only 20 and 44 cps upfield for the aliphatic ring protons and 4 cps downfield for the CH_3 protons.[4] In the Ba^{2+},F_2^{2-} complex, the diamagnetic anisotropy at the aliphatic ring protons is enhanced due to the presence of the second fluorenyl ring (see Figure 2).

The exchange rate of complexed I with noncomplexed I is much slower for $Ba^{2+}F_2^{2-}$ than for F^-,Na^+. At 60°, which represents the approximate coalescence temperature for the CH_3 peaks of the complexed and noncomplexed cyclic polyether at 0.1 M concentrations in pyridine, the rate constant for the reaction $Ba^{2+},F_2^{2-}–I + I^* \rightarrow Ba^{2+}F_2^{2-}–I^* + I$ is in the order of 500 M^{-1} sec^{-1}. For F^-,Na^+ this rate constant in THF[4] is close to 10^5 M^{-1} sec^{-1} and even higher in pyridine. The exchange reaction with the $Ba^{2+}F_2^{2-}$ complex is probably sterically hindered, but the Ba^{2+} ion is also more tightly bound to the cyclic polyether. Spectral studies show that in an equimolar mixture of $Ba^{2+}F_2^{2-}$, F^-,Na^+, and I in THF the cyclic polyether is complexed exclusively to Ba^{2+},F_2^{2-}.

When small quantities of triglyme or pentaglyme are added to a solution of Ba^{2+},F_2^{2-} in THF, one finds again approximately equal fractions of contact and separated ion pairs, and the same spectrum persists even in the pure glymes. Only when sufficient amounts of coordinating agents like ethylenediamine or hexamethylphosphoramide are added to the THF or dioxane solution of the salt can one observe complete solvent separation, although indications are that the separation occurs in two steps.

Finally, studies of proton abstraction reactions between $Ba^{2+}F_2^{2-}$ and 3,4-benzofluorene confirm one of our earlier findings,[5] *viz.*, the low reactivity of the free fluorenyl ion as compared to the F^-,Na^+ ion pair. The reaction with $Ba^{2+}F_2^{2-}$ shows a square-root dependence on $[Ba^{2+}F_2^{2-}]$, indicating that either F^- or Ba^{2+},F^- is the reactive species. The free ion rate constant is approximately 75 M^{-1} sec^{-1}, that for the Ba^{2+},F_2^{2-} ion pair less than 0.1 M^{-1} sec^{-1}. The high rate constant for F^-,Na^+ ion pair (>3000 M^{-1} sec^{-1}, see ref 5) was interpreted as indicative of the catalyzing role of the Na^+ ion. This, of course, is not possible for the Ba^{2+},F_2^{2-} ion pair where the Ba^{2+} is shielded by the two fluorenyl moieties.

Acknowledgment. The support of this research through a grant from the National Institutes of Health (Grant No. GM-15965) and the Petroleum Research Fund administered by the American Chemical Society is gratefully acknowledged.

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Deuterium as an Aromatic Substituent. Fluorine Chemical Shifts in the Monodeuteriofluorobenzenes

Sir:

Secondary deuterium isotope effects have been the subject of numerous studies in recent years.[1] However, relatively little quantitative data are available concerning the replacement of a specific protium, *viz.*, *ortho*, *meta*, or *para*, with deuterium.[2] Although these previous results have indicated that deuterium behaves as an electron donor, a consistent mechanistic explanation, which can account for the magnitudes of the effects, has not been forthcoming.[2a] We have therefore begun an investigation designed to elucidate the responsible interactions.

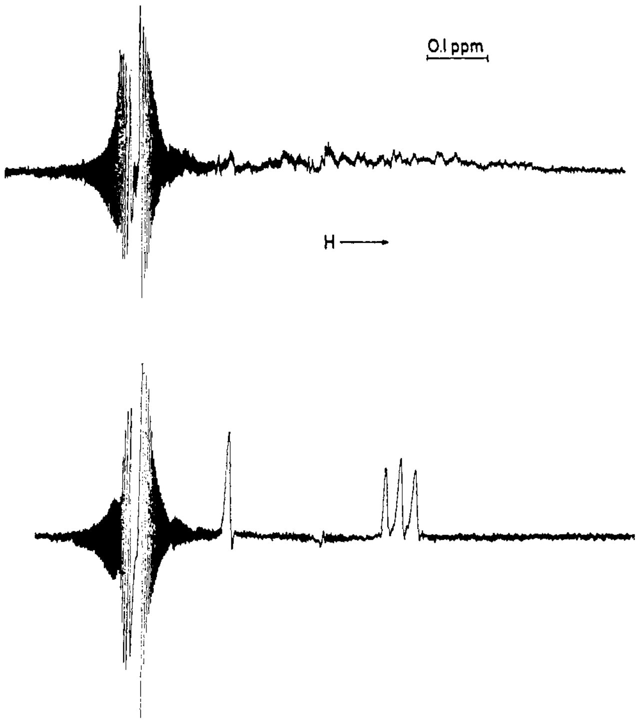

Figure 1. ^{19}F nmr spectrum of fluorobenzene-d_0 and fluorobenzene-2-d in methanol-O-d without, and with, proton decoupling. A higher spectrometer gain was used in the upper (undecoupled) trace.

Taft and coworkers[3] have elegantly shown that the ^{19}F chemical shifts in numerous fluorobenzenes are sensitive measures of substituent interactions. Using the method of Taft we have determined the ^{19}F chemical shifts of the three monodeuteriofluorobenzenes relative to fluorobenzene-d_0.[4] Our results bear on the nature of the deuterium interaction and indicate the potential contribution of direct nonbonded interactions to secondary isotope effects in aromatic systems.

Fluorobenzene-3-d and fluorobenzene-4-d were prepared according to Streitwieser and Mares.[5] Fluorobenzene-2-d was synthesized according to Bak.[6] The nmr samples contained 3–5% (volume) total fluorobenzene (composed of a 3:1 mixture of fluorobenzene-d_1–fluorobenzene-d_0) and 2% 1,1,2,2-tetrachlorotetrafluorocyclobutane (TCTFCB) as an internal lock and reference. The samples were degassed and sealed. The solvents employed were cyclohexane, methanol-

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Table I. Chemical Shifts[a] and DF Coupling Constants[b] for the Monodeuteriofluorobenzenes

	Fluorobenzene-2-*d*		Fluorobenzene-3-*d*		Fluorobenzene-4-*d*	
Solvent	$\int_{\mathrm{H}}^{\mathrm{D}}$	J_{DF}	$\int_{\mathrm{H}}^{\mathrm{D}}$	J_{DF}	$\int_{\mathrm{H}}^{\mathrm{D}}$	J_{DF}
Cyclohexane	0.285 ± 0.003	1.4 ± 0.08	0.008 ± 0.003	0.8 ± 0.08	0.011 ± 0.002	<0.2
Methanol-O-*d*	0.285 ± 0.003	1.3 ± 0.08	0.011 ± 0.003	0.9 ± 0.08	0.011 ± 0.002	<0.2
Trifluoroacetic acid-*d*	0.285 ± 0.003	1.3 ± 0.08	0.005 ± 0.003	0.9 ± 0.08	0.012 ± 0.002	<0.2

[a] Parts per million relative to fluorobenzene-d_0 [b] In hertz.

O-*d*, and trifluoroacetic acid-*d*. Concentrations of 5% or less are considered justifiable approximations to infinite dilution.[3]

Figure 1, top trace, shows the ^{19}F spectrum (recorded at 56.4 MHz on a Varian HA-60-IL spectrometer) of a mixture of fluorobenzene-2-*d* and fluorobenzene in methanol-O-*d*. The lock signal from TCTFCB is seen downfield from the complex pattern of the aromatic materials. In order to determine precise chemical shifts, it was decided to simplify the spectrum by eliminating all H–F coupling. This was accomplished by simultaneous irradiation at the proton magnetic resonance frequency. The resulting spectrum (bottom trace) contains a 1:1:1 triplet ($|J_{\mathrm{DF}}|$ = 1.3 Hz) for fluorobenzene-2-*d*; this multiplet is 0.285 ppm upfield from the single sharp resonance of fluorobenzene-d_0. Analogous results were obtained for the *meta* and *para* compounds, although the isotope shifts were significantly smaller and the resonance of fluorobenzene-4-*d* appeared as a singlet, implying that $|J_{\mathrm{DF}}| < 0.2$ Hz. The results are summarized in Table I.

The proton–fluorine coupling constants in fluorobenzene have been determined previously.[7] Using these data, we have calculated the corresponding deuterium–fluorine coupling constants ($J_{\mathrm{DF}} = 0.15J_{\mathrm{HF}}$)[8] and have obtained 1.41, 0.91, and 0.02 Hz for the *ortho*, *meta*, and *para* positions, respectively. These results agree with the coupling constants observed directly (Table I).

Within experimental error, the isotope effect on the ^{19}F chemical shifts and D–F coupling constants for the three deuterated fluorobenzenes are invariant to the solvents employed. These solvents were chosen since they produce significant variations in the relative chemical shifts of substituted fluorobenzenes.[3,9] Furthermore, no change in the isotopic chemical shift of fluorobenzene-4-*d* was noted, despite a 40% decrease in its concentration. This over-all invariance suggests that the observed shifts are a reflection of intramolecular interactions rather than medium effects.

The upfield direction of the isotopic shift is expected because the net shielding on fluorine should be increased by the deuterium. This effect has ample precedence from nmr studies[10] as well as chemical investigations.[2]

The magnitudes of the isotopic shifts vary markedly with deuterium position. The effect of an *ortho* deuterium is 25 and 35 times that of a *para* and *meta* deuterium, respectively. This contrasts sharply to deuterium kinetic effects in solvolytic reactions[2c] and carbanion formation,[2a] where smaller variations have been found.

Using Taft's equations relating ^{19}F chemical shifts of *meta*- and *para*-substituted fluorobenzenes to the substituent parameters σ_{I} and $\sigma_{\mathrm{R}}{}^0$,[3] our results demonstrate that the parameters for deuterium (relative to protium) are $\Delta\sigma_{\mathrm{I}} = -0.0011$[11] and $\Delta\sigma_{\mathrm{R}}{}^0 = -0.0001$. It can be inferred from these data that deuterium in the *meta* or *para* position interacts with a group in the 1 position primarily *via* an inductive mechanism rather than a mesomeric perturbation of the π system.[12]

It appears that an *ortho* deuterium creates an abnormally large isotope effect on the ^{19}F chemical shift. This may be the result of some direct F–D nonbonded interaction. In this regard, the difference between the lengths as well as the vibrational amplitudes of the C–H and C–D bonds may play a significant role. Additional discussion must await results from our investigations of polydeuterated fluorobenzenes and theoretical calculations concerning the effects of vibrational levels on chemical shifts.

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(8) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 188.

(9) In fact, the TCTFCB signal was 1.5 ppm upfield from the fluorobenzene-d_0 resonance in cyclohexane, but 0.1 to 0.4 ppm downfield in the polar media.

(10) (a) G. V. D. Tiers, *J. Am. Chem. Soc.*, **79**, 5585 (1957); (b) H. S. Gutowsky, *J. Chem. Phys.*, **31**, 1683 (1959); (c) M. Saunders, J. Plostnieks, P. S. Wharton, and H. H. Wasserman, *ibid.*, **32**, 317 (1960); (d) K. Schaumburg and C. Deverell, *J. Am. Chem. Soc.*, **90**, 2495 (1968).

(11) From the experimental pK_{a} of acetic acid-d_3, Streitwieser and Klein have calculated $\Delta\sigma_{\mathrm{I}} = -0.0012$ (see ref 2c).

(12) Corroborating evidence can be found in ref 2a and 2c.

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Received April 28, 1969

Diselenocyanatobis(2,2′-bipyridyl)iron(II), a Possible Iron(II) Analog of the Yellow Lifschitz Nickel(II) Complexes[1]

Sir:

Recently, it was demonstrated[2] that the compound *cis*-dithiocyanatobis(2,2′-bipyridyl)iron(II), [Fe(bipy)$_2$(NCS)$_2$], undergoes a transition between spin quintet and spin singlet electronic ground states at temperatures of 210–216°K, depending on the polymorph studied. X-Ray structural investigations[3] show that the transition is accompanied by a change of the Fe–N(bipy) bond length from 2.17 ± 0.02 to 2.03 ± 0.02 Å,[4] corresponding to the $t_{2g}{}^4e_g{}^2$ and $t_{2g}{}^6$ configurations of octahedral iron(II), respectively. Analogous transitions are encountered in the bis(1,10-phenanthroline) complexes [Fe(phen)$_2$(NCS)$_2$] and [Fe(phen)$_2$(NCSe)$_2$].[5,6]

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(1) This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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