# A CRITICAL EXAMINATION OF FLUORINE HYPERCONJUGATION IN AROMATIC SYSTEMS

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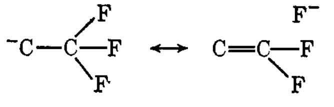
## Contents

## I. Introduction

Fluorine hyperconjugation or no-bond resonance (I) has



I

often been used to rationalize physical properties[2-5] and reactivity patterns[3,5,6] of organo fluorine compounds. Recent studies concerning the relative stability of various highly fluorinated aliphatic anions indicate that fluorine hyperconjugation plays no significant role in influencing aliphatic reactivity.[5,7] The purpose of the present review is to evaluate the importance of fluorine hyperconjugation in aromatic systems. Discussion will center on the Hammett behavior of the trifluoromethyl substituent for reactions involving the delocalization of negative charge. Auxiliary data gleaned from dipole moment and nuclear magnetic resonance (nmr) studies will also be presented. In the analysis which follows, the relative merits of fluorine hyperconjugation, and alternative models such as Sheppard's p-π effect[8] involving electron back-donation by fluorine lone pairs and the so-called π-inductive mechanism,[9] in which polar effects are considered dominant, will be considered as a means of rationalizing aromatic behavior.

## II. Physical Methods Relating to Fluorine Hyperconjugation

### A. DIPOLE MOMENTS

One of the classical methods by which resonance interactions have been detected is by means of dipole moments. In one approach the vector difference between the dipole moment of an aromatic compound ArX and that of its aliphatic analog RX is ascribed to resonance.[10] Such resonance moments, $\mu_r$, are listed for several substituents in Table I. The large magnitude of $\mu_r$ for the groups $-OCH_3$ or $-NH_2$, for example, is interpreted as indicating the important resonance capabilities of these substituents.[10] The small resonance moment of $CF_3$ has been interpreted as suggesting the importance of hyperconjugation.[3] However, rationalization in terms of the yet to be discussed π-inductive mechanism is equally plausible.

*Table I*

**Resonance Moments Derived from Monosubstituted Benzenes**[a]

| *Substituent* | $\mu_r$[b] | *Substituent* | $\mu_r$[b] |
|---|---|---|---|
| $N(CH_3)_2$ | 1.66 | F | 0.41 |
| $NH_2$ | 1.02 | $CH_3$ | 0.35 |
| $OCH_3$ | 0.8 | $CF_3$ | −0.2 |
| OH | 0.6 | CN | −0.45 |
| I | 0.50 | $COCH_3$ | −0.46 |
| Br | 0.43 | $CCl_3$ | −0.50 |
| Cl | 0.41 | $NO_2$ | −0.76 |

[a] Sutton, ref 10. [b] Defined as the vector difference $\mu(ArX) - \mu(RX)$; *i.e.*, corrections for the direction of the bond moments of $-NH_2$, $-N(CH_3)_2$, $-OH$, and $-OCH_3$ have been applied.

Perhaps a better method of detecting resonance effects with dipole moments is by means of substituent interactions. For example, the fact that the observed dipole moment of *p*-dimethylaminonitrobenzene (II) is significantly larger than that

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[1] Present address: Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, Calif. 91109.

[2] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, pp 314–316.

[3] J. D. Roberts, R. L. Webb, and E. A. McElhill, *J. Amer. Chem. Soc.*, **72**, 408 (1950).

[4] J. Hine, *ibid.*, **85**, 3239 (1963).

[5] D. Holtz, *Progr. Phys. Org. Chem.*, in press.

[6] S. Andreades, *J. Amer. Chem. Soc.*, **86**, 2003 (1964).

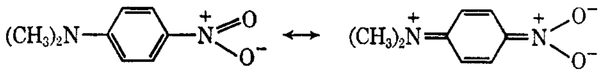
[7] A. Streitwieser, Jr., and D. Holtz, *ibid.*, **89**, 692 (1967).

[8] W. A. Sheppard, *ibid.*, **87**, 2410 (1965).

[9] (a) M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962, pp 155–156; (b) A. Streitwieser, Jr., and H. F. Koch, *J. Amer. Chem. Soc.*, **86**, 404 (1964); (c) A. Talvik, P. Zuman, and O. Exner, *Collect. Czech. Chem. Commun.*, **29**, 1266 (1964).

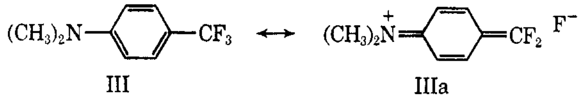
[10] L. E. Sutton in "Determination of Organic Structures by Physical Methods," Vol. 1, E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, pp 392–396.

calculated from the sum of the moments of dimethylaniline and nitrobenzene is usually interpreted as indicating the importance of resonance structure IIa to the ground state of the molecule. A significant contribution by such a resonance



II IIa

form would, of course, be predicted to cause an enhanced dipole moment. We might expect that a similar analysis for *p*-dimethylaminobenzotrifluoride (III) would allow comment on the relative importance of resonance structure IIIa to the ground state of this molecule.

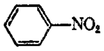
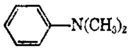
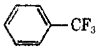
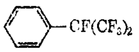
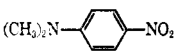
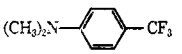
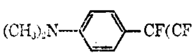


III IIIa

The data in Table II do indeed show an enhanced dipole moment for $p$-$CF_3C_6H_4N(CH_3)_2$. This was one of the pieces of evidence which Roberts[3] used in first suggesting the concept of fluorine hyperconjugation. However, it is to be noted that $p$-$(CF_3)_2CFC_6H_4N(CH_3)_2$ also shows an exalted dipole moment. As Sheppard[8] has pointed out, the similarity in the enhancement of the dipole moment for these two molecules suggests that fluorine no-bond resonance is not responsible for the enhancement. The only alternative to this conclusion is the postulate that no-bond resonance involving a $C$–$CF_3$ bond is as important as for C–F. This is clearly not the case since the stabilities of fluoride and trifluoromethide ion differ so vastly; the acidity of HF is at least 30 powers of ten greater than that of $HCF_3$.

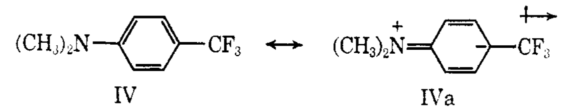
*Table II*

**Dipole Moments of Some Substituted Benzenes**

| *Compound* | Dipole moment, D: *Measd*[a] | *Calcd*[b] | *Diff* |
|---|---|---|---|
|  | 3.93 | | |
|  | 1.58 | | |
|  | 2.61 | | |
|  | 2.68 | | |
|  | 6.89 | 5.51 | 1.38 |
|  | 4.62 | 4.19 | 0.43 |
|  | 4.71 | 4.26 | 0.45 |

[a] Values taken from Sheppard, ref 8, and McClellan, ref 12. [b] By simple addition.

An alternative model seems to explain the data of Table I at least as well as fluorine hyperconjugation does. The moments of both $ArCF_3$ and $ArCF(CF_3)_2$ as well as the difference between $ArCF_3$ and $RCF_3$ can be adequately rationalized without hyperconjugation by a structure such as IVa in which the strongly electron-withdrawing perfluoroalkyl groups have polarized the aromatic $\pi$ electrons so as to cause an enhanced dipole moment. This so-called $\pi$-inductive mechanism is discussed in more detail below.



IV IVa

In closing this section, it seems relevant to point out that the dipole moments of the meta compounds $m$-$(CH_3)_2NC_6H_4CF_3$ and $m$-$(CH_3)_2NC_6H_4CF(CF_3)_2$ have never been measured. Arguments based on dipole moments relating to such subtle structures as IIIa have little value until it is shown that normal behavior is observed in molecules where such resonance is impossible.[11]

## B. NUCLEAR MAGNETIC RESONANCE

This physical method which has revolutionized many areas of organic chemistry (structural elucidation, fast kinetics, etc.) is also potentially capable of yielding *experimental* electron distributions in organic molecules. Although some work in this direction has been accomplished,[13] further advances await a more refined understanding of the relationship of actual electron distributions to observed magnetic phenomena. In this respect, nuclei whose chemical shifts are paramagnetic in origin ($^{19}F$, $^{13}C$, but not $^{1}H$) are especially valuable since other magnetic perturbations such as diamagnetism, functional group anisotropies, and ring current effects become secondary.[14,15]

Studies of substituent effects on $^{19}F$ nmr shifts have had some bearing on the question of the importance of fluorine hyperconjugation in aromatic systems. Taft and his coworkers have done an exhaustive amount of work rationalizing $^{19}F$ chemical shifts in substituted fluoro aromatics in terms of physical organic substituent parameters. For substituted fluorobenzenes they have found the following.

(1) Chemical shifts of meta substituents are adequately correlated in terms of Hammett-like inductive parameters ($\sigma_I$).[16] Para substituents require a combination of inductive and resonance parameters ($\sigma_I$ and $\sigma_{R^0}$).[17]

(2) The fluorine chemical shift is insensitive to solvent variation for most meta substituents. Solvent effects which do occur are systematic and can be attributed to donor–acceptor-type interactions related to the chemical properties of the solvent and the substituent, *e.g.*, $CF_3COOH + m$-$FC_6H_4NH_2$. The correlation of the fluorine chemical shift with parameters derived from reaction chemistry coupled with the absence of solvent effects is strong evidence that only *intramolecular*

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(11) Additional dipole moments of substituted benzotrifluorides: (a) H. Freiser, M. E. Hobbs, and P. M. Gross, *J. Amer. Chem. Soc.*, **71**, 111 (1949); (b) G. Kraus and A. B. Conciatori, *ibid.*, **72**, 2283 (1950); (c) P. E. Brown and T. DeVries, *ibid.*, **73**, 1811 (1951); (d) A. L. Meyers and T. DeVries, *ibid.*, **73**, 1813 (1951); (e) J. J. Conradi and N. C. Li, *ibid.*, **75**, 1785 (1953); (f) A. E. Lutskii, E. M. Obukhova, Z. M. Kanevskaya, and A. S. Gol'berkova, *Teor. Eksp. Khim.*, **2**, 264 (1966); *Theor. Exp. Chem. (USSR)*, **2**, 201 (1966).

(12) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco, Calif., 1963.

(13) For leading references see (a) R. W. Taft and J. W. Rakshys, Jr., *J. Amer. Chem. Soc.*, **87**, 4387 (1965); (b) F. M. Beringer and S. A. Galton, *J. Org. Chem.*, **31**, 1648 (1966).

(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959, pp 317, 344.

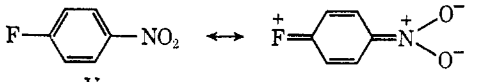
(15) C. Beguin, *Bull. Soc. Chim. Fr.*, 2711 (1964).

(16) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963).

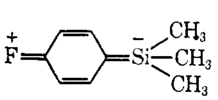
(17) R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).

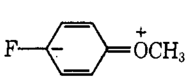
*electronic effects* are contributing to the fluorine chemical shift.[17,18]

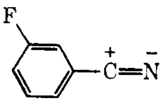
(3) The fluorine chemical shifts of para substituents are solvent invariant for *electron-donating groups*. However, electron-withdrawing substituents which are capable of resonance interaction with the para fluorine show shifts to lower field as solvent polarity is increased.[16] Taft has interpreted this phenomenon as due to an enhancement in polar solvents of resonance forms such as Va. It is found that charges must be at the periphery of the molecule to elicit a solvent response[19]; *i.e.*, structures such as VI, VII, and VIII


V Va

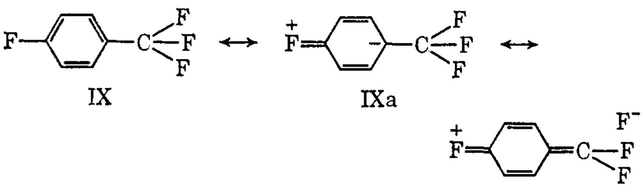
are solvent insensitive. Thus we have a potential probe to


VI


VII


VIII

distinguish between resonance structures IXa and IXb.


IX IXa IXb

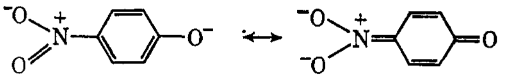
In fact, the $^{19}F$ nmr chemical shift of the ring fluorine in *p*-fluorobenzotrifluoride shows a small solvent dependence consistent with IXb;[19] *i.e.*, the analysis seems to indicate some role for fluorine hyperconjugation. On the other hand, Sheppard[8] has shown that the chemical shift of the trifluoromethyl fluorines of IX is insensitive to solvent changes. One would expect these fluorines to undergo solvent shifts also if IXb is truly important. Further, all of the para substituents which have been observed to cause solvent shifts are both electron withdrawing and resonance conjugating (CN, $NO_2$, $COOCH_3$, etc.) except possibly for the test substituent $CF_3$. To be sure that solvent shifts result from charge separation by resonance conjugation, the solvent dependence of para electron-withdrawing groups which are not resonance conjugating ($CH_2CF_3$, $CH_2Cl$, $CH_2NO_2$, etc.) should be determined. The importance of fluorine hyperconjugation to the observed chemical shifts is thus an open question.

In another study, Bumgardner[20] has written hyperconjugative resonance forms involving fluorine in explaining the $^{19}F$ chemical shifts of substituted benzotrifluorides. His conclusion is unwarranted owing to a paucity of examples. This system is unlikely to yield conclusive results even if more work is attempted because the substituent effects on the chemical shift for the substituted benzotrifluorides is an order of magnitude less than that found for the substituted fluorobenzenes.[21]

In conclusion it can be stated that no strong definitive picture regarding the importance of fluorine hyperconjugation in the ground state of molecules emerges from nmr studies to date.

## III. Reactivity Studies Relating to Fluorine Hyperconjugation

Perhaps the best and most reliable criterion for postulating a resonance effect for a particular substituent is the determination that multiple $\sigma$ constants are necessary to reproduce observed reactivity. For example, the ionization of benzoic acids and phenols requires two sigma constants ($\sigma$, $\sigma^-$) to describe satisfactorily the substituent behavior of the *p*-$NO_2$ group. This phenomenon is usually interpreted in terms of a resonance interaction (Xa) for the *p*-nitrophenolate ion which


X Xa

is not possible for the corresponding benzoate ion. Such an interpretation is further justified by the fact that in the case of *m*-$NO_2$, for which a resonance interaction such as Xa is not possible in either the phenolate or benzoate ions, one $\sigma$ constant serves to correlate the observed reactivity behavior.

A possible test, therefore, for the importance of fluorine hyperconjugation is whether or not a second $\sigma$ constant is necessary to correlate the substituent behavior of the *p*-trifluoromethyl group for reactions involving anions. A collection of $\sigma$ constants for the trifluoromethyl group derived from various reactions in which delocalization of negative charge is important is presented in Table III. For each reaction the least-squares regression line was calculated omitting the *m*- and *p*-$CF_3$ substituents; the reactivity of these two substituents was then used to calculate $\sigma_m(CF_3)$ and $\sigma_p(CF_3)$. Widely deviant as well as charged substituents were omitted from the least-squares calculation. Most commonly these were $CO_2^-$, *m*- and *p*-$NH_2$, *p*-I, and *p*-Ph. Groups whose $\sigma$ constants were not listed by Leffler and Grunwald[22] were also rejected. The results of these calculations differ slightly from the values reported by the original authors. Correlation coefficients were always better than 0.985. Representative plots of the Hammett correlations from which the $\sigma$ values of Table III were derived are displayed in Figure 1.

The $\sigma$ values derived for *p*-$CF_3$ in Table III are indeed exalted for reactions in which the delocalization of negative charge is important (reactions 2–9). Such behavior might be interpreted as indicating the importance of fluorine hyperconjugation. It is to be noted, however, that an enhancement in $\sigma$ value also occurs for *m*-$CF_3$! This is not the case for groups such as $NO_2$, CN, etc., which delocalize negative charge by classical resonance. For these groups only the para isomer shows an enhanced $\sigma$ value.

Perhaps the ratio, $\sigma_p/\sigma_m$, is a better indication of resonance participation. Typically, this ratio has a value of 1.14 ±

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[18] R. W. Taft, *J. Amer. Chem. Soc.*, 79, 1045 (1957).

[19] See ref 17, pp 3154–3156.

[20] C. L. Bumgardner, *J. Org. Chem.*, 28, 3225 (1963).

[21] R. W. Taft and L. Erickson, private communication.

[22] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, pp 173, 211.

*Table III*

**$\sigma$ Values Derived for the Trifluoromethyl Group from Various Reactions**

| *Reaction* | $\sigma_m$[a] | $\sigma_p$[a] | $\sigma_p/\sigma_m$ | *Slope*[b] | *Intercept*[b] | *Corr coeff*[b,c] | *Ref* |
|---|---|---|---|---|---|---|---|
| 1. Ionization of benzoic acids, 25°, in 50% ethanol–water | 0.42 | 0.53 | 1.26 | ... | ... | ... | 8 |
| 2. Ionization of anilines, 25°, in water | 0.47 | 0.63 | 1.34 | −2.78 ± 0.08 | 4.51 ± 0.03 | 0.993 (21) | 8, 24 |
| 3. Ionization of phenols, 25°, in water | 0.44 | 0.56 | 1.28 | −2.18 ± 0.04 | 9.90 ± 0.02 | 0.998 (14) | 25, 26 |
| 4. Sodium methoxide addition to para-substituted pentafluorobenzenes, 60°, in methanol | ... | 0.72 | ... | 4.85 ± 0.21 | 0.18 ± 0.11 | 0.996 (6) | 27, 28 |
| 5. $\alpha$-Tritium exchange of toluenes, 50°, with lithium cyclohexylamide in cyclohexylamine | 0.47 | 0.60 | 1.28 | 3.74 ± 0.16 | 0.01 ± 0.03 | 0.995 (8) | 9b, 29 |
| 6. Sodium thiophenoxide addition to substituted 2-nitrochlorobenzenes, 35°, in methanol | 0.44 | 0.63 | 1.43 | 4.46 ± 0.13 | 0.52 ± 0.06 | 0.994 (18) | 30 |
| 7. Sodium methoxide addition to 4-substituted 2-nitrochlorobenzenes, 50°, in methanol | ... | 0.74 | ... | 3.93 ± 0.12 | 0.02 ± 0.08 | 0.997 (9) | 31 |
| 8. Pyrrolidine addition to substituted 2-nitrochlorobenzenes, 45°, in benzene | ... | 0.73 | ... | 3.82 ± 0.16 | −0.06 ± 0.8 | 0.985 (19) | 32 |
| 9. Sodium methoxide addition to para-substituted chlorobenzenes, 50°, in methanol | ... | 0.65 | ... | 8.41 ± 0.19 | 0.15 ± 0.15 | 0.999 (4) | 33 |

[a] Calculated from the reactivity of the $CF_3$ substituent using the Hammett plot least-squares correlation parameters. [b] For least-squares correlation of Hammett plot. [c] Values in parentheses are the number of points present in the least-squares correlation.

0.05 when only inductive effects are important.[23] When resonance delocalization is possible this ratio ($\sigma_p^-/\sigma_m$) assumes a value in the range 1.75–1.84 (CN, $NO_2$, $SO_2CH_3$, $CO_2C_2H_5$) or even higher ($COCH_3$ = 2.32; $CH{=}CHNO_2$ = 2.59).[22]

The values observed for $\sigma_p/\sigma_m$ for $CF_3$ (1.28–1.43) in systems that require delocalization of negative charge are only slightly greater than the value (1.26) observed for the benzoic acids in which direct conjugation by fluorine hyperconjugation is impossible. It is difficult to interpret these numbers. Is the difference between 1.43 and 1.28 significant compared to 1.75, or are the enhancements of $p$-$CF_3$ exhibited in Figure 1 only experimental scatter from the correlation lines?

Taft has developed a methodology for separating aromatic substituent effects into their inductive and resonance components.[16,17,34,35] Using this approach, Sheppard[8] has examined a number of $m$- and $p$-perfluoroalkyl fluorobenzenes. The inductive ($\sigma_I$) and resonance ($\sigma_R$) effects of the groups $CF_3CF_2$–, $CF_3CF_2CF_2CF_2$–, $(CF_3)_2CF$–, and $(CF_3)_2C(OH)$– were determined from p$K_a$ measurements of benzoic acids and anilines and were in agreement with values determined from $^{19}F$ nmr chemical shifts. The results are presented in Table IV.

*Table IV*

**Substituent Parameters Derived for Various Perfluoroalkyl Groups**[a]

| *Substituent* | $\sigma_I$ | $\sigma_R$ | $\sigma_R^0$ |
|---|---|---|---|
| $CF_3$ | 0.33–0.44 | 0.18 | 0.10 |
| $CF_2CF_3$ | 0.41 | ... | 0.11 |
| $n$-$(CF_2)_3CF_3$ | 0.39 | ... | 0.11 |
| $CF(CF_3)_2$ | 0.25–0.48 | 0.17–0.26 | 0.04 |
| $C(OH)(CF_3)_2$ | 0.28–0.31 | 0.15 | 0.02 |

[a] Sheppard, ref 8.

Significantly, the inductive and resonance effects of the various perfluoroalkyl groups are similar to those of the $CF_3$ group. Therefore, fluorine no-bond resonance (IXb) cannot be contributing in an important way to the electronic structures of these molecules; if it were, $\sigma_R$ would be expected to be much larger for $CF_3$ than for the other groups investigated The only alternative to his conclusion is the postulate that no-bond resonance involving a C–$CF_3$ bond is as important as that for a C–F bond; *i.e.*, resonance structures XIa and XIb are of equal energy. This is clearly not the case since as

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(23) O. Exner, *Collect. Czech. Chem. Commun.*, **31**, 65 (1966).

(24) (a) D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworths, London, 1965. (b) A more recent determination (ref 8) of the p$K$ of $p$-trifluoromethylaniline is to be especially noted. Thus, coupled with the analysis of dipole moments presented above, we see that the evidence upon which the original suggestion for fluorine hyperconjugation was based (ref 3) is now obsolete and invalid.

(25) A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, 388 (1961).

(26) C. L. Liotta and D. F. Smith, Jr., *Chem. Commun.*, 416 (1968).

(27) J. Burdon, W. B. Hollyhead, C. R. Patrick, and K. V. Wilson, *J. Chem. Soc.*, 6375 (1963).

(28) K. C. Ho and J. Miller, *Aust. J. Chem.*, **19**, 423 (1966), report kinetic parameters for this reaction which deviate significantly from the results of ref 27 and give $\sigma_p(CF_3)$ = 0.82. The results of ref 27 seem more reliable because of a superior method of analyzing kinetic aliquots.

(29) A. Streitwieser, Jr., and D. Holtz, *J. Org. Chem.*, **35**, 4288 (1970).

(30) A. M. Porto, L. Altieri, A. J. Castro, and J. A. Brieux, *J. Chem. Soc. B*, 963 (1966).

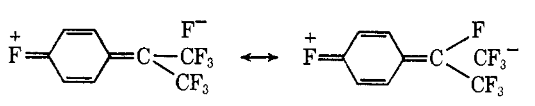
(31) J. Miller, *Aust. J. Chem.*, **9**, 61 (1956).

(32) W. Greizerstein, R. A. Bonelli, and J. A. Brieux, *J. Amer. Chem. Soc.*, **84**, 1026 (1962).

(33) J. Miller and W. Kaiyan, *J. Chem. Soc.*, 3492 (1963).

(34) R. W. Taft and I. G. Lewis, *J. Amer. Chem. Soc.*, **81**, 5343 (1959).

(35) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960).



XIa XIb

mentioned previously the acidities of HF and $HCF_3$ differ by at least 30 powers of ten. On the other hand, if fluorine hyperconjugation is totally insignificant then $\sigma_R(CF_3)$ should be zero. Perhaps the $\sigma_R$ constants are improperly scaled.

In a more recent study, Swain[36] has shown that all of the various types of $\sigma$ constants introduced over the years can be satisfactorily correlated in terms of two parameters $\mathcal{F}$ and $\mathcal{R}$. These parameters which are purported to represent the field (inductive) and resonance components, respectively, of a substituent correlate 43 different reaction series with an average correlation coefficient of 0.967. The magnitudes of $\mathcal{F}$ and $\mathcal{R}$ for a given substituent should give a measure of the relative importance of inductive and resonance interactions for that substituent. Inspection of Table V indicates that trifluoromethyl is a strong electron acceptor by resonance both in a relative and absolute sense. The $\mathcal{R}$ and $\mathcal{R}/\mathcal{F}$ values for trifluoromethyl (0.186, 0.29) are larger than those observed for the classical resonance substituents nitro (0.155, 0.14) and cyano (0.184, 0.22). The analysis suggests that hyperconjugation is an important component of trifluoromethyl substituent effects.

*Table V*

**Swain Substituent Parameters**[a]

| *Substituent* | $\mathcal{F}$ | $\mathcal{R}$ | $\lvert\mathcal{R}/\mathcal{F}\rvert$ |
|---|---|---|---|
| $NH_2$ | 0.037 | −0.681 | 18.4 |
| $OCH_3$ | 0.413 | −0.500 | 1.21 |
| $CH_3$ | −0.052 | −0.141 | 2.71 |
| H | 0.000 | 0.000 | ... |
| F | 0.708 | −0.336 | 0.47 |
| Cl | 0.690 | −0.161 | 0.23 |
| Br | 0.727 | −0.176 | 0.24 |
| I | 0.672 | −0.197 | 0.29 |
| $CF_3$ | 0.631 | 0.186 | 0.29 |
| CN | 0.847 | 0.184 | 0.22 |
| $NO_2$ | 1.109 | 0.155 | 0.14 |
| $COCH_3$ | 0.534 | 0.202 | 0.38 |
| $N(CH_3)_3^+$ | 1.460 | 0.000 | ... |

[a] Swain and Lupton, ref 36.

Swain has made a valuable contribution in that he has shown that the literal hoard of different $\sigma$ constants can all be expressed in terms of two parameters. However, it is not clear that the derived parameters, $\mathcal{F}$ and $\mathcal{R}$, are necessarily an adequate measure of the field and resonance components of substituent effects. Indeed the results presented above seem to indicate the opposite. Even if fluorine hyperconjugation were important, it is difficult to see how such an interaction could be more important than classical resonance. In this respect, $\mathcal{R}$ values indicate that the resonance interaction of methyl (−0.141) is almost as important as that of chloro (−0.161). Perhaps Swain's $\mathcal{R}$ values also contain an inductive component.

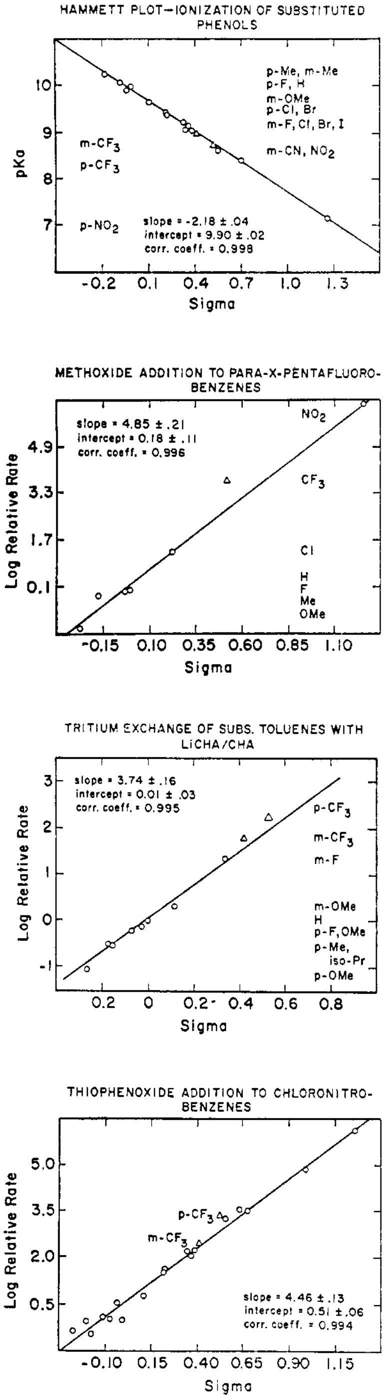


**Figure 1.** Representative Hammett plots for reactions involving delocalization of negative charge. *m*- and *p*-$CF_3$ are represented by the symbol Δ and have been omitted from the calculation o the least-squares line.

Swain defined $\mathcal{F}$ as identical with the substituent constant $\sigma'$ derived from the 4-substituted bicyclo[2.2.2]octane-1-carboxylic acids.[37] There is little question then that $\mathcal{F}$ is a valid measure of inductive effects. To obtain $\mathcal{R}$ values, Swain assumed that the resonance effect of the trimethylammonium group, $(CH_3)_3N^+$–, is zero. The derivation of $\mathcal{R}$ for all sub-

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[36] C. G. Swain and E. C. Lupton, Jr., *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

[37] (a) J. D. Roberts and W. T. Moreland, Jr., *ibid.*, **75**, 2167 (1953); (b) H. D. Holtz and L. M. Stock, *ibid.*, **86**, 5189 (1964); (c) F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, **89**, 5678 (1967).

stituents follows by employing a given substituent's $\mathcal{F}$, and $\sigma_p$ values in conjunction with eq 1 with $r_p$ set equal to unity.

$$\sigma_p = f_p\mathcal{F} + r_p\mathcal{R} \qquad (1)$$

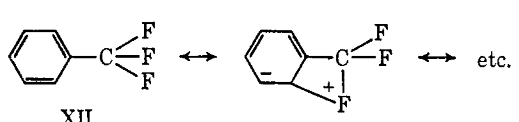
The parameter $\mathcal{R}$, as defined, may not be a good measure of the resonance component of a substituent. Problems relating to the relative magnitude of $\mathcal{R}$ for various substituents have already been raised above. Of more theoretical concern is the fact that Swain's methodology defines the resonance component for dipolar substituents on the basis of the behavior of an ionic substituent. Since ionic and dipolar substituent effects may be fundamentally different and since most common substituents are dipolar in nature, it would seem to be more reasonable to try to define resonance contributions in terms of a dipolar substituent.

Two alternative ways of defining $\mathcal{R}$ may be suggested. Previous sections have shown the large role inductive effects play in influencing the reactivity of fluoroalkyl substituents. One might hypothesize therefore that $\mathcal{R}$ for trifluoromethyl is zero. Such a hypothesis, of course, defines a set of $\mathcal{R}$ values for all substituents. Alternatively, the $\mathcal{R}$ component of substituents $CH_2X$ could be taken as zero. Such substituents[23,38] are insulated from the $\pi$ system of the aromatic nucleus by a methylene group and would be expected to have negligible resonance components. It would be interesting to investigate the consequences of these two alternative methods of defining $\mathcal{R}$.

## *IV. Alternative Rationalizations*

### A. THE p–π MECHANISM

In an important paper Sheppard[8] has investigated substituent effects on $^{19}F$ nmr shifts for several systems, including $CF_3C_6H_4X$, and has chosen to explain his results in a novel manner. He interprets the substituent behavior of the trifluoromethyl group in terms of an interaction of the unshared p electrons of the fluorine atom with the $\pi$ system of the aromatic ring. Electron density is returned to the ring partly counteracting the normal electron-withdrawing effect of fluorine. This p–$\pi$ effect is illustrated in the resonance structures below.



XII XIIa

Unfortunately, the argument on which Sheppard postulates this effect is unconvincing. Sheppard considers first the two kinds of fluorines in arylsulfur pentafluorides (Figure 2). The apex fluorine cannot interact directly with the $\pi$ system of the ring, and its chemical shift should be influenced by only normal inductive and resonance effects transmitted through the molecule. In agreement with this idea, the chemical shift of the apex fluorine is found to correlate directly with the ordinary Hammett $\sigma$ parameters. On the other hand, he argues, the chemical shift of the basal fluorines should be influenced not only by normal inductive and resonance effects but also, if it exists, by the effect of the p–$\pi$ interaction. Hence, according to Sheppard, the difference between the chemical shift of the apex and basal fluorines should be a direct measure of the extent of the p–$\pi$ interaction and should correlate directly with the $\pi$-system charge density. Sheppard now says that the $\pi$-system charge density is roughly proportional to the ordinary Hammett $\sigma$ parameters and since $\Delta\delta$ (chemical shift difference between apex and basal fluorines) correlates linearly with $\sigma$, the reality of the p–$\pi$ interaction is proven. A similar analysis of the benzotrifluoride chemical shifts again using the chemical shift of the apex fluorine of $SF_5$ as a standard for the contribution from inductive and resonance effects gives correlation lines of the same slope although with slightly displaced intercepts. This indicates that the p–$\pi$ mechanism must be important for the trifluoromethyl group also.

*Table VI*

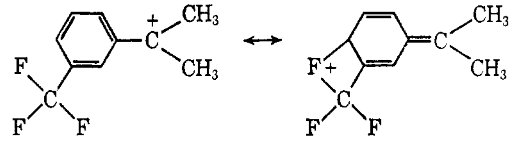
**$\sigma$ and $\sigma^+$ Constants for Trifluoromethyl**

| | $\sigma$ | $\sigma^+$ |
|---|---|---|
| $m$-$CF_3$ | 0.42[a] | 0.52[b] |
| $p$-$CF_3$ | 0.53[a] | 0.61[b] |

[a] Sheppard, ref 8. [b] Brown and Okamoto, ref 39.

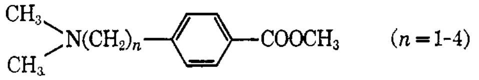
The trouble with this analysis is, of course, that all of the chemical shifts investigated correlate with the Hammett $\sigma$ constants. It is reasonable to expect that fluorines in different chemical environments will respond with different sensitivities (different rhos) to the Hammett parameters. This is exactly what is observed. There appears to be no reason to postulate a special effect such as the p–$\pi$ mechanism to rationalize such normal behavior.

This is not to belittle Sheppard's suggestion for it is novel and worthy of consideration. Other evidence, however, suggests that the p–$\pi$ mechanism is not important for the aromatic trifluoromethyl group. If the p–$\pi$ mechanism were important, then $\sigma^+$ should be considerably less in value than $\sigma$ for $m$-$CF_3$, that is to say that contributions from resonance structure XIIIa should accelerate the rate of solvolysis of $m$-trifluoromethylcumyl chloride.



XIII XIIIa

In fact, $\sigma^+ > \sigma$ for both $m$- and $p$-$CF_3$ and the p–$\pi$ interaction mechanism fails an important test (Table VI). Stock[40] using essentially a similar argument has also criticized the p–$\pi$ mechanism. Further, Smith and Menger[41] have recently studied the spectral properties and the basic hydrolysis kinetics of the aminoalkyl benzoates, XIV. Back-bonding effects, if indeed they are significant, should be as important in XIV as they



XIV

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[38] O. Exner, *Tetrahedron Lett.*, 815 (1963).

[39] H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4980 (1958).

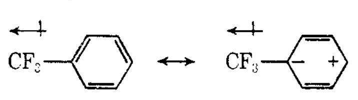
[40] Reference 37c, p 5682.

[41] J. H. Smith and F. M. Menger, *J. Org. Chem.*, **34**, 77 (1969).

are in Sheppard's perfluoroalkyl aromatics. The results as measured by spectral shifts and intensities gave no indication of any p–$\pi$ interaction in either the ground (ir) or excited (uv) states of XIV. The kinetic results were also in agreement with this conclusion.[42] It can therefore be concluded that the p–$\pi$ effect is unimportant in influencing the chemistry of the $CF_3$ group.[42a]

## B. THE $\pi$-INDUCTIVE MECHANISM

The above analyses do not eliminate fluorine hyperconjugation as a possible mechanism for stabilization. More significantly *they do not require its postulation* either. In light of the material presented in previous sections, it seems most reasonable to interpret the reactivity behavior of the trifluoromethyl substituent without the use of fluorine hyperconjugation. We choose instead an inductive model, the so-called $\pi$-inductive effect.[9] This model, illustrated by XVa, represents the strong electron-withdrawing effect of the trifluoromethyl group as a dipole external to the benzene ring polarizing the $\pi$ system so as to enhance the delocalization of negative charge. The model is consistent with the following facts: (1) the more than normal enhancement of reactivity by the *p*-$CF_3$ group in reactions requiring delocalization of negative charge (Table III); (2) the difference in dipole moment between trifluoromethyl-substituted aromatic and aliphatic compounds and the enhanced dipole moments of molecules such as *p*-trifluoromethylaniline; (3) the similarity in $\sigma_R$ parameters for several perfluoroalkyl groups as determined by Sheppard[8] from p$K_a$ and $^{19}F$ nmr measurements; (4) the correlation of the methoxide-catalyzed hydrogen isotope exchange rates of 9-substituted fluorenes, including 9-$CF_3$, with the inductive substituent parameter $\sigma_I$;[43] (5) the success in rationalizing large reactivity differences in highly fluorinated aliphatic systems solely in terms of inductive effects.[5]



XV XVa

It should also be mentioned, without losing sight of the limitations of the molecular orbital method, that a self-consistent field molecular orbital calculation by Wright has shown the quantitative feasibility of the $\pi$-inductive model.[44,45] For his calculation, Wright represented the trifluoromethyl group by a dipole external to the benzene ring and calculated the loss in $\pi$-bonding energy for the reaction $ArCH_3 \rightarrow ArCH_2^-$. The ratio of this energy loss for a dipole in the para position as compared to the meta position was found to be 1.27–1.38 depending on the value assumed for the dielectric constant of the medium intervening between the dipole and the benzene ring. The range of these numbers agrees well with the experimental values found for $\sigma_p/\sigma_m$ for the reactions listed in Table III.

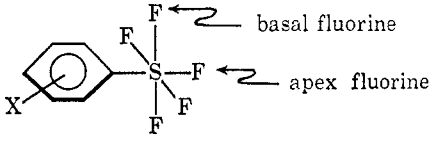


**Figure 2.** Arylsulfur pentafluoride illustrating the apex and basal fluorines.

The $\pi$-inductive model is much superior in rationalizing the above facts than either the fluorine hyperconjugation model or Sheppard's p–$\pi$ interaction mechanism. The shortcomings of these latter two models have already been well noted in previous sections. Sheppard[8] has criticized the $\pi$-inductive model on the grounds that it is unable to explain the substituent behavior of groups such as $-N(CH_3)_3^+$, $-ICl_2$, and $-N(CF_3)_2$. He is correct, but then neither of the two alternative models do any better. Another criticism of the $\pi$-inductive mechanism for the $CF_3$ group has been that it does not explain why the relative values of the inductive and resonance components of the Hammett constants ($\sigma_I$ and $\sigma_R$) are so different from those of the $C(CN)_3$ group[46] which presumably can influence reactivity only by inductive effects. Although Wright's calculation[44] does not satisfactorily resolve this problem, it does show that the stabilizing influence of the trifluoromethyl group in a situation urgently requiring electron delocalization can be quantitatively described satisfactorily in terms of polarization of the aromatic $\pi$ system by the dipole moment associated with $CF_3$. That is, inductive effects adequately rationalize the substituent behavior of the trifluoromethyl group in an aromatic system. Considering all of the available evidence, the $\pi$-inductive model best describes the behavior of perfluoroalkyl groups in aromatic systems at the present time.

## *V. Conclusion*

In this article we have made a critical analysis of the importance of the popular concept of fluorine hyperconjugation in influencing the physical properties and reactivity patterns of aromatic systems containing perfluoroalkyl substituents. The conclusion is reached that fluorine hyperconjugation is unimportant as a primary factor in influencing physical properties and reactivity patterns. Alternative rationalizations have been explored, and it is concluded that at the present time a model based on polar (inductive) effects best describes the substituent effects of perfluoroalkyl groups.

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(42) It is recognized that a better evaluation of the p–$\pi$ hypothesis could have been made if the meta-substituted counterparts of XIV had also been studied.

(42a) For a recent paper on this point, see K. J. Klabunde, *J. Amer. Chem. Soc.*, **92,** 2427 (1970).

(43) A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89,** 693 (1967). The number of substituents on which the correlation line for this study is based must be increased before great weight can be given to the results of this work.

(44) J. S. Wright, Ph.D. Thesis, University of California, Berkeley, 1968, pp 168–192.

(45) D. Holtz, Ph.D. Thesis, University of California, Berkeley, 1968, pp 188–194.

(46) W. A. Sheppard and R. M. Henderson, *J. Amer. Chem. Soc.*, **89,** 4446 (1967).