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Theoretical Study of *Endo* Selectivity in the Diels−Alder Reactions between Butadienes and Cyclopropene

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The *endo* selectivity in the Diels−Alder reactions of some substituted butadienes with cyclopropene has been investigated theoretically. Electron delocalization between a diene and the dienophile has been presented in terms of pairs of interaction orbitals. In addition to the principal orbital interactions to form new σ bonds between the diene and the dienophile, the cyclopropene occupied interaction orbital shows significant amplitudes on the methylenic hydrogens to overlap *in phase* with the paired unoccupied interaction orbital of butadiene at the backbone C_2 and C_3 carbons. The contribution of this secondary orbital interaction to the stabilization of the transition state has been estimated numerically. It has been demonstrated that neither electron delocalization nor the electrostatic interaction interprets preference of the *endo*-addition over the *exo*-addition, but the sum of the two terms has been found to show a correlation with the difference in the barrier heights for the two modes of cycloadditions.

Introduction

The *endo* selectivity in the Diels−Alder reactions has been established in experiments,[1,2] but the mechanism of bringing about the selectivity is a subject of controversy. The pioneering theory formulated by Alder and Stein has been known as the rule of “maximum accumulation of double bonds”.[3] The *endo* preference has also been discussed on the basis of inductive forces,[4] electrostatic forces associated with charge transfer between dienes and dienophiles,[5] the differential volumes of activation,[6] differential polarities of the transition state,[7] the pre-reactive van der Waals complexes,[8] and some other factors.[9,10] On the other hand, Herndon and Hall suggested that the orbitals would overlap more efficiently at the reaction sites of the diene and the dienophile in the *endo*-transition state than in the *exo*-transition state.[11] Woodward and Hoffmann pointed out first the significance of secondary orbital interactions between the atoms of the diene and dienophile molecules that are not bonded in the adduct.[12]

Cyclopropene was shown experimentally to add to butadiene with *endo* selectivity.[13,14] Apeloig and Matzner have studied the secondary orbital interactions with respect to the Diels−Alder reaction between cyclopropene and various dienes,[15] by applying the frontier orbital theory.[16] Similar argument has also been applied to understand the preference for the *endo*-transition structure of the ene reaction of cyclopropene and propene.[17] Apeloig and Matzner assumed that the integral expressing the interaction between the backbone carbons C_2 and C_3 of butadienes and the methylenic hydrogen of cyclopropene was proportional to the Mulliken overlap population calculated for the *endo*-transition-state structure.[15] The presence of a nice correlation between the second-order perturbation energy and the difference in the activation energies for the *exo*- and *endo*-transition states, ΔE_a(*exo* − *endo*), was demonstrated.

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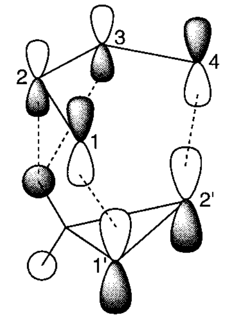
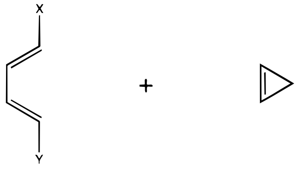
In that study, the secondary orbital interactions have been included in the transition-state calculations, and therefore the effect has already been evaluated in the Mulliken overlap populations calculated for the *endo*-transition structure. Then, it is not easy to understand why the second-order perturbation energy ΔE evaluated by the square of the overlap populations divided by the energy gap between the frontier orbitals should show a linear correlation with the ΔE_a(*exo* − *endo*). That is, if the secondary orbital interaction governs the *endo* selectivity, the overlap population should show a linear correlation with ΔE_a.



We examine in this study the Diels−Alder reactions between cyclopropene and butadienes having some substituent groups in conjugation with the diene framework, by applying a configuration analysis of the wave function and a paired interaction orbital scheme.[18,19] In examining the secondary orbital interaction, we may refer here to its meaning. The secondary orbital interactions have been defined so far within the framework of the frontier orbital theory.[12,15a] Gleiter argued also the secondary orbital interactions in terms of the frontier orbitals.[20] The frontier orbitals have the largest amplitude on the reaction sites, and therefore other occupied and/or unoccupied MOs will show large amplitude on the site of secondary interactions. Other MOs may also play significant roles in determining the stereoselectivity. Thus, we use the term "secondary orbital interactions" to specify the orbital interactions that occur in the regions outside the reaction sites. We attempt here to take all the occupied and unoccupied MOs into account.



1 : X = Y = H
2 : X = H, Y = BH_2
3 : X = H, Y = CN
4 : X = H, Y = F
5 : X = H, Y = OH
6 : X = H, Y = (C≡CH)
7 : X = Y = BH_2
8 : X = Y = CN
9 : X = Y = F
10 : X = Y = OH
11 : X = Y = (C≡CH)

Table 1. Energy Difference between the *Exo* and *Endo* Transition States for the Diels−Alder Reaction between Cyclopropene and Butadienes

	ΔE_a(*exo* − *endo*) (kJ/mol)		
diene	RHF/6-31G*	MP2/6-31G* [a]	B3LYP/6-31G* [a]
1	8.279	12.350	8.477
2	11.590	15.671	11.270
3	9.328	13.503	9.158
4	6.542	10.850	5.893
5	8.553	12.701	7.407
6	8.519	12.866	8.533
7	14.493	18.936	14.510
8	10.600	14.564	9.368
9	4.842	9.355	4.200
10	9.918	13.498	8.372
11	8.592	12.980	7.753

[a] Structures optimized at the RHF/6-31G* level.

Method of Calculations

Full geometry optimization of all the reactants and the *exo*- and *endo*-transition states for the additions was carried out at the RHF level by using the GAMESS program, with the 6-31G* basis set, to compare with the arguments in a previous study.[15a,21] All the transition states were confirmed to have an imaginary mode of vibration. We performed then single-point energy calculations at the MP2/6-31G*//RHF/6-31G* level and the B3LYP calculations on the structures optimized at the RHF/6-31G* level by using the Gaussian 94 program.[22]

Results and Discussion

The differences in the activation energies calculated for the *exo*- and *endo*-additions are summarized in Table 1. It is seen that nonsubstituted butadiene **1** favors the *endo*-addition of cyclopropene. It has been reported that B3LYP and QCISD(T) calculations give reasonable values of the activation energy for the Diels−Alder reaction between **1** and cyclopropene,[23,24] whereas CASSCF and RHF calculations give larger values,[15a,23,24] and the calculation at the MP2 level gives a smaller value.[15a,23] The difference in the barrier heights for the *exo*- and *endo*-additions has been estimated to be ~8.4 kJ/mol by means of the B3LYP and QCISD(T) calculations.[23,24] The MP2 calculations in the present study are seen to give somewhat larger values for the difference in barrier heights compared with the B3LYP calculations, as has been pointed out previously for the addition of **1**.[23] Electron-withdrawing substituents, BH_2 and CN, on butadiene are shown to enhance the *endo* selectivity, whereas electron-donating substituents, F and OH, suppress the selectivity. The OH group has a somewhat strange effect, as shown by **10**.

To see the orbital interactions, we expanded first the wave function of the reacting system in terms of electron configurations of two fragment species, a diene and a

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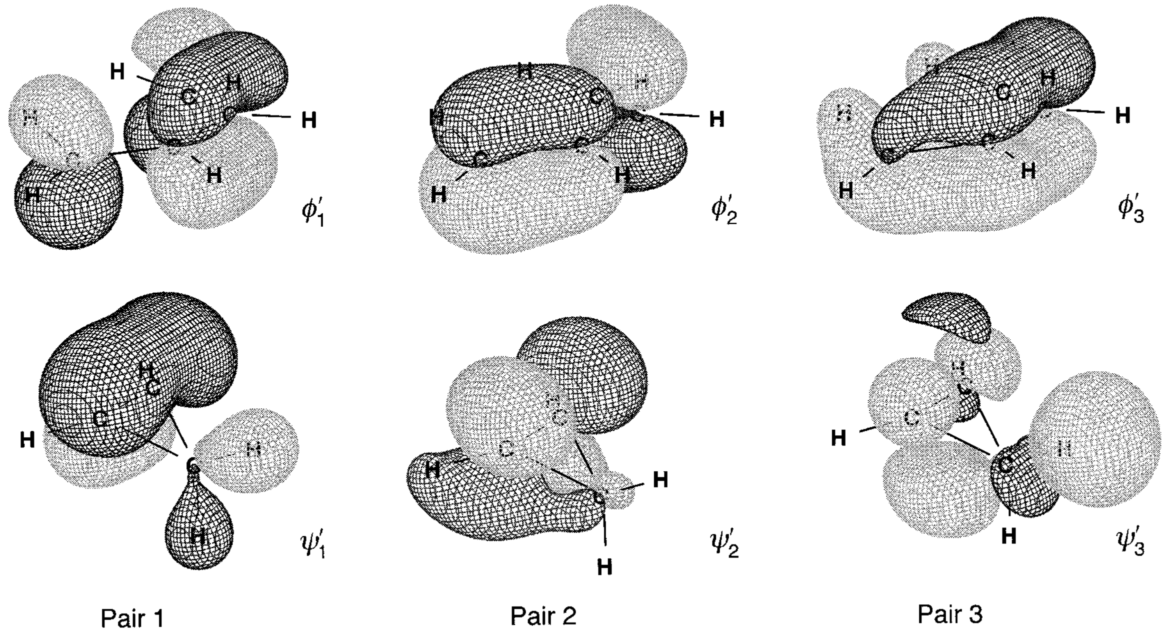
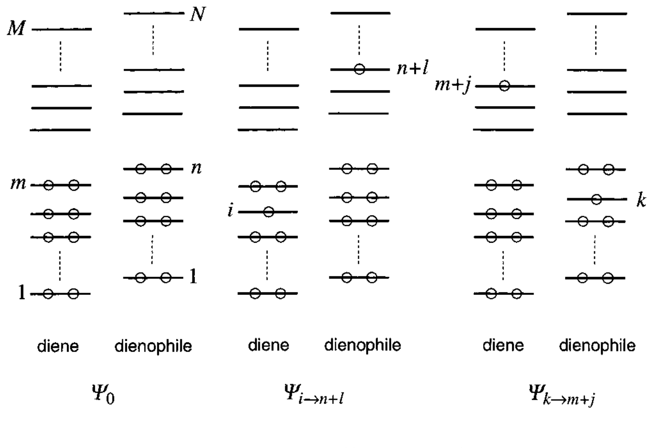


Figure 1. Pairs of interacting orbitals participating in electron delocalization at the *endo*-transition state of the addition of cyclopropene to butadiene.

cyclopropene, frozen to their geometries at the transition state. We applied the method of configuration analysis.[18] Electron delocalization is described principally by the mixing in of one-electron-transferred configurations $\Psi_{i\rightarrow n+l}$ and $\Psi_{k\rightarrow m+j}$ into the original configuration, Ψ_0, in which the diene and the dienophile retain their electron configurations in an isolated state. Many other electron configurations appear at the same time, including local excitation of electrons in the diene part and in the dienophile part, to reduce the bias in electron distribution caused by delocalization of electrons.[18] Each electron configuration is expressed as usual by a determinant or determinants of the fragment MOs with a singlet spin function.



Then, by utilizing the coefficients of electron-transferred configurations, we have carried out simultaneous unitary transformations of MOs within each of the two fragment species.[19] The orbital transformations have been made for the combinations of the occupied MOs of one fragment, e.g., the cyclopropene, and the unoccupied MOs of the other fragment, a diene. As a result, electron delocalization is represented for the most part by the two pairs of hybrid MOs of the fragments, (ϕ'_1; ψ'_1) and (ϕ'_2; ψ'_2), which are illustrated in Figure 1 for the addition of **1**. Here, the orbital ϕ'_1 is given by a linear combination of the unoccupied MOs ϕ_{m+j} of **1** and the orbital ψ'_1 by a linear combination of the occupied MOs ψ_k of cyclopropene. This pair of orbitals, denoted here by pair 1, represents electron delocalization from cyclopropene to **1**. On the other hand, the orbital ϕ'_2 consists of the occupied MOs ϕ_i of **1** and the orbital ψ'_2 of the unoccupied MOs ψ_{n+l} of cyclopropene. This pair of interaction orbitals, pair 2, stands for electron delocalization from **1** to cyclopropene. One sees that the two pairs look very similar to the HOMO−LUMO interactions in this small system.

Interestingly, the interaction orbital of cyclopropene in pair 1 has significant amplitudes on the methylenic hydrogens. This pair of orbitals demonstrates clearly the presence of the secondary orbital interaction pointed out by Apeloig and Matzner.[15a] The interaction orbitals very similar in shape to pair 1 have also been obtained for the addition of cyclopropene to other dienes. The butadienes which carry substituent groups in conjugation with the diene π system generate the interaction orbitals localized effectively on the diene framework by combining the unoccupied π-type MOs. On the other hand, the secondary orbital interaction is not allowed by symmetry in pair 2. The interaction has also been shown to be negligibly small in pair 2 for the monosubstituted butadienes without the symmetry plane. Instead, the secondary orbital interaction appears in an additional pair of interaction orbitals (pair 3) that shows a very weak electron delocalization from the diene part to the dienophile part.

The aim of this study is to examine if the stabilization brought about by the secondary orbital interactions is large enough to control the *exo*/*endo* selectivity in this reaction. The wave function is now given in terms of electron configurations of the transformed fragment orbitals. The energy of the original electron configuration, $<\Psi_0\,|H|\,\Psi_0> = H_{0,0}$, is not affected at all by the orbital transformations. Electron delocalization from the cyclopropene part to the butadiene part is represented by the

Table 2. Differences in Stabilization Due to Electron Delocalization and in Electrostatic Interactions between the *Exo* and *Endo* Transition States for the Diels–Alder Reaction between Cyclopropene and Butadienes[a]

	electron delocalization			Coulomb
diene	pair 1[b]	pair 2[c]	pair 3[c]	interaction
1	3.844	−2.832	0.917	0.758
2	4.676	−3.454	0.893	3.449
3	4.544	−3.117	0.817	0.372
4	3.517	−2.668	0.820	−0.280
5	2.963	−2.820	0.874	2.571
6	4.176	−3.014	0.835	0.825
7	5.159	−3.610	0.884	7.588
8	5.212	−3.518	0.736	0.064
9	3.238	−2.559	0.734	−1.411
10	1.520	−2.249	0.799	4.929
11	4.279	−3.297	0.749	0.630

[a] Calculated at the RHF/6-31G* level, in kJ/mol. [b] Electron delocalization from cyclopropene to a diene. [c] Electron delocalization from a diene to cyclopropene.

mixing in of the electron-transferred configuration, denoted here by Ψ_I, in which an electron has been shifted from ψ'_1 of the cyclopropene to ϕ'_1 of a diene in pair 1, starting from Ψ_0. Then, we have calculated exactly the expectation values of the total Hamiltonian for the reacting system with respect to the original and electron-transferred configurations.[18a,25] The stabilization arising from delocalization of electrons from cyclopropene to a diene may be estimated by utilizing perturbation theory.[26] The interaction in this system does not seem, however, to be weak enough to apply the second-order perturbation scheme at the transition state. Thus, we have evaluated the stabilization by $2C_0C_I(H_{0,I} - S_{0,I}H_{0,0})$, where $S_{0,I}$ signifies the overlap integral between Ψ_0 and Ψ_I and C_0 and C_I indicate, respectively, the coefficients of Ψ_0 and Ψ_I in the wave function of the reacting system. The coefficients C_0 and C_I have been obtained directly from the wave function by expanding it in terms of the electron configurations of the two reacting species.[18] The strength of electron delocalization from the butadiene part to the cyclopropene part has been estimated similarly, by taking the electron configuration Ψ_{II} in which an electron has been shifted from ϕ'_2 of a diene to ψ'_2 of the cyclopropene in pair 2.

The stabilization due to electron delocalization from the cyclopropene part to the diene part (pair 1) has been calculated to be −72.48 kJ/mol for the *exo*-transition state and −76.32 kJ/mol for the *endo*-transition state in **1**, in favor of the *endo*-selectivity. The stabilization has been found to be the largest in **8** with two CN groups, −88.35 and −93.56 kJ/mol, and the smallest in **10** with two OH groups, −70.39 and −71.91 kJ/mol, for the *exo*- and *endo*-additions, respectively. The differences in stabilization energies are presented in Table 2. Electron-withdrawing substituents on butadiene are shown to enhance electron delocalization from the cyclopropene part to the diene part. On the other hand, it is interesting to see that the stabilization brought about by electron delocalization from **1** to cyclopropene (pair 2) is not very similar in the *exo*-addition and in the *endo*-addition. It has been calculated to be −85.42 kJ/mol for the *exo*-addition and −82.59 kJ/mol for the *endo*-addition in favor of the *exo*-transition state. This suggests that the substituent groups have an opposite effect in pair 2 to the substituent effect observed in pair 1. The stabilization due to electron delocalization from the diene part to the cyclopropene part has been calculated actually to be the largest in **10**, −94.78 and −92.53 kJ/mol, and the smallest in **8**, −69.12 and −65.60 kJ/mol, for the *exo*- and *endo*-additions, respectively.

The dienes having an ethynyl group, **6**, and two ethynyl groups, **11**, give slightly larger stabilization compared with **1** in delocalization from the cyclopropene part, but give slightly smaller stabilization in delocalization from the diene part. The ethynyl group seems to oppose, though very small in magnitude, the normal electron demand in the Diels–Alder reaction.[27] Electron delocalization between the orbitals in pair 3 is very weak, bringing only −4.90 and −5.82 kJ/mol of stabilization to the *exo*- and *endo*-transition states for the reaction of **1**, respectively, in favor of the *endo*-addition. However, the difference in the orbital interactions in this pair is not affected significantly by the substituent groups, as shown in Table 2.

Secondary orbital interactions have been demonstrated, as a whole, to favor the *endo*-addition of cyclopropene to **1**. The *endo*-addition is seen to be more favored in the dienes having electron-withdrawing groups, **2**, **3**, **6**, **7**, **8**, and **11**, whereas it is less favored in the dienes having electron-donating groups, **4**, **5**, **9**, and **10**.[28] One finds, however, that the difference in stabilization due to electron delocalization is not large enough to interpret the difference between the barrier heights for the *exo*- and *endo*-additions, presented in Table 1. Houk and co-workers showed that the electrostatic interactions were of crucial importance in explaining the facial selectivity in nucleophilic additions to carbonyl bonds.[29] Then, we have estimated the electrostatic interactions E_Q by utilizing the wave functions of the isolated diene and dienophile molecules frozen to the geometries that they have at the transition state.[26] As summarized in Table 2, the electrostatic interaction favors the *endo*-addition, except for the cases of **4** and **9**. It is very strong in **7** and in **10**. The strange behavior of **10** in ΔE_a(*exo* − *endo*) observed in Table 1 seems to be understood in this context.

In the ene reaction of propene with cyclopropene, only the combination of the LUMO of the former and the HOMO of the latter has been suggested to provide a secondary orbital interaction.[17] The secondary orbital interaction is shown also in the present systems mainly by the first pair of orbitals, representing electron delocalization from the cyclopropene part to the diene part. The difference in the sum of the two energy terms, the stabilization brought about by the electron delocalization, E_1, and the stabilization due to the electrostatic interaction, E_Q, is plotted in Figure 2 against ΔE_a(*exo* − *endo*) obtained by the B3LYP calculations. One finds a nice correlation between them. Though some other factors, e.g., polarization induced by electron delocalization, are supposed to be operating to counterbalance the *exo* preference of the orbital interactions in pair 2 and to fill the gap between the two theoretically calculated quantities in Figure 2, the present analysis suggests that the

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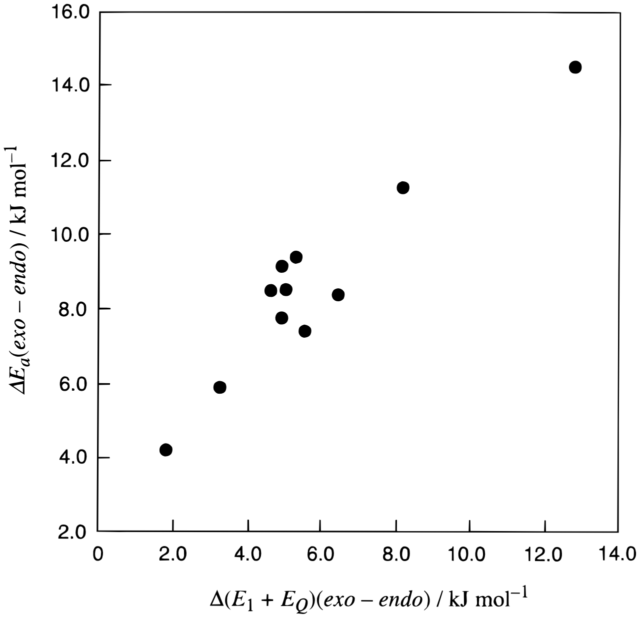

Figure 2. Relation between the difference in the activation energies for the *exo*- and *endo*-additions and the stabilization due to the secondary orbital interactions and the electrostatic interactions in the addition of cyclopropene to butadienes.

secondary orbital interaction depicted in pair 1 and the electrostatic interaction are responsible together for the *endo* selectivity in the Diels−Alder additions of cyclopropene to butadienes.

Conclusion

We have studied the *endo* selectivity in the Diels−Alder reactions of some substituted butadienes with cyclopropene theoretically, by applying the paired transformations of the diene and dienophile MOs. In addition to the principal interactions to form new σ bonds between a diene and the dienophile, the cyclopropene occupied interaction orbital shows significant amplitudes on the methylenic hydrogens. One of the hydrogens overlaps *in phase* with the paired unoccupied interaction orbital of the diene at the backbone carbons, C_2 and C_3, as has been discussed in the literature. We have attempted to estimate the strength of this secondary orbital interaction, by combining a configuration analysis of the wave function for the reacting system and calculations of the integrals representing the orbital interactions between the dienes and the dienophile. The contribution of electrostatic interaction to the stabilization of the *exo*- and *endo*-transition states has also been estimated. It has been clarified that neither electron delocalization nor the electrostatic interaction interprets the difference in the barrier heights for the *endo*-and *exo*-additions, but the sum of the two terms has been found to show a good correlation with the energy difference. The present study suggests some difficulty of ascribing the difference in the activation energies to one or two specific energy terms, in a quantitative sense. We believe, however, that recognition of the strength of secondary orbital interactions relative to the magnitude of activation energies will be of use in discussing the stereoselectivity in related reactions.

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Supporting Information Available: Information on the geometries and energies of the species examined in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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