Theoretical Studies of the Electrocyclic Reaction Mechanisms of Hexatriene to Cyclohexadiene

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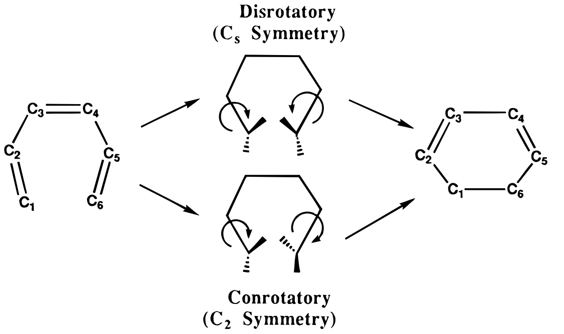
The potential energy surfaces for electrocyclic reactions of hexa-1,3,5-triene were calculated by ab initio molecular orbital methods. The transition states of two electrocyclic reaction pathways (conrotatory and disrotatory) for hexa-1,3,5-triene were obtained. Both transition states are a true transition state. The transition state of the disrotatory pathway is about 11 kcal/mol lower in energy than that of the conrotatory pathway. The reaction path through cis−trans isomerization from cZc-hexa-1,3,5-triene to cyclohexa-1,3-diene was proposed. The conrotatory and the disrotatory reaction pathways were also characterized by the CiLC-IRC method.

1. Introduction

Pericyclic reactions may be the most important class of organic reactions. The mechanisms of these reactions have been the subject of the most heated and interesting controversies. The orbital symmetry rules such as the Woodward−Hoffmann rule[1] and the frontier orbital theory[2] defined the concept of a pericyclic reaction. The rules served not to settle mechanistic questions but to raise the stakes on what were already lively controversies.

In our previous papers,[3−5] the electrocyclic reaction mechanisms for butadiene and disilylbutadiene were reported. From the analysis of these reaction paths by a configuration interaction (CI)-localized molecular orbital (LMO) CASSCF calculation along the IRC pathway (CI-LMO-CAS//IRC: CiLC-IRC), the differences between the conrotatory and the disrotatory mechanisms were explained by the biradical character of the terminal atoms. For the transition states on the conrotatory and the disrotatory pathways, the energy difference from the orbital phase (orbital symmetry rules) was estimated for butadiene (10.6 kcal/mol) and 1,4-disilylbutadiene (3.4 kcal/mol). The comparison of the conrotatory and the disrotatory mechanisms for diene and triene is interesting in the characterization of a electrocyclic reaction.

It is known that the electrocyclic reaction for hexa-1,3,5-triene occurs through the disrotatory path (C_s symmetry) for thermal excitation and not through the conrotatory path (C_2 symmetry).



The groups of Houk[6,7] and Baldwin[8] have calculated the transition-state geometry of the disrotatory reaction pathway for the electrocyclic isomerization of cyclohexa-1,3-diene to hexa-1,3,5-triene by ab initio MO methods. They pointed out that the activation energy for the ring closure is 26 kcal/mol by the MP2/6-31G*//RHF calculation level. However, the conrotatory reaction path and the difference of energy barrier heights between the disrotatory and the conrotatory pathways are, to our knowledge, unknown.

In the present paper, we report the potential energy surfaces for the disrotatory and the conrotatory pathways of electrocyclic reactions of hexa-1,3,5-triene by the CASSCF MO calculation level. These electrocyclic reaction pathways are also analyzed by CiLC-IRC methods.

2. Methods of Computation

Geometries of all stationary points were optimized at a complete active space (CAS) self-consistent-field (SCF) method[9] with a 6-31G(d,p) basis set[10,11] using the Gaussian94 program package[12] and were characterized as minima or saddle points by calculation of the harmonic vibrational frequencies using analytical second derivatives.[13,14] For the CASSCF calculation, six active spaces corresponding to three π and π* orbitals for hexa-1,3,5-triene and related systems were included. All configurations in active spaces were generated. Single-point energies were determined at a multiconfigurational second-order Møller−Plesset perturbation (MP2/CAS) 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 disrotatory and the conrotatory 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[4,19−21] 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 localization 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

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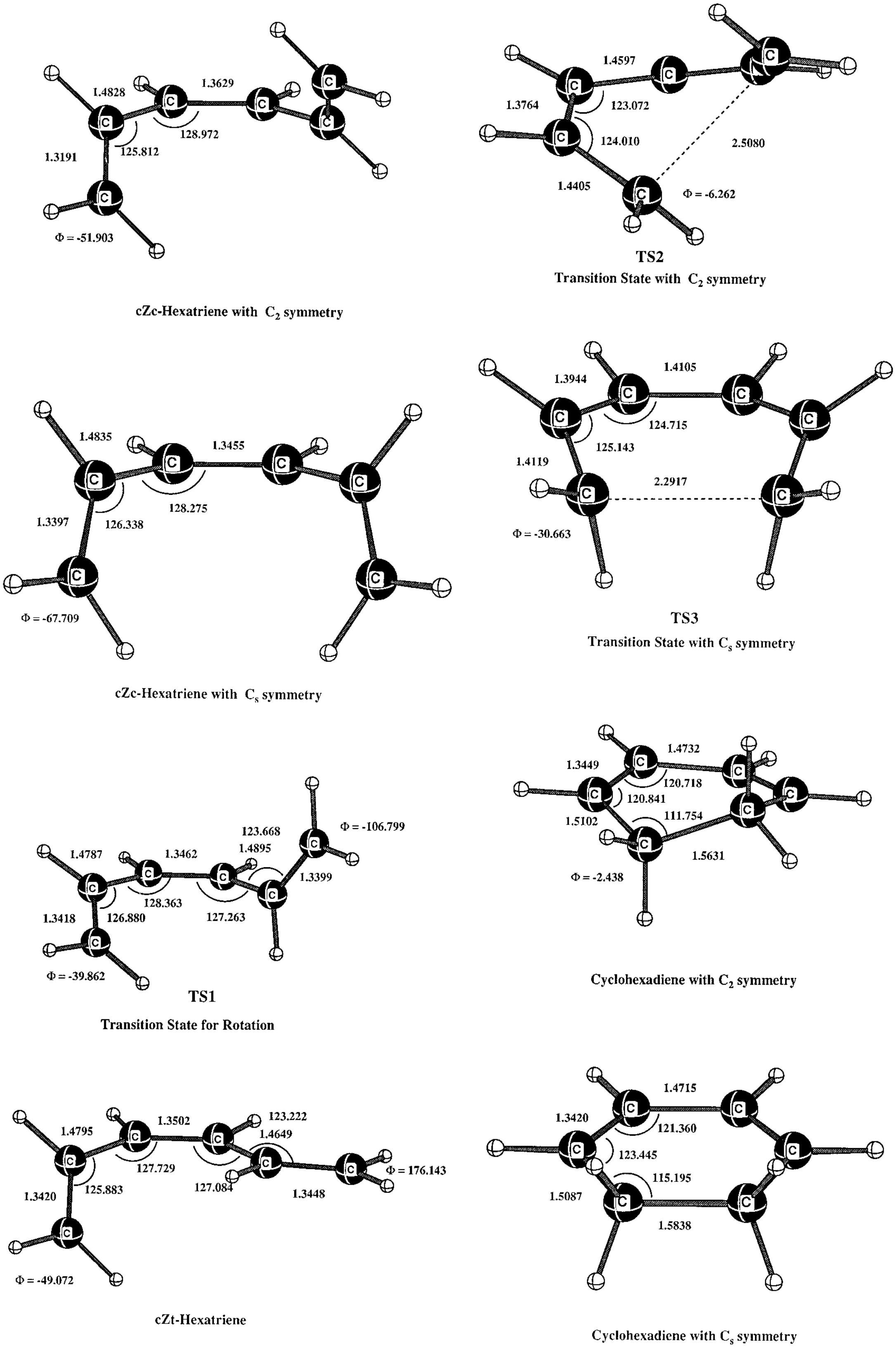


cZc-Hexatriene with C_2 symmetry

TS2
Transition State with C_2 symmetry

cZc-Hexatriene with C_s symmetry

TS3
Transition State with C_s symmetry

TS1
Transition State for Rotation

Cyclohexadiene with C_2 symmetry

cZt-Hexatriene

Cyclohexadiene with C_s symmetry

Figure 1. Stationary point geometries (in Å and deg) for electrocyclic reaction of hexatriene at the CAS/6-31G(d,p) level. Φ is the dihedral angle between planes of $C_1-C_2-C_3$ and $C_2-C_3-C_4$ or between planes of $C_6-C_5-C_4$ and $C_5-C_4-C_3$.

functions. The calculated total energy by the CI method in the process corresponds to that by the CAS−SCF calculation. The calculation procedures are repeated along the IRC pathway, which we call a CiLC-IRC analysis for the procedures. From the analysis of the results, 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.[22]

3. Results and Discussions

3.1. Reaction Pathways. The stationary point geometries for electrocyclic reactions of hexatriene are shown in Figure 1, and

TABLE 1: Total Energies (in hartree) for Stationary Points for Electrocyclic Reaction of Hexatriene

	CAS/6-31G(d,p)	MP2/CAS/6-31G(d,p)	CAS/6-311+G(d,p)	MP2/CAS/6−3111+G(d,p)
cZc-hexatriene (C_2)	−231.890 56	−232.609 06	−231.933 71	−232.773 48
cZc-hexatriene (C_s)	−231.888 54	−232.607 65	−231.931 97	−232.772 06
cZt-hexatriene	−231.897 64	−232.615 40	−231.940 94	−232.779 75
cyclohexadiene (C_2)	−231.917 10	−232.647 48	−231.958 23	−232.811 02
cyclohexadiene (C_s)	−231.914 25	−232.643 54	−231.955 06	−232.806 23
TS1 (rotation)	−231.888 86	−232.607 26	−231.932 39	−232.772 02
TS2 (conrotatory)	−231.816 06	−232.533 12	−231.857 99	−232.697 60
TS3 (disrotatory)	−231.832 00	−232.550 58	−231.874 47	−232.714 14

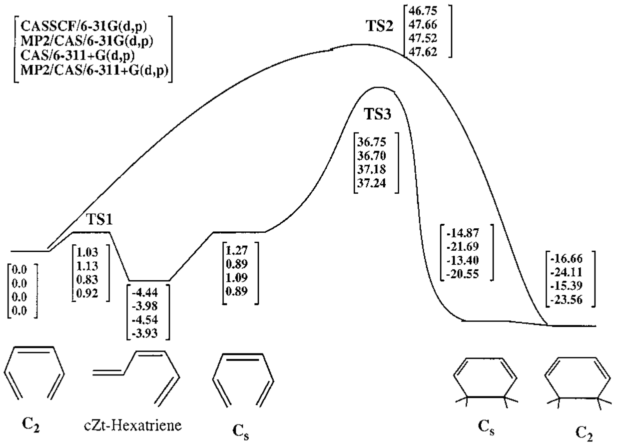


Figure 2. Potential energy profile along the minimal energy pathway for the cyclic reaction of hexatriene. The energy values are in given in kcal/mol at the CAS/6-31G(d,p), MP2/CAS/6-31G(d,p), CAS/6-311+G-(d,p), and MP2/CAS/6-311+G(d,p) levels.

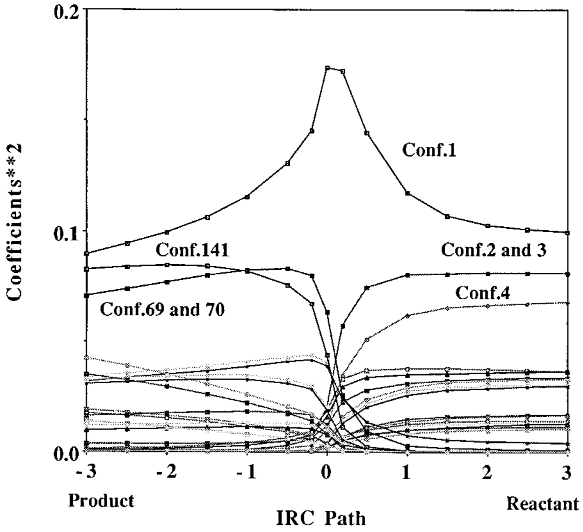


Figure 3. Square of CI coefficients of the CiLC-IRC along the conrotatory pathway for electrocyclic reaction of hexatriene. The unit of IRC is bohr × amu$^{1/2}$.

total energies are listed in Table 1. These potential energy surfaces are also depicted in Figure 2. For cZc-hexa-1,3,5-triene, two structures were obtained with C_2 and C_s symmetries by the CAS/6-31G(d,p) calculation level. The calculated hexatriene with C_2 symmetry is a real minimum structure, and the structure of hexatriene with C_s symmetry has one negative eigenvalue (45 cm^{-1}) with a″ symmetry for the force-constant matrix. The structure of hexatriene with C_s symmetry leads to cZt-hexatriene without an energy barrier and is the transition state for the rotations of C_2-C_3 and of C_4-C_5 bond axes. The energy difference between cZc-hexatriene with C_s symmetry and cZt-hexatriene is 4.8 kcal/mol at the MP2/CAS/6-311+G(d,p) level. The transition state between cZt-hexatriene and cZc-hexatriene with C_2 symmetry is TS1, which has an energy barrier of 4.9 kcal/mol above cZt-hexatriene by the MP2/CAS/6-311+G(d,p) calculation level. The total energy of TS1 is almost the same as that of cZc-hexatriene with C_s symmetry. The structure of cZc-hexatriene with C_2 symmetry is about 4.0 kcal/mol higher in energy than that of cZt-hexatriene. Accordingly, the energy barrier height from cZc-hexatriene with C_2 symmetry to cZt-hexatriene is only 0.9 kcal/mol at the MP2/CAS/6-311+G(d,p) calculation. Consequently, geometry alternation between C_2 and C_s symmetry types for cZc-hexatriene occurs easily through cZt-hexatriene.

For the electrocyclic reaction of hexatriene, two transition states TS2 and TS3 were found for C_2 (conrotatory) and C_s (disrotatory) symmetries by the CAS/6-31G(d,p) method, respectively. Both structures of TS2 and TS3 are real transition states and have only one negative eigenvalue for the force-constant matrix. The transition state of the disrotatory pathway (C_s symmetry) is about 10.4 kcal/mol lower in energy than that of the conrotatory pathway (C_s symmetry). This energy difference corresponds to the energy (10.6 kcal/mol) arising from the orbital phase for the electrocyclic reaction of butadiene. From a comparison of the geometry parameters for the transition states of the disrotatory and the conrotatory pathways, the transition state with C_s symmetry is a midway point of the reaction from alternation of the C−C bonds; the largest difference in the bond distances of C_1-C_2, C_2-C_3 and C_3-C_4 is only 0.02 Å length. On the other hand, the transition state with C_2 symmetry is a later point in the reaction. The largest difference in the bond distances of C_1-C_2, C_2-C_3 and C_3-C_4 of the transition state with C_2 symmetry is 0.08 Å length.

For cyclohexadiene, two structures with C_2 and C_s symmetries were obtained, respectively. The structure with C_s symmetry has one negative eigenvalue for the force-constant matrix and is the transition state for the interconversion of cyclohexadienes with C_2 symmetry. The structure with C_s symmetry is 3 kcal/mol higher in energy than that with C_2 symmetry.

As a result, the reaction pathway (disrotatory) with the lower energy barrier allowed by the orbital symmetry rules leads to the reactant and the product with C_s symmetry. However, both the reactant and the product are unstable. On the other hand, the reaction pathway (conrotatory) with the higher energy barrier leads to the stable reactant and product.

3.2. CiLC−IRC Analysis. To study the reaction mechanisms for the disrotatory and the conrotatory pathways, the CiLC-IRC analysis was performed. The weights of CI coefficients by the CiLC-IRC method for the conrotatory and the disrotatory pathways are displayed in Figures 3 and 4, respectively. Some configurations for the large weights of CI coefficients in Figures 3 and 4 are shown in Figure 5. From Figures 3 and 4, the weights of configurations 2, 3, and 4 decrease from the reactant side to the transition state (the product side), and the weights of configurations 69, 70, and 141 increase from the transition state (the reactant side) to the product side. Then two groups of these configurations cross at the vicinity of the transition states. That is, configurations 2 and 3 could be described as the

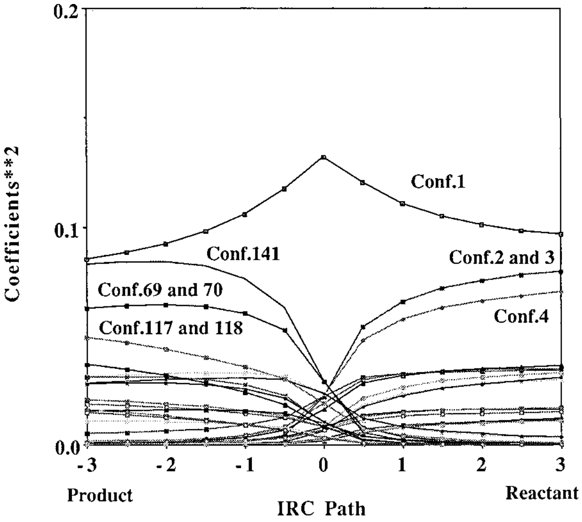
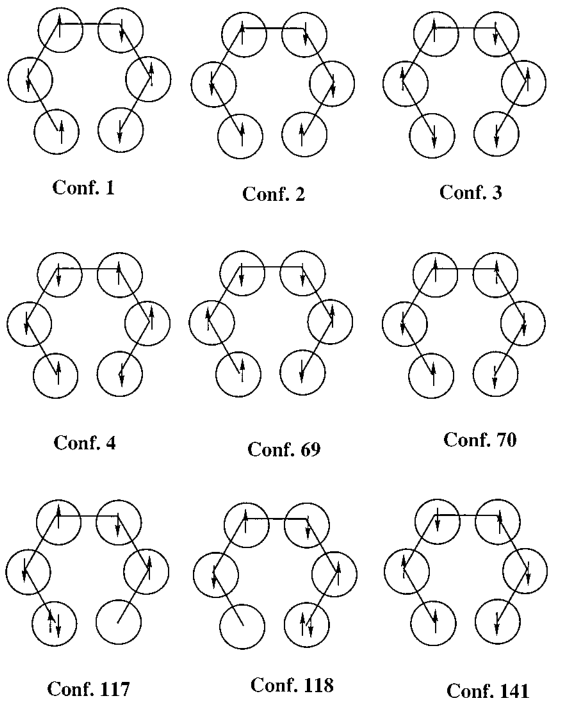


Figure 4. Square of CI coefficients of the CiLC-IRC along the disrotatory pathway for electrocyclic reaction of hexatriene. The unit of IRC is bohr × amu$^{1/2}$.


Conf. 1 Conf. 2 Conf. 3

Conf. 4 Conf. 69 Conf. 70

Conf. 117 Conf. 118 Conf. 141

Figure 5. Some electronic configurations for CiLC-IRC analysis.

interaction of triplet coupling between the terminal carbon atoms of hexatriene, and configurations 69 and 70 could be described as the interaction of singlet coupling between the new bond formation atoms (the terminal carbon atoms for the reactant). As a result, variations in the weights of configurations 2, 3, 69, and 70 along the reaction pathways mean bond formation for the terminal atoms of hexatriene. Configuration 4 could be described as the interaction of triplet coupling between C_2 and C_3 (and C_4 and C_5) atoms, and configuration 141 could be described as the interaction of singlet coupling between C_2 and C_3 (and C_4 and C_5) atoms. Consequently, variations in the weights of configurations 4 and 141 mean the exchange of Kekule's structures (of π orbitals) for the reactant and the product. The above results for the configurations (2, 3, 4, 69, 70, and 141) show the common mechanism for the electrocyclic reaction of hexatriene. The obvious difference for the disrotatory and the conrotatory pathways is variation in the weight of configuration 1. Configuration 1, which is the reference state, could be described as α and β spins located alternately on each carbon atom of hexatriene. On the conrotatory path, configuration 1 is located in a small interval in the vicinity of the transition state along the IRC pathway. That is, other configurations (2, 3, 4, 69, 70, 141, etc.) decrease "suddenly" in the small interval of the IRC pathway. On the other hand, the weight of configuration 1 along the disrotatory pathway changes slowly. Of course, the small peak of the weight of configuration 1 for the disrotatory pathway locates at the vicinity of the transition state. Nevertheless, the height of the peak for the disrotatory pathway is naturally less than that for the conrotatory pathway. From the comparison of the CiLC-IRC analysis for both reaction pathways, the conrotatory reaction with C_2 symmetry occurs with a sudden variation of the spin-state rearrangement.

Conclusion

The potential energy surfaces for the electrocyclic reactions of hexatriene were calculated by the ab initio MO methods. Two reaction pathways were found: disrotatory with C_s symmetry and conrotatory with C_2 symmetry. The energy barrier height of the transition state for the disrotatory pathway is about 10 kcal/mol lower than that for the conrotatory pathway. The transition state for the disrotatory pathway links the two transition structures of C_s symmetry. The reactant (cZc-hexatriene with C_s symmetry) is the transition state of cis–trans isomerization to cZt-hexatriene, and the product (cyclohexadiene with C_s symmetry) is also the transition state of conversion to cyclohexadiene with C_2 symmetry. Consequently, the lowest energy path of the electrocyclic reaction is the disrotatory type and occurs through the cis–trans-isomeization (cZt-hexatriene).

The CiLC-IRC analysis was performed for the disrotatory and the conrotatory reaction pathways. The conrotatory pathway, which is symmetry forbidden from the orbital symmetry rules, is characterized by "sudden variation" of the configurations.

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