

the intensity should tend toward zero, as in sterically twisted anisole.<sup>12</sup>

The first expectation is qualitatively confirmed in the observed spectra (Table I).<sup>13</sup> We do wish, however, to emphasize that no reliance can be placed on the magnitude of the observed increase because of the overlapping band problem.

**Acknowledgment.** The authors thank Dr. Edward Gregorek for the intensity measurements of the <sup>1</sup>L<sub>b</sub> bands in the fluorothioanisoles and Mr. Joseph Rakshys for the F n.m.r. measurements. We are indebted to Professor G. Illuminati for supplying samples of compounds I–III.

(12) L. J. Frolen and L. Goodman, *J. Am. Chem. Soc.*, **83**, 3405 (1961).

(13) On the other hand, the CT band (shifted to ~2500 Å. in thioanisole) decreases in intensity upon steric twisting.

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## Concerning Linear Relationships between the $\sigma$ and $\pi$ Electron Effects of Unshared Pair Substituents. The Role of $\pi(p-d)$ Conjugation<sup>1</sup>

Sir:

Evidence that both donor 3p and acceptor 3d (or 4p) orbitals of sulfur are utilized in the interaction of the thiomethoxy group with the benzene ring is presented in the companion paper.<sup>2</sup> This conclusion is further confirmed and extended by the comparison of the ground-state  $\sigma$  and  $\pi$  electronic properties of the methyl derivatives of the first- and second-row elements of groups IV-B to VII-B. We report herein these electronic properties as determined by the F<sup>19</sup> n.m.r. shielding effects in *m*- and *p*-fluorophenyl derivatives. The evidence is timely in connection with current interest in linear relationships between substituent  $\sigma$  and  $\pi$  electron effects (*i.e.*, linear  $\sigma_I$ - $\sigma_R$  or  $\sigma_{(m)}$ - $\sigma_{(p)}$  relationships).<sup>3,4</sup>

The F n.m.r. shielding parameter,  $f_{H}^{m-X}$  (for the *m*-X substituted fluorobenzene relative to internal fluorobenzene) is directly related to  $\sigma_I$ , the inductive reactivity parameter based upon substitution at carbon having only  $\sigma$  bonds, *i.e.*, -CH<sub>2</sub>-X.<sup>5</sup> For this reason it has been proposed that the predominating contribution to  $f_{H}^{m-X}$  results from changes in the C-F  $\sigma$  bond moment produced by the polarization imposed by the C(Ar)-X  $\sigma$  bond<sup>6</sup>; that is,  $f_{H}^{m-X}$  may be regarded as essentially a  $\sigma$  electron effect parameter.

For -R *para* substituents, the F n.m.r. shielding parameter,  $f_{m-X}^{p-X}$  (for the *p*-X substituted fluorobenzene

(1) This work was supported in part by the National Science Foundation.

(2) L. Goodman and R. W. Taft, *J. Am. Chem. Soc.*, **87**, 4385 (1965).

(3) (a) N. L. Bauld, Abstracts, 139th National Meeting of the American Chemical Society, St. Louis, Mo., March 1961; (b) D. H. McDaniel, *J. Org. Chem.*, **26**, 4692 (1961); (c) C. Y. Meyers, *et al.*, *J. Am. Chem. Soc.*, **86**, 2944 (1964); C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 389 (1964).

(4) R. W. Taft, *et al.*, *J. Am. Chem. Soc.*, **85**, 3146 (1963).

(5) R. W. Taft, *et al.*, *ibid.*, **85**, 709 (1963), and earlier references.

(6) R. W. Taft, *et al.*, Abstracts, Meeting of the Society of Applied Spectroscopy, Cleveland, Ohio, Sept. 30, 1964, paper 91.

relative to its *meta* isomer as internal reference), is directly related to  $\sigma_R^0$ , the resonance reactivity parameter which is presumably based upon the contribution of the net  $\pi$  electron effect to normal *para*  $\sigma$  values.<sup>4</sup> This shielding parameter is also directly related to MO theory ground-state  $\pi$  electron charge density at the *para* carbon atom (bonded to F).<sup>7</sup> Evidently the predominating contribution to  $f_{m-X}^{p-X}$  results from the localization of  $\pi$  electronic charge in the C-F region produced by a net delocalization of  $\pi$  electrons into the ring from X ( $f_{m-X}^{p-X}$  positive) or from the ring into X ( $f_{m-X}^{p-X}$  negative). Accordingly,  $f_{m-X}^{p-X}$  may be taken as the  $\pi$  electron effect parameter.

Compelling evidence for these assignments is provided by the following additional considerations. Values of  $f_{m-X}^{p-X}$  in general cover an order of magnitude greater range than values of  $f_H^{m-X}$ .<sup>4,5</sup> Nevertheless, there are recently obtained data available for 14 substituents for which  $f_{m-X}^{p-X} = 0.0 \pm 0.4$  p.p.m., whereas the  $f_H^{m-X}$  values cover a range from -7.2 to +0.7 p.p.m.<sup>4,5,8</sup> The structures of these substituents<sup>9</sup> are such that it is reasonable to propose that in the ground state there is very little net flow of  $\pi$  charge either in or out of the benzene ring.

In Figure 1 the  $\pi$  electron effect parameter,  $f_{m-X}^{p-X}$ , is plotted *vs.* the  $\sigma$  electron effect parameter,  $f_H^{m-X}$ .

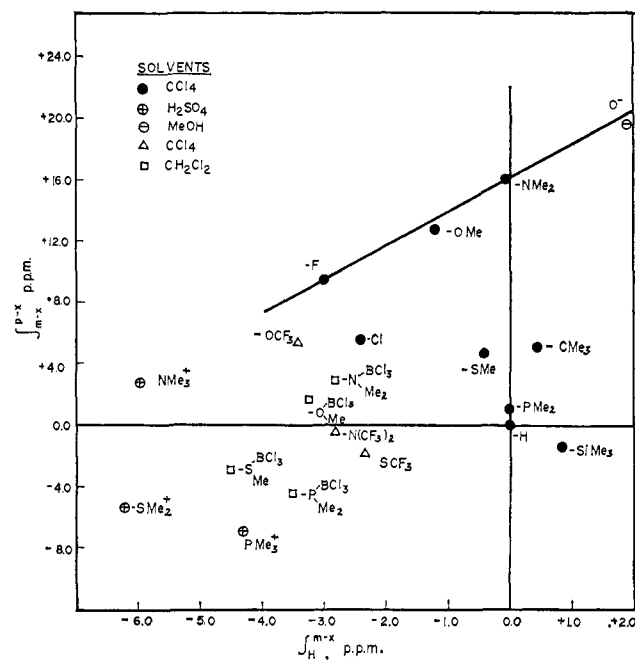


Figure 1. Relationship between  $\pi$  and  $\sigma$  electron effects of substituents on F n.m.r. shielding in *m*- and *p*-FC<sub>6</sub>H<sub>4</sub>X compounds (X is as indicated): ordinate, the  $\pi$  electron effect parameter; abscissa, the  $\sigma$  electron effect parameter.

The closed circles give the results (obtained in CCl<sub>4</sub> solutions by the previously reported method<sup>b</sup>) for the

(7) (a) R. W. Taft, *et al.*, *J. Chem. Phys.*, **38**, 380 (1963); (b) G. E. Maciel and J. J. Natterstad, *ibid.*, **42**, 2427 (1965); (c) T. K. Wu and B. P. Dailey, *ibid.*, **41**, 2796; and references therein.

(8) Unpublished results; G. E. Maciel, *J. Am. Chem. Soc.*, **86**, 1269 (1964); R. West, private communication; W. A. Sheppard, private communication.

(9) These substituents are Sn(CH<sub>3</sub>)<sub>3</sub>, Ge(CH<sub>3</sub>)<sub>3</sub>, C(OCH<sub>3</sub>)<sub>3</sub>, H, CH<sub>2</sub>Cl, P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, CH<sub>2</sub>NH<sub>3</sub><sup>+</sup>, CCl<sub>3</sub>, N(CF<sub>3</sub>)<sub>3</sub>, SOCH<sub>3</sub>, N(COF)CF<sub>3</sub>, N(COF)<sub>2</sub>, C(CN)<sub>3</sub>, and ICl<sub>2</sub>.

methyl derivatives of the first and second rows of the elements of groups IV-B–VI-B and the VII-B elements. Two features are noteworthy. First, values of  $f_{\text{H}}^{m-x}$  increase in the familiar substituted carbon electronegativity order  $F < Cl < OCH_3 < SCH_3 < N(CH_3)_2 < P(CH_3)_2 < C(CH_3)_3 < Si(CH_3)_3$ , whereas values of  $f_{m-x}^{p-x}$  do not. Second, values of  $f_{m-x}^{p-x}$  for the unshared pair substituents of the first row (F,  $OCH_3$ ,  $N(CH_3)_2$ ) increase linearly with  $f_{\text{H}}^{m-x}$ , whereas the unshared pair substituents of the second row (Cl,  $SCH_3$ , and  $P(CH_3)_2$ ) do not follow this simple relationship. Instead, net  $\pi$  electron donation to the ring decreases in this order for the latter substituents. Evidently the donor  $\pi(2p_{\text{C}}-3p_{\text{X}})$  interaction is increasingly opposed by the acceptor  $\pi(2p_{\text{C}}-3d_{\text{X}})$  interaction.<sup>2</sup>

Linear relationships (of slope  $\sim 2$ ) of  $f_{m-x}^{p-x}$  vs.  $f_{\text{H}}^{m-x}$  (i.e.,  $\sigma_{\text{R}}$  vs.  $\sigma_{\text{I}}$ ) have been shown<sup>4</sup> to hold within families of united atom-like substituents, each family involving variations within the same kind of  $\pi(p-p)$  conjugative interaction mechanism.<sup>10</sup> For such a family of substituents the  $\pi$  and  $\sigma$  electrons find themselves under essentially the same relative constraints of the effective nuclear fields. This condition provides the basis of the linear  $\sigma_{\text{I}}-\sigma_{\text{R}}$  (or  $\sigma_{\text{I}}-\sigma$ ) relationship. If additional conjugative interaction mechanisms are introduced by the substitution, decay of the linear  $\sigma_{\text{I}}-\sigma_{\text{R}}$  relationship accordingly follows (e.g.,  $CH_3O$  and  $CH_3OCOO$ , etc.<sup>4</sup>). The  $\pi(p-d)$  interaction involved with the second-row unshared pair substituents constitutes an extension of the  $\pi$  electron framework (over that for simple  $\pi(p-p)$  interaction) which we believe results in the substantial dispersion observed in the  $f_{m-x}^{p-x}$  vs.  $f_{\text{H}}^{m-x}$  plot (Figure 1).

The results of this and the previous investigations<sup>4,11</sup> may be summarized in the generalization that the observed substituent effects are anticipated to be linear with  $\sigma_{\text{I}}$ , if within the family of substituents the  $\pi$  electron effects involve variations within a single predominant interaction mechanism.

Figure 1 also includes results (in the indicated solvents) for the methyl derivatives of the elements of groups V-B and VI-B complexed with  $BCl_3$  ( $\square$ ), the corresponding perfluoromethyl derivatives ( $\Delta$ ), and the "onium" ion salts ( $\oplus$ ). In these substituents the positive charge imposed upon the central atom is expected to increase the  $\pi(p-d)$  acceptor action.<sup>12,13</sup> When  $\pi(p-p)$  interaction alone operates, the limiting effect of the positive charge is expected to be a near-zero value of  $f_{m-x}^{p-x}$ . This expectation is indeed realized since  $f_{m-x}^{p-x}$  is either a small positive or essentially zero value for all of these derivatives of the first-row elements. When both 3p and 3d orbitals are utilized, the effect of an appreciable positive charge is expected to render these (classically saturated) substituents net  $\pi$  electron acceptors (+R). In accord, the  $\pi$  electron

effect parameter,  $f_{m-x}^{p-x}$ , is substantially negative for all of the derivatives of the second-row elements.

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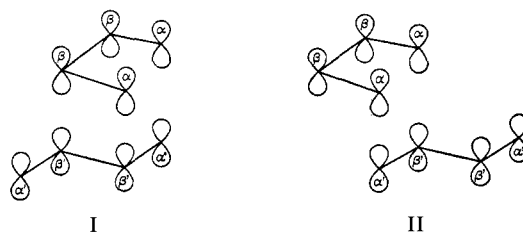
Received June 17, 1965

## Orbital Symmetries and *endo-exo* Relationships in Concerted Cycloaddition Reactions

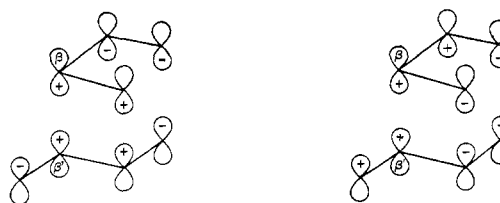
Sir:

We have previously shown the utility of orbital symmetry relationships and correlation diagrams in rationalizing and predicting the stereochemical course and concerted nature of electrocyclic reactions, intermolecular cycloadditions, and sigmatropic rearrangements.<sup>1</sup> We now show how these methods may be extended to yield further insight into the origins of secondary conformational effects in concerted cycloaddition reactions.

Consider the Diels–Alder addition of butadiene to itself, as a concerted  $4 + 2$  cycloaddition reaction.<sup>1</sup> *A priori*, this reaction might take place through either of two alternative transition states, I or II. The *endo* approach, I, is distinguished from the *exo*, II,



mainly by the proximity of a  $\beta$  and a  $\beta'$  orbital in the former. Any secondary interaction among occupied diene and dienophile molecular orbitals will contribute only in a very minor way to the total energy, since such an interaction will increase the energy of some levels while decreasing the energy of others. The significant interactions will come from the symmetry-allowed mixing of unoccupied with occupied levels.<sup>2</sup> In the case at hand, inspection of diagrams III and IV reveals at once that either possibility for such mixing leads to bonding, i.e., energy lowering, interaction of the proxi-



Mixing of highest occupied "diene" orbital (top) with lowest unoccupied "olefin" orbital (bottom)

III

Mixing of lowest unoccupied "diene" orbital (top) with highest occupied "olefin" orbital (bottom)

IV

(10) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963, p. 141.

(11) R. W. Taft, R. H. Martin, and F. W. Lampe, *J. Am. Chem. Soc.*, **87**, 2490 (1965).

(12) D. P. Craig, *J. Chem. Soc.*, 997 (1959).

(13) For confirmatory experimental results, cf. the following: (a) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, Chapter 17, and references therein; (b) C. C. Price and S. Oae, "Sulfur Bonding," Ronald Press Co., New York, N. Y., 1962, Chapter 5; (c) F. G. Bordwell and P. J. Bouton, *J. Am. Chem. Soc.*, **78**, 87 (1956); (e) W. A. Sheppard, *ibid.*, **85**, 1314 (1963), and earlier references; (d) C. E. Griffin, *et al.*, *J. Org. Chem.*, **30**, 97 (1965).

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2511 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); see also H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965), and K. Fukui, *Tetrahedron Letters*, 2009 (1965).

(2) This has also been stressed by K. Fukui ["Molecular Orbitals in Chemistry, Physics and Biology," P.-O. Löwdin and B. Pullman, Ed., Academic Press Inc., New York, N. Y., 1964, p. 525].