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Theoretical Studies on the Electrocyclic Reactions of Bis(allene) and Vinylallene. Role of Allene Group

Shogo Sakai

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan

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The reaction mechanisms of the electrocyclic ring closure of bis(allene) and vinylallene were studied by ab initio MO methods. The conrotatory and disrotatory pathways of the electrocyclic reactions from bis(allene) to bis(methylene)cyclobutene were determined by a CASSCF method. The transition state on the conrotatory pathway is 26.8 kcal/mol above bis(allene) and about 23 kcal/mol lower than that on the disrotatory pathway at a MRMP calculation level. The activation energy on the conrotatory pathway is lower by 23 kcal/mol than that of the electrocyclic reaction of butadiene. This lower energy barrier comes from the interactions of the "side π orbitals" of the allene group. The interaction of the "vertical π orbitals" of the allene group is predominant at the early stage of the reaction. The activation energy of the electrocyclic reaction of vinylallene is about 8.5 kcal/mol higher than that on the conrotatory pathway of bis(allene).

1. Introduction

The electrocyclic reactions of polyenes have been studied extensively both theoretically and experimentally. The orbital symmetry rules such as the Woodward−Hoffmann rule[1] and the frontier orbital theory[2] defined the concept of an electrocyclic reaction. The rules served not to settle mechanistic questions but to raise the stakes on what were already lively controversies.

In our previous papers, the electrocyclic reaction mechanisms for hexatriene,[3,4] butadiene,[5−7] and the analogous compounds[8] were reported. By a CiLC-IRC analysis on the basis of an ab initio molecular orbital theory, the difference of the mechanisms between the conrotatory and the disrotatory reactions was explained with the biradical character of the terminal atom.

Pasto and co-workers[9] investigated experimentally the reaction of bis(allene) to bis(methylene)cyclobutene rearrangement. At thermal conditions in the gas phase at low pressure at 300−350 °C, they showed that the ring-closure reaction of bis(allene) occurs through the same conrotatory process as the cyclic reaction of butadiene. They[10] also indicated that the reaction of vinylallene is the same ring-closure process as that of bis(allene). For the cyclic reaction of vinylallene, the substituted effects on vinyl group have been studied experimentally[11−15] and theoretically.[16] However, the role of two types π orbitals (vertical π and side π' orbitals) of the allene group for the cyclization of bis(allene) and/or vinylallene is not known well. In simple consideration, the "side π' orbital" and the "vertical π orbital" of allene group are orthogonal, and the vertical π orbital relates with the cyclization and the side π' orbital does not. However, for the products (bis(methylene)cyclobutene and/or methylenecyclobutene) of the ring closure reaction, the π orbital in the ring part (cyclobutene) probably interacts with the π orbital of methylene group, which may be produced from the side π' orbital of the allene group. The conrotatory mechanism of cyclization of butadiene occurs continually. Namely, the π bond orbital in the ring part interacts not only with the vertical π orbital of allene group but also with the side π orbital during the cyclic process. However, the mechanisms of orbital interactions along the reaction process are, to our knowledge, unknown, although the entropies of the reactions were calculated by theoretical methods.

In this paper we report the potential energy surfaces of electrocyclic reactions for the conrotatory and the disrotatory pathways of bis(allene) and for vinylallene by a CASSCF MO calculation level. These electrocyclic reaction pathways are analyzed by a CiLC-IRC method. Especially the role of allene group for the cyclization was focused as the analysis.

2. Theoretical Methods

Geometries of all stationary points were optimized at a complete active space (CAS) self-consistent-field (SCF) method[17] with a 6-31G(d) basis set[18] and were characterized as minima or saddle points by calculation of the harmonic vibrational frequencies using analytical second derivatives. For the CASSCF calculation, eight active spaces corresponding to four π and π^* orbitals for bis(allene) and related systems and six active spaces corresponding to three π and π^* orbitals for vinylallene and related systems were included. All configurations in active spaces were generated. Additional calculations were performed to obtain improved energy comparisons: the calculation with the CASSCF-optimized structures with electron correlation incorporated through the multiconfigurational theories (MRMP)[19] with the 6-31G(d) basis set. The intrinsic reaction coordinate (IRC)[20,21] was followed from the transition state toward both reactants and products.

To interpret the mechanisms on the closing 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[22−24] with the 6-31G(d) basis set. The CASSCF is calculated to obtain a starting set of orbitals for the localization procedure. After carrying out the CASSCF procedure, the CASSCF-optimized orbitals were localized by the Boys localization procedure.[25] The calculated localized orbitals are very atomic in nature. By use of the localized MOs as a basis, a full CI with determinants level is used to generate electronic structures and their relative

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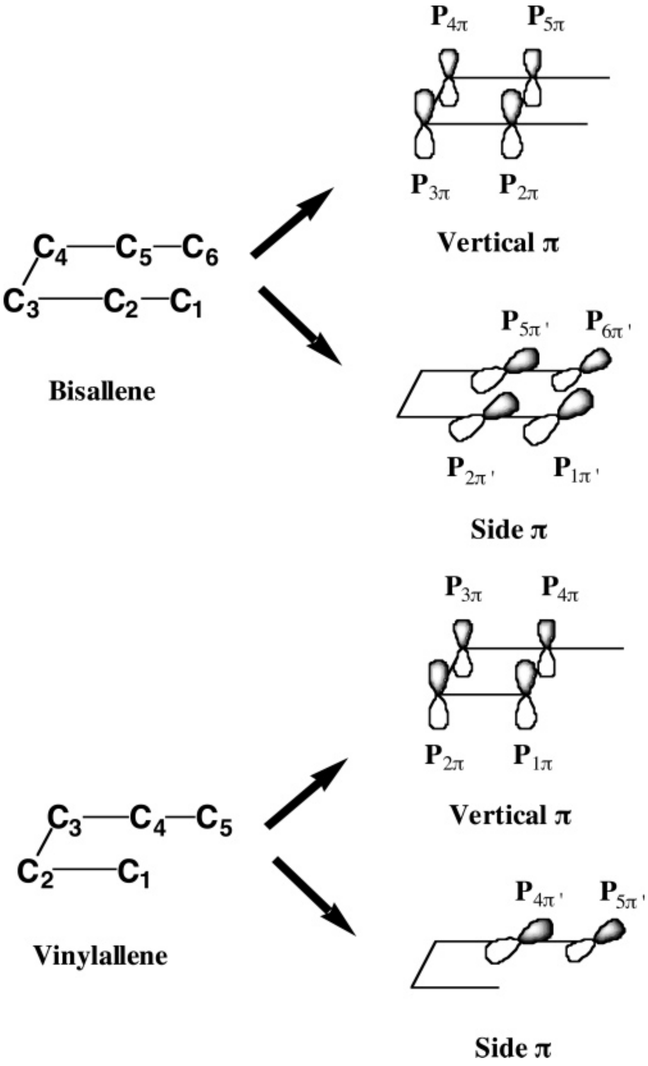
SCHEME 1



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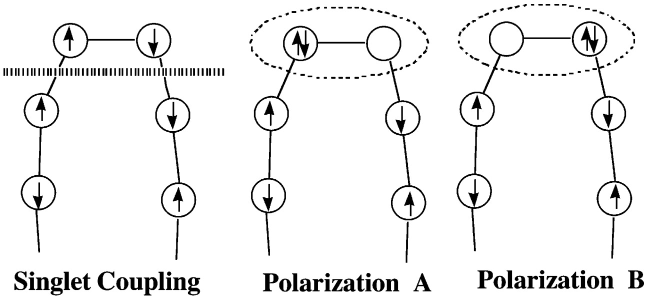


weights in the atomic orbital-like wave functions. The calculated total energy by the CI method in the process corresponds to that by the CASSCF calculation. The calculation procedures are repearted along the IRC pathway, which we call a CiLC-IRC analysis for the procedures. For CI configurations, each bond was assigned by the terms of the singlet coupling and polarization as shown in Scheme 2. In this scheme, the dotted line denotes a triplet coupling (antibonding) between the orbitals, and an ellipse denotes an ionic coupling (polarization). It was postulated that the singlet coupling and polarization terms could be describing the electronic structure of one bond, and this description is related to a usual presentation by the valence bond (VB) theory. This procedure has been used for many reaction mechanism analyses.[26]

TABLE 1: Total Energies (hatrees) and the Relative Energies (kcal/mol) for Stationary Points of Electrocyclic Reactions of Bis(allene) and Vinylallene

	total energy		relative energy	
	CASSCF	MRMP	CASSCF	MRMP
bis(allene) (C_{2v})	−230.678257	−231.335930	0.0	0.0
TS (conrotatory: C_2)	−230.626090	−231.293307	32.74	26.75
TS (disrotatory: C_s)	−230.601948	−231.256786	47.89	49.67
bis(methylene)cyclobutene	−230.702003	−231.360355	−14.90	−15.32
vinylallene	−192.825278	−193.382945	0.0	0.0
TS	−192.756859	−193.326771	42.94	35.25
methylenecyclobutene	−192.822857	−193.385673	1.52	−1.71

The CiLC-IRC analysis and MRMP calculations were performed using the GAMESS software pakage,[27] and the others were carried out using Gaussian03.[28]

3. Results and Discussion

3.1. Reaction Pathways.

3.1.1. Bis(allene). The stationary points geometries for electrocyclic reactions of bis(allene) are shown in Figure 1, and the total energies and the relative energies are listed in Table 1. The calculated stationary points structure of bis(allene) has C_{2v} symmetry. Namely the vertical π orbitals of $C_2-C_3-C_4-C_5$ are orthogonal to the side π' orbitals of C_1-C_2 and C_5-C_6 bonds.

For the electrocyclic reaction path of bis(allene), two reaction pathways of the corotatory (C_2 symmetry) and the disrotatory (C_s symmetry) can be considered. The transition state on the conrotatory pathway has one negative eigenvalue (-831 cm^{-1}) for the force constant matrix, which corresponds to the reaction coordinate. The transition state on the disrotatory pathway has two negative eigenvalues; one (-640 cm^{-1}) corresponds to the reaction coordinate and the other (-173 cm^{-1}) has a″ symmetry. Consequently, the transition state on the conrotatory pathway is a real transition state, and on the disrotatory pathway is not real one (a second-order saddle point). The second-order saddle point as the transition state on the disrotatory pathway can be seen the disrotatory transition state of the cyclization of butadiene. Although the second-order saddle point is not a true transition state, the characterization of the disrotatory pathway is interesting in the field of the reaction mechanism theory. The interesting point for the conrotatory pathway of bis(allene) is the transition state structure with the dihedral angle $C_2-C_3-C_4-C_5$ of nonzero (14.5°). The dihedral angle of $C_2-C_3-C_4-C_5$ is zero for both bis(allene) and bis(methylene)cyclobutene. Namely, the cyclization of bis(allene) along the IRC pathway does not occur through a least motion path. The center bond C_3-C_4 of the transition state is about 0.08 Å shorter than that of bis(allene) and the C_2-C_3 (or C_4-C_5) bond is 0.07 Å longer than that of bis(allene). The C_1-C_2 (or C_5-C_6) bond of the transition state is only 0.016 Å longer than that of the reactant (bis(allene)). Accordingly, the side π' bonds of C_1-C_2 and C_5-C_6 may not be contributed for the deformation from the reactant to the transition state. The central bond C_3-C_4 of the transition state is about 0.01 Å longer than the C_2-C_3 (or C_4-C_5) bond, whereas the central bond length of the conrotatory transition state of the cyclization of butadiene is about 0.08 Å shorter than the side bonds. Namely, the conrotatory pathway of bis(allene) has an early transition state and that of butadiene has a latter transition state. This conforms to the Hammond postulation:[29] the cyclization of bis(allene) is an exothermic reaction and that of butadiene is an endothermic reaction. The energy barrier height at the conrotatory transition state of bis(allene) is about 27 kcal/mol above bis(allene) and is about 22.5

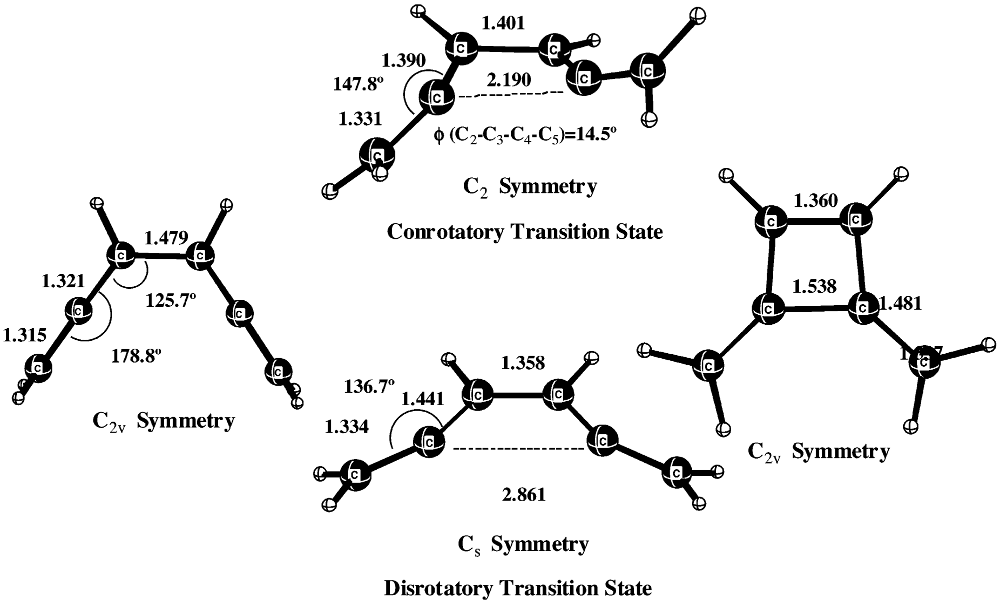


Figure 1. Stationary point geometries (in angstrom and degrees) for electrocyclic reaction of bis(allene) at the CASSCF/6-31G(d) level.

kcal/mol lower than that of butadiene at the MRMP calculation level. The cyclization of bis(allene) is an exothermic process at 15 kcal/mol, and of butadiene is an endothermic one. This corresponds to the fact that the ring closer reaction of bis(allene) occurs and the ring opening reaction of cyclobutene occurs experimentally.

For the disrotatory transition state of bis(allene), the central bond length of C_3-C_4 is about 0.08 Å shorter than that of C_2-C_3 (or C_4-C_5) and is shorter than those of bis(methylene)-cyclobutene and bis(allene). From the variation of the central bond along the reaction path, the conrotatory reaction occurs smoothly (monotonically), but the disrotatory reaction does not occur smoothly. This is similar to the cyclization of butadiene. Although the C_2-C_5 length of the conrotatory transition state is about 0.67 Å shorter than that of the disrotatory transition state, the angle of $C_1-C_2-C_3$ (and/or $C_4-C_5-C_6$) of conrotatory transition state is about 11° larger than that of the disrotatory transition state. This probably means that the electronic rearrangement at C_2 and C_5 atoms of the disrotatory transition state is larger than that of the conrotatory transition state. This may correspond to the diradical character at the terminal carbon of the disrotatory cyclic reaction of butadiene as shown in the previous paper.[5]

The variations of some geometrical parameters of the cyclizations of bis(allene) along the conrotatory (C_2 symmetry) and the disrotatory (C_s symmetry) pathways were shown in Figures 2 and 3. For the conrotatory pathway, the dihedral angle of $C_2-C_3-C_4-C_5$ increases from the reactant side until the point of about 4.5 bohr × amu$^{1/2}$ of the IRC path and decreases from the point of IRC to the products via the transition state. Namely, the maximum point (about 32°) of the dihedral angle exists at the region of about 4.5 bohr x amu$^{1/2}$ of the IRC path. The rotation of the vertical π and the side π' orbitals on the C_1-C_2 (C_5-C_6) and/or C_2-C_3 (C_4-C_5) bond axes occurs from the same region of the maximum point of the dihedral angle (see the variations of a dihedral angles of $H_7-C_6-C_4-C_3$ and $H_8-C_6-C_4-C_3$ in Figure 2a). The large variation of the distance of C_2-C_5 bond occurs also at the region between 5 and -4.5 bohr x amu$^{1/2}$ on the IRC pathway. Accordingly, the reaction can be classified in two periods. One is the preparation period for the new bond formation and the other is the bond formation period. On the other hand, the distance of the C_2-C_5 bond along the disrotatory IRC pathway changes monotonically from the region of about 5 bohr x amu$^{1/2}$ to that of over -10 bohr x amu$^{1/2}$ (see Figure 3b).

3.1.2. Vinylallene. The stationary point geometries for electrocyclic reaction of vinylallene are shown in Figure 4, and the total energies and the relative energies are also listed in Table 1. The structure of vinylallene has a C_s symmetry and the vertical π orbitals of $C_1-C_2-C_3-C_4$ are orthogobal to the side π' orbitals of C_4-C_5. The product, methylenecyclobutene, has also a C_s symmetry. The transition state has one negative eigenvalue (-863 cm^{-1}) for the force constant matrix, which corresponds to the reaction coordinate. The dihedral angle of $C_1-C_2-C_3-C_4$ at the transition state is 17.5° and is larger by 3° than that of the conrotatory transition state of bis(allene) system. The C_1-C_4 bond length of the transition state is about 0.02 Å longer than the corresponding one of the conrotatory transition state of bis(allene) system and is almost 0.65 Å shorter than that of the disrotatory transition state. The transition state of cyclic reaction of vinylallene is a conrotatory type from the geometrical parameters, and this corresponds to the previous experimental results.[10] The variation of some geometrical parameters of the cyclization of vinylallene along the IRC pathway is shown in Figure 5. The dihedral angle of $C_1-C_2-C_3-C_4$ increases from the reactant side until the point of about 4.5 bohr x amu$^{1/2}$ and decreases from the point of IRC to the product side via the transition state. This variation is very similar to that on the conrotatory pathway of bis(allene). The maximum point (about 33°) of the dihedral angle exists at the region of about 4.5 bohr x amu$^{1/2}$ of IRC path. The rotation of the vertical π and the side π' orbitals on the C_3-C_4 and/or C_4-C_5 bond axes occurs from the same region of the maximum point of the dihedral angle (see the variation of the dihedral angles of $H_6-C_5-C_3-C_2$ and $H_7-C_5-C_3-C_2$ in Figure 5a). The large variation of the C_1-C_4 length occurs from the same region of the IRC path. Consequently, the cyclization mechanism of vinylallene is similar to that of bis(allene) and can be also classified to two periods (the preparation period of the new bond formation and the period of the bond formation).

The heats of reactions of bis(allene), vinylallene, and butadiene are -15.3, -1.7, and 9.2 kcal/mol at the MRMP

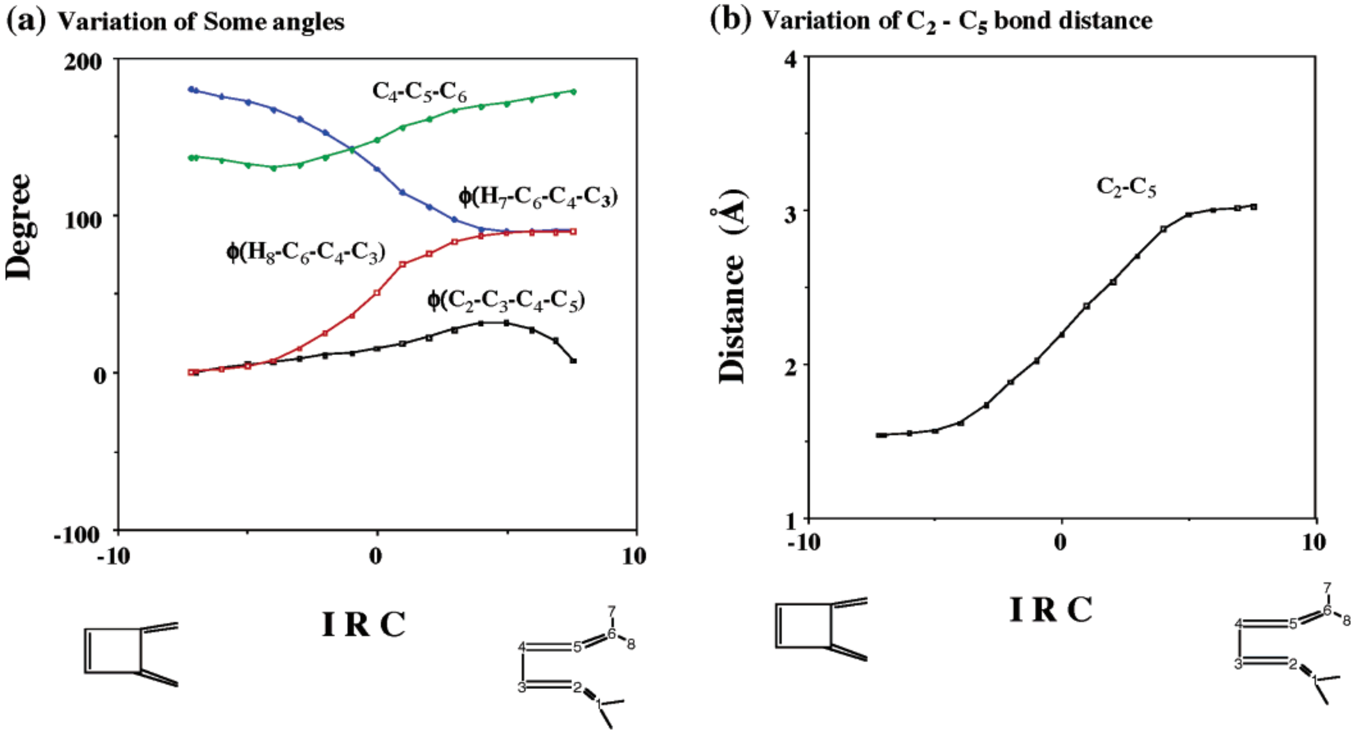


Figure 2. Variation of some geometrical parameters along the conrotatory IRC pathway of electrocyclic reaction of bis(allene).

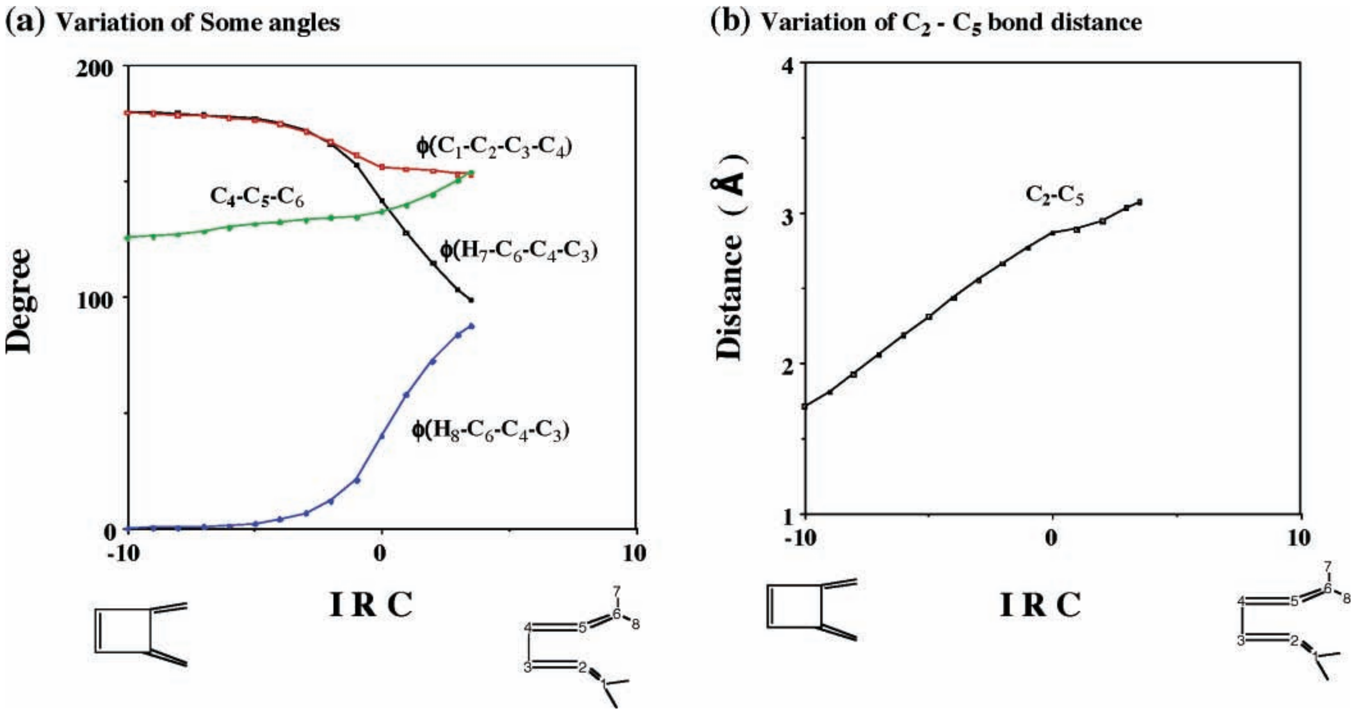


Figure 3. Variation of some geometrical parameters along the disrotatory IRC pathway of electrocyclic reaction of bis(allene).

calculation level, respectively. The activation energies of the conrotatory transition state of bis(allene), the transition state of vinylallene, and the conrotatory transition state of butadiene are 26.75, 35.25, and 49.3 kcal/mol, respectively. The heat of reaction of cyclization of vinylallene is about 13.6 kcal/mol smaller than that of bis(allene). This energy difference probably comes from the π resonance energies. Namely, bis(dimethylene)cyclobutene is a six-π-orbital system of the hexatriene type and methylenecyclobutene is a four-π-orbital system of the butadiene type. The difference of the activation energies of bis(allene) and vinylallene probably comes from the same reason as the heat of reactions. Namely, the vertical π orbitals of $C_1-C_2-C_3-C_4$ of vinylallene at the transition state are probably not orthogonal to the side π' orbitals of the C_4-C_5 bond. Although the vertical $p_4\pi$ orbital of the C_4 atom is orthogonal to the side $p_4\pi'$ orbital of the C_4 atom, the vertical $p_4\pi$ orbital of the C_4 atom does not have to be orthogonal to the side $p_5\pi'$ orbital of the C_5 atom. Accordingly, there is a possibility of the formation of a six-π-orbital resonance system of $p_1\pi-p_2\pi-p_3\pi-p_4\pi-p_5\pi'-p_4\pi'$ as the hexatriene type at the transition state. In this case, two sets of the orbital interaction for the bond formation of C_1-C_4 can be considered at the transition state.

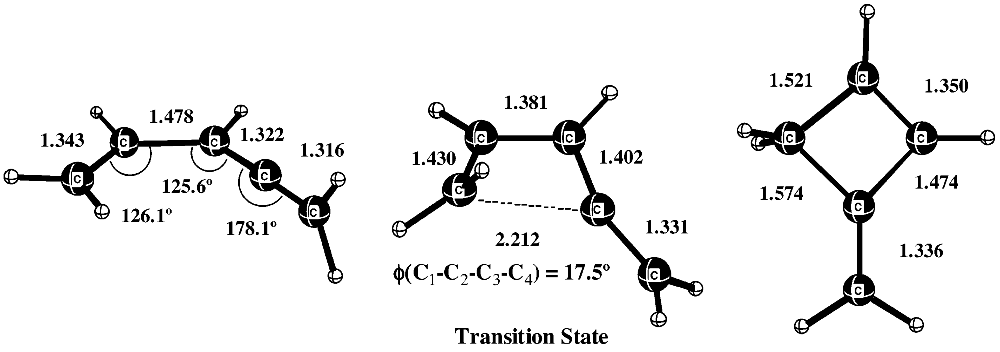


Figure 4. Stationary point geometries (in angstroms and degrees) for electrocyclic reaction of vinylallene at the CASSCF/6-31G(d) level.

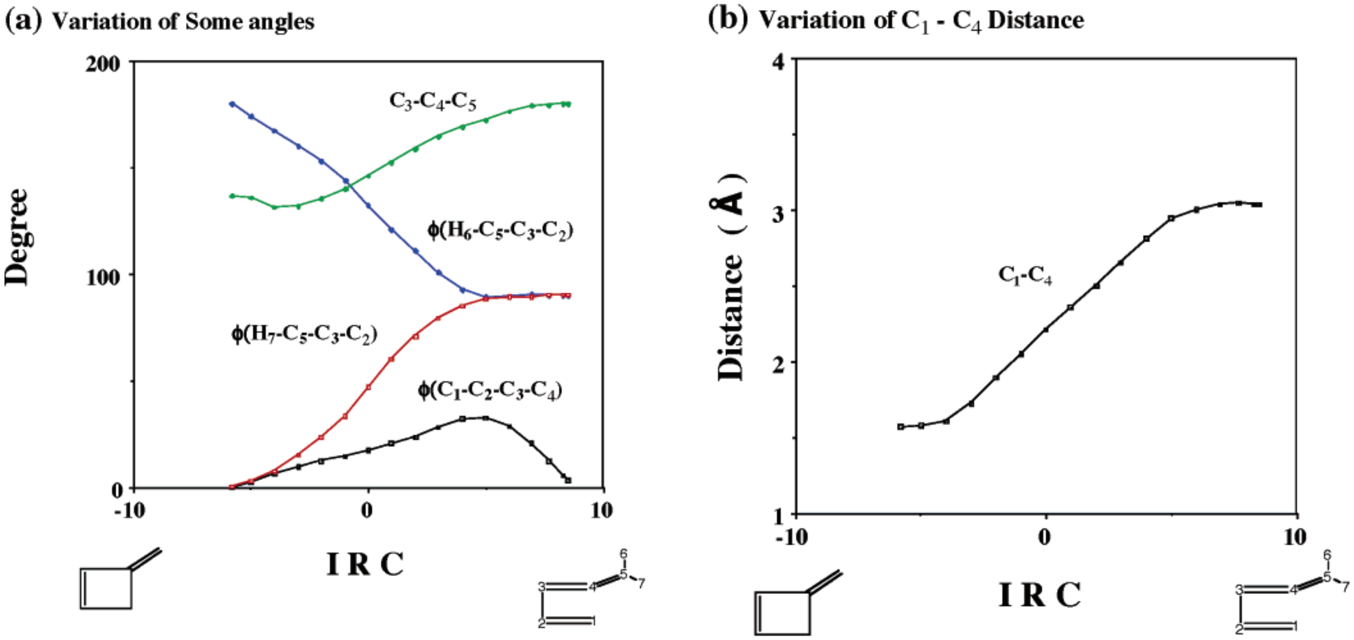
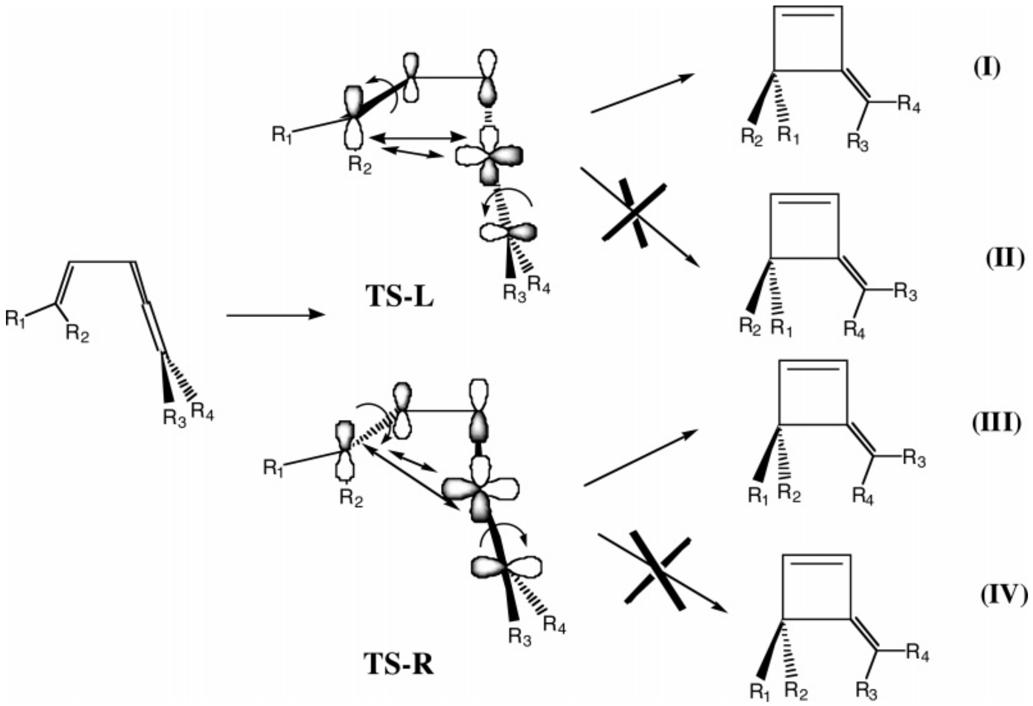


Figure 5. Variation of some geometrical parameters along the IRC pathway of electrocyclic reaction of vinylallene.

One is the interaction between the vertical $p_1\pi$ and $p_4\pi$ orbitals as the cyclization of butadiene. Another is the interaction of the vertical $p_1\pi$ and the side $p_4\pi'$ as the cyclization of hexatriene. From the orbital symmetry rules, the orbital interactions of the vertical−vertical $p_1\pi-p_4\pi$ and the vertical−side $p_1\pi-p_4\pi'$ have to be in-phase in the HOMO. Two types transition states can be obtained as shown in Scheme 3, where the orbital phase of the vertical p orbitals of $C_1-C_2-C_3-C_4$ indicate the HOMO as that of butadiene and the orbital phase of the side p orbitals of C_4-C_5 indicate the HOMO as that of ethylene. One is the structure (TS-L) of the lower level of allene part on the plane of $C_1-C_2-C_3$ and another is that (TS-R) of the upper level. Two transition states are enantiomorphs. These conformations depend on the direction of the rotation of the dihedral angle of $C_1-C_2-C_3-C_4$. For the lower level of the allene structure (TS-L), the methylene group of C_1 has to rotate to the left on the C_1-C_2 axis because of the interaction of the lower lobe of the vertical $p_1\pi$ and the upper lobe of the vertical $p_4\pi$ orbitals being in-phase in the HOMO of four-electron four-orbital system (and also the six-electron six-orbital system). Then, there are two possibilities of the rotation of the methylene part of allene. If the methylene group rotates to the left on the C_4-C_5 bond axis (the same direction of rotation of methylene group of C_1), the outward lobe of the side $p_5\pi'$ orbital interacts with the upper lobe of the vertical $p_4\pi$ orbital. Then the inward lobe of the side $p_4\pi'$ orbital interacts with the lower lobe of the vertical $p_1\pi$ orbital in-phase in the HOMO of the six-electron six-orbital system. However, if the methylene group of allene rotates to the right on the C_4-C_5 axis, the inward lobe of the side $p_5\pi'$ orbital interacts with the upper lobe of the vertical $p_4\pi$ orbital. Then the side $p_4\pi'$ orbital interacts with the vertical $p_1\pi$ orbital out-of-phase in the HOMO of six-electron six-orbital system, and this means destabilization. For the structure (TS-R) of the upper level of allene for the plane of $C_1-C_2-C_3$, the methylene group of C_1 rotates to the right on the C_1-C_2 axis because of the interaction of the vertical $p_1\pi$ and the vertical $p_4\pi$ orbitals being in-phase in the HOMO. Then, the methylene group of allene rotates to the right on the C_4-C_5 axis because of the interaction of the vertical $p_1\pi$ and the side $p_4\pi'$ orbitals being in-phase in the HOMO of the six-electron six-orbital system. Therefore, the possible products of the reaction are I and III. Both I and III are produced in-phase in the HOMO and can be stabilized in energy. From the results, if the dihedral angle of $C_1-C_2-C_3-C_4$ of vinylallene is not zero by the influence of the substitution groups on the C_1 or C_5 atom, the torquoselectivity occurs for the electrocyclic reactions.

3.2. CiLC Analysis. The weights of some orbital interactions along the IRC pathways for the conrotatory and disrotatory cyclic reactions of bis(allene) by the CiLC analysis were shown in Figures 6 and 7. The weights of the singlet coupling and polarization terms of some orbital interactions along the conrotatory and disrotatory IRC pathways are shown in the Supporting Information. For the conrotatory pathway in Figure 6, the weights of the interactions of the vertical−vertical $p_2\pi-$

SCHEME 3



$p_3\pi$ orbitals and the vertical−vertical $p_3\pi-p_4\pi$ orbitals cross at the region of the transition state. The weight of the side−side $p_1\pi'-p_2\pi'$ orbital interaction decreases rapidly in the region of the transition state. The bond formation of C_2-C_5 is composed of three types of orbital interactions; the vertical−vertical $p_2\pi-p_5\pi$, the side−side $p_2\pi'-p_5\pi'$, and the side−vertical $p_2\pi'-p_5\pi$ ($p_2\pi-p_5\pi'$). The weight of the orbital interaction of the vertical−vertical $p_2\pi-p_5\pi$, which is the similar to the orbital interaction of the cyclic reaction of butadiene, is a little larger than those of the side−side $p_2\pi'-p_5\pi'$ and the side−vertical $p_2\pi'-p_5\pi$ ($p_2\pi-p_5\pi'$) in the region of before the transition state along the reaction path. After the transition state, the interactions of the side−side $p_2\pi'-p_5\pi'$ and the side−vertical $p_2\pi'-p_5\pi$ ($p_2\pi-p_5\pi'$) are larger than that of the vertical−vertical $p_2\pi-p_5\pi$. Consequently, the conrotatory reaction of bis(allene) occurs through three processes. The first process is the increasing of dihedral angle ($C_2-C_3-C_4-C_5$), which relates to the lowest vibration mode of bis(allene). After that, the interaction between the vertical $p_2\pi$ and the vertical $p_5\pi$ orbitals occurs. To increase in the orbital interaction, the vertical $p_2\pi$ and the vertical $p_5\pi$ orbitals rotate conrotatory on the C_2-C_3 and C_4-C_5 bond axes, respectively. Then the orthogonality between the side $p_1\pi'$ (or $p_6\pi'$) and the vertical $p_2\pi$ (or $p_5\pi$) orbitals collapses, and the eight-orbital eight-electron interaction ($p_2\pi'-p_1\pi'-p_2\pi-p_3\pi-p_4\pi-p_5\pi-p_6\pi'-p_5\pi'$) system is formed. After the formation of eight-orbital eight-electron system, the interactions of the side−side $p_2\pi'-p_5\pi'$ and the vertical−side $p_2\pi-p_5\pi'$ ($p_2\pi'-$

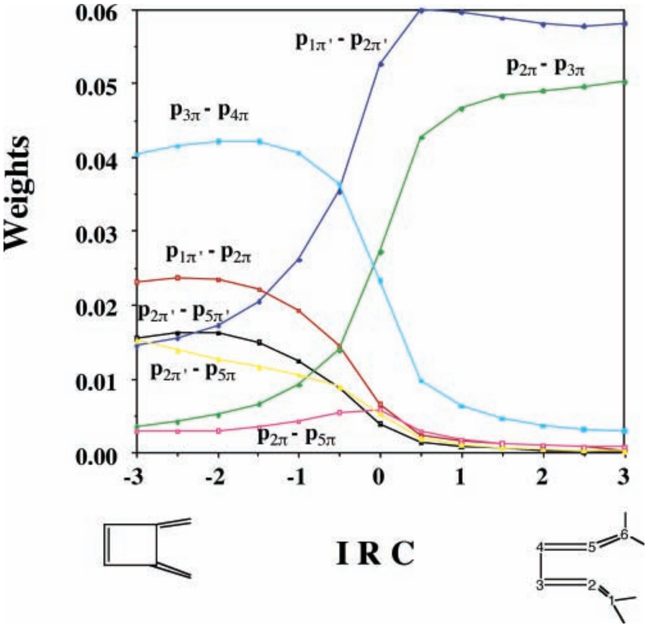


Figure 6. Weights of some orbital interactions by CiLC analysis along the conrotatory IRC pathway of electrocyclic reaction of bis(allene).

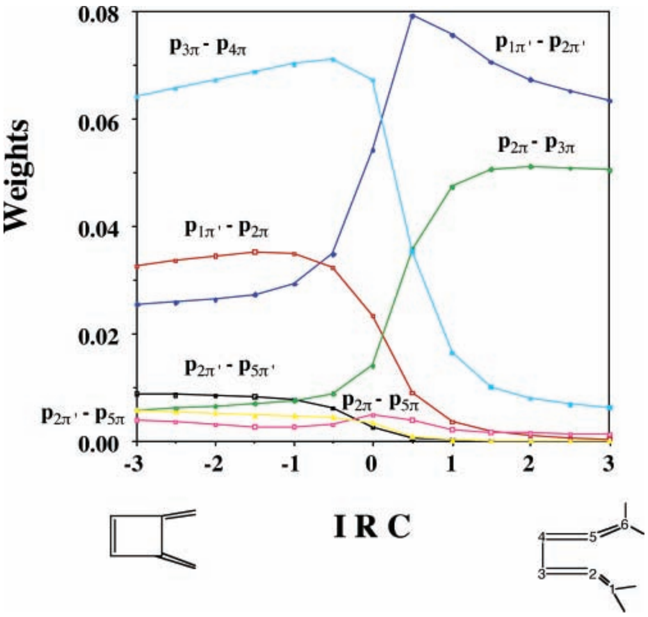


Figure 7. Weights of some orbital interactions by CiLC analysis along the disrotatory IRC pathway of electrocyclic reaction of bis(allene).

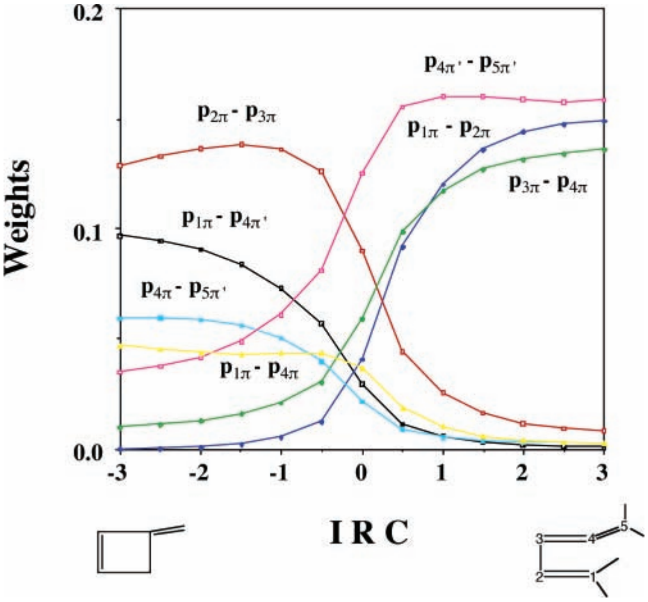


Figure 8. Weights of some orbital interactions by CiLC analysis along the IRC pathway of electrocyclic reaction of vinylallene.

$p_5\pi$) become favorable. Therefore, the cyclic reaction of bis(allene) is not as simple a conrotatory mechanism as that of butadiene.

On the disrotatory reaction path of bis(allene), the bond exchange of the vertical−vertical $p_2\pi-p_3\pi$ and the vertical−vertical $p_3\pi-p_4\pi$ occurs in the region before the transition state. This mechanism is the same as for the conrotatory pathway. For the C_2-C_5 bond formation, the weight of the orbital interaction of the vertical−vertical $p_2\pi-p_5\pi$ is larger than those of the side−side $p_2\pi'-p_5\pi'$ and the side−vertical $p_2\pi'-p_5\pi$ ($p_2\pi-p_5\pi'$) in the region before the transition state. This is also similar to that on the conrotatory path of bis(allene). However, the bond interaction of the vertical−vertical $p_2\pi-p_5\pi$ on the disrotatory pathway is very different from that on the conrotatory. Although the orbital interaction of the vertical−vertical $p_2\pi-p_5\pi$ on the conrotatory pathway is composed from both the singlet coupling and the polarization terms, that on the disrotatory pathway occurs through a biradical state (no polarization terms at the transition state). The difference of the bond formation between the conrotatory and disrotatory mechanisms is similar to that of cyclic reaction of butadiene, as shown in the previous paper.[5]After the transition state, the bond formation of the vertical−vertical $p_2\pi-p_5\pi$, the side−side $p_2\pi'-p_5\pi'$ and the side−vertical $p_2\pi'-p_5\pi$ ($p_2\pi-p_5\pi'$) on the disrotatory path is very slow. This can also be shown from the comparison of the variations of the distance of C_2-C_5 bond along the conrotatory and disrotatory pathways (see Figures 2b and 3b). The orbital interactions of the side−side $p_2\pi'-p_5\pi'$ and the side−vertical $p_2\pi'-p_5\pi$ ($p_2\pi-p_5\pi'$) occur biradically from the weights of the singlet coupling and polarization terms (see Figures S2d,e and S1d,e in the Supporting Information). Thus, the bond formation of C_2-C_5 including three types orbital interactions on the disrotatory pathway is a biradical process and that on the conrotatory is a concerted process. The orbital interaction of the side−side $p_1\pi'-p_2\pi'$ on the conrotatory path decreases from the region near the transition state and the orbital interaction of the side−vertical $p_1\pi'-p_2\pi$ increases from the same region. For the disrotatory pathway, the orbital interaction of the side−side $p_1\pi'-p_2\pi'$ changes rapidly near the transition state. The rapid variation may correspond to the C_2-C_5 bond formation of the biradical type on the disrotatory path.

The weights of some orbital interactions along the IRC path of the cyclic reaction of vinylallene by CiLC analysis were shown in Figure 8. The weights of the singlet coupling and the polarization terms of some orbital interactions along the IRC pathway are also in the Supporting Information. The weights of the orbital interactions of the vertical−vertical $p_1\pi-p_2\pi$ and the vertical−vertical $p_3\pi-p_4\pi$ bonds decrease smoothly along the IRC pathway from the reactant side to the product side, and that of the vertical−vertical $p_2\pi-p_3\pi$ increases along the IRC pathway. The weights of the orbital interaction of the vertical−vertical $p_1\pi-p_2\pi$ and the vertical−vertical $p_3\pi-p_4\pi$ bonds cross that of the vertical−vertical $p_2\pi-p_3\pi$ at the region of near the transition state. For the bond formation of C_1-C_4, the weight of the orbital interaction of the vertical−vertical $p_1\pi-p_4\pi$ is larger than that of the vertical−side $p_1\pi-p_4\pi'$ in the region before the transition state. In the region after the transition state, the weight of the orbital interaction of the vertical−side $p_1\pi-p_4\pi'$ becomes much larger than that of the vertical−vertical $p_1\pi-p_4\pi$. Namely, the cyclization of vinylallene is the butadiene-like cyclic mechanisms before the transition state. The large variation of the orbital interactions of the side−side $p_4\pi'-p_5\pi'$ and the vertical−side $p_4\pi-p_5\pi'$ occur near the transition state, and these weights of the orbital interactions cross after the transition state.

4. Conclusion

The potential energy surfaces of the electrocyclic reactions of bis(allene) and vinylallene were calculated by the ab initio CAS-SCF methods. The energy barrier of the transition state of the electrocyclic reaction of bis(allene) on the conrotatory pathway is 26.75 kcal/mol above bis(allene). The energy barrier height is lower by 22.6 kcal/mol than that of butadiene[5] and 10.5 kcal/mol lower than that on the disrotatory pathway of hexatriene.[4] The low energy barrier of the transition state of bis(allene) arises from the orbital interactions of the side π' orbitals and the vertical π orbitals. Namely, the orthogonality between the side π' orbital ($p_1\pi'$ and $p_6\pi'$) and the vertical π orbital ($p_2\pi$ and $p_5\pi$) collapsed near the transition state. Then the electrocyclic reaction system changes from a four-electron four-orbital system such as butadiene to an eight-electron eight-orbital system. This orbital interaction mechanism along the IRC pathway was also explained by the CiLC analysis.

For the electrocyclic reaction of vinylallene, the geometrical variation from the reactant (vinylallene) with C_s symmetry to the transition state is similar to that on the conrotatory pathway of bis(allene). Therefore, the reaction mechanism is the same as that on the conrotatory pathway of bis(allene). The transition state is 8.5 kcal/mol higher than that on the conrotatory pathway of bis(allene). This probably comes from fewer orbital interaction sets for new σ bond formation than that of bis(allene). Namely, the new σ bond of bis(allene) is formed from four-orbital interactions: the vertical π−vertical π ($p_2\pi-p_5\pi$), the vertical π−side π ($p_2\pi-p_5\pi'$ and $p_2\pi'-p_5\pi$), and the side π−side π ($p_2\pi'-p_5\pi'$). For vinylallene, the new σ bond is formed from two orbital interactions: the vertical π−vertical π ($p_1\pi$ -$p_4\pi$) and the vertical π−side π ($p_1\pi-p_4\pi'$).

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Supporting Information Available: Figures of weights of singlet coupling and polarization terms of some orbital interactions by CiLC analysis. This materual is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Verlag Chemie: Weinheim, Germany, 1970.

(2) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.

(3) Sakai, S. *J. Phys. Chem. A*, in press.

(4) Sakai, S.; Takane, S. *J. Phys. Chem. A* **1999**, *103*, 2878.

(5) Sakai, S. *J. Mol. Struct. (THEOCHEM)* **1999**, *461*−*462*, 283.

(6) Sakai, S. *Chem. Phys. Lett.* **1998**, *287*, 263.

(7) Sakai, S. *Chem. Phys. Lett.* **2000**, *319*, 687.

(8) Lee, P. S.; Sakai, S.; Horstermann, P.; Roth, W. R.; Kallel, E. A.; Houk, K. N. *J. Am. Chem. Soc.* **2003**, *125*, 5839.

(9) Pasto, D. J.; Yang, S. H. *J. Org. Chem.* **1989**, *54*, 3544.

(10) Pasto, D. J.; Kong, W. *J. Org. Chem.* **1989**, *54*, 4028.

(11) Toda, F.; Garratt, P. *Chem. Rev.* **1992**, *92*, 1685.

(12) Murakami, M.; Amii, H.; Itami, K.; Ito, Y. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1476.

(13) Lopez, S.; Rey, J. G.; Rodriguez, J.; Lera, A. R. *Tetrahedron Lett.* **1995**, *36*, 4669.

(14) Delas, C.; Urabe, H.; Sato, F. *J. Am. Chem. Soc*. **2001**, *123*, 7937.

(15) Murakami, M.; Ashida, S.; Matsuda, T. *J. Am. Chem. Soc*. **2004**, *126*, 10838.

(16) Lopez, S.; Rodriguez, J.; Rey, J. G.; Lera, A. R. *J. Am. Chem. Soc.* **1996**, *118*, 1881.

(17) Roos, B. In *Advances in chemical physics*; Lawley, K. P., Ed.; Wiley: New York, 1987; Vol. 69, Part II, p 399.

(18) Hariharan, P. C.; Pople, J. A. *Theo. Chim. Acta* **1973**, *28*, 213.

(19) Nakano, H. *J. Chem. Phys.* **1993**, *99*, 7983.

(20) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 416.

(21) Ishida, K.; Morokuma, K.; Komornicki, A. *J. Chem. Phys.* **1977**, *66*, 2153.

(22) Cundari, T. R.; Gordon, M. S. *J. Am. Chem. Soc*. **1991**, *113*, 5231.

(23) Sakai, S. *J. Phys. Chem. A* **1997**, *101*, 1140.

(24) Sakai, S. *Int. J. Quantum Chem.* **1998**, *70*, 291.

(25) Foster, J. M.; Boys, S. F. *Rev. Mod. Phys.* **1960**, *32*, 300.

(26) Sakai, S. *J. Phys. Chem. A* **2006**, *110*, 6339 and the references in it.

(27) Schmidt, M. W.; Buldridge, K. K.; Boatz, J. A.; Jensen, J. H.; Koseki, Gordon, M. S.; Nguyen, K. A.; Windus, T. L.; Elbert, S. T. *QCPE Bull.* **1990**, *10*, 52.

(28) Frisch, K. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheseman, J. R.; Montgomery, J. A.; Vreven, T., Jr.; Kudin, K. N.: Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, D.; Raghavachari, K.; Foresman, J, B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003.

(29) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.