

A NEW ESTIMATION OF SECONDARY INTERACTIONS  
CONTROLLING THE STEREOSELECTIVITY OF DIELS-ALDER REACTIONS

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The perturbational calculations have been quite successful in interpreting the stereoselectivities of a variety of reactions.<sup>1</sup> The endo/exo selectivity of Diels-Alder reactions has been correlated with the stabilization in the endo orientation of dienophile substituents.<sup>2-4</sup>

The intermolecular stabilization energies estimated for reactant aggregates may well predict the stereochemistry of reaction, if the aggregates resemble the transition state. According to Hammond's postulate,<sup>5</sup> the fact that the Diels-Alder reaction is highly exothermic suggests that it has a reactant-like transition state. However, the large negative entropy of activation<sup>6</sup> indicates that the transition state is in a highly oriented form. Diels-Alder reactions should thus differ significantly from the so-called molecular complexation. This suggests an innate difference in the roles of the primary (i.e., bond-forming) and the secondary (i.e., nonbonding) interactions at the transition state. For such systems, the estimation of secondary interactions from the conventional molecular-complex approximation, which allows no essential discrimination between the primary and secondary interactions, would not be quite adequate. Here presented is an approach to the estimation of the secondary interaction influencing specifically the bond-forming process at the primary sites.

According to the perturbational Hückel molecular orbital theory,<sup>7</sup> the change in the partial bond order between r and s of the jth molecular orbital by the interaction between t and u is given in terms of the mutual bond polarizability,  $\pi_{rs,tu}^j$ , and the resonance integral increment,  $\Delta H_{tu}$ :

$$\Delta P_{rs,tu}^j = \pi_{rs,tu}^j \cdot \Delta H_{tu} \quad (1)$$

where

$$\pi_{rs,tu}^j = \sum_{i \neq j} \frac{(c_{ir}c_{js} + c_{jr}c_{is})(c_{it}c_{ju} + c_{jt}c_{iu})}{\epsilon_j - \epsilon_i} \quad (2)$$

Within the framework of this approximation, summation of  $\pi_{rs,tu}^j$  for all occupied orbitals weighted by the coefficients of the localized molecular orbital for the bond r-s gives a new expression for the mutual bond polarizabilities  $T_{rs,tu}$ :

$$T_{rs,tu} = \sum_j^{\text{occ}} (u_{rs}^j)^2 \cdot \pi_{rs,tu}^j \quad (3)$$

where  $u_{rs}^j$  is an element of the unitary transformation matrix of the bond r-s from the canonical to the localized MO:

$$\phi_{rs} = \sum_j^{\text{occ}} u_{rs}^j \cdot \psi^j \quad (4)$$

The new index  $T_{rs,tu}$  thus obtained may be termed a specific mutual bond polarizability, which represents an influence of the secondary interaction on the primary bond-formation process and may be taken as a measure of the "steric" effect between t and u.

The endo/exo stereoselectivity was examined for the addition of butadiene to acrolein. Calculations were carried out by using Hückel MO's in which the resonance integrals at the reaction sites,  $\Delta H_{16}$  and  $\Delta H_{45}$ , were taken to be  $0.1\beta$ . The molecular orbitals obtained were transformed into localized molecular orbitals according to the method by Trindle.<sup>8</sup> Table 1 lists the elements of the unitary transformation matrix ( $u_{rs}^j$ ) for the newly forming bonds.

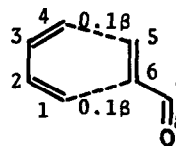


Table 2 summarizes the specific mutual bond polarizabilities in units of  $\beta$  for the secondary interacting sites. Since a synchronous formation of two  $\sigma$  bonds is supposed in the Diels-Alder reaction,<sup>6</sup> the polarizabilities for two reaction sites have been added up. Significantly large positive values are found for  $T_{27}$  and  $T_{38}$ , indicating that both the bonds C(1)—C(6) and C(4)—C(5)

Table 1. Elements of the Unitary Transformation Matrix to the Localized Molecular Orbitals (LMO)

LMO	HMO			
	$\psi_1$	$\psi_2$	$\psi_3$	$\psi_4$
$\phi_{16}$ (bond 1—6)	-0.500	-0.069	-0.772	0.386
$\phi_{45}$ (bond 4—5)	0.195	0.240	0.303	0.901

Table 2. Specific Mutual Bond Polarizabilities in the Addition of Butadiene to Acrolein<sup>a)</sup>

rs \ tu	$T_{rs,tu}$ (1/ $\beta$ )			
	2—7	2—8	3—7	3—8
1—6	0.109	0.155	0.133	0.494
4—5	0.093	-0.345	-0.110	0.369
Total ( $T_{tu}$ ) <sup>b)</sup>	0.202	-0.190	0.023	0.863

a) For the numbering, refer to the text.

b)  $T_{tu} = T_{16,tu} + T_{45,tu}$

are strengthened when the atoms C(2) and C(3) are brought into proximity with C(7) and O(8), respectively. Clearly, the C(2)—C(7) interaction is greater in the endo orientation than in the exo geometry, because of the smaller inter-nuclear distance. Likewise, the C(3)—O(8) interaction would be significant only in the endo orientation of s-cis acrolein. These secondary interactions are thus expected to favor the endo orientation in the formation of new  $\sigma$  bonds. The results well account for the predominant formation of endo adducts in the Diels-Alder reaction.

The present calculation neglects the intermolecular stabilization which may arise directly from the interaction between secondary sites. This approximation would need some explanations. The role of attractive secondary interactions has been stressed in interpreting the stereoselectivity of Diels-Alder reactions.<sup>2-4</sup> However, the direct group interaction estimated for stable molecules is dominantly repulsive<sup>9</sup> in the region of intermolecular separations at which the transition state molecules are generally supposed to locate.<sup>10</sup> The situation may suggest

that somewhat different modes of intermolecular forces are operative in the reaction. The most distinctive features of reaction should be the electronic reorganization accompanying the bond formation. The apparent contradiction could be reconciled by assuming the secondary interaction to be such an effect on the primary bond formation as described above.

An interesting application of the treatment here presented would be found in the explanation of the deviation from the endo-rule of methacrylic dienophiles.<sup>11</sup> In previous reports,<sup>12</sup> we concluded that the apparent endo-preference of the methyl substituent is due to its attractive interaction with the endo-part of the diene rather than the steric repulsion of the methyl group. The results might well be accounted for from the standpoint as presented in this article. Details of such treatments will be reported elsewhere.

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