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# Molecular Orbital Treatment of *Para* Orientation in the Diels-Alder Reactions of 2-Substituted Butadienes with Methyl Acrylate[1]

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The intermolecular orbital method was applied to the orientation phenomena in the Diels-Alder reactions of 2-R-butadienes (R=Me, Ph, Cl, and CN) with methyl acrylate assuming the parallel biplanar transition state geometries. Although qualitatively correct predictions of *para* orientation (major isomer) were obtained with the calculated overlap energies, it is suggested that the non-bonding interactions are overestimated. The simple perturbational molecular orbital method, which takes only the interactions at the terminal positions into account, was also unsatisfactory. However, frontier orbital interactions provided qualitatively correct prediction of the major isomeric product in every case.

The general *ortho*/*para* orientation in the Diels-Alder reactions between unsymmetrical dienes and dienophiles is questionable with regard to its rationalization in terms of organic electronic theory.[3,4] The experimental vindication of the orientation rule was ill-founded.[3] We recently determined the kinetically controlled isomer ratios of the adducts from 1-Me-, 2-Me-, 2-Ph-, 2-Cl-, 2-CN-, and 2-CF$_3$-butadienes with methyl acrylate.[5] We are satisfied that the enigmatic orientation rule was qualitatively correct and this led us to seek an explanation.

Since the multicenter mechanism of the Diels-Alder reactions is generally accepted, we have to take into account a number of electronic interactions contributing to the energies of the transition states in order to make a reasonable prediction of the orientation. The relative importance of these contributing factors may not be estimated by the qualitative argument of organic electronic theory. Thus the present problem requires an estimate of various contributing factors by computation.

Feuer *et al.*[4] used a perturbational molecular orbital method (PMO) with considerable success, but their dienes were limited to methyl and phenyl substituted butadienes. For explaining the *ortho*/*para* orientation by electron-releasing substituents alone, the electronic theory is sufficient.[6] But the real difficulty with this theory lies in rationalizing the same *ortho*/*para* orientation also by the substituents of opposite polarity. Therefore, in order to know whether the PMO treatment gives a satisfactory solution of the problem or not, the cases with electron-releasing substituents and electron-withdrawing substituents must be studied by application of the PMO method. In this article we describe the results of some attempts of explanation of the orientation phenomena[7] in the Diels-Alder reactions of methyl acrylate with 2-substituted butadienes using the intermolecular orbital (IMO)[8] and the PMO methods.

## Method

In the first part of the study the interaction energies $\Delta E_{\text{overlap}}$ of multicenter [4+2] transition states were calculated by the IMO method with the formula,[9]

$$\begin{aligned}\Delta E_{\text{overlap}} = & -\sum_{rr'}(q_r+q_{r'})\eta_{rr'}S_{rr'} \\ & -2\sum_{j}^{\text{occ}}\sum_{k'}^{\text{vac}}\Big(\sum_{rr'}C_{jr}C_{k'r'}\eta_{rr'}\Big)^2/(E_{k'}-E_j) \\ & -2\sum_{k}^{\text{vac}}\sum_{j'}^{\text{occ}}\Big(\sum_{rr'}C_{kr}C_{j'r'}\eta_{rr'}\Big)^2/(E_k-E_{j'}) \qquad (1)\end{aligned}$$

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[2] To whom inquiries should be addressed.

[3] J. Sauer, *Angew. Chem.*, **79**, 76 (1967).

[4] J. Feuer, W. C. Herndon, and L. H. Hall, *Tetrahedron*, **24**, 2575 (1968).

[5] T. Inukai and T. Kojima, *J. Org. Chem.*, **36**, 924 (1971).

[6] For example, J. S. Meek, B. T. Poon, R. T. Merrow, and S. J. Cristol, *J. Amer. Chem. Soc.*, **74**, 2669 (1952).

[7] The term *orientation* in this article is used to mean the choice of the major isomeric product.

[8] J. Salem, *J. Amer. Chem. Soc.*, **90**, 543 (1968).

[9] See Reference 8 for the definition of various symbols.

The first summation denotes the repulsion between $\pi$-electron shells of a diene and dienophile. The second summation (hereafter called term 2) denotes the stabilization due to delocalization of $\pi$-electrons of a diene to the vacant orbitals of a dienophile, and the third summation (term 3) that due to delocalization of $\pi$-electrons of a dienophile to the vacant orbitals of a diene. The unprimed and primed suffixes refer to a diene and dienophile, respectively. The wave functions and energy values for the isolated reactants were calculated by the simple Hückel method. The Hückel parameters used are listed in Table 1. Further parametrization employed is

$$\eta_{rr'}/S_{rr'} = 3\beta \text{ (for all } r \text{ and } r')^{8)}$$

where $\beta$ is the standard resonance integral of benzene.

TABLE 1. HÜCKEL PARAMETERS USED[a)]

| Coulomb parameter, $h(X)$ | | Resonance parameter, $k_{x-x'}$ | |
|---|---|---|---|
| $h(\dot{C})$ | 0 | C—C | $S/S_0$ |
| $h(\dot{O})$ | 1.5 | C—O, carbonyl | 0.85 |
| $h(\ddot{O})$ | 2.0 | C—O, ether | 0.6 |
| $h(\dot{N})$ | 0.5 | O—Me | 0.3 |
| $h(\ddot{C}l)$ | 2.0 | C—N, nitrile | 1.19 |
| $h(\ddot{M}e)$ | 2.0[b)] | C—Cl | 0.37 |
| | | C—Me | 0.7[b)] |

a) $\alpha_x = \alpha_c + h(X)\beta$; $\beta_{x-x'} = k_{x-x'}\beta$.
b) The heteroatom model of methyl group.

The geometries of the reactant molecules were assumed to be planar and constructed from the probable bond angles and lengths.[10)] The transition state model were constructed by putting the reactants in parallel planes at 3.2 Å distance;[11,12)] there are eight transition state geometries corresponding to possibilities of *para* and *meta* orientation, *endo* and *exo* stereochemistry, and cisoid and transoid conformation of C=C–C=O moiety of methyl acrylate—only two of these are illustrated in Fig. 1.

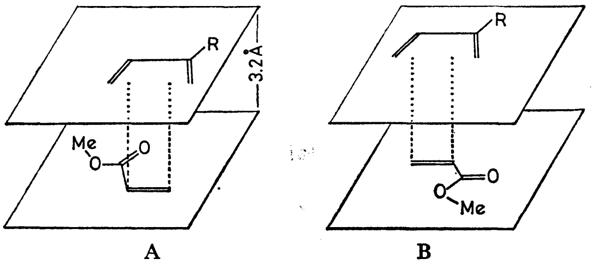

Fig. 1. Transition State Models. A, *para*, *endo*, cisoid; B, *meta*, *exo*, transoid.

The required overlap integrals $S_{rr'}$ were calculated by

$$S_{rr'} = S_{rr'}(\sigma\sigma)\cos^2\theta_{rr'} - S_{rr'}(\pi\pi)\sin^2\theta_{rr'} \quad (2)$$

where $\theta_{rr'}$ is the angle between the interatomic line and the normal on the molecular plane (Fig. 2). $S_{rr'}(\sigma\sigma)$ and $S_{rr'}(\pi\pi)$ are known through the extensive tables by Mulliken *et al.*[13,14)]

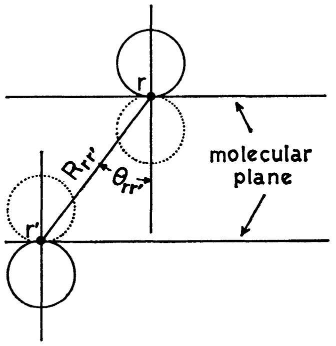

Fig. 2.

Calculation of $\Delta E_{\text{overlap}}$ was performed using a computer program which reads seqular determinants for a pair of isolated reactant molecules and the appropriate overlap matrix $((S_{rr'}))$ for each transition state geometry, and gives the desired energy terms of Eq. 1.

In the second half of the study the same simplest PMO method as that used by previous workers was used.[4)] Thus the perturbational energies, $E_p$, for the four-center transition states were calculated considering only the terminal interactions, *i.e.*, those between the two pairs of atoms at which $\sigma$-bonds will close (Eq. 3).[15)] The Hückel parameters used are those listed in Table 1.

$$E_p = 2[\sum_m^{\text{occ}}\sum_n^{\text{vac}} - \sum_m^{\text{vac}}\sum_n^{\text{occ}}](a_{mr}b_{ns} + a_{mu}b_{nv})^2\gamma^2/(E_m - E_n) \quad (3)$$

## Results and Discussion

The results by the IMO method for *endo* addition of the cisoid methyl acrylate are shown in Table 2. The main features of interest are:

1) $\Delta E_{\text{overlap}}$ gives correct predictions of *para* orientation by all the substituents.

2) The delocalization energy, namely term 2 plus term 3 of eq 1, indicates *meta* orientation by Ph and CN groups and practically null selectivity in the cases of Me and Cl. It is the repulsion term that makes $\Delta E_{\text{overlap}}$ turn out to be *para* directing.

3) The calculations of the delocalization energy taking only the frontier orbitals into account lead to correct orientation in all cases.

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10) Butadiene skeleton [A. Almenningen *et al.*, *Acta Chim. Scand.*, **12**, 1221 (1958)] was assumed to be maintained in all the 2-substituted butadienes. Bond lengths between $C_{(2)}$ (butadiene) and substituent atoms are: $C_{(2)}$—$C_{\text{methyl}}$, 1.50 Å; $C_{(2)}$—$C_{\text{phenyl}}$, 1.46 Å $C_{(2)}$—Cl, 1.70 Å; $C_{(2)}$—$C_{\text{cyano}}$, 1.44 Å, $R_{C\equiv N}$, 1.16 Å. Based on the three-dimensional structure of methyl acrylate [T. Ukaji, This Bulletin, **32**, 1275 (1959)], the following flat structure was assumed: $C_{(1)}=C_{(2)}$, 1.36 Å; $C_{(2)}$—$C_{(3)}$, 1.44 Å; $C_{(3)}$—$O_{(4)}$, 1.36 Å; $O_{(4)}$—$C_{(5)\text{methyl}}$, 1.46 Å; $C_{(3)}=O_{(6)}$, 1.22 Å; $\angle C_{(1)}C_{(2)}C_{(3)}$, 120°; $\angle C_{(2)}C_{(3)}O_{(4)}$, 125°; $\angle C_{(2)}C_{(3)}O_{(6)}$, 120°; $\angle C_{(3)}O_{(4)}C_{(5)}$, 115°.

11) W. C. Herndon and L. H. Hall, *Theor. Chim. Acta*, **7**, 4 (1967).

12) P. Markov and P. N. Skancke, *Acta. Chim. Scand.*, **23**, 1295 (1969).

13) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

14) Those unavailable in the tables were calculated using the appropriate master formula (Reference 13) with the aid of the numerical values of $A_k(p)$, $B_k(pt)$ integrals given by Kotani *et al.* [M. Kotani, A. Amemiya, E. Ishiguro, and T. Kimura, "Tables of Molecular Integrals," Maruzen Co., Ltd, Tokyo (1963)].

15) See Reference 4 for the definition of various symbols.

Table 2. Interaction energies (in units of $\beta$) by IMO method for reactions of 2-substituted butadienes with cisoid methyl acrylate by *endo* mechanism

| Substituent | | Repulsion | Delocalization | $\Delta E_{\text{overlap}}$ | $\Delta E_{\text{frontier}}$[a] |
|---|---|---|---|---|---|
| Me | *para* | −0.0272 | 0.0178 | −0.0094 | 0.0153<br>(0.0140) |
| | *meta* | −0.0340 | 0.0175 | −0.0165 | 0.0138<br>(0.0126) |
| Ph | *para* | −0.0271 | 0.0176 | −0.0094 | 0.0123<br>(0.0108) |
| | *meta* | −0.0318 | 0.0186 | −0.0132 | 0.0099<br>(0.0083) |
| Cl | *para* | −0.0270 | 0.0177 | −0.0093 | 0.0158<br>(0.0144) |
| | *meta* | −0.0292 | 0.0177 | −0.0116 | 0.0152<br>(0.0138) |
| CN | *para* | −0.0268 | 0.0176 | −0.0093 | 0.0148<br>(0.0130) |
| | *meta* | −0.0301 | 0.0190 | −0.0111 | 0.0142<br>(0.0123) |

a) The frontier orbital interaction energy, *i.e.* the sum of delocalization energies relative to the highest occupied MO(diene)—lowest vacant MO(dienophile) interaction and the highest occupied MO(dienophile)—lowest vacant MO(diene) interaction. The energy for the former interaction alone is shown in parentheses.

Table 3. Interaction energies (in units of $\beta$) by IMO method for reactions of 2-substituted butadienes with cisoid methyl acrylate by *exo* mechanism

| Substituent | | Repulsion | Delocalization | $\Delta E_{\text{overlap}}$ | $\Delta E_{\text{frontier}}$[a] |
|---|---|---|---|---|---|
| Me | *para* | −0.0216 | 0.0148 | −0.0068 | 0 0117<br>(0.0102) |
| | *meta* | −0.0218 | 0.0147 | −0.0071 | 0.0110<br>(0.0096) |
| Ph | *para* | −0.0214 | 0.0146 | −0.0068 | 0.0099<br>(0.0083) |
| | *meta* | −0.0215 | 0.0150 | −0.0065 | 0.0093<br>(0.0075) |
| Cl | *para* | −0.0214 | 0.0148 | −0.0066 | 0.0117<br>(0.0102) |
| | *meta* | −0.0214 | 0.0147 | −0.0068 | 0.0114<br>(0.0099) |
| CN | *para* | −0.0213 | 0.0145 | −0.0068 | 0.0110<br>(0.0092) |
| | *meta* | −0.0212 | 0.0151 | −0.0061 | 0.0110<br>(0.0090) |

a) See Table 2, footnote a.

4) These statements are qualitatively valid also when the transoid conformation of methyl acrylate is assumed.

Similar results for *exo* addition of the cisoid methyl acrylate are listed in Table 3. In this case both the $\Delta E_{\text{overlap}}$ and delocalization energy predict preferred formation of *meta* isomer for Ph and CN, in disagreement with experimental facts.[5] The discrepancies are reasonable since the *exo* geometry is evidently improbable in view of the general *endo* rule of the Diels-Alder reactions.[3,16] Similar results are obtained for the transoid methyl acrylate *endo* addition.

The above apparent success with $\Delta E_{\text{overlap}}$ for *endo* is only superficial, however, as is evident if we compare the results of *endo* (Table 2) and *exo* (Table 3) mechanism. Thus the $\Delta E_{\text{overlap}}$ values for the *endo* mechanism are greater (higher $\Delta H^{\neq}$) than the corresponding values for the *exo* mechanism: this erroneous prediction of general predilection for the *exo* addition comes from the excessively large repulsion energy calculated for the *endo* transition state model as shown by exact figures (Tables 2 and 3).

Inclusion of the classical Coulomb potential $\Delta E_{\text{polar}}$ given by Eq. 4[17] does not give improved results. According to the results (Table 4), 2-Ph- and 2-CN-

$$\Delta E_{\text{polar}} = \sum_{r}\sum_{r'} \Delta q_r \Delta q_{r'} / R_{rr'}$$

$$\Delta E = \Delta E_{\text{overlap}} + \Delta E_{\text{polar}} \qquad (4)$$

butadienes should react by the *exo* mechanism in disagreement with Alder's *endo* rule.

Appropriateness of the value of the interplanar distance (3.2 Å) assumed in the present study is questionable. Furthermore, the assumption of a parallel biplanar transition state is debatable although it has usually been made.[11,12,18] Since it is known experimentally that the *endo* mechanism only slightly exceeds the *exo* generally in the Diels-Alder reactions of acyclic dienes,[19] the non-bonding interactions might not be strong enough to pull the reactants close together into

Table 4. Comparison of $\Delta E^{a}$ (Eq. 4) for *endo* and *exo* addition of cisoid methyl acrylate

| Substituent | Geometry | | $\Delta E_{\text{polar}}$ | $\Delta E_{\text{overlap}}$[b] | $\Delta E$ |
|---|---|---|---|---|---|
| 2-Me | *para* | *endo* | −0.81 | +0.65 | −0.16 |
| | | *exo* | +0.20 | +0.47 | +0.67 |
| | *meta* | *endo* | −0.91 | +1.14 | +0.23 |
| | | *exo* | +0.22 | +0.49 | +0.71 |
| 2-Ph | *para* | *endo* | 0 | +0.65 | +0.65 |
| | | *exo* | 0 | +0.47 | +0.47 |
| | *meta* | *endo* | 0 | +0.91 | +0.91 |
| | | *exo* | 0 | +0.45 | +0.45 |
| 2-Cl | *para* | *endo* | −0.24 | +0.64 | +0.40 |
| | | *exo* | +0.05 | +0.46 | +0.51 |
| | *meta* | *endo* | −0.29 | +0.79 | +0.50 |
| | | *exo* | +0.03 | +0.47 | +0.50 |
| 2-CN | *para* | *endo* | +1.08 | +0.64 | +1.72 |
| | | *exo* | +0.22 | +0.47 | +0.69 |
| | *meta* | *endo* | +1.42 | +0.77 | +2.19 |
| | | *exo* | +0.26 | +0.42 | +0.68 |

a) In kcal/mol.

b) Calculated from the values in Tables 2 and 3 with a conversion factor of $\beta = -3$ eV (the spectroscopic value of benzene resonance integral.[8])

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[16] J. G. Martin and R. K. Hill, *Chem. Rev.*, **61**, 537 (1961).

[17] A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, **91**, 3793 (1969).

[18] N. Tyutyulkov and P. Markov, *Monatsh. Chem.*, **96**, 2030 (1965); *ibid.*, **99**, 861 (1968); P. Markov and N. Tyutyulkov, *ibid.*, **97**, 1229 (1966); K. Somekawa, T. Matsuo, and S. Kumamoto, This Bulletin, **42**, 3499 (1969).

[19] T. Inukai and T. Kojima, *J. Org. Chem.*, **32**, 869 (1967); O. Korver, T. L. Kwa, and C. Boelhouwer, *Tetrahedron*, **25**, 4109 (1969); T. L. Kwa, O. Korver, J. W. Hartgerink, and C. Boelhouwer, *ibid.*, **24**, 5711 (1968).

TABLE 5. PERTURBATION ENERGIES (IN UNITS OF $\gamma^2/\beta$) BY PMO METHOD FOR REACTIONS OF 2-SUBSTITUTED BUTADIENES WITH METHYL ACRYLATE

| Substituent | | $E_p$ | $E_{\mathrm{frontier}}$[a)] |
|---|---|---|---|
| Me | *para* | 1.6046 | 1.1098 (0.5391) |
| | *meta* | 1.5504 | 0.9983 (0.4336) |
| Ph | *para* | 1.5731 | 0.9616 (0.4726) |
| | *meta* | 1.5466 | 0.8406 (0.3347) |
| Cl | *para* | 1.5668 | 1.0710 (0.4819) |
| | *meta* | 1.5518 | 1.0397 (0.4523) |
| CN | *para* | 1.5291 | 0.9115 (0.4431) |
| | *meta* | 1.5459 | 0.9072 (0.4115) |

a) See Table 2, footnote a.

a near parallel *endo* geometry, making a more open geometry likelier.[20)] Our present calculation, therefore, might have overestimated the non-bonding interactions. To make matters worse, the calculated orientation is influenced by the delicate balance of counteracting factors.

An alternative approach is to neglect the non-bonding interactions altogether and see whether qualitatively correct predictions can be obtained.[4)] The perturbation energies $E_p$ by the PMO method are shown in Table 5. The preferred orientation is predicted correctly in Me, Ph, and Cl cases, but not in the CN case. Thus the claim for successful rationalization of the orientation rule resulted from the hasty conclusion arising from incomplete analysis of the problem.[4)]

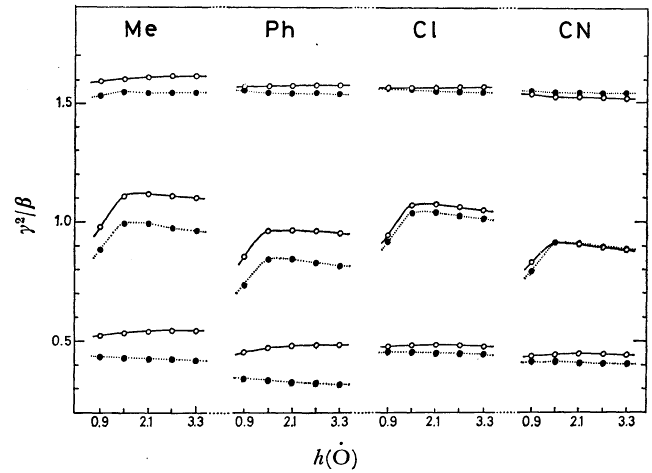

Fig. 3. Perturbation Energy Terms as Functions of $h(\dot{O})$. Upper Curves, Ep; Middle Curves, $E_{\mathrm{frontier}}$; Bottom Curves, Highest Occupied MO (Diene)—Lowest Vacant MO (Dienophile). —○— *Para*, ···●··· *Meta*.

The frontier orbital interactions, however, agree with the experimental orientation in all the cases, and the delocalization energy corresponding to the highest occupied MO(diene)→lowest vacant MO(dienophile) plays a decisive role in conducing to correct predictions.

Variation of the Coulomb parameter $\mathrm{h}(\dot{\mathrm{O}})$ of the dienophile from 0.9 to 3.3, far beyond the reasonable range for methyl acrylate itself, did not alter the orientations in terms of both the $E_p$ and $E_{\mathrm{frontier}}$ as shown in Fig. 3. This is in line with the fact that the *ortho*/*para* orientation rule holds over a wide range of dienophile polarity.[3,5,19,21)]

It may be appropriate to emphasize the importance of the frontier orbitals in determining reactivity.[22)] Their role was undervalued[4)] because of the fact that $E_{\mathrm{frontier}}$ constitutes only a moderate fraction of total $E_p$. This reasoning is not convincing, because the most easily perturbed highest occupied MO will play a greater role, in the real transition state, than that allotted to it by the perturbational calculation as Fukui and Fujimoto discussed in general terms.[23)] Therefore, unless one treats the transition state more realistically, including the hybridization change *etc.* of the reactants, the full term calculation may turn out to be less accurate, in spite of its formal preciseness, than the frontier orbital method. In fact attention to the frontier orbital interactions alone rather than the full term value was found to be a more judicious choice at least for predictive purposes. Furthermore, the diene→dienophile delocalization part of $E_{\mathrm{frontier}}$ plays a decisive role in giving right predictions (Table 5 and Table 2).

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20) *Endo* dimerization of cyclopentadiene could be explained by considering only the interactions at the terminal positions when an interplanar angle of 60° was assumed for the *endo* transition state: W. C. Herndon and L. H. Hall, *Tetrahedron Lett.*, **1967**, 3095.

21) J. Kazan and F. D. Greene, *J. Org. Chem.*, **28**, 2965 (1963); T. Inukai and T. Kojima, *ibid.*, **31**, 1121 (1966); W. M. Daniewski and C. E. Griffin, *ibid.*, **31**, 3236 (1966); C. M. Wynn and P. S. Klein, *ibid.*, **31**, 4251 (1966); J-C. Soula, D. Lumbroso, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, **1966**, 2059; T. Kojima and T. Inukai, *J. Org. Chem.*, **35**, 1342 (1970).

22) K. Fukui in "Modern Quantum Chemistry," Vol. 1 (Edited by O. Sinanoglu), p. 49, Academic Press, New York (1965).

23) K. Fukui and H. Fujimoto, This Bulletin, **42**, 3399 (1969).