coupling mechanisms between the free radical and P atoms seem unlikely. Indeed, since $U_{\infty P}$ for $P(O)Cl_3$ is more positive than that for several trivalent compounds, *strong* indirect coupling mechanisms resulting from exchange polarization and/or complexation at substituent sites are suggested.

Evidence for a direct coupling mechanism related to the distance of closest approach[3] comes from the dialkyl phosphites. As noted above, H directly bonded to P leads to relatively large scalar rates. Since H contains no available p or d orbitals, there is no *a priori* reason to expect it to promote strong complex formation. This leaves direct coupling of the radical with the electrons about P, which is highly favored because of the small size of H. We note, however, that conjugative mechanisms cannot be ruled out entirely.

The effect of long-range conjugation *via* the molecular system is demonstrated by $(C_6H_5O)_2P(H)O$ which shows a more positive enhancement than any dialkyl phosphite and by $(C_6H_5O)_3P$ which is more positively enhanced than any $(RO)_3P$. In particular, the phenyl group is larger than the methyl group, eliminating a predominant direct effect. A possible interpretation involves the greater ability of the aromatic system to transmit spin information to P *via* exchange polarization of or complexation with delocalized orbitals, in accord with previous interpretations for aromatic fluorocarbons.[10] If this is true, we might expect analogous variations in both α and τ_s.

Sulfur vs. Oxygen. Since sulfur is more polarizable than oxygen, we might expect thio-substituted compounds to show more scalar coupling than their oxygenated analogs if scalar coupling is transmitted through the molecular π system. Alternatively, a direct coupling mechanism would favor oxygen because it is smaller than sulfur. The experimental results, both for the phenylthiophosphonic halides and for the thioalkyl phosphites, show that neither possibility dominates and suggests the presence of competing mechanisms.

Concluding Remarks. If the lone-pair orbital is considered to be a substituent with a negligible steric effect, then, with the exception of sulfur and oxygen, the only two double-bonded substituents tested, ultimate enhancements decrease with increasing substituent size. In order of increasing polarization, $RO < C_6H_5 < Br < Cl < H <$ lone pair. This strongly suggests a scalar coupling process which includes unpairing of electrons directly bonded to phosphorus, even in compounds which are relatively well shielded sterically. On the other hand, long-range coupling *via* delocalized orbitals is required and may be the most important coupling process for some systems. The nature of these mechanisms, which incorporate variations in α, τ_s, and d, should become more clear after additional measurements are performed. In particular, quantitative high-field measurements with several of these unusually stable systems would be of great value in determining the relative contributions of the various parameters.

Anisotropy of Fluorine Chemical Shifts in Substituted Fluorobenzenes

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Abstract: Fluorine chemical-shift anisotropies of some *para*-substituted fluorobenzenes have been determined in nematic liquid crystal solution. Changes in anisotropies relative to fluorobenzene have been correlated with Taft's inductive and resonance parameters. For fluorobenzene maximum shielding occurs along the axis perpendicular to the aromatic ring.

Various attempts have been made to calculate fluorine chemical shifts in aryl fluorides or to correlate calculated π-electron densities and π-bond orders with the observed isotropic shifts.[1-8] The analysis of magnetic resonance spectra of molecules dissolved in nematic liquid crystal solvents provides details of the anisotropy of the shielding tensor[9,10] which should, in prin-

ciple, permit a further test of calculations of chemical shifts. The semiempirical theory of Karplus and Das[1] is attractive in this respect since it expresses the shielding in terms of localized bond parameters. This theory, and the extension by Prosser and Goodman,[2] demonstrated the importance of π charge densities in determining the fluorine chemical shift which has led to the correlation of the π densities with isotropic chemical shifts. Such approaches have been fairly successful providing no *ortho* substituents are present. The inclusion of long-range interactions produced a more satisfactory over-all correlation,[6] obviating the need for the "*ortho* effect," but the theoretical basis of the π-electron density calculations employed in this correlation has been questioned.[11]

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All these methods, however, are aimed at correlating the isotropic chemical shift; furthermore, changes in the σ framework are ignored or included empirically. To compare the anisotropies of the fluorine chemical shifts it seemed advisable to employ the original Karplus and Das theory, but an attempt to calculate the anisotropies in various fluorobenzenes, using the original Karplus and Das parameters, was unsuccessful.[12] Several causes could be responsible. The theory might be oversimplified by the neglect of all orbitals except those on the central atom. The parameters chosen may not be the most suitable. The assumption was made that the average excitation energy was constant and also isotropic. We considered that it might be more profitable to seek a correlation between shielding anisotropies and an empirical parameter which reflects changes in electron distribution. In the present paper we describe such a correlation with Taft inductive and resonance parameters.[13]

Experimental Section

Samples were obtained from commercial sources and used without further purification. Deuteration of p-fluorophenol and p-fluoroaniline was achieved by repeated exchange with deuterium oxide. Solute concentrations were in the range 30–33 mol % in a mixed liquid crystal consisting of 4,4′-di-n-hexyloxy- (61.7%), 4,4′-di-n-pentyloxy- (34.8%), and 4,4′-di-n-butoxyazoxybenzene (3.5%). Spectra were recorded with a modified Varian DP60 spectrometer as previously described.[14] Fluorine chemical shifts were measured from external trifluoroacetic acid and corrected to internal carbon tetrafluoride.[12]

Results

The solute molecules discussed here have C_{2v} symmetry (or effectively so for p-fluoroaniline and p-fluorophenol), and therefore two motional constants are required to describe the mean orientation.[15] To solve the nmr spectrum it is not usually possible to obtain analytical expressions for transition frequencies and intensities if a large number of magnetically inequivalent nuclei are present. However, for *para*-substituted fluorobenzenes, a first-order perturbation treatment leads to quite precise expressions since the direct dipole coupling between *ortho* protons is about an order of magnitude larger than any of the other dipolar coupling constants. While the present work was in progress, McLean, *et al.*,[16] published an account of the method as applied to molecules with D_{2h} symmetry and the details are not included here. For molecules which are not symmetrically substituted D_{HH}^m and $D_{HH}^{m'}$ may not be equal and there may be a chemical-shift difference between protons. In the first-order approximation the proton spectra should consist of 24 lines symmetrically placed relative to the center at $\frac{1}{2}(\nu_{H_2} + \nu_{H_4})$, but two pairs of lines are separated by $\frac{3}{4}(J_{HH}^m + J_{HH}^{m'}) + \frac{3}{2}J_{HH}^p$, a quantity of about 4 to 5 Hz, and cannot be resolved in the spectra. The proton half-spectrum thus consists of five doublets separated by $\frac{1}{2}(J_{HF}^o + J_{HF}^m + D_{HF}^o + D_{HF}^m)$. The general appearance of the spectra depends upon the relative signs and magnitudes of the two quantities $\frac{1}{2}(D_{HH}^m + D_{HH}^{m'})$ and D_{HH}^p, and on their signs relative to D_{HH}^o.

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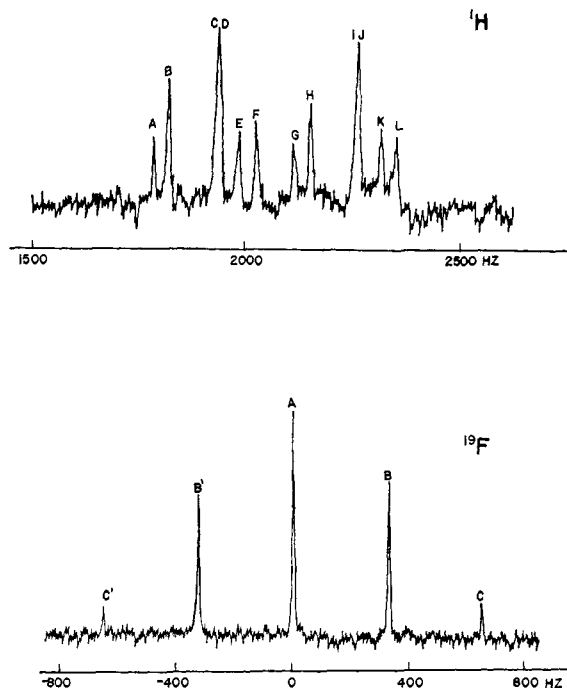
Figure 1. Proton and fluorine magnetic resonance spectra of p-chlorofluorobenzene dissolved in nematic liquid crystal solvent. Only the high-field half of the proton spectrum is shown.
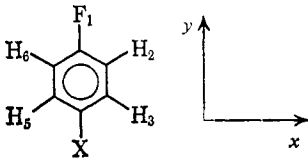
The fluorine magnetic resonance spectra consisted of a quintet (1:4:6:4:1) separated by $\frac{1}{2}(J_{HF}^o + J_{HF}^m + D_{HF}^o + D_{HF}^m)$. The proton and fluorine spectra of p-chlorofluorobenzene are shown in Figure 1. Analysis of the spectra gives values for $\frac{1}{2}(D_{HH}^m + D_{HH}^{m'})$, D_{HH}^p, D_{HH}^o, and $\frac{1}{2}(J_{HF}^o + J_{HF}^m + D_{HF}^o + D_{HF}^m)$. Since the sign of D_{HH}^o is negative,[15] the proton resonance spectra of p-chloro-, p-bromo-, p-nitrofluorobenzene, and p-fluorobenzonitrile correspond to the case with opposite signs for $\frac{1}{2}(D_{HH}^m + D_{HH}^{m'})$ and D_{HH}^p with the positive term having the larger magnitude. The actual signs of these two terms and the signs and magnitudes of D_{HF}^o and D_{HF}^m were made on the basis of reasonable geometry: $r(C-C) = 1.39$ Å, $r(C-H) = 1.08$ Å, $r(C-F) = 1.31$ Å. Literature values were used for the respective J_{HF}^o and J_{HF}^m.[17-19] The motional constants were then obtained by fitting $\frac{1}{2}(D_{HH}^m + D_{HH}^{m'})$ and $\frac{1}{2}(D_{HF}^o + D_{HF}^m)$ to the observed spectra.

In order to eliminate one of the chemical shift terms, and to reduce the dipolar coupling between the ring protons and those of the substituent, the spectra of p-fluorophenol and p-fluoroaniline deuterated in the substituent position were recorded. The proton spectrum of p-fluoroaniline-d_2 showed only two very broad peaks with a separation of about 3600 Hz. The fluorine spectrum showed a quintet with each peak further split into quintets of separation 22 Hz and intensity ratio 1:2:3:2:1. Since it was impossible to derive a value for $\frac{1}{2}(D_{HH}^m + D_{HH}^{m'})$, the motional constants were obtained from the experimental values of $(D_{HF}^o + D_{HF}^m)$ and $\frac{3}{2}D_{HH}^o$, which was assumed to be equal to the separation of the two broad peaks in the proton spectrum. The spectrum of p-fluorophenol-d did not

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Table I. Spectral Parameters for *para*-Substituted Fluorobenzenes

Substituent	$D_{HH}°$	$\frac{1}{2}(D_{HH}^m + D_{HH}^{m'})$	D_{HH}^p	$D_{HF}°$	D_{HF}^m	$J_{HF}°$	J_{HF}^m	$C_{3z^2-r^2}$	$C_{x^2-y^2}$	δ, ppm Nematic[a]	δ, ppm Isotropic
p-Chloro	−2754.5	133.9	−26.4	−346.3	−317.9	8.1	4.7	−0.2974	−0.2843	51.13 ± 0.04 (67°)	53.64 ± 0.05 (96°)
p-Bromo	−3044.4	161.8	−21.3	−337.5	−346.3	8.2	4.8	−0.3158	−0.3185	50.41 ± 0.07 (65°)	53.09 ± 0.05 (91°)
p-Cyano	−3341.5	184.4	−19.2	−338.2	−374.2	8.6	5.8	−0.3357	−0.3499	37.40 ± 0.05 (64°)	41.21 ± 0.04 (93°)
p-Nitro	−3246.3	128.2	−46.8	−492.6	−380.4	8.2	4.8	−0.3721	−0.3230	34.44 ± 0.05 (65°)	40.97 ± 0.02 (93°)
p-Hydroxy-*d*	−1787.9	45.4	−45.4	−391.5	−236.3	8.1	5.0	−0.2489	−0.1819	61.62 ± 0.04 (67°)	63.12 ± 0.02 (91°)
p-Amino-*d*₂	−2428 ± 50			−304.7	−271.6	8.1	5.0	−0.2560	−0.2411	65.58 ± 0.02 (65°)	65.77 ± 0.04 (91°)

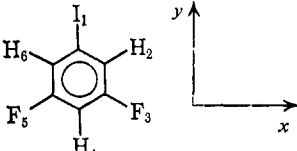[a] Relative to CF₄. Mean of five determinations.

show any evidence of deuterium–proton or deuterium–fluorine coupling but the proton spectrum showed only three doublets due to the coincidence of lines caused by the near equality of $|\ ^1/_2(D_{HH}^m + D_{HH}^{m'})|$ and $|D_{HH}^p|$.

The difference in chemical shift between the two pairs of protons in the *para*-substituted fluorobenzenes should shift the center of the inner ten lines of the proton spectrum relative to the center of the outer ten lines. Within the experimental errors only the spectrum of *p*-nitro-fluorobenzene required such a correction. A chemical-shift difference between H₂ and H₃ of 90 Hz was required to account for the spectral asymmetry of 4 Hz.

The first-order pertubation treatment gave almost exact frequencies for most of the observable transitions. Second-order corrections were generally about 3 Hz and the largest correction was 7 Hz for two lines (C and I) in the spectrum of *p*-nitrofluorobenzene. Final parameters are given in Table I.

The theoretical spectrum of 3,5-difluoroiodobenzene was computed using the program and method described previously.[14] The rms deviation of all observed lines from their computed frequencies was 2.5 Hz. Final parameters are given in Table II.

Discussion

For the molecules considered here, the chemical shift in the nematic phase is given by[15]

$$\bar{\sigma}_{zzi} = \frac{1}{3}(\sigma_{xxi} + \sigma_{yyi} + \sigma_{zzi}) +$$

$$C_{3z^2-r^2}\left(\frac{2}{3}\right)(5)^{-1/2}\left[\sigma_{zzi} = \frac{1}{2}(\sigma_{xxi} + \sigma_{yyi})\right] +$$

$$C_{x^2-y^2}(3)^{1/2}(5)^{-1/2}(\sigma_{xxi} - \sigma_{yyi}) \quad (1)$$

where σ_{xx}, σ_{yy}, and σ_{zz} are the diagonal components of the nuclear screening tensor. The first term on the right-hand side of eq 1 is the chemical shift in the isotropic phase and thus eq 1 can be rearranged to the form

$$A[\sigma_{aa} - \frac{1}{2}(\sigma_{bb} + \sigma_{cc})] + B[\sigma_{bb} - \sigma_{cc}] = C \quad (2)$$

while at the same time the molecule fixed axes *x*, *y*, and *z* are rewritten as transformed to axes *a* (perpendicular to the molecular plane), *b* (along the C–F bond), and *c* (in the molecular plane and perpendicular to the C–F bond). In Table III the values of the coefficients *A*, *B*, and *C* in

Table II. Spectral Parameters for 3,5-Difluoroiodobenzene

i	j	D_{ij}	D_{ij}^{pseudo}	J_{ij}
2	3	−1040.3		8.5
2	4	−221.8	6.0	2.5
2	5	−91.6		−1.0
2	6	−146.9		1.5
3	4	−699.6		9.0
3	5	−99.5		7.2

$C_{3z^2-r^2} = -0.2869$ 	 $C_{x^2-y^2} = -0.0420$
$\nu_{H_2} = 0$ 	 $\nu_{H_4} = 5.0$ Hz
¹⁹F chemical shift (nematic 67°) = 37.74 ± 0.04 ppm[a]
(isotropic 95°) = 45.95 ± 0.02 ppm

[a] Internal CF₄.

Table III. Coefficients *A*, *B*, and *C* from Eq 2

Substituent	*A*	*B*	C^a
p-Fluoro	1.0	−0.684	31.7 ± 1.0
p-Chloro	1.0	−0.827	28.2 ± 1.0
p-Bromo	1.0	−0.873	28.5 ± 1.3
p-Cyano	1.0	−0.903	38.0 ± 1.0
p-Nitro	1.0	−0.752	58.8 ± 1.2
p-Hydroxy	1.0	−0.633	20.1 ± 1.0
p-Amino	1.0	−0.816	2.4 ± 1.0
m-Fluoro	1.0	−0.170	74.4 ± 2.0
3,5-Difluoroiodo	1.0	0.063	95.5 ± 1.5
1,3,5-Trifluoro	1.0	0	102.0 ± 1.5
Fluorobenzene	1.0	−0.424	50.0

[a] Standard deviation of five measurements. In parts per million (ppm).

eq 1 are listed for the compounds studied here and also for fluorobenzene,[15] *m*- and *p*-difluorobenzene,[12] and 1,3,5-trifluorobenzene.[14]

It is usual in attempts to calculate fluorine chemical shifts to assume that the "paramagnetic" contribution is dominant. Furthermore the shifts are measured relative to fluorobenzene with the additional assumption that the average excitation energy remains constant. According to the Karplus and Das theory[1] the changes in the components of the chemical shift, relative to the reference compound fluorobenzene, are given by

$$\Delta\sigma_{aa} = \sigma_{oa}(S_r - 1)\Delta I \qquad (3)$$

$$\Delta\sigma_{bb} = \sigma_{ob}(\Delta\rho) \qquad (4)$$

$$\Delta\sigma_{cc} = \sigma_{oc}[(S_r - \rho_r - 1)\Delta I + (S_r + I_r)\Delta\rho] \qquad (5)$$

where S_r is the S hybridization of the reference compound; $\Delta I = I - I_r$ and $\Delta\rho = \rho - \rho_r$ are the changes in ionic character and double-bond character. The terms σ_{oa}, etc., are given by $\sigma_{oa} = e^2h^2/m^2c^2\Delta E_a\langle 1/r^3\rangle_{2p}$, etc.; i.e., the average excitation energy is taken to be anisotropic. The lack of suitable values for ΔI and $\Delta\rho$ and the absence of any data on the anisotropy of the average excitation energy make it difficult to apply these equations. The theory is inadequate when applied to the calculation of anisotropies using the original parameters of Karplus and Das.[1]

Taft[13] has correlated his inductive and resonance parameters with the isotropic ^{19}F chemical shifts with success for a large number of meta- and para-substituted fluorobenzenes. The isotropic chemical shift, relative to fluorobenzene, is given by eq 6[20] with σ_R equal to zero for meta substituents.[22]

$$\bar{\sigma} = -29.7\sigma_R - 6.1\sigma_I \qquad (6)$$

We assume a direct proportionality between ΔI and σ_I and between $\Delta\rho$ and σ_R so that the Taft parameters can be incorporated into eq 3 to 5. A least-squares fit was made to the experimental data for 11 non-ortho-substituted fluorobenzenes with the constants of proportionality and $\{\sigma_{aa} - {}^1/_2(\sigma_{bb} + \sigma_{cc})\}$ and $(\sigma_{bb} - \sigma_{cc})$ for fluorobenzene as the unknown parameters, to give

$$\Delta\sigma_{aa} = 18.2\sum\sigma_I \qquad (7)$$

$$\Delta\sigma_{bb} = -58.7\sigma_R \qquad (8)$$

$$\Delta\sigma_{cc} = -36.5\sum\sigma_I - 30.4\sigma_R \qquad (9)$$

The sum of eq 7-9, of course, equals eq 6.

A change in ionic character of the carbon-fluorine band, has opposite effects upon $\Delta\sigma_{aa}$ and $\Delta\sigma_{cc}$ as shown by their dependence on σ_I. Within the context of the Karplus and Das theory both σ_{aa} and σ_{cc} should increase with increasing ΔI, and the effect can be interpreted in terms of a negative average excitation energy ΔE_a. The occurrence of negative average excitation energies has been recognized as a consequence of this approximation[23,24] but does not mean, however, that the resulting contribution to the chemical shift is diamagnetic. It may be responsible for the high-shielding component along the a axis.

Table IV lists the values of the anisotropy terms, the calculated values of C from substitution in eq 2, and the calculated and experimental isotropic chemical shifts. The standard deviation in C is 3.0 ppm and in $\bar{\sigma}$ is 1.4 ppm. The largest deviations occur for p-nitrofluorobenzene and p-fluorobenzonitrile. This is not unexpected since these +R substituents exhibit solvent-dependent chemical shifts[21] and do not obey eq 6 strictly.

Table IV. Anisotropy Values[a] of Fluorine Chemical Shifts of Substituted Fluorobenzenes

	$\{\sigma_{aa} - {}^1/_2(\sigma_{bb} + \sigma_{cc})\}$	$\{\sigma_{bb} - \sigma_{cc}\}$	C_{calcd}	$\bar{\sigma}_{calcd}$	$\bar{\sigma}_{exptl}$
Fluorobenzene	62.5	30.1	49.7	0	0
p-Fluoro	67.2	58.1	27.4	6.3	6.6
p-Chloro	71.7	52.4	28.3	2.5	2.7
p-Bromo	71.7	51.0	27.1	2.1	2.1
p-Cyano	84.4	44.7	43.2	−6.0	−9.8
p-Nitro	90.1	46.0	55.4	−8.2	−10.0
p-Hydroxy	52.5	51.7	19.9	11.2	12.1
p-Amino	41.5	44.0	5.6	14.2	14.8
m-Fluoro	81.5	48.0	73.1	−3.2	−3.0
3,5-Difluoroiodo	95.4	63.0	99.3	−5.5	−5.0
1,3,5-Trifluoro	100.5	68.0	100.5	−6.3	−5.8

[a] In parts per million (ppm).

The values so obtained for the anisotropy of fluorobenzene may be compared with those of Snyder[15] and Chan and Dubin.[25] Snyder obtained $\sigma_{aa} - {}^1/_2(\sigma_{bb} + \sigma_{cc}) = +159$ ppm and $(\sigma_{bb} - \sigma_{cc}) = +250$ ppm. Since these results are based upon the invalid assumption that the results for fluorobenzene and hexafluorobenzene are consistent, the lack of agreement is not surprising. Our results disagree with those of the molecular beam magnetic resonance determination, both in sign and magnitude. Buckingham, et al.,[26] have warned that appreciable systematic errors could arise in measurements of chemical shift anisotropies due to environmental effects upon solute molecules on going from the nematic to the isotropic phase. However, Dailey, et al.,[27] have shown recently that the solvent anisotropy effect for protons may be less serious than has been believed. A shift of 10 Hz in the fluorine resonance would cause an additional uncertainty of about ±2 ppm in the anisotropy. It is unrealistic to hold these effects responsible for the disagreement between the anisotropies from nematic liquid crystal and molecular beam measurements since substitution of Chan and Dubin's values in eq 2 for fluorobenzene gives a value of −150 ppm for C. The considerable disagreement between the two methods may arise from the different assumptions used in each treatment[28] and emphasizes the need for further investigation, both theoretical and experimental.

(20) This equation is preferred to a later expression[21] since it led to smaller deviations. The results, however, are unchanged.
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