

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  $\pi(2p_{(C)}-3p_{(X)})$  interaction is increasingly opposed by the acceptor  $\pi(2p_{(C)}-3d_{(X)})$  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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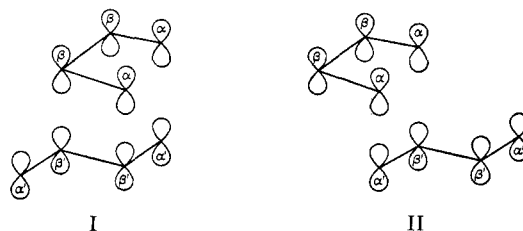
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## Orbital Symmetries and *endo-exo* Relationships in Concerted Cycloaddition Reactions

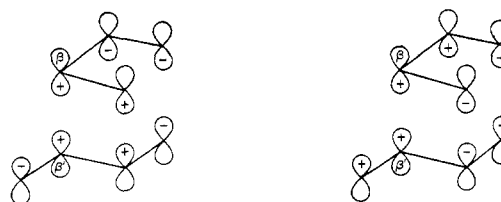
Sir:

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).

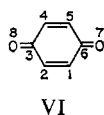
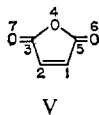
(12) D. P. Craig, *J. Chem. Soc.*, 997 (1959).

(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); (d) W. A. Sheppard, *ibid.*, **85**, 1314 (1963), and earlier references; (e) 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].

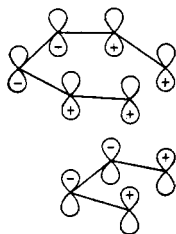
mate  $\beta$  and  $\beta'$  orbitals. Thus, the *endo* transition state (I) for this  $4 + 2$  concerted cycloaddition reaction is stabilized *vis-a-vis* the *exo* alternative (II) by symmetry-controlled secondary orbital interactions. Similar circumstances obtain for all of the  $4 + 2$  concerted cycloaddition reactions we have considered. For example, our extended Hückel calculations reveal that for maleic anhydride (V) and *p*-benzoquinone (VI), the relevant low-lying antisymmetric unoccupied dienophile orbitals are



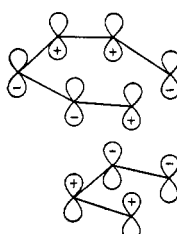
$$\chi_4 = 0.442(\psi_1 - \psi_2) + 0.506(\psi_5 - \psi_3) - 0.343(\psi_6 - \psi_7) \quad (\text{V})$$

$$\chi_5 = 0.306(\psi_1 - \psi_2 - \psi_4 + \psi_5) + 0.461(\psi_6 - \psi_3) - 0.368(\psi_7 - \psi_8) \quad (\text{VI})$$

The orbital symmetry relationships signaled here provide a simple quantum chemical basis for the large body of experience summarized in the Alder *endo* addition rule.<sup>3</sup> Our treatment differs from previous proposals, which have emphasized the roles of inductive forces,<sup>4</sup> electrostatic forces consequent upon charge transfer between diene and dienophile,<sup>5</sup> and maximum accumulation of unsaturation.<sup>3</sup> In particular it is now clear that in some cases the orbital interactions among unsaturated centers involved in a concerted cycloaddition reaction will be such as to raise, rather than lower, the energy of the *endo* transition state, and lead to a preference for *exo* addition, insofar as symmetry factors are dominant; inspection of the relevant orbital diagrams (VII and VIII) for the (as yet unobserved)



VII



VIII

symmetry-allowed  $6 + 4$  combination<sup>1</sup> indicates that it is such a case. By contrast, the symmetry-allowed  $8 + 2$  and  $2 + 2 + 2$  cycloadditions<sup>1</sup> should resemble the  $4 + 2$  process and proceed by preference through *endo* transition states; there is already evidence for that preference in one example of the latter process.<sup>6</sup>

The dimerization of cyclobutadiene is a special case of much interest, considered in the light of orbital symmetry relationships. If, as seems likely, there is substantial bond localization in that highly reactive

(3) K. Alder and G. Stein, *Angew. Chem.*, **50**, 514 (1937); K. Alder, *Ann.*, **571**, 157 (1951); K. Alder and M. Schumacher, *Fortschr. Chem. Org. Naturstoffe*, **10**, 1 (1953). For exceptions to the rule, cf. J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962).

(4) A. Wassermann, *J. Chem. Soc.*, 825, 1511 (1935); 432 (1936); *Trans. Faraday Soc.*, **35**, 841 (1939).

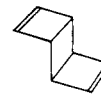
(5) R. B. Woodward and H. Baer, *J. Am. Chem. Soc.*, **66**, 645 (1944).

(6) R. C. Cookson, J. Dance, and J. Hudec, *J. Chem. Soc.*, 5416 (1964).

molecule, one can delineate, *a priori*, the possibilities of  $2 + 2$ ,  $2 + 4$ , and  $4 + 4$  cycloadditions. Our selection rules<sup>1</sup> require a preference for the concerted  $2 + 4$  process, and indeed evidence that this path is favored has very recently been brought forward.<sup>7</sup> Examination of secondary orbital interactions along the lines set down in this communication reveals further that the *endo* process, leading to the *syn* dimer (IX), should be favored over the alternative *exo* combination, which



IX



X

would give the *anti* dimer (X). The formation of both *syn* and *anti* dimers in reactions initiated with a variety of possible cyclobutadiene precursors has been reported, but in those experiments in which there was the greatest likelihood of the transitory existence of a free cyclobutadiene the predicted *endo* process was observed.<sup>8</sup>

(7) G. Wittig and J. Weinlich, *Chem. Ber.*, **98**, 471 (1965).

(8) R. Criegee, *Angew. Chem.*, **74**, 703 (1962), and references therein; P. S. Skell and R. J. Peterson, *J. Am. Chem. Soc.*, **86**, 2530 (1964), and references therein.

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## Orbital Symmetries and Orientational Effects in a Sigmatropic Reaction

Sir:

The 3,3 sigmatropic shift<sup>1</sup> (I  $\rightarrow$  II) in hexa-1,5-dienes (the Cope rearrangement) has been shown<sup>2</sup> to proceed



I



II

more easily through a four-center chair-like transition state (III) than through the six-center boat-like alter-



III



IV

native (IV). It is the purpose of this communication to suggest that orbital symmetry relationships<sup>1,3</sup> play a predominant role in determining that preference.

A correlation diagram<sup>3</sup> for the molecular orbitals involved in the rearrangement is illustrated in Figure 1. The levels are classified as symmetric (S) or antisymmetric (A) with respect to the mirror plane in the boat-

(1) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 2511 (1965).

(2) W. von E. Doering and W. R. Roth, *Tetrahedron*, **18**, 67 (1962); *Angew. Chem.*, **75**, 27 (1963).

(3) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965); cf. also H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).