Concerning the Relative Importance of π Inductive Effects and Polar Field Effects on ^{19}F Chemical Shifts in Aromatic Derivatives

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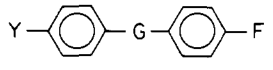
Abstract: ^{13}C chemical shifts for ammonio derivatives of aromatic compounds, molecular orbital calculations for the same compounds, and correlations of ^{13}C chemical shifts for 4-substituted biphenyls with σ_I and σ_R all indicate that π polarization is an important mechanism of transmission of polar substituent effects and appears to be the dominant polar effect on ^{19}F chemical shifts in aryl fluorides. The constant in the Buckingham electric field equation $A = 27 - 34 \times 10^{-12}$ for C-F bonds. This value is used to show that direct field effects are unimportant in most aryl fluorides. Molecular orbital calculations for β,β-difluorostyrenes show that the π component of C(sp^2)-F bonds is relatively insensitive to direct field effects, thus accounting for the relative unimportance of these effects upon ^{19}F chemical shifts in aryl fluorides.

There is a continuing controversy concerning the importance of π-inductive and polar electric field effects on ^{19}F chemical shifts in aromatic derivatives.[2,3] Taft and co-workers have interpreted the observed σ_I dependence of ^{19}F chemical shifts for a series of systems **1** in terms of π-inductive effects:[2]



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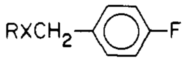
Similarly, the enhanced σ_I dependence of ^{19}F chemical shifts in 10-substituted 9-fluoroanthracenes (**2**) relative to 4-substituted fluorobenzenes (**3**) has been attributed to π-inductive effects.[2a,3] On the other hand, Adcock and co-workers have argued that polar field contributions are more important than π-inductive effects, based on ^{19}F chemical shifts for the systems **4–8**:[4]



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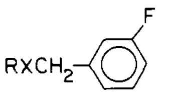

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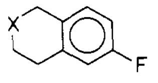

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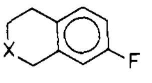

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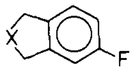

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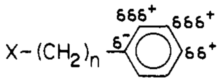
Schulman and co-workers[5] have analyzed ^{13}C chemical shifts for 4-substituted biphenyls (**9**) using the FMMF approach to substituent effects.[6] In contrast with both other groups, they concluded that the ^{13}C chemical shifts are insensitive to field/inductive effects and that only mesomeric effects are important. Thus using similar aromatic derivatives, different groups have either concluded that π-inductive effects contribute to ^{19}F chemical shifts,[2,3] that polar electric field effects are more important,[4,6] or that neither effect is important.[5]

Based on ^{13}C chemical shifts and molecular orbital calculations for phenylalkane,[7] styrene,[8] and phenylacetylene[9] derivatives, we concluded that field-induced polarization of the phenyl π-electron system is an important mechanism of transmission of polar substituent effects. Further evidence for π polarization has been reported recently.[4,10,11] We now present evidence demonstrating significant π polarization in **1–9,** thus reconciling the contradictory conclusions of other groups.[2-5] The importance of direct field effects is also evaluated.

Results and Discussion

A. Evidence for π-Polarization Effects. Exocyclic polar or charged groups in phenylalkanes induce π-electron density changes which can be represented schematically by:[7]



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This seemed inconsistent with the claim that field/inductive effects are unimportant in 4-substituted biphenyl derivatives.[5] To test the latter conclusion, ^{13}C chemical shifts were measured for 4-ammoniobiphenyl in CF_3CO_2H. These shifts, expressed relative to the isoelectronic 4-methylbiphenyl in the same solvent[12] (see Table I), indicate π-electron density changes in the unsubstituted phenyl group which are identical with **10.** Therefore, we correlated the ^{13}C chemical shifts for the other 4-substituted biphenyls[5] with Taft's σ_I and $\sigma_R{}^0$ constants.[13,14] Results of these correlations are summarized in Table I. The pattern of ρ_I values is amazingly similar to the actual chemical shifts for 4-ammoniobiphenyl and to the chemical shift and π-electron density patterns in phenylalkane derivatives.[7] Since ^{13}C chemical shifts in similar systems appear to reflect π-electron density changes,[7-9] these results indicate that polar substituents successively polarize the two phenyl groups. Thus, π polarization appears to be an important mechanism for transmission of polar effects in the biphenyl system. The failure of Schulman et al. to detect this effect can be attributed to a weakness in the FMMF treatment; it assumes that the only polar effects are direct field effects.[6]

Molecular orbital calculations for ammonio derivatives of **1** have shown that phenyl π polarization leads to proportionate changes in the 2p(π)-electron density of the attached fluorine.[9] Results for further derivatives (Table II) show a close parallel between carbon and fluorine π-electron density changes and ρ_I values for these derivatives, confirming that the σ_I dependence of **1** and the enhanced σ_I dependence for **2** relative to **3** reflect π-polarization effects. This explanation can also account for the observation that ρ_R decreases more rapidly than ρ_I as phenyl group conjugation decreases in **1**[2] since π polarization involves both a conjugative component and a through-space component which is present even when conjugation is destroyed.[8,9] Thus the major features of the field/inductive de-

Table I. (a) ^{13}C Chemical Shifts for 4-Ammoniobiphenyl (in CF_3COOH) Relative to 4-Methylbiphenyl and (b) Correlations of ^{13}C Chemical Shifts for Other 4-Substituted Biphenyls with σ_I and σ_R^0

		Correlations with halogens				Correlations without halogens			
Carbon	$\delta_{^{13}C}$[a]	ρ_I[b]	ρ_R	r[c]	SD[d]	ρ_I	ρ_R	r	SD
4	−9.64	e							
3	−5.82	e							
2	+1.92	+2.87 ± 0.78	−1.21 ± 0.53	0.799	0.54	+1.90 ± 0.23	−0.84 ± 0.15	0.968	0.14
1′	+5.97	+5.77 ± 0.99	+15.05 ± 0.67	0.993	0.69	+6.26 ± 1.08	+14.96 ± 0.70	0.996	0.66
1′	−2.33	−2.86 ± 0.39	−1.25 ± 0.27	0.956	0.27	−3.17 ± 0.16	−1.14 ± 0.10	0.997	0.09
2′	+0.19	+0.53 ± 0.19	+1.02 ± 0.13	0.949	0.14	+0.41 ± 0.22	+1.11 ± 0.14	0.973	0.13
3′	+0.28	+0.37 ± 0.11	+0.32 ± 0.07	0.905	0.07[f]	+0.49 ± 0.11	+0.26 ± 0.07	0.960	0.06
4′	+1.45	+1.94 ± 0.06	+2.13 ± 0.04	0.999	0.04	+2.00 ± 0.06	+2.09 ± 0.04	1.000	0.04

[a] ^{13}C chemical shifts in ppm relative to 4-methylbiphenyl. Low field shifts are positive. Correlations were also performed using the same sign convention. [b] Weighting factors in correlation: $\delta = \delta_0 + \rho_I\sigma_I + \rho_R\sigma_R^0$. Experimental data from ref 5. [c] Multiple correlation coefficient. [d] Standard deviation between calculated and experimental values. [e] No correlations were performed for C(4) and C(3) since these carbon shifts may not reflect changes in ground-state electron density.[7] [f] Standard deviation comparable with experimental error.

Table II. Comparison of Carbon and Fluorine π-Charge Densities ($\times 10^4$) for Ammonio Derivatives of **1**, **2**, and **3** and ρ_I Values from ^{19}F Chemical Shift Correlations for the Same Derivatives in CCl_4

Compd	G	$q_{C\pi}$[a]	$q_{F\pi}$	ρ_I[b]
1	$-CH_2-$	+199	+29	−1.95
1	$-N{=}CH-$	+329	+45	−2.56
1	$-CH{=}CH-$	+311	+42	−2.95
1	$-N{=}N-$	+329	+45	−3.22
1	-[c]	+349	+48	−3.98
3		+564	+97	−8.13
2		+1155	+155	−13.18

[a] Carbon π-charge density for carbon to which fluorine is attached (positive sign indicates decreased electron density). [b] Data from ref 2a. Negative sign arises from the sign convention for ^{19}F chemical shifts (low field shift negative). [c] - indicates biphenyl. Calculations carried out with a dihedral angle of 21° between the two phenyl groups. The reported dihedral angle for biphenyl is 19-23° [P. L. Britton, C. L. Cheng, R. W. LeFevre, L. Radom, and G. L. Ritchie, *J. Chem. Soc. B*, 2100 (1971)].

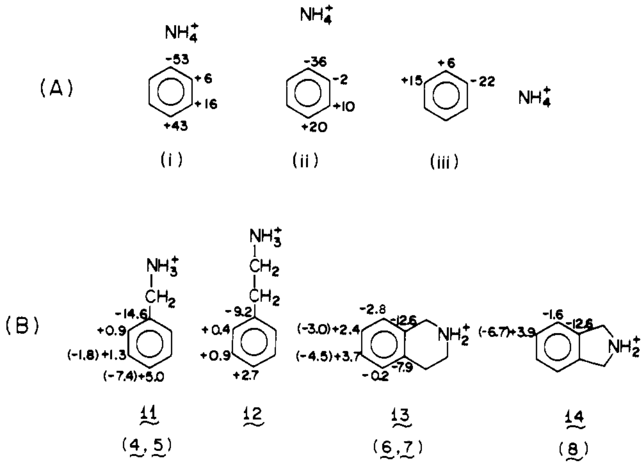
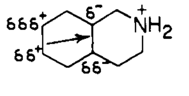


Figure 1. (A) π-electron charge densities ($\times 10^3$) for C_6H_6–NH_4^+ pairs. (i) NH_4^+ same distance from benzene ring as $-NH_3^+$ in benzylammonium ion (ii) and (iii) NH_4^+ same distance from benzene ring as in phenethylammonium ion. (B) ^{13}C chemical shifts for $-NH_3^+$ and $-NH_2^+-$ derivatives relative to $-CH_3$ or $-CH_2-$ derivatives and, in brackets, ^{19}F chemical shifts for the corresponding $-NH_3^+$ and $-NH_2^+-$ derivatives (**4–8**), relative to $-CH_3$ or $-CH_2-$ derivatives.[4] Note that ^{13}C and ^{19}F chemical shifts use a different sign convention (low field shifts are respectively positive and negative).

pendence of ^{19}F chemical shifts in **1–3** and ^{13}C chemical shifts in **9** can be accounted for by π polarization.

Recently Adcock and co-workers have shown that ^{19}F chemical shifts for **4–8** depend critically on the orientation of X relative to the ^{19}F probe (see Figure 1 for results where X = NR_2^+), an observation which they attribute in part to the polarizability of the phenyl group.[4] Results of CNDO/2 calculations for benzene-NH_4^+ pairs confirm that π polarization depends critically on the orientation of the charged group (see Figure 1). Therefore, the ^{13}C chemical shifts were measured for **11–14**, relative to the analogous CH_2 or CH_3 derivatives (Figure 1). It is seen that **11**, **12**, and **14** show π-polarization patterns similar to the benzene-NH_4^+ pairs while **13** is intermediate between **11** and **14**, consistent with a charged group intermediate between a vertex and an edge of a benzene ring (see **15**, arrow indicates direction of electron polarization). The only inconsistency concerns C(3) and C(6) which show high field shifts in **13** and **14** while the benzene-NH_4^+ pairs would suggest low field shifts. This probably reflects ring strain.[15] The most important observation is that the ^{13}C chemical shifts of the appropriate carbons in **11–14** parallel the ^{19}F chemical shifts in **4–8** (Figure 1). This confirms that the polar effects on ^{19}F chemical shifts in **4–8** can be attributed to an orientation-dependent π-polarization effect.



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Therefore, we conclude that the reported chemical shifts in **1–9** are all consistent with the presence of a significant π-polarization effect. In fact, our results indicate that π polarization is the dominant polar effect upon chemical shifts in these derivatives. This does not rule out the presence of other forms of π-inductive effects (such as orbital repulsion effects[16]) as well as direct field effects (particularly in **2** and **3**, see below). However, it does indicate that π polarization is a much more important mechanism of transmission of polar effects than has generally been accepted.[16,17]

B. The Importance of Through-Space (Direct) Electric Field Effects upon ^{19}F Chemical Shifts in Aromatic Derivatives. The best compounds for evaluating the importance of field effects upon ^{19}F chemical shifts are 4-substituted β,β-difluorostyrenes (**16**). By analogy with 4-substituted styrenes, substituent-induced changes in $\delta_{F(a)} - \delta_{F(b)}$ should reflect through-space field effects (see Figure 2). Rae and Smith have reported ^{19}F chemical shifts for seven derivatives of **16**.[19] These data can be used to evaluate A in the Buckingham equation for linear electric field effects:[20,21]

Table III. Comparison of Estimated Direct (Through-Space) Field Contributions to ^{19}F Chemical Shifts for Nitro Derivatives of **1**, **2**, and **3**

Compound	Direct field contribution (ppm)[a]	Total field/inductive contribution[b]	% direct field contribution
3	−1.87 (−2.36)	−5.28	35 (45)
2	−1.87 (−2.36)	−8.50	22 (28)
Triphenylmethane	−0.23 (−0.30)	−1.27	18 (24)
Biphenyl	−0.26 (−0.33)	−2.59	10 (13)
trans-Stilbene	−0.13 (−0.16)	−1.65	8 (10)
Diphenyl sulfide[c]	−0.20 (−0.25)	−2.98	7 (8)

[a] Estimated from eq 1 using $A = 2.7 \times 10^{11}$ and (in brackets) $A = 3.4 \times 10^{11}$. Low field shifts are negative. [b] Estimated from ρ_I values from $\sigma_I - \bar{\sigma}_R$ correlations of ^{19}F chemical shifts of **1**, **8**, and **9** in CCl_4.[2a] The total field/inductive contribution was taken as $0.65\rho_I$, based on $\sigma_I = 0.65$ for the NO_2 group.[15] [c] Assuming a C-S-C angle of 109.5°.

Table IV. Calculated (CNDO/2) Charge Densities ($\times 10^4$) for 4-Substituted (β,β-Difluorostyrenes (**16**) Expressed Relative to X = H ($\alpha = 128.5°$)

	X						
	NMe_2	OCH_3	CH_3	F	CN	NO_2	NH_3^+
$q_{F(a)}\sigma$	−15[a]	−5	−5	+13	+18	+48	+200
$q_{F(b)}\sigma$	−15	−9	−4	0	+8	+23	+60
$q_{F(a)}\pi$	−19	−12	−5	−2	+9	+27	+88
$q_{F(b)}\pi$	−19	−12	−5	−2	+8	+25	+75
$q_{C(\beta)}\pi$	−200	−124	−55	−30	+65	+222	+651
$q_{C(\alpha)}\pi$	+101	+58	+28	0	−39	−134	−445
$\Delta q_F\sigma$	0	+4	−1	+13	+10	+25	+140
$\Delta q_F\pi$	0	0	0	0	+1	+2	+13

[a] Negative sign indicates increased electron density.

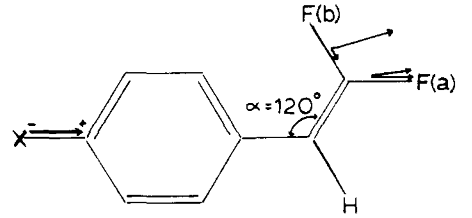

Figure 2. 4-Substituted β,β-difluorostyrene (**16**). For $\alpha = 120°$ and for a unit dipole placed 0.9 Å from C(4) along the C(4)-X bond axis, $E_z(F(a)) = 6.64 \times 10^3$ esu and $E_z(F(b)) = -0.61 \times 10^3$ esu. The corresponding values for $\alpha = 128.5°$ are $E_z(F(a)) = 6.12 \times 10^3$ esu and $E_z(F(b)) = 0.62 \times 10^3$ esu.

$$\Delta(\delta_{F(a)} - \delta_{F(b)}) = -A[E_z(C\text{-}F(a)) - E_z(C\text{-}F(b))] \quad (1)$$

where E_z(C-F) is the field component (due to the substituent group) acting along the C-F bond. E_z values were calculated at the midpoints of C-F bonds, using σ bond moments for individual substituents[22] and assuming standard bond lengths and bond angles.[23] In addition, E_z was calculated with the C(1)-C(α)-C(β) angle, $\alpha = 128.5°$, a value estimated from CNDO/2 calculations in which energy was minimized. The latter value is closer to experimental values of α in related derivatives.[8] Plots of $\Delta\delta$ vs. ΔE_z yielded $A = +27 \times 10^{12}$ for the standard geometry and $A \simeq +34 \times 10^{12}$ for the energy-minimized geometry. These A values should be at least semiquantitatively correct. They are intermediate between previously reported values of 10×10^{-12} [24] and 47×10^{-12} [25] for C-F bonds.[26]

Using these values of A, the Buckingham equation can be used to predict electric field contributions for various derivatives of **1**. Calculated contributions for nitro derivatives are given in Table III. Total field/inductive contributions were estimated from $0.65\rho_I$ ($\sigma_I = +0.65$ for NO_2[13]), using previously reported values of ρ_I.[2a] The results suggest that field effects represent about 40% of total field/inductive effects in fluorobenzenes (**2**). However, in derivatives of **1**, field effects are only a minor fraction of total field/inductive effects, as previously suggested.[2a] Derivatives **4**-**8** should have intermediate field contributions (ca. 25%).

To better understand the relative insensitivity of ^{19}F chemical shifts to direct field effects, CNDO/2 calculations were performed for derivatives of **16** using the energy-minimized geometry with $\alpha = 128.5°$ (see Table IV). $\Delta q_F\sigma$ (= $q_{F(a)}\sigma - q_{F(b)}\sigma$) provides a measure of the direct field effect, due to preferential field-induced polarization of the C(β)-F(a) bond (see Figure 2). The calculations indicate variations in $\Delta q_F\sigma$ which are similar in sign and magnitude to those for the corresponding styrene derivatives.[8]

While $\Delta q_F\sigma$ reflects through-space field effects, $q_{F(a)}\pi$ and $q_{F(b)}\pi$ show nearly equal changes, suggesting that *these parameters are relatively insensitive to direct field effects.* Instead, through-bond effects alter π-electron density at C(β) with resultant transfer of π-electron density between C(β) and both F(a) and F(b) (this can be regarded as a change in C(β)-F π-bond order). This is most apparent at F(b) since $q_{F(b)}\pi$ is proportional to $q_{C(\beta)}\pi$:[28]

$$q_{F(b)}\pi = 0.1 q_{C(\beta)}\pi \quad (2)$$

$\Delta q_F\pi$ does show a slight field dependence due to field-induced polarization of the partial C(β)-F(a)π bond, but only for highly polar groups. This accounts for the relative insensitivity of ^{19}F chemical shifts to direct field effects since there is general agreement that ^{19}F chemical shifts in aromatic derivatives primarily reflect changes in fluorine π-electron density.[28,29] Thus although direct field effects lead to significant C-F σ-bond polarization, ^{19}F chemical shifts are relatively insensitive to these effects compared with substituent effects transmitted through the π-electron system.

Conclusions

Analysis of the chemical shifts of derivatives **1–9** indicates that polarization of the intervening π-electron system is a significant mechanism of transmission of polar substituent effects in all of these derivatives.

Calculations based on the Buckingham equation indicate that direct field effects are important only in 4-substituted fluorobenzenes and 10-substituted 9-fluoroanthracenes. The relative insensitivity of ^{19}F chemical shifts to direct field effects arises because direct field effects act primarily by polarizing the C–F σ bonds while ^{19}F chemical shifts are mainly sensitive to variation in π-electron density.[30]

Experimental Section

Chemical shift measurements and molecular orbital calculations were carried out using previously reported procedures.[7,8]

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(17) π polarization could be regarded as a form of field effect.[4,18] However, we prefer to regard it as a π-inductive effect since the polarization is enhanced in conjugated systems.[2,8,9]

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(30) NOTE ADDED IN PROOF. Further evidence for π polarization effects has recently been obtained from ^{13}C chemical shifts for derivatives of **11**, **13**, and **14** with polar substituents [W. Adcock, B. D. Gupta, and W. Kitching, *J. Org. Chem.*, **41**, 1498 (1976)].

Aromatic Substitution in the Gas Phase. Ambident Behavior of Halo- and Dihalobenzenes toward D_2T^+. Tritiodeprotonation vs. Tritiodehalogenation

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Abstract: The gas-phase electrophilic attack of radiolytically formed D_2T^+ ions on halo- and dihalobenzenes was investigated in homogeneous systems formed by a large excess (760 Torr) of D_2 labeled with DT and containing at low concentrations (ca. 1 Torr) the aromatic substrate and a thermal radical scavenger (O_2). Analysis of the labeled products demonstrated two major reaction pathways, i.e., tritiodeprotonation, yielding the tritiated substrate or its isomers, and tritiodehalogenation. The relative rate of the two competing reactions is mainly determined by the nature of the halogen atom(s) contained in the substrate, the extent of dehalogenation increasing in the order Br $\leq$ Cl $\ll$ F. The results suggest two distinct mechanisms for the major reaction channels, as tritiodeprotonation appears to depend on the attack of D_2T^+ on the aromatic π system, while tritiodehalogenation requires the attack of the gaseous electrophile to the n center(s) of the substrate. The above conclusions, independently supported by appropriate ion cyclotron resonance and chemical ionization mass spectrometric data, are compared with the results obtained with different gaseous electrophiles and in related reactions occurring in solution.

Introduction

Novel experimental techniques[2-4] that allow the isolation of the final products and the determination of the *substrate* and *positional* selectivity of the electrophile have been extensively applied to the study of aromatic substitutions in the gas phase, i.e., in a reaction environment entirely free from the complicating effects of solvation and ion pairing that invariably affect