On the MO Perturbation Theory of Molecular Rearrangements

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The relationship between two simple Hückel MO perturbation treatments of electrocyclic reactions formerly proposed has been examined. The reason why the two different approaches give the same prediction with regard to the favorable paths of the reactions has been established numerically. A calculation of the thermal ring-closing of butadiene has been carried out, including both sigma and pi electrons.

In 1965, Woodward and Hoffmann suggested a selection rule for electrocyclic reaction of conjugated molecules.[1] Various intramolecular reactions as well as intermolecular reactions between two systems have been discussed on the basis of the symmetry properties of the molecular orbitals (MO) of the reactants and the product.[2-18] Since then, several theories for unimolecular reactions have been proposed.[19-24] Some MO and valence-bond (VB) calculations of the favorable course of electrocyclic reactions have also been carried out.[25-29] Among the theoretical approaches to the electrocyclic rearrangements of open conjugated chains, we can find two types of MO perturbation treatments on the level of the simple Hückel approximation.[5] One is to discuss the path of molecular rearrangements by examining the energy change caused by the introduction of a resonance integral between the two termini of a chain, representing the starting of ring-closing by the overlapping of the two terminal atomic orbitals (AO).[5a,b] The other is to apply a partitioning technique to the reaction; thereby, the ring-closing of a conjugated chain can be regarded as if it were an intersystem four-center interaction between the two fragments of a molecule.[5d] The basic idea of the partitioning technique originated from the perturbation theory for the intermolecular interaction of two independent systems has been developed successfully in numerous unimolecular reactions.[5d,f,30] In this paper, we intend first to examine the relationship between these perturbation approaches to molecular rearrangements and then to present some numerical results on the electrocyclic rearrangement of butadiene calculated by use of the extended Hückel MO wave function, in order to observe the behavior of sigma and pi electrons in the reaction.

Simple Hückel MO Perturbation Theory for Unimolecular Rearrangements

Let us first discuss the perturbation theory of the simple Hückel MO method.[31] When the resonance integral between the AO's r and s, represented by β_{rs}, varies by a small amount, $\Delta\beta_{rs}$, that between the

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AO's t and u by an amount of $\Delta\beta_{tu}$, and so on, the change in the electronic energy is given by:

$$\Delta E \cong 4\sum_{i}^{\text{occ}}\sum_{(r,s)} c_r{}^{(i)}c_s{}^{(i)}\Delta\beta_{rs} + 2\sum_{i}^{\text{occ}}\sum_{j}^{\text{uno}} \frac{\{\sum_{(r,s)}(c_r{}^{(i)}c_s{}^{(j)}+c_r{}^{(j)}c_s{}^{(1)})\Delta\beta_{rs}\}^2}{\varepsilon_i-\varepsilon_j} \tag{1}$$

where $c_r{}^i$ is the coefficient of the AO r in the MO i, where ε_i is its energy, and where $\overset{\text{occ}}{\sum}$ and $\overset{\text{uno}}{\sum}$ imply the summation over all the occupied and over all the unoccupied MO's respectively. Therefore, in the case of the ring-closing between the two termini r and s of a polyene, the energy change associated with this process is given approximately by:

$$\Delta E \cong 2P_{rs}\gamma\beta_{rs} \tag{2}$$

where P_{rs} is the mobile bond-order between the π AO's at the termini and where $\gamma\beta_{rs}$ is the resonance integral standing for the interaction. Since $\gamma\beta_{rs}$ and the overlap integral, s_{rs}, are opposite in sign, the positive $\gamma\beta_{rs}$ corresponds to the conrotatory, and the negative $\gamma\beta_{rs}$, to the disrotatory, ring-closing (Fig.1).

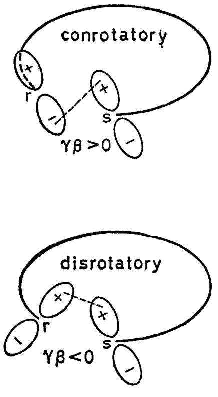


Fig. 1. A schematic representation of conrotatory and disrotatory ring-closing of a polyene.

In the ground-state of butadiene, P_{14} is negative, so the reaction should take place preferentially in such a way as to make $\gamma\beta_{14}$ positive. On the contrary, P_{14} is positive in the first excited-state in favor of the disrotatory ring-closing. The thermal and photochemical ring-closing of hexatriene should take place dominantly in a fashion opposite to that in the case of butadiene, because P_{16} is positive in the ground-state and negative in the first excited-state. In general, P_{rs} is negative in the ground-state and positive in the first excited-state for polyenes with $4n$-electrons, while it is positive in the ground-state and negative in the excited-state for polyenes with $4n+2$ electrons.[5a] The conclusion thus derived from the intramolecular first-order perturbation energy was found to be in excellent agreement with the experimental results and with the results of other theoretical approaches.

When we employ the partitioning technique, we can regard a ring-closing of a conjugated chain as a cyclic interaction between two fragments of a molecule (Fig. 2). The interaction energy between them can be given by (in the ground-state):

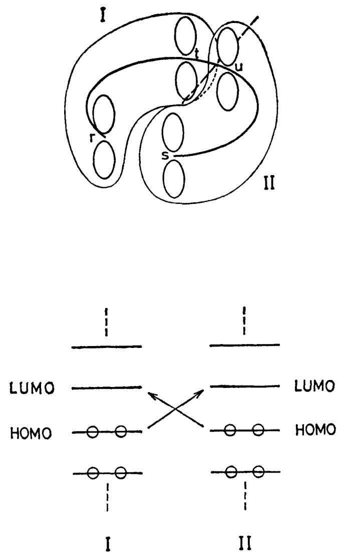


Fig. 2. A schematic representation of partitioning of a polyene into two fragments and the mode of orbital overlap interaction.

$$\Delta E' \cong 2\Big(\sum_{i}^{\text{occ}}\sum_{j}^{\text{uno}}-\sum_{i}^{\text{uno}}\sum_{j}^{\text{occ}}\Big)\frac{(c_r{}^{(i)}c_s{}^{(j)}\gamma\beta+c_t{}^{(i)}c_u{}^{(j)}\beta)^2}{\varepsilon_i-\varepsilon_j} \tag{3}$$

if we can assume that the interaction is sufficiently weak as to be called a "perturbation." Equation (3) tells us that the most favorable mode of interaction is determined by the orbital overlap interaction of the occupied MO's of one fragment and the unoccupied MO's of the other fragment. When the highest occupied (HO) MO of one part happens to be degenerate with the lowest unoccupied (LU) MO of the other, the interaction energy can be approximated by:

$$\Delta E' \cong -2|c_r{}^{(\mathrm{HO})}c_s{}^{(\mathrm{LU})}\gamma\beta+c_t{}^{(\mathrm{HO})}c_u{}^{(\mathrm{LU})}\beta| \tag{4}$$

Even not in such a condition, the interaction between the HOMO of one part and the LUMO of the other part, and the converse, play dominant roles in determining the favorable mode of interaction, in general, because the denominators of these terms in Eq. (3) are obviously smaller than those of the other terms.

When a polyene is partitioned into two odd electron fragments, the interaction energy is given by;

$$\Delta E' \cong -|c_r{}^{(\mathrm{SO})}c_s{}^{(\mathrm{SO}')}\gamma\beta+c_t{}^{(\mathrm{SO})}c_u{}^{(\mathrm{SO}')}\beta| \tag{5}$$

where SO and SO′ mean the singly-occupied nonbonding MO's of the two fragments.

Let us now consider the thermal ring-closing of butadiene (Fig. 3). When we divide butadiene into two ethylenic parts, the HOMO (S)–LUMO (A) interaction favors the *anti*-mode interaction. Here, S denotes the symmetric MO's with $c_r{}^{(i)}c_t{}^{(i)}>0$ and A indicates the antisymmetric MO's with $c_r{}^{(i)}c_t{}^{(i)}<0$; we may call the mode of interaction in which β and $\gamma\beta$ possess the same sign "*syn*-interaction," and that in which β and $\gamma\beta$ have different signs, "*anti*-interaction."[5c] The case of division into an allylic part and a single p AO also shows that the interaction should take place preferentially in the *anti*-mode. Accordingly, thermal ring-closing takes place dominantly in a conrotatory fashion.

The interaction between an ethylenic part and a

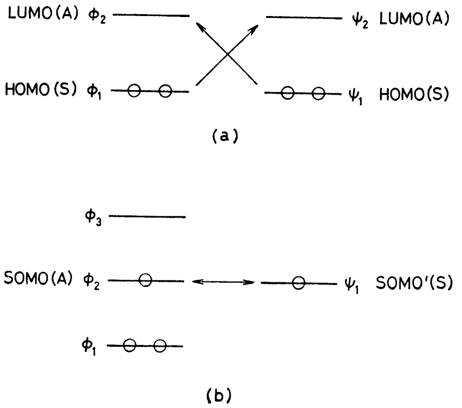


Fig. 3. Orbital overlap interaction in thermal ring-closing of butadiene.
(a) Division into two ethylenic parts
(b) Division into an allylic part and a single *p* AO

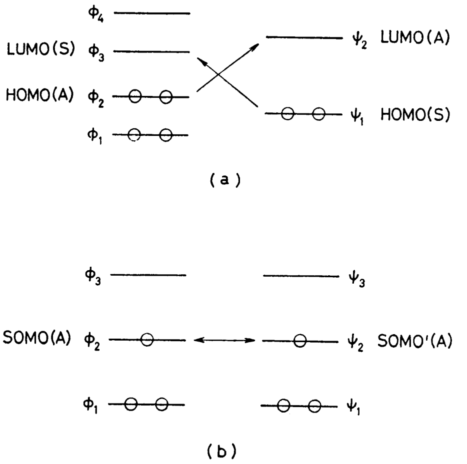


Fig. 4. Orbital overlap interaction in thermal ring-closing of hexatriene.
(a) Division into ethylenic and butadienic part
(b) Division into two allylic parts

butadienic part, and the interaction between two allylic parts, both prefer *syn*-interaction in the ground-state (Fig. 4). Therefore, the ring-closing of hexatriene is liable to occur in a disrotatory manner.

In order to discuss the favorable mode of photochemical reactions, we divide a conjugated chain into two parts, in which one has an excited-electron configuration. In this case, the interaction between SOMO and HOMO and the interaction between SOMO' and LUMO are predominant (Fig. 5).

$$\Delta E' \cong -\left|(c_r{}^{(\mathrm{SO})}c_s{}^{(\mathrm{HO})}\gamma\beta + c_t{}^{(\mathrm{SO})}c_u{}^{(\mathrm{HO})}\beta)^2 + (c_r{}^{(\mathrm{SO}')}c_s{}^{(\mathrm{LU})}\gamma\beta + c_t{}^{(\mathrm{SO}')}c_u{}^{(\mathrm{LU})}\beta)^2\right|^{1/2} \tag{6}$$

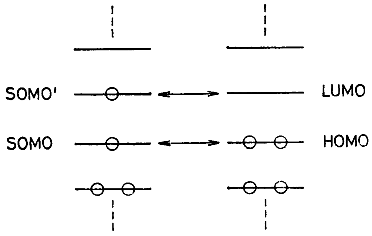


Fig. 5. Mode of orbital overlap interaction in photochemical ring-closing.

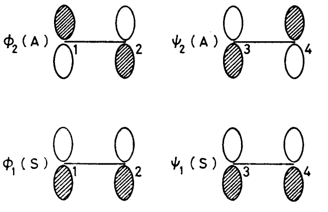
Equation (6) corresponds to the case in which SOMO degenerates with HOMO, and SOMO', with LUMO.[5b,32] In some cases, one of the two interaction terms is more important than the other. Consequently, the photochemical ring-closing of butadiene prefers the *syn*-interaction, and that of hexatriene, the *anti*-interaction. In general, the cyclic interaction between two fragments of a polyene with $4n$ electrons takes place preferentially in the *anti*-mode in the ground-state and in the *syn*-mode in the excited-state, while the interaction between two fragments of a polyene possessing $4n+2$ electrons favors the *syn*-mode in the ground-state and the *anti*-mode in the excited-state.[5d]

The Relation between Two Perturbation Approaches

As has been mentioned above, the rule derived from the partitioning analysis of orbital interactions in the thermal and photochemical ring-closing of conjugated chains can give the same prediction as the rule deduced from the intramolecular first-order perturbation. Now, let us discuss the relation between these two approaches to molecular rearrangements by means of some numerical calculations.

TABLE 1. DIVISION OF BUTADIENE MO'S INTO ETHYLENE MO'S

	MO's of butadiene[a]			
	φ_1	φ_2	φ_3	φ_4
ϕ_1	0.688	0.688	0.163	−0.163
ϕ_2	0.163	−0.163	−0.688	−0.688
ψ_1	0.688	−0.688	0.163	0.163
ψ_2	0.163	0.163	−0.688	0.688



$\phi_i = c_1{}^{(i)}\chi_1 + c_2{}^{(i)}\chi_2$ $\psi_j = c_3{}^{(j)}\chi_3 + c_4{}^{(j)}\chi_4$

a) MO's of butadiene are numbered in the order of increasing energy.

The four π MO's of butadiene can be expressed by linear combinations of the bonding and antibonding π MO's of two ethylenic fragments (Table 1). It should be noted that the signs of the coefficients depend on how the arbitrary factor, ±1 is assigned the real MO's of two ethylenic parts. Here and in what follows, we always choose the signs of the MO's so as to make $c_t{}^{(i)}c_u{}^{(j)}>0$, where t and u are the AO's between which the partition of a chain is made, and where i and j denote the MO's of the two fragments. By the use of the coefficients listed in Table 1, the first-order perturbation energy given by Eq. (2) for

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[32] C. Nagata, A. Imamura, Y. Tagashira, M. Kodama, and N. Fukuda, *J. Theor. Biol.*, **9**, 357 (1965).

the thermal ring-closing of butadiene can be rewritten as:

$$\varDelta E = 0.8944\{(c_1{}^{(1)}c_4{}^{(2)}+c_1{}^{(2)}c_4{}^{(1)})\gamma\beta + (c_2{}^{(1)}c_3{}^{(2)}+c_2{}^{(2)}c_3{}^{(1)})\beta\} - 0.8944\beta$$

where 0.8944β is the conjugation stabilization of the 2,3-π bond and is common to both the conrotatory and disrotatory processes. The bonding and *anti*-bonding interactions between ϕ_1 and ψ_1 compensate for each other in the simple Hückel MO approximation. Consequently, the energy change associated with the thermal ring-closing can be represented by the interaction of occupied and unoccupied MO pairs, $\phi_1-\psi_2$ and $\psi_1-\phi_2$. Since ϕ_1 and ψ_1 are S MO's and ϕ_2 and ψ_2 are A MO's, the interaction should take place in the *anti*-mode. In the photochemical reaction, the energy change is expressed as:

$$\varDelta E = 1.0000\{(c_1{}^{(1)}c_4{}^{(1)}+c_1{}^{(2)}c_4{}^{(2)})\gamma\beta + (c_2{}^{(1)}c_3{}^{(1)} + c_2{}^{(2)}c_3{}^{(2)})\beta\} + 0.4472\{(c_1{}^{(1)}c_4{}^{(2)}+c_1{}^{(2)}c_4{}^{(1)})\gamma\beta + (c_2{}^{(1)}c_3{}^{(2)}+c_2{}^{(2)}c_3{}^{(1)})\beta\} - 1.4472\beta$$

where 1.4472β is the conjugation energy of the 2,3-π bond in the first excited-state. It can be seen that the interaction between ϕ_1 and ψ_1 and the interaction between ϕ_2 and ψ_2 play dominant roles.

When we divide butadiene into an allylic part and a single p AO, the energy change is given by:

$$\varDelta E = 2(0.2236c_1{}^{(1)}+0.9487c_1{}^{(2)}+0.2236c_1{}^{(3)})\gamma\beta + 2(0.2236c_3{}^{(1)}+0.9487c_3{}^{(2)}+0.2236c_3{}^{(3)})\beta - 1.7888\beta$$

where 1.7888β is the conjugation energy of the 3,4-π bond in the ground-state. We can see that the favorable mode of interaction is governed by the two SOMO's.

Next, let us consider the ring-closing of hexatriene. In case of the division of hexatriene into a butadienic part (ϕ_1, ϕ_2, ϕ_3, ϕ_4) and an ethylenic part (ψ_1, ψ_2), the interaction between ϕ_2 and ψ_2 and the interaction between ϕ_3 and ψ_1 predominate in the thermal ring-closing in favor of the *syn*-interaction, whereas the interaction between ϕ_2 and ψ_1 and the interaction between ϕ_3 and ψ_2 make major contributions to the energy change in the excited-state in favor of the *anti*-interaction (Table 2). The division of hexatriene into two allylic fragments shows the importance of the interaction between two SOMO's in the thermal ring-closing:

Table 2. Contributions of orbital interactions to the energy change in the ring-closing of hexatriene

	Thermal		Photochemical	
	ψ_1(S)	ψ_2(A)	ψ_1(S)	ψ_2(A)
ϕ_1 (S)	0.009	0.352	0.105	0.278
ϕ_2 (A)	−0.004	0.917	0.909	0.447
ϕ_3 (S)	0.917	−0.004	0.447	0.909
ϕ_4 (A)	0.352	0.009	0.278	0.105

ψ: MO's of ethylenic part, ϕ: MO's of butadienic part

$$\varDelta E = 0.0692\{(c_1{}^{(1)}c_6{}^{(1)}+c_1{}^{(3)}c_6{}^{(3)})\gamma\beta + (c_3{}^{(1)}c_4{}^{(1)} + c_3{}^{(3)}c_4{}^{(3)})\beta\} + 0.3418\{(c_1{}^{(1)}c_6{}^{(2)}+c_1{}^{(3)}c_6{}^{(2)} + c_1{}^{(2)}c_6{}^{(1)}+c_1{}^{(2)}c_6{}^{(3)})\gamma\beta + (c_3{}^{(1)}c_4{}^{(2)}+c_3{}^{(3)}c_4{}^{(2)} + c_3{}^{(2)}c_4{}^{(1)}+c_3{}^{(2)}c_4{}^{(3)})\beta\} + 0.2418\{(c_1{}^{(1)}c_6{}^{(3)} + c_1{}^{(3)}c_6{}^{(1)})\gamma\beta + (c_3{}^{(1)}c_4{}^{(3)}+c_3{}^{(3)}c_4{}^{(1)})\beta\} + 1.8616(c_1{}^{(2)}c_6{}^{(2)}\gamma\beta + c_3{}^{(2)}c_4{}^{(2)}\beta) - 1.5697\beta$$

The numerical results given above with respect to the thermal and photochemical ring-closing of butadiene and hexatriene have shown that the orbital overlap interaction between HOMO and LUMO (in the case of the partitioning of a polyene into two even electron systems) or between SOMO and SOMO′ (in the case of the partitioning of a polyene into two odd electron systems) plays a dominant role in controlling the stereochemical course of the thermal reaction, while the orbital overlap interaction between HOMO and SOMO and that between LUMO and SOMO′ are important in the photochemical ring-closing. This may be the reason why the partitioning analysis can give the same prediction as that of the first-order perturbation approach; at the same time it suggests that the two approaches to the molecular rearrangements can be equivalent in an approximate sense. The partitioning technique supplies us with the simplest way of discussing the molecular rearrangements in MO terms, regardless of whether any symmetry is retained throughout the reactions or not.

Inclusion of Sigma Electrons

Parr and his collaborators introduced the integral Hellmann-Feynman theorem to calculate the rotation barrier of ethane, obtaining a value of 2.4 kcal/mol; this is in good agreement with the experimental value of 2.9 kcal/mol.[33] Here we will present the results of calculation derived from the application of the theorem, though in a very approximate sense, to the ring-closing of butadiene. Let us consider a state, p, corresponding to a point on the reaction coordinate in the neighborhood of the initial state, i. Then, the energy change by going from i to p is given by;

$$\varDelta E = E_p - E_i = \frac{\langle \Psi_i|\varDelta H|\Psi_p\rangle}{\langle \Psi_i|\Psi_p\rangle} \qquad (7)$$

$$\varDelta H = H_p - H_i$$

where H is the Hamiltonian operator of the system. If we can assume here that the wave function, Ψ_p, is expanded by the wave functions of the state, i:

$$\Psi_p = \Psi_i + \lambda\Psi_i{}^{(1)} + \lambda^2\Psi_i{}^{(2)} + \cdots \qquad (8)$$

the energy change can be represented by:

$$\varDelta E = \langle \Psi_i|\varDelta H|\Psi_i\rangle + \lambda\{\langle \Psi_i|\varDelta H|\Psi_i{}^{(1)}\rangle - \langle \Psi_i|\varDelta H|\Psi_i\rangle\langle \Psi_i|\Psi_i{}^{(1)}\rangle\} + \lambda^2\{\langle \Psi_i|\varDelta H|\Psi_i{}^{(2)}\rangle + \cdots\} + \cdots \qquad (9)$$

The use of the matrix sum rule leads us to the same result as that obtained by Salem.[20] It should be noted that Eq. (7) holds only for the exact wave func-

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[33] a) H. J. Kim and R. G. Parr, *J. Chem. Phys.*, **41**, 2892 (1964). b) R. W. Wyatt and R. G. Parr, *ibid.*, **43**, s217 (1965).

tion. The concrete forms of $\Psi_i^{(1)}$, $\Psi_i^{(2)}$, $\cdots$, are not necessarily easily obtainable, in general. However, as long as we are concerned with the beginning stage of the reaction, λ is small and the energy change can be measured by taking only the first term, to the roughest approximation:

$$\langle\Psi_i|\Delta H|\Psi_i\rangle = \int\rho_{ii}(1)H'(1)\mathrm{d}\tau_1 + \Delta V_{\mathrm{nn}} \tag{10}$$

$$\rho_{ii}(1) = N\int\Psi_i^*(1, 2, \cdots, N)\Psi_i(1, 2, \cdots, N)\mathrm{d}\tau_2\cdots\mathrm{d}\tau_N$$

where ΔV_{nn} is the change in the nuclear repulsion energy and where N is the number of electrons in the system. The change in the Hamiltonian operator due to the change in the relative positions of the nuclei associated with ring-closing is given by:

$$H' = \sum_{\mu}\sum_{k}\left(\frac{1}{r_{\mu k}^{p}} - \frac{1}{r_{\mu k}^{i}}\right) \tag{11}$$

where μ and k denote the nucleus and the electron respectively, and where

$$r_{\mu k}^{i} = |\boldsymbol{r}_k - \boldsymbol{r}_\mu|$$

$$r_{\mu k}^{p} = |\boldsymbol{r}_k - \boldsymbol{r}_\mu'| = |\boldsymbol{r}_k - (\boldsymbol{r}_\mu + \Delta\boldsymbol{R})| = |r_{\mu k}^{i} - \Delta\boldsymbol{R}| \tag{12}$$

The deformation, $\Delta\boldsymbol{R}$, is given by:

$$\Delta\boldsymbol{R} = \Delta x\cdot\boldsymbol{i} + \Delta y\cdot\boldsymbol{j} + \Delta z\cdot\boldsymbol{k}$$

where $\boldsymbol{i}$, $\boldsymbol{j}$, and $\boldsymbol{k}$ are unit vectors in a three-dimensional space. Thus, we have;

$$\frac{1}{r_{\mu k}^{p}} - \frac{1}{r_{\mu k}^{i}} \cong \frac{x - A_x}{(r_{\mu k}^{i})^3}\Delta x + \frac{y - A_y}{(r_{\mu k}^{i})^3}\Delta y + \frac{z - A_z}{(r_{\mu k}^{i})^3}\Delta z \tag{13}$$

where (A_x, A_y, A_z) is the Cartesian coordinate of the nucleus, μ. Consider the rotation of the methylene group about the carbon-carbon axis by an angle of ω (Fig. 6). By this rotation, hydrogen changes its position from (A_x, A_y, A_z) to (A_x', A_y', A_z'). Here, we have:

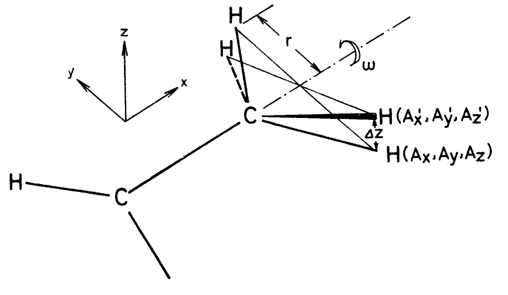

Fig. 6. A schematic representation of the rotation of methylene about carbon-carbon bond axis.

$$A_x' = A_x$$

$$A_y' = A_y + r(1 - \cos\omega) \cong A_y + \frac{1}{2}r\omega^2 \tag{13}$$

$$A_z' = A_z + r\sin\omega \cong A_z + r\omega - \frac{1}{6}r\omega^3$$

Since we are concerned with the beginning stage of the reaction, we may disregard the second- and third-order terms with respect to ω. Therefore, we obtain:

$$\Delta x = \Delta y = 0,\ \Delta z = r\omega \tag{15}$$

By the use of the MO wave function for the ground-state, the diagonal element of the first-order density matrix is given by:

$$\rho_{ii}(1) = 2\sum_{i}^{\mathrm{occ}}\phi_i(1)^2 \tag{16}$$

When the MO's ϕ_i are given, as usual, by the linear combinations of AO's, we obtain:

$$\Delta E \cong 2\sum_{i}^{\mathrm{occ}}\sum_{\mu}\sum_{r}\sum_{s}c_r^{(i)}c_s^{(i)}\int\chi_r\frac{z - A_z}{r_{\mu\mathrm{k}}^3}\chi_s\mathrm{d}\tau\cdot\Delta z + \Delta V_{\mathrm{nn}} \tag{17}$$

where χ_r and χ_s are the AO's. It can be seen that Eq. (17) has much the same form as Eq. (2), derived from the simple Hückel MO perturbation. A calculation was made with respect to the thermal ring-closing of butadiene by use of the extended Hückel MO's (Table 3).[34] The integrals necessary for the calculation of the energy change were computed by the formula derived by Matsuoka, expanding the Slater AO's into the Gaussian basis set.[35] In the extended Hückel MO approximation, the sum of the energies of doubly-occupied MO's can be a measure of the total energy of the system in the ground-state.[36] Table 3 shows that π electrons favor a conrotatory ring-closing, while σ electrons prefer a disrotatory ring-closing. Furthermore, it is demonstrated that π electrons play a major role in determining the stereochemical course of the electrocyclic rearrangement of butadiene. The results given here are very approximate and can never be a quantitative measure for distinguishing the favorable reaction path. However, this calculation provides us with some information of the energetic aspects of two possible modes of the ring-closing of butadiene, including both the σ and π electrons.

TABLE 3. ENERGY GRADIENT IN THE THERMAL RING-CLOSING OF BUTADIENE AT $|\omega| = 5°$

	Conrotatory	Disrotatory
ΔE_σ[a]	−4.036	−4.236
ΔE_π[a]	−1.265	−0.772

a) In eV/Bohr-radius unit.

In this paper, we have limited ourselves to the electrocyclic reaction of butadiene and hexatriene in order to accentuate the relation between different perturbation approaches. The methods presented here can be applied, in principle, to any kind of molecular rearrangement.

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