^{3,7} It also appears from a comparison of ASIS effects in H₃BNMe₃ and H₃BP(OMe)₃ that geometrically fixed group contributions to the molecular dipole are not necessary for strong ASIS effects. Furthermore, our results on ASIS phenomena in coordination complexes show that solutes which are large compared to the aromatic solvent molecules can display sizable aromatic shifts even if they possess no net molecular dipole.⁷ It seems reasonable to conclude at this time that opposite ASIS effects caused by "face-on" and "edge-on" collision of solvent molecules to oppositely charged regions of a solute can occur in nonrigid systems provided that (a) the solute is large enough to accommodate both types of geometrical clustering and (b) the solute possesses either an overall dipole moment or, in the absence of a net moment, localized bond or group dipoles. Furthermore, protons which are acidic possess the same ASIS properties as hydridic hydrogens provided there is adjacent to the acidic hydrogen a properly oriented concentration of negative charge as in the polycyclic ortho esters.³

In contrast to POCH₃ or PCH₃ protons which experience aromatic shifts expected for locations in positive regions of local or molecular dipoles, the ¹⁹F nuclei bonded to phosphorus manifest ASIS effects which are the reverse in both solvents. The sizable downfield shift of the ¹⁹F nuclei in benzene for the adducts contrasts with the 0.04- and 0.23-ppm upfield shift reported for F₃CH in this solvent compared to CCl₄ and cyclohexane, respectively.⁸ To explain the fluoroform result, Smith and Ihrig⁸ invoked a model involving the interaction of the proton with the benzene π cloud *via* the sixfold axis of the solvent which accounts for the strong shielding (*ca.* 1 ppm) of the solute hydrogen. The benzene molecule in such a collision complex would then also be sufficiently close to the fluorines to account for their upfield shift in benzene.⁸ Our results suggest that the deshielding periphery of a benzene molecule(s) is attracted by the relatively high

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concentration of negative charge arising from the $(\delta^-)\text{F}-\text{P}(\delta^+)$ bond dipole and the fluorine lone pairs.

In the series $\text{H}_3\text{BP}(\text{OMe})_3$, $\text{H}_3\text{BPF}(\text{OMe})_2$, $\text{H}_3\text{BPF}_2(\text{OMe})$, the CH_3 and BH_3 protons produce increasing and decreasing ASIS effects, respectively, in both aromatic solvents. Increasing the electronegativity of phosphorus along the series by fluorine substitution of OMe groups would tend to render both the CH_3 and BH_3 protons more acidic and this is also reflected in the increased deshielding of these nuclei in the series (Table I). The reason for the opposite progression of the ASIS effect at fluorine for the last two members of

the series in C_6F_6 and C_6D_6 is not clear and it may be related to variations in solvent cluster geometries arising from differing steric requirements of the two solutes and/or a domination of van der Waals solute-solvent interactions.⁹

Acknowledgments. The authors thank the National Science Foundation (Grants GP-28684 and GP-8306) and the Robert A. Welch Foundation for financial support.

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Complexes of Nucleophiles with Rare Earth Chelates. I. Gas Chromatographic Studies^{1a} of Lanthanide Nuclear Magnetic Resonance Shift Reagents

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Abstract: The present study reports the retention of many different ethers, ketones, alcohols, esters, olefins, and alkanes by gas-chromatographic columns with liquid phases composed of solutions of tris- β -diketonate rare earth chelates in squalane. The dependence of the interaction on the nature of the organic solute, the nature of the chelate ligand, the radius of the metal ion, and the degree of polymerization was investigated. The more nucleophilic organic compounds, for example, tetrahydrofuran (THF), were found to undergo much stronger interaction with the metal chelates than the less basic solutes. The Er(III) chelates of fluorinated β -diketonates (for example, the new ligand 3-trifluoroacetyl-*d*-camphorate anion, facam) underwent a much greater interaction with the nucleophiles than similar nonfluorinated Er(III) compounds. The retention time of THF increases exponentially with the inverse of the metal ionic radius in the facam chelates. The data indicate that this effect is due to a decrease in the extent of polymerization of the chelates with decreasing radius. In squalane, over the concentration range studied, the polymeric form of Tb(facam)₃ appears to be a dimer; molecular weight determinations support this conclusion. The regularities observed in the gc data can be used to predict the efficacy of various rare earth chelates as nmr shift reagents. Since the structure of tris(2,2,6,6-tetramethyl-3,5-heptanedionato)erbium(III) is trigonal prismatic in the solid state, a reaction scheme is postulated in which a fused monocapped trigonal-prismatic dimer dissociates in solution to yield a monomer with a trigonal-prismatic structure. It is this monomer to which a donor becomes bonded to form a monocapped trigonal-prismatic adduct in both the gc and nmr studies.

Specific interactions between solutes and stationary phases have been employed in gas chromatography (gc) to resolve many mixtures which have proven difficult to separate by other means.²⁻¹² The forma-

tion of hydrogen-bonded associates was used in resolving racemic mixtures on asymmetric phases.³ Metal salts and complexes have been found very useful in resolving other mixtures. For example, the affinity of the Ag(I) ion for the π electrons of olefins was used to efficiently separate alkenes from alkanes.⁴ The association constants of the unstable Ag(I) olefin complexes have been measured as a function of the alkene structures,⁶⁻⁸ and the equilibrium constant for the association of Cl^- with SbCl_3 has been measured as a function of the size of the alkali metal ion in the liquid phase.⁵

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