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# Theoretical Analysis of Concerted and Stepwise Mechanisms of Diels−Alder Reaction between Butadiene and Ethylene

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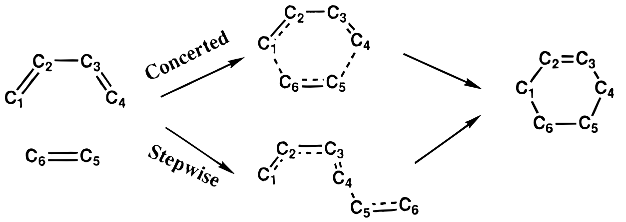
The concerted and the stepwise mechanisms of the Diels−Alder reaction between butadiene and ethylene were studied by ab initio MO methods. For the stepwise mechanism, three process are included: the first process is the formation of biradical intermediate with a transition state, the second is the rotation for the new bond axis with a transition state, and the third is the other bond formation without an energy barrier. The transition state for the first process has a higher energy barrier of 4 kcal/mol than that for the second process at the CAS-MP2/6-311+G(d,p) calculation level. For the concerted mechanism, the energy barrier height of the transition state is 2.7 kcal/mol lower than that of the first process of the stepwise mechanism by the CAS-MP2/6-311+G(d,p) level. Both reaction mechanisms were analyzed by a CiLC−IRC method. The CiLC−IRC analysis shows the nature of the aromaticity for the transition state of the concerted mechanism. The CiLC−IRC analysis also shows that the transition state of the second process of the stepwise mechanism causes from the static energy as the rotational barrier of methyl group.

## 1. Introduction

The Diels−Alder reactions may be the most important class of organic reactions. The mechanisms of the reactions have been the subject of the most heated and interesting controversies.[1−9] The parent reaction of butadiene and ethylene is concerted, but the activation barrier for the stepwise mechanisms is only a few kcal/mol higher. Houk and co-workers[5,9] calculated the transition states for the Diels−Alder reaction between butadiene and ethylene by a MCSCF MO and a density functional method. They found the synchronous transition state for the concerted pathway and the transition state of biradical formation for the stepwise pathway. For the stepwise process, their attempts to locate the transition state for the closure of biradical intermediate to cyclohexene were unsuccessful. In their papers,[9] the energy barrier for the concerted transition state was predicted to be lower, between 2.3 and 7.7 kcal/mol, than that of the stepwise. Because the concerted and stepwise mechanisms are so close in energy, there is still doubt about which mechanism occurs for each substituted case. It is interesting in the classification of electronic mechanisms for the concerted and the stepwise reactions.



In our previous papers,[10,11] the electrocyclic reaction mechanisms for butadiene, disilylbutadiene, and hexatriene were characterized by a configuration interaction (CI)/localized molecular orbital (LMO) CASSCF calculation along the IRC pathway (CiLC−IRC) method. From the analysis of those reaction pathways by the CiLC−IRC method, the differences between the conrotatory and the disrotatory mechanisms were explained by the biradical character of the terminal atoms. For the Diels−Alder reactions, the characterization of the mechanisms of the concerted and the stepwise is important for the estimation of the reaction pathway occurs for substituted case.

In the present paper, we report the potential energy surfaces for the concerted and stepwise reactions by the CASSCF and CAS-MP2 calculation levels. These reaction pathways are analyzed by CiLC−IRC methods.

## 2. Computational Approach

All equilibrium and transition state geometries were determined with analytically calculated energy gradients at a complete active space self-consistent field (CASSCF) method[12] with the split-valence plus polarization 6-31G(d,p) set.[13,14] For the CASSCF calculation, six active orbitals corresponding to two $\pi$ and $\pi^*$ orbitals for butadiene and $\pi$ and $\pi^*$ for ethylene and related systems were included. All configurations in active spaces were generated. Frequency calculations were performed to determine the nature of each stationary point. Single-point energies were determined at a multiconfigurational second-order M$\phi$ller−Plesset perturbation (CAS-MP2) method[15] with a 6-311+G(d,p) basis set[16] using the CASSCF-optimized structures. The intrinsic reaction coordinate (IRC)[17,18] was followed from the transition state toward both reactants and products.

To interpret the mechanisms of the concerted and the stepwise pathways, a configuration interaction (CI), localized molecular orbital (LMO) CASSCF calculation along the IRC pathway (CiLC−IRC) was carried out following a method described elsewhere[10,11,19−21] with the 6-31G(d,p) basis set. (1) The CASSCF is calculated to obtain a starting set of orbitals for the localization procedure. (2) After the CASSCF procedure is carried out, the CASSCF-optimized orbitals are localized. The six CASSCF-optimized MOs are subjected to the Boys localiza-

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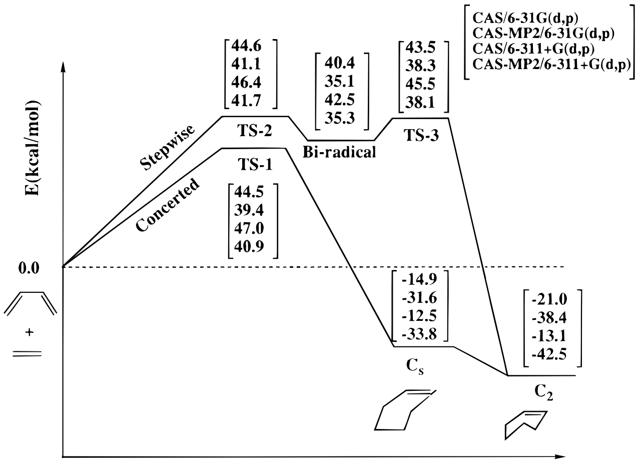


**Figure 1.** Potential energy profile along the minimal energy pathway for the concerted and the stepwise mechanisms of the Diels−Alder reaction of butadiene and ethylene. The energy values are given in kcal/mol at the CAS/6-31G(d,p), CAS-MP2/6-31G(d,p), CAS/6-311+G(d,p), and CAS-MP2/6-311+G(d,p) levels.

**TABLE 1: Total Energies (in Hartree) for Stationary Points for the Diels−Alder Reactions of Butadiene and Ethylene**

| | CASSCF 6-31G(d,p) | CAS-MP2 6-31G(d,p) | CASSCF 6-311+G(d,p) | CAS-MP2 6-311+G(d,p) |
|---|---|---|---|---|
| concert TS1 | −232.98315 | −233.72999 | −233.02491 | −233.89435 |
| cyclohexene ($C_s$) | −233.08483 | −233.85008 | −233.12666 | −234.02031 |
| cyclohexene ($C_2$) | −233.09454 | −233.86143 | −233.12814 | −234.03469 |
| stepwise TS2 | −232.97997 | −233.72428 | −233.02278 | −233.89006 |
| biradical | −232.98770 | −233.73474 | −233.03005 | −233.90113 |
| stepwise TS3 | −233.98254 | −233.72957 | −233.02510 | −233.89646 |

tion procedure. The calculated localized orbitals are very atomic in nature. (3) By use of the localized MOs as a basis, a full CI with determinants level is used to generate electronic structures and their relative weights in the atomic orbital-like wave functions. The total energy calculated by the CI method in the process corresponds to that by the CASSCF calculation. (4) The calculation procedures from (1) to (3) are repeated along the IRC pathway, which we call a CiLC−IRC for the procedures. From the CiLC−IRC analysis of the reactions, we can see the change of electronic state on the basis of atomic-like orbitals.

The calculations of the CiLC−IRC analysis were performed with the GAMESS program package,[23] and the others were used by the GAUSSIAN98 program package.[24]

## 3. Results and Discussions

The total energies of the stationary points for the concerted and the stepwise pathways of the Diels−Alder reaction between butadiene and ethylene are listed in Table 1, and their geometries are provided as Supporting Information. The potential energy surfaces including the zero-point energy corrections are drawn in Figure 1.

**3.1. Concerted Mechanism.** The geometry parameters of the transition state on the concerted pathway are similar to those of the previous calculations.[5,9] Namely, the $C_1-C_2$ (and $C_3-C_4$) bond lengths are almost equal to the $C_2-C_3$ bond length. The difference between the $C_1-C_2$ (or $C_3-C_4$) and $C_2-C_3$ bond lengths is only 0.002 Å. For the comparison of geometry parameters between the ethylene part and butadiene part, the difference between the $C_1-C_2$ and $C_5-C_6$ bond lengths is also small (0.006 Å). Therefore, each bond length for ethylene and butadiene has an almost similar value. However, we cannot say that the concerted transition state has “the aromatic structure” from the geometry parameters, because of lack of aromatic nature for the $C_1-C_6$ and $C_4-C_5$ bonds.

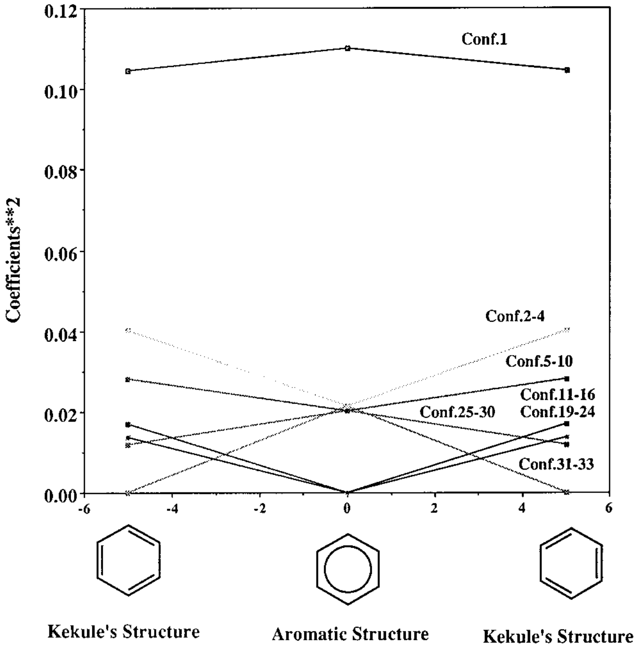
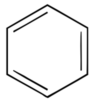
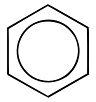
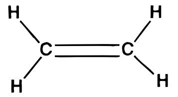


**Figure 2.** Square of CI coefficients by the CiLC calculation for Kekule’s structure and aromatic structure.

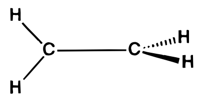
To study the aromatic nature by the CiLC−IRC analysis, we will analyze the electronic structure of benzene. For benzene, the alternation of two structures is treated: one is the Kekule’s structure (**1**) and the other is aromatic structure (**2**). For the Kekule’s structure, the C═C bond length (1.338 Å) of ethylene (**3**) was used for the C═C double bond parts of **1** and the C−C bond length (1.489 Å) of twisted ethylene (**4**) was used for the C−C single bond parts of **1**. The geometry parameters of benzene (**2**), ethylene (**3**), and twisted ethylene (**4**) were optimized by the CASSCF/6-31G(d,p) level. The CiLC calculations were performed for two structures of benzene (**1** and **2**).


(1) Kekule's Structure


(2) Aromatic Structure



(3) Ethylene



(4) Twisted Ethylene

The weights of CI coefficients by the CiLC method are shown in Figure 2. The small values (<0.001) of the weights were neglected in Figure 2. Some configurations for the large weights of CI coefficients in Figure 2 are displayed in Figure 3. In Figure 3, dotted line denotes a triplet coupling (antibonding) between the orbitals, and an ellipse denotes an ionic coupling. From Figure 2, the weight of configuration 1, the reference state, does not change much for both structures. The weights of configurations 2−10 decrease from the Kekule’s structure to the aromatic structure, and the weights of configurations 25−33 increase. Then, the weights of configurations of two groups (2−10 and 25−33) become almost the same values at the aromatic structure. Configurations 2−4 could be described as the interaction of singlet coupling for each double bond of the Kekule’s structure. Configurations 5−10 could be described as the

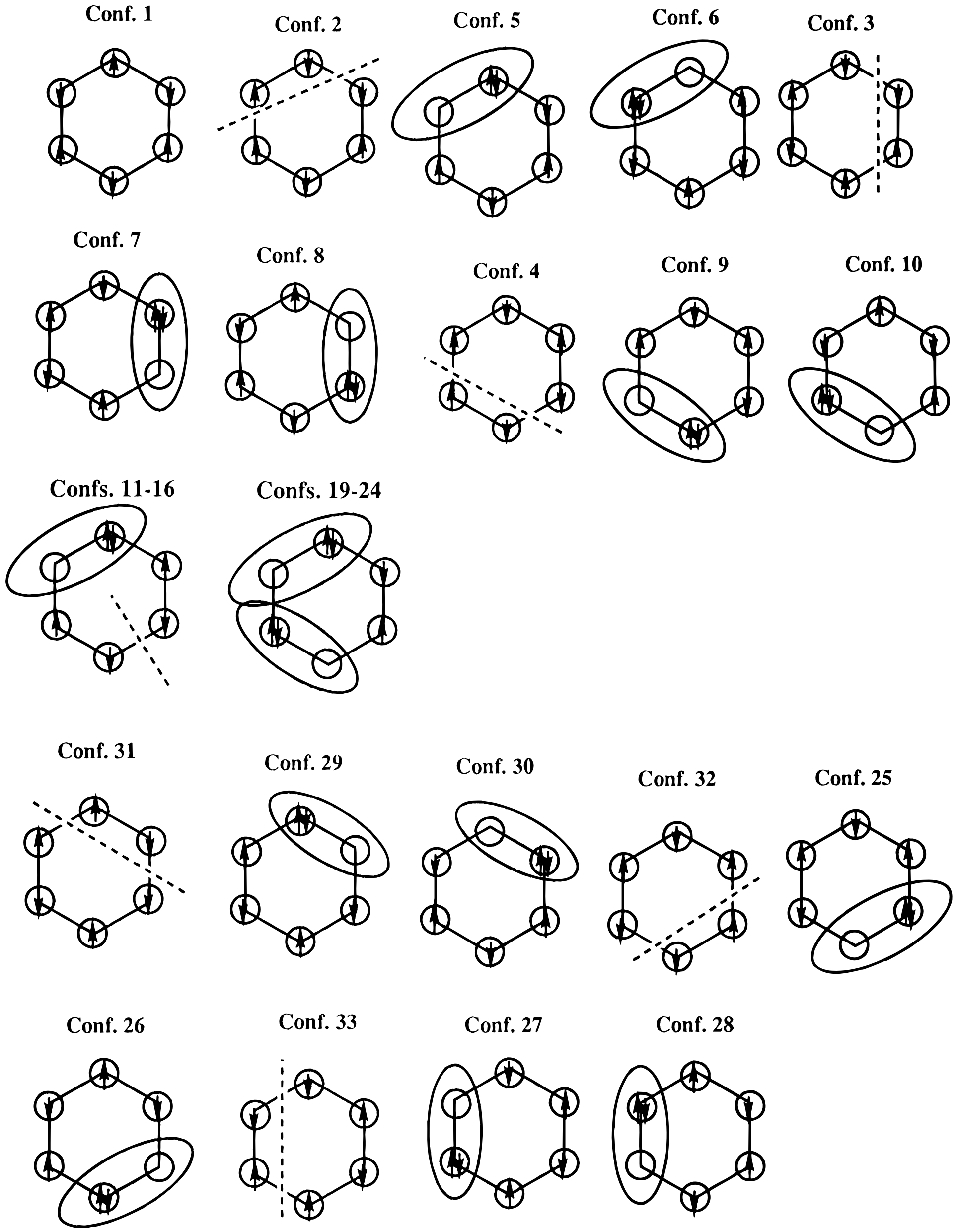
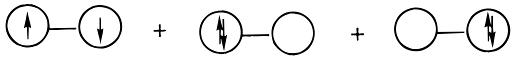


**Figure 3.** Some electronic configurations of benzene for CiLC analysis.

polarization for the double bond parts of the Kekule's structure. Therefore, configurations 2−4 and 5−10 could be described as the bonding for the double bond parts of the Kekule's structure. In fact, the $\pi$ bonding of ethylene can be described as the singlet coupling between $p_\pi$ orbitals plus two polarization terms as shown below. On the other hand, configurations 25−30 and 31−33 could be described as the bonding for the single bond parts of the Kekule's structure. Configurations 11−16 and 19−24 could be described as the higher order excitation terms. From the above results, it can be said that the aromatic structure of benzene type is singlet coupling plus polarization terms for all six bonds.



To study the reaction mechanism for the concerted pathway of butadiene and ethylene, the CiLC−IRC analysis was performed. The weights of CI coefficients by the CiLC−IRC method for the concerted pathway are displayed in Figure 4. Some configurations for the large weights of CI coefficients in Figure 4 are shown in Figure 5. Configuration 1 is the reference state (alternative spin for neighboring atoms) and has a maximum weight at the transition state. The large weights of configurations for the reactants side (butadiene + ethylene) decrease into the products side (cyclohexene), and the large weights for the products side increase from the region before the transition state. Thus, both groups of configurations cross at the transition state. This means that the maximum variation of the electronic states from both sides of the reactants and products occurs at the transition state. We can say this transition state is governed completely by the electronic state. This is very different from the mechanisms of the cyclization of butadiene as shown in the previous paper.[10] For the reactants side, configurations 148, 125, and 126 could be described as the singlet coupling of spins for the double bonds of Kekule's structure, and configurations 67, 68, 37, 50, 38, and 49 show the polarization terms for the double bonds of Kekule's structure. Namely, configurations 148, 67, and 68 could be described as the $\pi$ bonding of ethylene part, configurations 125, 37, and 50

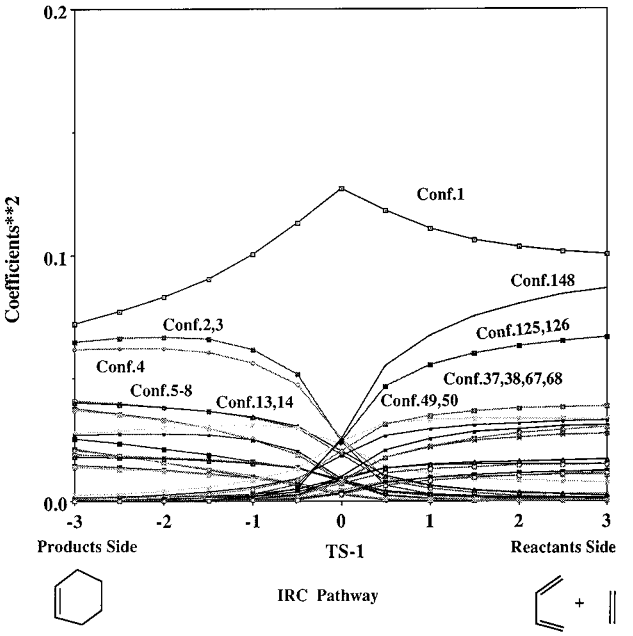


**Figure 4.** Square of CI coefficients of the CiLC-IRC along the concerted pathway for the Diels−Alder reaction of butadiene and ethylene. The unit of IRC is bohr amu$^{1/2}$.

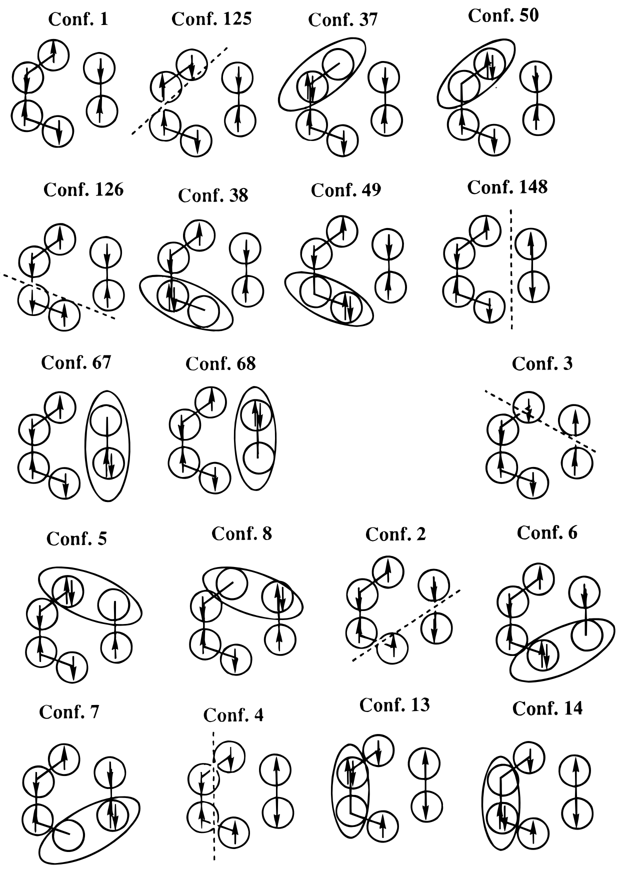


**Figure 5.** Some electronic configurations of the concerted pathway of butadiene and ethylene for CiLC-IRC analysis.

could be described as the $\pi$ bonding of $C_3$−$C_4$ of butadiene part, and configurations 126, 38, and 49 could be described as the $\pi$ bonding of $C_1$−$C_2$ of butadiene part. Therefore, configurations with large weights for the reactants side show the $\pi$ bonds of Kekule's structures of butadiene and ethylene. On the other hand, for the products side, configurations 2, 3, and 4 could be described as the bonding for $C_1$−$C_6$, $C_4$−$C_5$, and $C_2$−$C_3$ bonds, respectively. Configurations 6, 7, 5, 8, 13, and 14 are the polarization terms of new $\sigma$ bonds and $\pi$ bond of $C_2$−$C_3$. Namely, configurations 2, 6, and 7 could be described as a new $\sigma$ bond of $C_1$−$C_6$, configurations 3, 5, and 8 could be described as a new $\sigma$ bond of $C_4$−$C_5$, and configurations 4, 13, and 14 could be described as a $\pi$ bond of $C_2$−$C_3$. The variation of configurations along the IRC pathway corresponds to the Diels−Alder reaction mechanism on the basis of Kekule's structure. It is significant that the weights of these configurations show almost the same values at the transition state. This corresponds to the aromatic nature of benzene molecule. Namely, configurations of new $\sigma$ bonds and $\pi$ bonds contribute almost the same weights to the electronic state of the transition state. From the above results, it is concluded that the transition state of the concerted pathway has the aromatic nature.

The energy barrier height for the concerted transition state is 44.5 kcal/mol above the reactants (s-cis butadiene + ethylene), by the CASSCF/6-31G(d,p) level. By the larger basis set (6-311+G(d,p)), the energy barrier becomes to 47.0 kcal/mol. For our best calculation (CAS-MP2/6-311+G(d,p)), the energy barrier is 40.9 kcal/mol, and this value is still higher than the experimental observation (27.5 kcal/mol).[25] The energy difference between our calculated values and experimental observation for the energy barrier may be ascribed to the lack of dynamical correlation effects.[26]

The concerted reaction proceeds from the transition state (TS-1) with the conservation of $C_s$ symmetry and leads to cyclohexene with $C_s$ symmetry. However, the force constant matrix of cyclohexene with $C_s$ symmetry has one negative eigenvalue (57 cm$^{-1}$ for a$''$ symmetry). Hence, the reaction pathway from TS-1 to cyclohexene has a branching point (bifurcation),[27] which is caused by symmetry breaking.[28,29] Cyclohexene with $C_s$ symmetry is a transition state for alternation of cyclohexene with $C_2$ symmetry. Thus, the stable structure of cyclohexene has $C_2$ symmetry. Cyclohexene with $C_2$ symmetry is 8.7 kcal/mol lower in energy than that with $C_s$ symmetry at the CAS-MP2/6-311+G(d,p) level. The heat of reaction is exothermic by 42.5 kcal/mol at the CAS-MP2/6-311+G(d,p) calculation level, and corresponds to the experimental observation of 40 kcal/mol.[25]

**3.2. Stepwise Mechanism.** For the stepwise mechanism, the first process is the formation of an anti intermediate biradical product with a transition state (TS-2). The geometry parameters of the stepwise anti biradical transition state (TS-2) and anti intermediate biradical are good agreements to the previous values.[5,9] The energy barrier height of the stepwise anti biradical transition state (TS-2) is 2.7 kcal/mol above that of the concerted transition state (TS-1) at the CAS-MP2/6-311+G(d,p) level. Including the zero-point energy corrections, the energy barrier of TS-2 becomes only 0.8 kcal/mol above that of TS-1. The transition state (TS-3) of the second process locates on the reaction pathway between anti intermediate biradical and cyclohexene, and the geometry is shown in Scheme 1. The energy barrier height of the transition state (TS-3) of the second process is 2.8 kcal/mol above the intermediate biradical and is lower by 3.6 kcal/mol than that of the anti biradical transition state (TS-2).

To characterize the stepwise reaction mechanisms, the CiLC−IRC analysis was performed. The weights of CI coefficients by the CiLC−IRC method for the formation reaction pathway (the first process) of anti-intermediate biradical are displayed in Figure 6. Some configurations for the large weights of CI configurations in Figure 6 are shown in Figure 7. The maximum weight of configuration 1, the reference state, locates at the

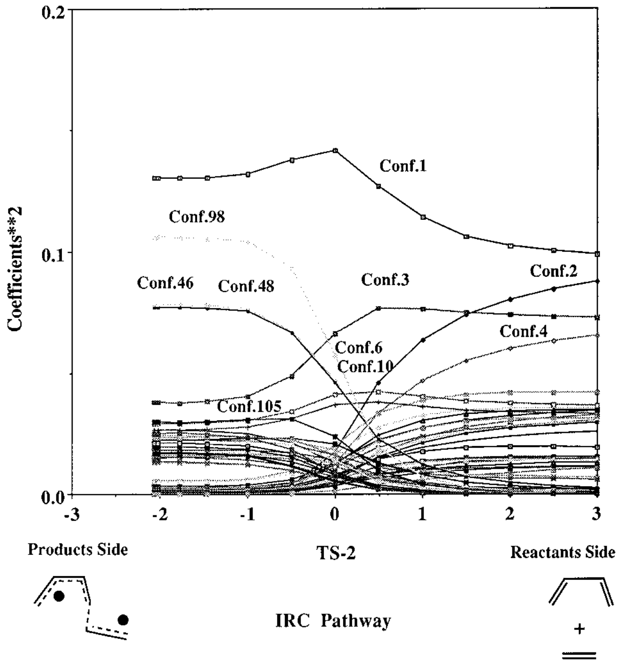
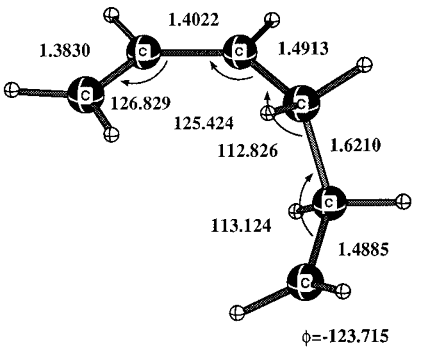


**Figure 6.** Square of CI coefficients of the CiLC−IRC along the first process of the stepwise pathway for the Diels−Alder reaction of butadiene and ethylene. The unit of IRC is bohr amu$^{1/2}$.

## SCHEME 1



**Stepwise Transition State for Second Process**

**TS-3**

transition state. This means that the variation of the electronic state for reaction dominates the location of the transition state. The weights of configuration 2 and 4 decrease from the reactants side (butadiene + ethylene) to the transition state. That is, configurations 2 and 4 could be described as the triplet coupling (antibonding) of the new $C_4-C_5$ bond and the $C_2-C_3$ bond (the single bond for Kekule's structure of butadiene). The weights of configurations 98, 46, and 48 increase from the region of the transition state to the products side (biradical intermediate). Configuration 98 could be described as the division of three parts (allyl, $C_1-C_2-C_3$; new $\sigma$ bond, $C_4-C_5$; and radical, $C_6$) and configurations 46 and 48 could be described as the polarization terms of new $\sigma$ bond. Thus, configurations 98, 46, and 48 represent the bonding of new $\sigma$ bond ($C_4-C_5$). While the weight of configuration 3 decreases at the vicinity of the transition state from the reactants side, the weight of configuration 3 is still large for the products side. The weights of configurations 6 and 10 (polarization of $C_1-C_2$ $\pi$ bond) do not change much from the reactants side to the products side. That is, the Kekule's structure of anti intermediate biradical should be described as **5**. It is considered that a substituted group to the $C_3$ position affects the pathway for the Diels−Alder reaction. Consequently, the stabilization of the radical at the $C_3$ position with a substituted group leads to the low-energy barrier of the anti biradical transition state.

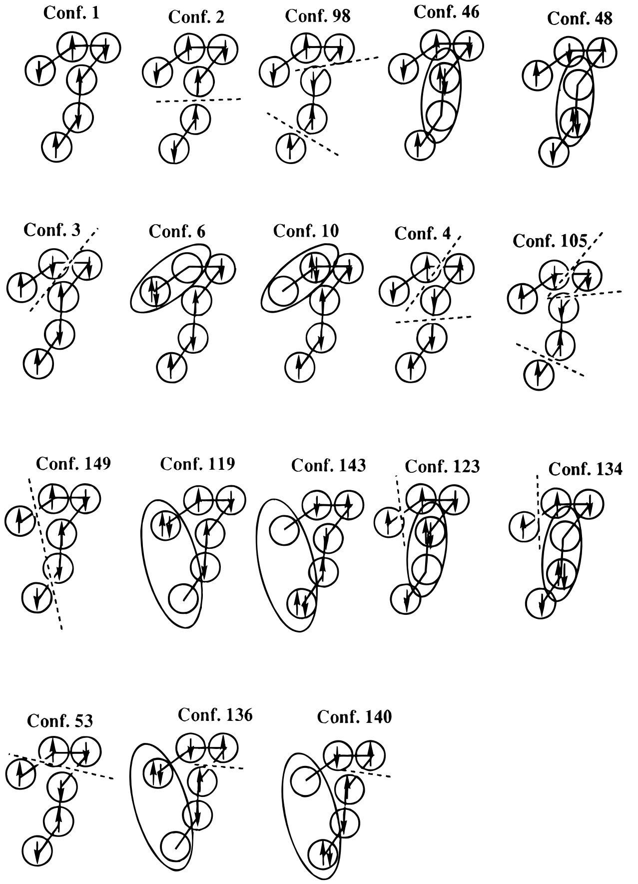
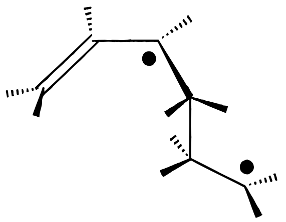


**Figure 7.** Some electronic configurations of the stepwise pathway for CiLC-IRC analysis.



**(5)**

The second process from anti intermediate biradical was studied by the CiLC−IRC analysis. The weights of CI coefficients by the CiLC−IRC method for the region of the transition state (TS-3) of the second process are displayed in Figure 8. Some configurations for the large weights of CI coefficients in Figure 8 are the same as those in Figure 7. In Figure 8, the weights of configurations do not change much for the region around the transition state (TS-3) for the second process. This means that the transition state (TS-3) is not dominated by the variation of the electronic state and is dominated by the steric effects of the rotation of the $C_5-C_6$ bond against the $C_4-C_5$ bond axis.

The weights of CI coefficients by the CiLC method along the variation of $C_1-C_6$ bond distance for the region (the third process) from after the transition state (TS-3) of the second process to cyclohexene are shown in Figure 9. The bond formation of $C_1-C_6$ begins from the $C_1-C_6$ bond distance of

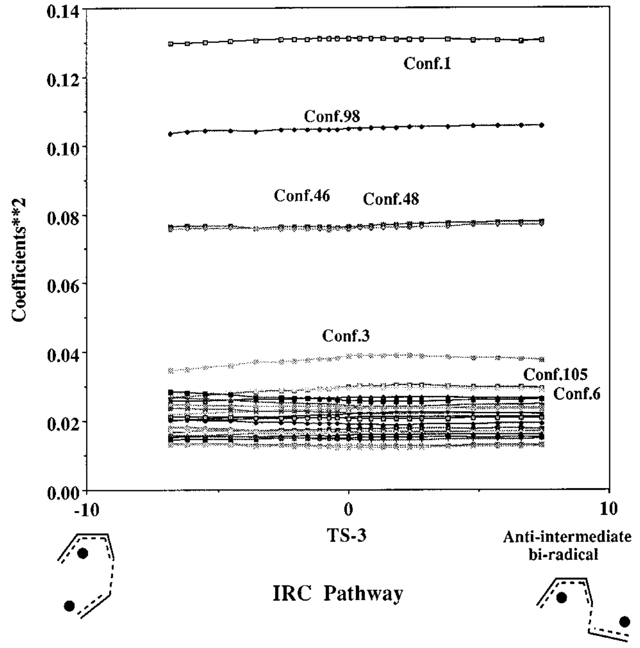


**Figure 8.** Square of CI coefficients of CiLC-IRC along the second process of the stepwise pathway for the Diels−Alder reaction of butadiene and ethylene. The unit of IRC is bohr amu$^{1/2}$.

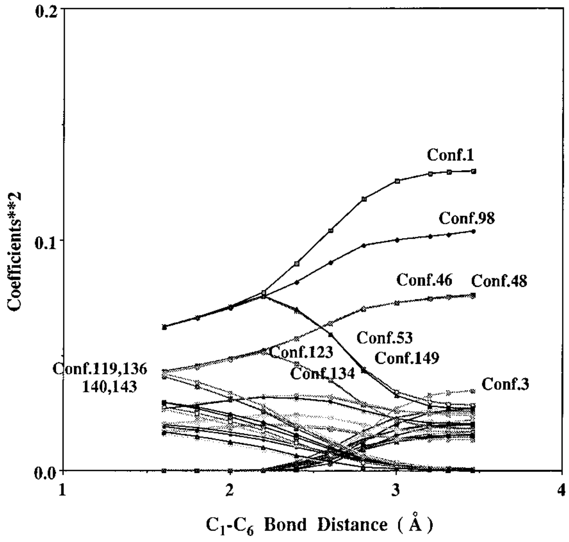


**Figure 9.** Square of CI coefficients of CiLC-IRC along the $C_1-C_6$ bond distance.

about 3.0 Å, and the shape of the system changes from pseudo-$C_s$ symmetry type to $C_2$ symmetry type without a barrier. Finally, both bonds $C_1-C_6$ and $C_4-C_5$ are formed for the same weights of configurations.

## 4. Conclusion

The potential energy surfaces for the concerted and the stepwise mechanisms of the Diels−Alder reaction between butadiene and ethylene were calculated by the CASSCF and CAS-MP2 methods. For the concerted mechanism, the CiLC−IRC analysis shows that the transition state has the aromatic nature of a benzene molecule. Namely, configurations of four $\pi$ bonds and two new $\sigma$ bonds contribute almost the same weights to the electronic state of the transition state. For the stepwise mechanism, three processes are included. The first process is the formation of biradical intermediate with the transition state, and the energy barrier height is 2.7 kcal/mol lower than that of the concerted reaction. The second is the rotation for the new bond axis; the energy barrier height is 4 kcal/mol lower than that of the first process. Recently, Houk and co-workers[30] found the transition state of the similar structure as TS-3 for the Diels−Alder reaction of cyclopentadiene and ethylene. The third process is the formation of the other bond without a barrier. From the CiLC−IRC analysis, the transition state of the first process is dominated by the variation of the electronic state, and the transition state of the second process is dominated by the steric effects.

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**Supporting Information Available:** Figure showing stationary point geometries for the concerted and the stepwise mechanisms for Diels−Alder reaction of butadiene and ethylene. This material is available free of charge via the Internet at http://pubs.acs.org.

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