

SCF MO CNDO/2 CONSIDERATIONS ON THE DIELS-ALDER REACTION

AN ETHYLENE-CIS-BUTADIENE SYSTEM

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Abstract—The semi-empirical SCF MO CNDO/2 theory was applied to the addition reaction of ethylene and *cis*-butadiene and theoretical investigations on the Diels-Alder reaction mechanism were performed. In the calculations of the system, molecular structures (bond lengths and hybridization conditions of atoms) and geometrical relationship of reactant molecules were determined so that the total energy of the system was minimized. Variations of interaction energy, molecular and electronic structures, and geometrical relationship of two molecules were obtained along the reaction process.

INTRODUCTION

RECENT development of the MO theory¹ makes it possible to describe all valence electron systems of rather large molecules. Some organic chemical reactions have been studied with these MO methods.² The purpose of the present study is the theoretical approach to the Diels-Alder reaction with an MO theory for all valence electrons. In the theoretical investigations on the Diels-Alder reaction, these MO theories are applicable to the system of diene and dienophile molecules. The total energy and the electronic structure of the system calculated by these methods along the reaction process are useful to understand the reaction mechanism.

Total energy of the system containing two reactant molecules in three dimensional space can be expressed as;

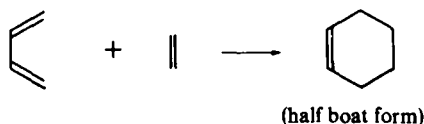
$$E_{\text{total}} = f(\mathbf{R}, x_1, x_2, \dots, y_1, y_2, y_3) \quad (1)$$

where \mathbf{R} is the vector from some reference point in one molecule to that in the other one and indicates the approaching condition (distance and direction) of two molecules, x_i 's are parameters to specify the molecular structure (bond lengths and bond angles) of each molecule, and y_j 's, parameters to specify geometrical relationship between two molecules in three dimensional space. The values of x_i 's and y_j 's vary as the reaction proceeds. Theoretical calculations on the system described by \mathbf{R} , therefore, should be performed using the molecular structures and the geometrical relationship of two molecules which are determined so that the total energy of the system is minimized. Namely, the energy and electronic structures of the system in the reaction process should be calculated with the values of x_i 's and y_j 's which satisfy the following conditions;

$$\frac{\delta E_{\text{total}}}{\delta x_i} = 0 \quad (i = 1, 2, \dots) \quad (2)$$

$$\frac{\delta E_{\text{total}}}{\delta y_j} = 0 \quad (j = 1, 2, 3) \quad (3)$$

In the present MO theoretical study on the Diels–Alder reaction, the simplest case was taken into account: addition reaction of ethylene and *cis*-butadiene leading to cyclohexene (half boat form). The procedure was based on the above considerations.



PROCEDURE

A. Molecular orbital method

The SCF MO CNDO/2 method³ was applied to an ethylene-*cis*-butadiene system. In the present study, bond lengths and bond angles of reactant molecules are determined so that the total energy of the system is minimized. An MO theory to be used, therefore, has to lead to some success in evaluation of molecular geometry. The CNDO/2 method gives good equilibrium bond lengths and bond angles of molecules.⁴ On the other hand, heats of atomization, heats of reactions, and bonding energies calculated by this method are in most cases much too high.⁵ However, the calculated heats of atomization of hydrocarbons are uniformly higher than experimental ones,⁶ and this indicates that the discussions on the changes in total energy and molecular and electronic structures of reactant molecules in the reaction process are performable by the CNDO/2 method.

B. Reaction process

The reaction process considered in the present study was a completely concerted one (one step and one stage). Fig 1 illustrates an ethylene-*cis*-butadiene system. The butadiene carbon skeleton is placed on the *xy* plane symmetrically with respect to the *x'z'* plane (= *xz* plane). In Fig 1, Q represents the center of the C—C single bond of ethylene fragment in the addition product, the cyclohexene molecule. This is the origin of the *x'*, *y'*, *z'* system and is on the *xz* plane. The followings are derived from the reason that the reaction process considered is a completely concerted one.

(i) Ethylene and *cis*-butadiene fragments have symmetrical conformations with respect to the *x'z'* plane. The center of the ethylene fragment, C in Fig 1, is always on the *x'z'* plane.

(ii) The vector R can be represented by CQ and θ , where CQ is the distance between the center of the ethylene C—C bond and the origin of the *x'*, *y'*, *z'* system, and θ is the angle between CQ and the *x'* axis.

(iii) Parameters y_j 's are reduced to only single variable ϕ which represents the angle between two planes, one containing the butadiene carbon skeleton and the other bisecting the HCH angle of the ethylene fragment (Fig 2). In this case, the following equation is used instead of Eqs (3).

$$\frac{\delta E_{\text{total}}}{\delta \phi} = 0 \quad (4)$$

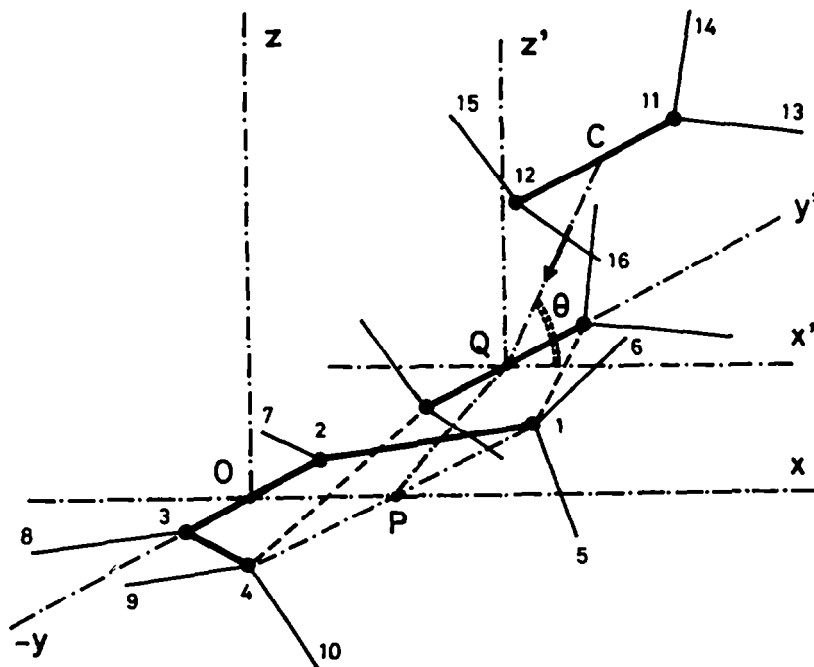
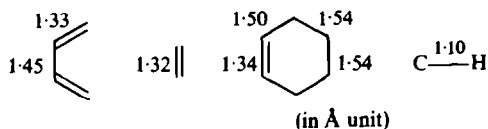


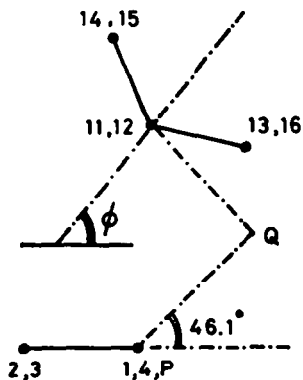
FIG 1. An ethylene-cis-butadiene system

C. Molecular structure

Bond lengths of reactant and resultant molecules used are;



Bond angles used are those derived from sp^2 or sp^3 approximation on hybridization of C atoms. From the C–C bond lengths shown here, the minimum energies were

FIG 2. Definition of an angle ϕ . The molecular system is projected along the y axis

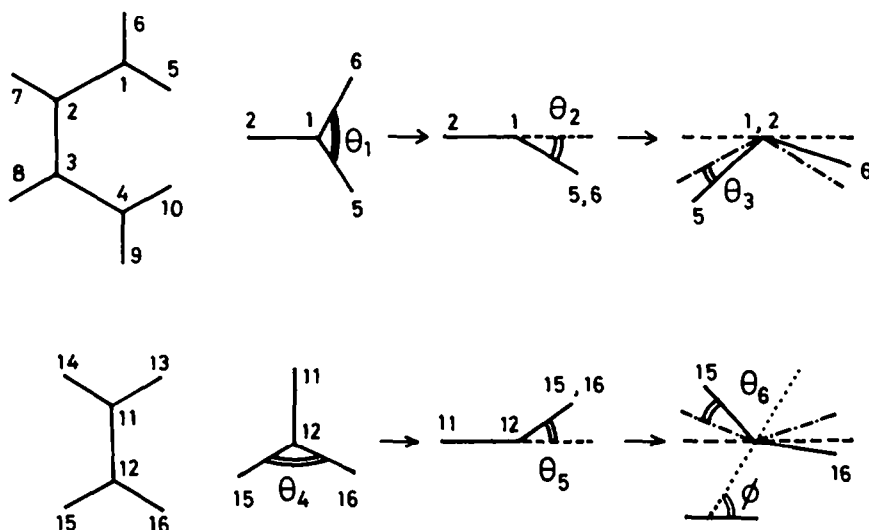


FIG 3. Definition of angles $\theta_1 \sim \theta_6$, which locate the protons in the reaction process

obtained by the CNDO/2 calculations for the ethylene and *cis*-butadiene molecules. As the reaction proceeds, hybridization of C atoms changes. H atoms on ethylene and on 1,4 positions of butadiene are no longer on their molecular planes. Coordinates of these H atoms were calculated with angles, $\theta_1 \sim \theta_2$ and ϕ , illustrated in Fig 3. All C—H bonds were fixed at 1.10 Å in the course of the reaction. Thus variables x_i 's in the present system are: two C—C bond lengths of the *cis*-butadiene fragment, one C—C bond length of the ethylene fragment and five angles, $\theta_1 \sim \theta_5$. Values of these parameters before and after the addition reaction are listed in Table 1.

TABLE 1. VALUES OF MOLECULAR PARAMETERS x_i BEFORE AND AFTER THE ADDITION REACTION

x_i	x_i^{Isolated}	x_i^{Adduct}
R(C ₁ —C ₂)	1.33 Å	1.50 Å
R(C ₂ —C ₃)	1.45	1.34
R(C ₁₁ —C ₁₂)	1.32	1.54
θ_1, θ_4	120°	109.5°
θ_2, θ_5	0	54.7°
θ_3	0	46.2°

D. Assumption on x_i

Variables should be determined so that the total energy of the system is minimized along the reaction process. There are eleven degrees of freedom in the potential surface of the present system; a distance CQ and an angle θ to locate the center of ethylene C—C bond, eight parameters x_i to specify the molecular structure, and an angle ϕ to specify the geometrical relationship of reactant molecules. It seems impossible that calculations are carried out with the optimum values of x_i and ϕ

determined from Eqs. (2) and (4). The assumption was made that the changes in x_i 's were mutually related. Then, degrees of freedom associated with molecular structure were reduced to only one, Δ , a measure of variation in molecular structure. Values x_i 's in the reaction process were calculated by;

$$x_i = x_i^{\text{isolated}} + \Delta(x_i^{\text{adduct}} - x_i^{\text{isolated}}) \quad (5)$$

Eqs (2) are therefore reduced to the following single restriction.

$$\frac{\delta E_{\text{total}}}{\delta \Delta} = 0 \quad (6)$$

RESULTS AND DISCUSSION

The total energies of the system were calculated for a number of approaching conditions and energy contours were plotted. They are given in Fig 4. Total energies

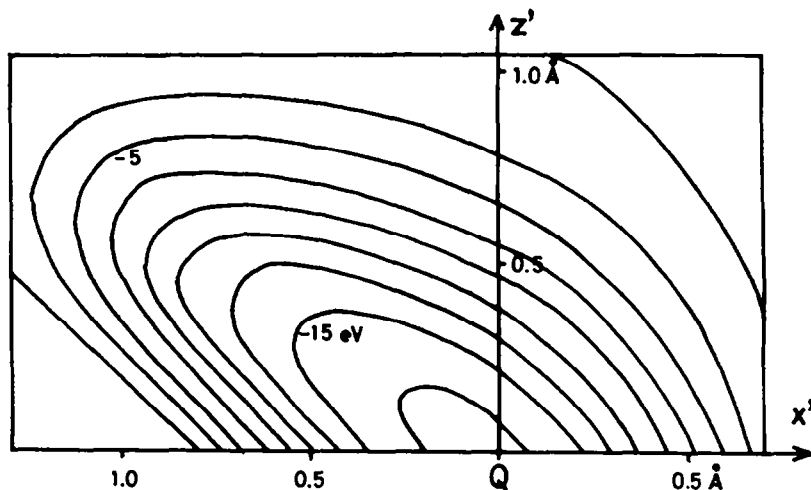


FIG 4. Energy contours plotted on the $x'z'$ plane

in this figure were those calculated with the optimum value of Δ determined from Eq (6) and with $\phi = 46.1^\circ$, the value of $\angle QPx$. The optimum ϕ determined from Eq (4) should be used in the present calculations. However, results at several approaching conditions with optimum values of ϕ showed that there are no essential changes in the tendency of energy contours appearing in Fig 4. Namely, a large stabilization energy is expected for the system in which the ethylene molecule is placed just above the *cis*-butadiene molecule. This implies that the approach of ethylene to *cis*-butadiene from this direction should be favorable in the addition reaction.

Figure 5 shows the total energies of the system as a function of the distance CQ for two approaches, $\theta = 135^\circ$ and $\theta = 90^\circ$. The total energy depends to some extent on ϕ . However, the situation appearing in Fig 4 is not seriously modified. Stabilization of the system is remarkable in the reaction process of $\theta = 135^\circ$ in comparison with that of $\theta = 90^\circ$. When $\theta = 135^\circ$, great stabilization of the system happens at $CQ = 1.5 \text{ \AA}$; this corresponds to 2.0 \AA distance between C atoms of ethylene and those at 1,4 positions of butadiene. It should be noted that there are no energy maxima

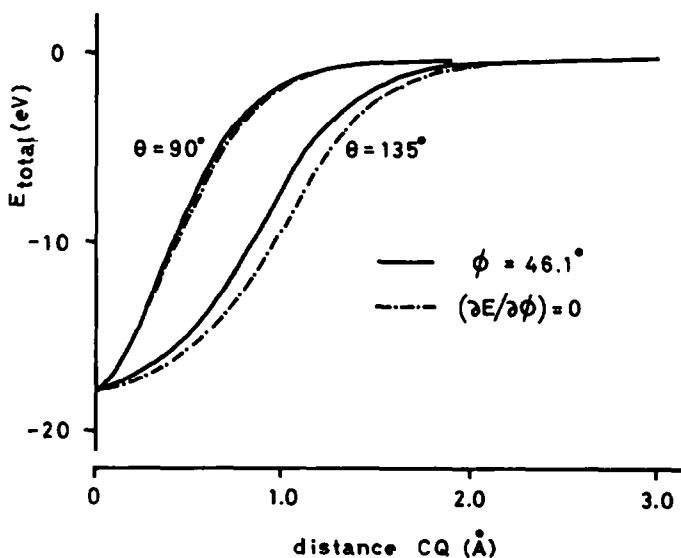


FIG 5. Variation of the total energy of the ethylene-cis-butadiene system

corresponding to the transition states of the reaction in total energy curves. This is perhaps due to the present CNDO/2 method by which high stabilization energies are obtained.

The variations of ϕ and Δ with CQ are shown in Fig 6. Dashed lines in the figures indicate the range where total energy is different from the minimum value within 0.1 eV. When $CQ > 2.0 \text{ \AA}$, ϕ is uncertain because of weak interaction of two molecules. When $CQ = 1.5 \sim 2.0 \text{ \AA}$, a coplanar orientation of two molecules ($\phi = 90^\circ$) is favored. Then, ϕ approaches to the values of the addition product, about 46° . As a whole, variation of ϕ is parallel to the maximum overlap principle between $2p(\pi)$

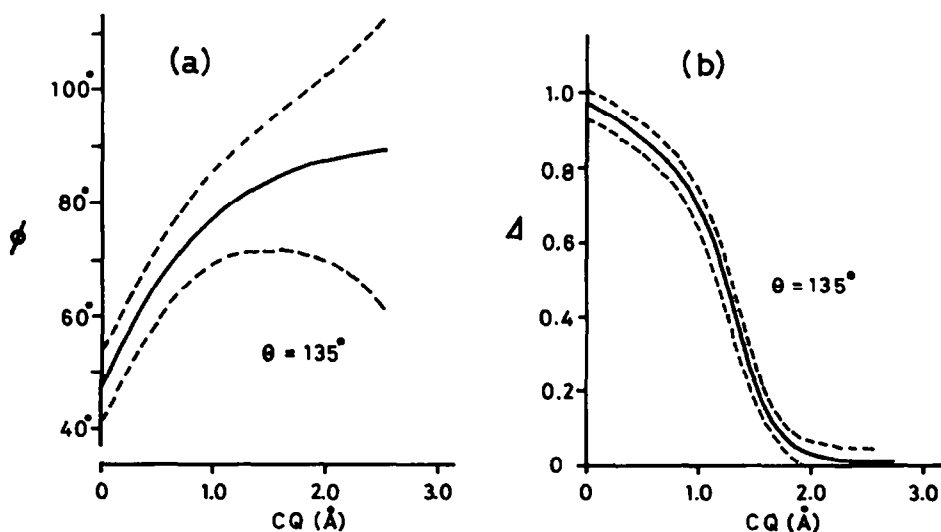


FIG 6. Variations of (a) ϕ and (b) Δ

orbitals* of ethylene and of 1,4 positions of butadiene. Remarkable change in molecular structure is expected in the range of $CQ = 1.5 \sim 0.8 \text{ \AA}$. Thus theoretical approach to the Diels-Alder reaction by only π -electron interactions can be performable when two molecules are apart from each other by $CQ > 1.5 \text{ \AA}$. It is noted that the distance $CQ = 1.5 \text{ \AA}$ corresponds to the distance $R_{1,11}$ or $R_{4,12}$ of 2.0 \AA .

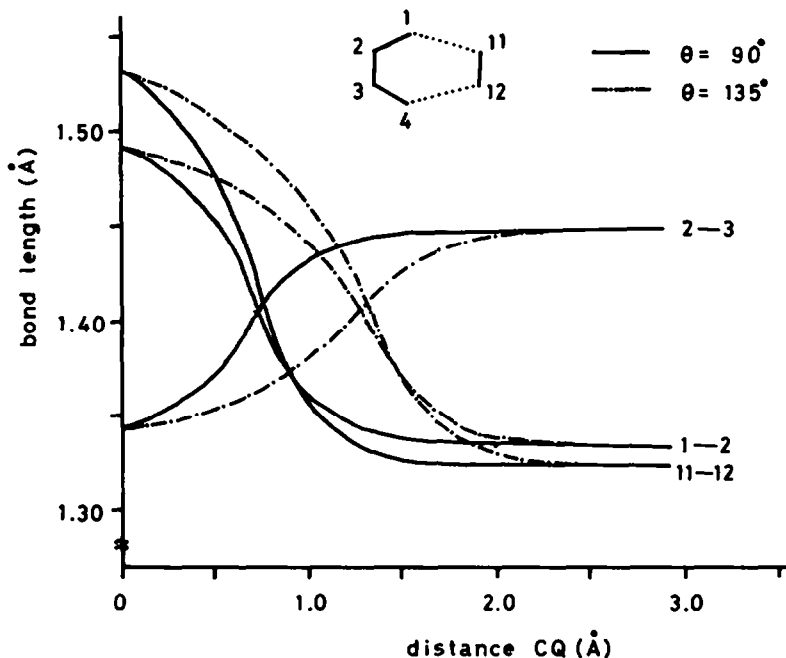


FIG 7. Variations of C—C bond lengths

Variations of C—C bond lengths with the distance CQ are given in Fig 7. The C—C double bond lengths $C_1=C_2$ and $C_{11}=C_{12}$, for example, become long with the approach of two molecules and finally come to those of C—C single bonds. For $\theta = 135^\circ$, remarkable changes in C—C bond lengths occur in the range of $CQ = 1.5 \sim 0.8 \text{ \AA}$ as seen in the change of molecular structure. This implies that changes in hybridizations of C atoms of the reactant molecules, $sp^2 \rightarrow sp^3$ or $sp^3 \rightarrow sp^2$, occur in this range of reaction process.

Interaction energies between two atoms A and B, E_{AB} , were calculated by the following equation;

$$E_{AB} = \sum_r^A \sum_s^B (2P_{rs}\beta_{rs} - \frac{1}{2}P_{rs}^2\gamma_{AB}) + (Z_A Z_B R_{AB}^{-1} - P_{AA}V_{AB} - P_{BB}V_{BA} + P_{AA}P_{BB}\gamma_{AB}) \quad (7)$$

* During the reaction, the 2p orbitals (π -orbitals) of ethylene and *cis*-butadiene are no longer pure because of the changes in molecular structures. The "p-orbitals" here are the effective orbitals which will form new bonds between two molecules.

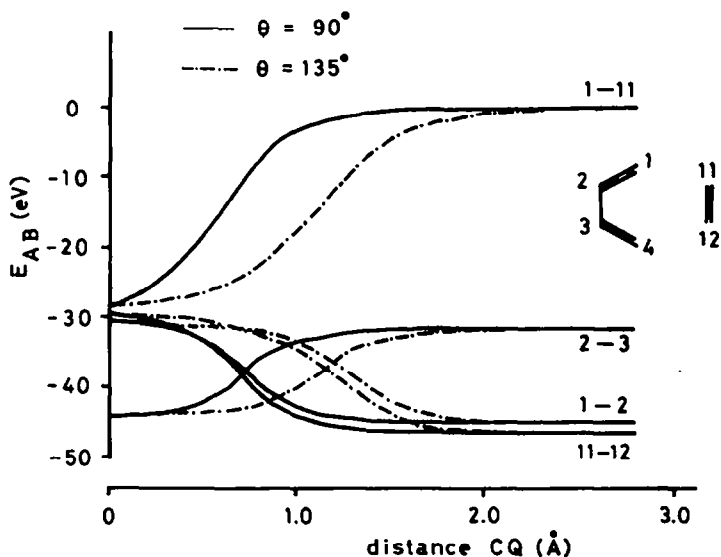


FIG 8. Variations of interaction energies E_{AB} between atoms A and B

where notations are the same as those of Pople *et al.*⁵ Calculated energies E_{AB} depend considerably on atomic distances R_{AB} and the changes in E_{AB} are similar to those in bond lengths (Fig 8). Interaction energies $E_{1,2}$ and $E_{11,12}$ of isolated reactant molecules are larger than that of $E_{2,3}$ according to the nature of C—C bonds, a single bond or a double bond. The situation is in the opposite direction in the addition product, cyclohexene, where the natures of C—C bonds are reversed. Interaction energies at secondary centers, $E_{2,11}$ and $E_{3,12}$, were negligible in comparison with those at primary centers, $E_{1,11}$ and $E_{4,12}$.

Electron distribution in the system varies as the reaction proceeds. Fig 9 shows the electron population in the ethylene fragment with the distance CQ. At the first stage of the reaction, electron population in the ethylene fragment increases with increasing proximity of two molecules. For $\theta = 135^\circ$, 0.1 electrons transfer from *cis*-

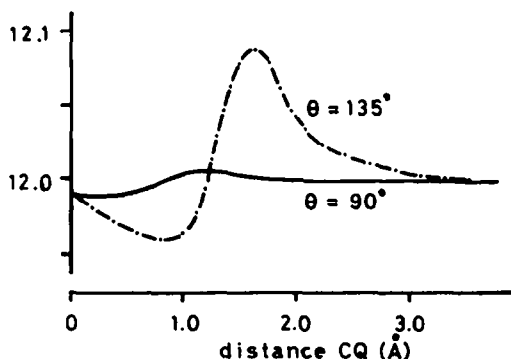


FIG 9. Variation of the electron population in the ethylene fragment

butadiene to ethylene at $CQ = 1.5 \text{ \AA}$. The Diels–Alder reaction is accelerated by the dienophile with an electron-attractive group. This suggests an important role of a charge transfer structure in stabilization of the system. Considering little variation of molecular structure at large distance, $CQ > 1.5 \text{ \AA}$, the stabilization of the system in the first stage of the reaction process should be caused by π -electron transfer from a diene to a dienophile.

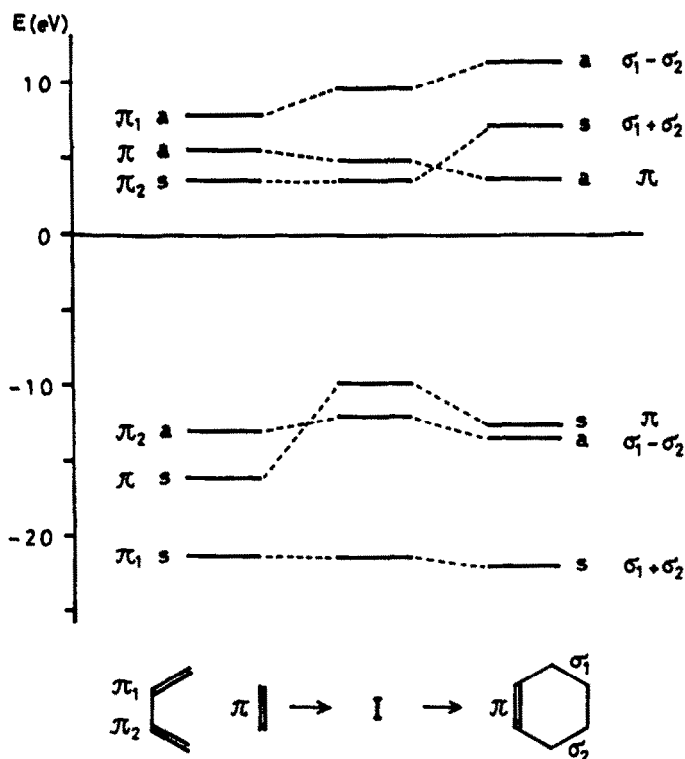


FIG 10. Variations of six reactant π -levels

The correlation diagram relating reactant MO levels with resultant MO levels is sometimes important to understand a reaction mechanism. The complete level diagram for the present reaction was considerably complex because of the strong mixing of π -orbitals with σ -orbitals during the reaction. Fig 10 illustrates only six reactant π -levels along the reaction process. The system denoted by I corresponds to that for $\theta = 135^\circ$ and $CQ = 1.2 \text{ \AA}$. Because of the strong mixing of the π -levels with σ -levels, variation of six π -MO levels can not be considered independently of the other orbitals. Thus, in spite of the usefulness of the MO level diagram along the reaction process (Fig 10), the correlation diagram relating only π -orbitals is of little value in quantitative discussions on the Diels–Alder reaction mechanism.

CONCLUSION

The SCF MO CNDO/2 theoretical study of an ethylene-*cis*-butadiene system gave the following results on the concerted Diels–Alder addition reaction of these molecules;

(1) The approach of ethylene to *cis*-butadiene from the direction just above the *cis*-butadiene molecular plane is favored.

(2) The orientation of two molecules is coplanar in the first step of the reaction. As the reaction proceeds, it changes so as to satisfy the maximum overlap principle between $2p(\pi)$ orbitals of ethylene and those at 1,4 positions of *cis*-butadiene.

(3) Changes in molecular structures of reactant molecules, C—C bond lengths and hybridization conditions of C atoms, occur when distances $R_{1,11}$ and $R_{4,12}$ are less than 2.0 Å. Great stabilization of the system also is expected in this region.

(4) Interaction energies between atoms, $E_{1,11}$ and $E_{4,12}$, change in a similar fashion as in the molecular structure. Interaction at secondary centers is of negligible order.

(5) π -Electron transfer from a diene to a dienophile is clearly expected in the first stage of the Diels–Alder reaction.

(6) Because of the strong mixing of π - and σ -orbitals, the correlation diagram relating only π -orbitals is of little value in quantitative discussions on the reaction mechanism.

Calculations were carried out on the HITAC 5020 computer at the Computation Center of The University of Tokyo.

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