

Criteria for pericyclic and pseudopericyclic character of electrocyclization of (Z)-1,2,4,6-heptatetraene and (2Z)-2,4,5-hexatriene-1-imine

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Abstract The electrocyclic reaction mechanisms of (Z)-1,2,4,6-heptatetraene and (2Z)-2,4,5-hexatriene-1-imine were studied by ab initio MO methods. The activation energy barrier height of the electrocyclic reaction of (Z)-1,2,4,6-heptatetraene is extremely a low energy barrier of 8.58 kcal/mol by a MRMP method. The activation energy barrier height of the electrocyclic ring closure of the *trans*-type of (2Z)-2,4,5-hexatriene-1-imine is lower by 3.18 kcal/mol than that of (Z)-1,2,4,6-heptatetraene. These low energy barriers come from some orbital interactions relating to allene group. For the reaction of (Z)-1,2,4,6-heptatetraene, the interactions of the vertical and side π orbitals of the allene group with another terminal π orbital are important at the transition state. The interaction of the vertical π orbital of allene group with a lone pair orbital of N atom is dominant at the transition state of the reaction of the *trans*-type of (2Z)-2,4,5-hexatriene-1-imine. The electrocyclic mechanism of the *cis*-type of (2Z)-2,4,5-hexatriene-1-imine was also discussed.

1 Introduction

Pseudopericyclic reactions were originally defined by Lemal and co-workers [1] as pericyclic reactions in which there is a disconnection in the cyclic overlapping of the active orbitals because of the presence of orthogonal orbital systems. Recently there has been an interesting controversy [2] concerning the intimate nature of bonding at the transition states for the electrocyclization of (Z)-1,2,4,6-heptatetraene and its

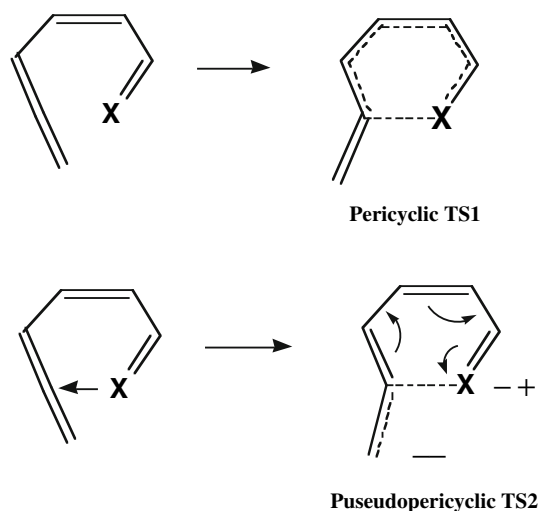
heterosubstituted analogues, (2Z)-2,4,5-hexatriene-1-imine and (2Z)-2,4,5-hexatrienal. It is whether the reactions occur through a nucleophilic addition of pseudopericyclic nature via transition state. There are two possible reaction processes. One is a pericyclic disrotatory electrocyclization via transition state TS1 as shown in Scheme 1, and the other is a pseudopericyclic nucleophile addition of the heteroatom lone pair via transition state TS2.

DeLear et al. [3,4] calculated the transition states of electrocyclic reactions of (Z)-1,2,4,6-heptatetraene, (2Z)-2,4,5-hexatriene-1-imine, and (2Z)-2,4,5-hexatrienal by the B3LYP method. They concluded that the cyclic reaction of (Z)-1,2,4,6-heptatetraene occurs through the disrotatory mechanism with a pericyclic and aromatic TS1, and the cyclic reactions of heterosubstituted analogues (2Z)-2,4,5-hexatriene-1-imine and (2Z)-2,4,5-hexatrienal involve a nucleophilic addition of the lone pair electron of heteroatom through a pseudopericyclic and not an aromatic TS2. On the other hand, Rodriguez-Otero and Cabaleiro-Lago [5,6] also studied the mechanisms of cyclic reactions of (Z)-1,2,4,6-heptatetraene, (2Z)-2,4,5-hexatriene-1-imine, and (2Z)-2,4,5-hexatrienal by the B3LYP calculations. They concluded that the three processes were essentially disrotatory pericyclic electrocyclization even through they are assisted by the electron lone pair on the heteroatom. These reactions were also discussed from the viewpoint of electro density [7,8].

From the above-reported evidence, the criteria between pericyclic and pseudopericyclic mechanisms for (Z)-1,2,4,6-heptatetraene and its heterosubstituted analogues is not clear because of inadequate definition of pseudopericyclic reaction and the lack of the intimate nature of electronic states at these transition states. With the aim of searching for more insight concerning the reaction mechanisms of these systems, we will analyze the mechanisms by a CiLC-IRC method. The CiLC-IRC method is a combination of configuration

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Scheme 1

interaction (CI), localized molecular orbital (LMO), and complete active space self-consistent field (CASSCF) analysis along the reaction pathway.

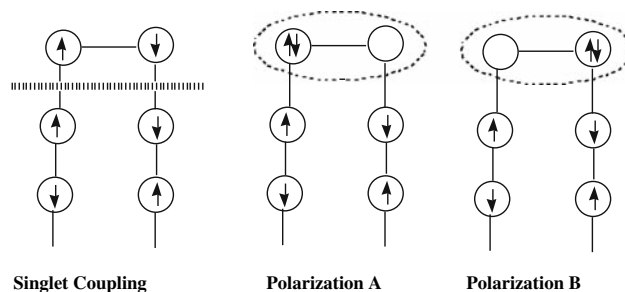
In this paper, the reaction mechanisms of electrocyclic reaction of (Z)-1,2,4,6-heptatetraene and (2Z)-2,4,5-hexatriene-1-imine were proposed by the CiLC-IRC analysis. The criteria of pericyclic and pseudopericyclic character of these reactions are also discussed.

2 Theoretical methods

For the electrocyclic reactions of (Z)-1,2,4,6-heptatetraene and (2Z)-2,4,5-hexatriene-1-imine, the equilibrium geometries of the reactants, products, and transition states were determined with analytically calculated energy gradients using the complete active space (CAS) self-consistent-field (SCF) method [9], following initial calculations using density functional theory with the 6-31G(d) basis set [10]. In our previous paper [11], the role of two types π orbitals (vertical π and side π orbitals) of allene group for the cyclization of bisallene and vinylallene was pointed out by the CiLC-IRC analysis. Therefore, eight active orbitals and eight electrons for (Z)-1,2,4,6-heptatetraene and nine active orbitals and ten electrons for (2Z)-2,4,5-hexatriene-1-imine were selected for CASSCF calculations, and all configurations in the active spaces were generated. For (Z)-1,2,4,6-heptatetraene, the eight-orbitals active space corresponds to eight p-orbitals of four π orbitals and four π^* orbitals relating the bond forming and breaking process. For (2Z)-2,4,5-hexatriene-1-imine, the nine-orbitals active space corresponds to those for (Z)-1,2,4,6-heptatetraene plus the lone pair orbital of nitrogen atom. Additional calculations were performed to obtain improved energy comparisons: the energy calcu-

lations at the CASSCF-optimized structures with electron correlation incorporated through the multiconfigurational second order Møller–Plesset perturbation theory (MRMP) [12]. The density functional calculations were also performed. The density functional employed was the Becke7s three parameter nonlocal exchange functional with the Lee, Yang, and Parr correlation function (B3LYP) [13–15]. The intrinsic reaction coordinate (IRC) [16,17] was followed from the transition structure toward both the reactants and the products at the CASSCF and/or B3LYP levels.

To interpret the electronic mechanisms of the reaction processes, configuration interaction (CI) localized molecular orbital (LMO)-CASSCF analyses were carried out according to a method described in detail elsewhere [18–20] using the 6-31G(d) basis set. In this analysis, the CASSCF wavefunction was initially constructed to obtain the starting set of orbitals for the localization procedure, after which the CASSCF optimized orbitals were localized by the Boys localization procedure [21]. Using the resulting localized MOs as a basis, a direct full CI [22] was performed to generate the electronic structures and their relative weights in the atomic orbital-like wave functions. These analyses were carried out along the intrinsic reaction coordinate (IRC) of each reaction. The total energy, as calculated by the CI procedure, corresponds to that by the CASSCF calculation, and the relative weights of the electronic states having different CI configurations were expected to indicate the variations of electronic bond-forming or bond-breaking. The CI procedure is referred to hereafter as the CiLC-IRC method. 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). The variation of the weights of these special configurations for each bond along the IRC pathway was most important. Therefore, it was postulated that the singlet coupling and polarization terms could be describing the electronic structure of one bond, and that this description is related to a usual presentation by the valence bond (VB) theory. Interpretation using such an approach has been successful for interpreting some reaction mechanisms,



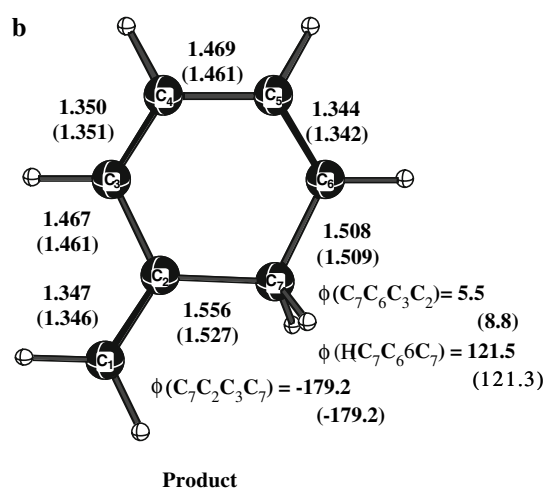
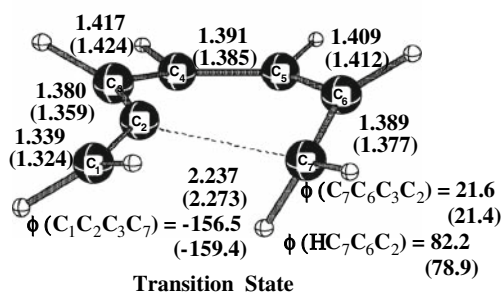
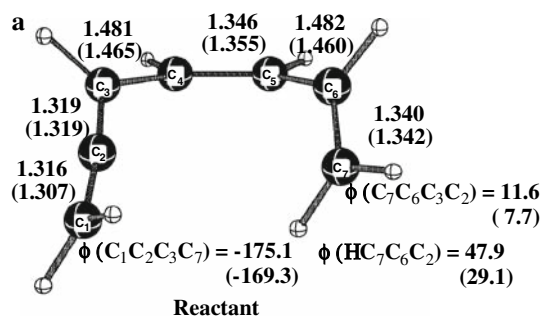
Scheme 2

as reported in previous papers [11, 23–31]. Calculations for the CiLC-IRC analysis were performed using the GAMESS software package [32]. Other calculations were carried out using Gaussian03 program [33].

3 Results and discussion

3.1 (Z)-1,2,4,6-heptatriene

The stationary point geometries for [1,5]-electrocyclic reaction of (Z)-1,2,4,6-heptatriene are shown in Fig. 1, and the total energies and the relative energies are listed in Table 1.



From the comparison of the CC bonds of the reactants and the transition state, the transition state is an early transition state. It has been considered that the cyclic reaction of (Z)-1,2,4,6-heptatriene is the similar reaction mechanism to that of cZc-hexatriene, which occurs through the disrotatory reaction pathway with C_s symmetry. The approximate shape of the C₂ – C₃ – C₄ – C₅ – C₆ – C₇ part of the reactant, (Z)-1,2,4,6-heptatriene, is similar to the C_s symmetry shape of cZc-hexatriene which lead to the disrotatory pathway. Of course, the dihedral angle of cZc-hexatriene [34] corresponding to $\phi(C_7C_6C_3C_2)$ of (Z)-1,2,4,6-heptatriene is zero degree for both reactant and transition state on the disrotatory pathway. But the dihedral angle of $\phi(C_7C_6C_3C_2)$ of (Z)-1,2,4,6-heptatriene is 11.6° at the CASSCF level, and the dihedral angle of the transition state increases in 21.6°. The increasing of the dihedral angle at the transition state indicates that the cyclic reaction mechanism of (Z)-1,2,4,6-heptatriene is not entirely the same to that of cZc-hexatriene. If the cyclization mechanism of (Z)-1,2,4,6-heptatriene is the same to that of cZc-hexatriene on the symmetry allowed disrotatory path, the dihedral angle of $\phi(C_7C_6C_3C_2)$ for the transition state has to reduce to near 0°.

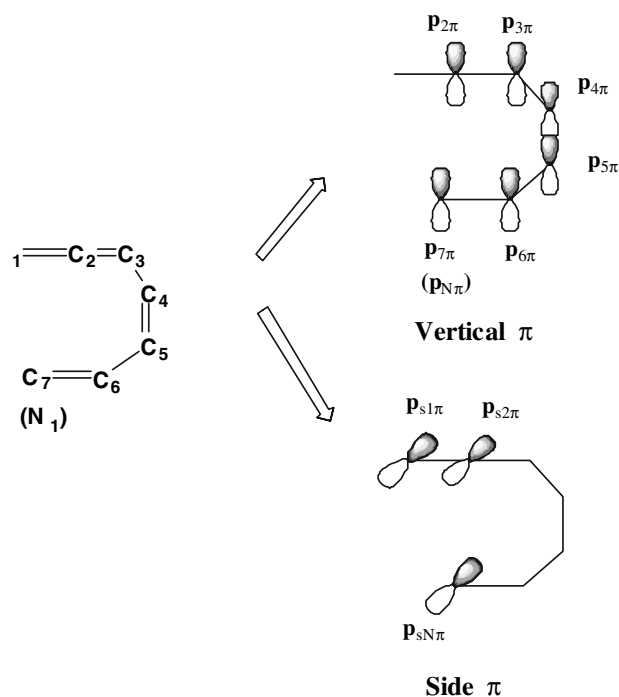


Fig. 1 Stationary point geometries (in angstroms and degrees) for electrocyclic reaction of (Z)-1,2,4,6-heptatriene at the CASSCF/6-31G(d) and the B3LYP/6-31G(d) levels. The B3LYP values are indicated in parentheses

To study the variation of each bond along the reaction path, the electronic weights of the bonds by the CiLC analysis along the CASSCF IRC pathway are shown in Fig. 2. The exchange between the π bonds ($p_{2\pi}$ – $p_{3\pi}$, $p_{4\pi}$ – $p_{5\pi}$, and $p_{6\pi}$ – $p_{7\pi}$) of the reactants side and that ($p_{3\pi}$ – $p_{4\pi}$ and $p_{5\pi}$ – $p_{6\pi}$) of the product side occurs smoothly at near the

Table 1 The total energy (hartree) and the relative energy (kcal/mol) for the stationary points of the electrocyclic reaction of (Z)-1,2,4,6-heptatetraene and (2Z)-2,4,5-hexatriene-1-imine

	Total energy		Relative energy	
	CASSCF	CAS-MP2	CASSCF	CAS-MP2
(Z)-1,2,4,6-heptatetraene	–269.72893	–270.551948	0.0	0.0
Transition State	–269.69452	–270.50581	21.59	8.58
Product	–269.78659	–270.58207	–36.19	–39.28
(2Z)-2,4,5-hexatriene-1-imine				
<i>Trans</i> -type	–285.73489	–286.55025	0.0	0.0
Transition state	–285.70369	–286.54164	19.58	5.40
Product	–285.79195	–286.61491	–35.81	–40.58
<i>Cis</i> -type	–285.73583	–286.55172	0.0	0.0
Transition state	–285.68837	–286.52896	29.79	14.29
Product	–285.79195	–286.61491	–35.22	–39.66

transition state. From the new σ bond formation, the bonds of the side-vertical $p_{s2\pi}-p_{7\pi}$ and the vertical-vertical $p_{2\pi}-p_{7\pi}$ grow up from near the transition state, and the weights of the bonds are almost equal in the region from $0.5 \text{ bohr} \times \text{amu}^{1/2}$ to $-0.5 \text{ bohr} \times \text{amu}^{1/2}$ of the IRC. The equal weights of the bonds of the side-vertical $p_{s2\pi}-p_{7\pi}$ and the vertical-vertical $p_{2\pi}-p_{7\pi}$ correspond to the dihedral angle of $\phi(C_7C_6C_3C_2)$ of the transition state of (Z)-1,2,4,6-heptatetraene. Namely the orbital $p_{7\pi}$ have to interact with the orbitals of the side $p_{s2\pi}$ and the vertical $p_{2\pi}$ at the same time keeping with in-phase of the $p_{7\pi}$ and $p_{2\pi}$ orbitals (disrotatory pathway). For the region of the product side from $-0.5 \text{ bohr} \times \text{amu}^{1/2}$ of the IRC, the weight of the orbital interaction of the side-vertical $p_{s2\pi}-p_{7\pi}$ is larger than that of the vertical-vertical $p_{2\pi}-p_{7\pi}$. This means the side π orbital of $p_{s2\pi}$ have a important role of the cyclic reaction, and the cyclic reaction is not the typical disrotatory mechanism as that of *c*(Z)c-hexatriene. Such cyclization mechanism including allene is similar to that of bisallene and vinylallene as shown in the previous paper [9]. The variation of the weights of the orbital interaction of the side-vertical $p_{s2\pi}-p_{7\pi}$ and the vertical-vertical $p_{2\pi}-p_{7\pi}$ corresponds to that of the reduction of the side-side $p_{s1\pi}-p_{s2\pi}$ orbital interaction. The side-vertical $p_{s1\pi}-p_{2\pi}$ orbital interaction grows up from the transition state and the increase of the orbital interaction is a little later than those of the orbital interactions of the side-vertical $p_{s2\pi}-p_{7\pi}$ and the vertical-vertical $p_{2\pi}-p_{7\pi}$. Namely the reaction mechanism can be discriminated between the π bond exchange in the ring and π - σ bonds exchange. The activation energy barrier of the cyclic reaction of (Z)-1,2,4,6-heptatetraene is 8.5 kcal/mol, and is much lower than that (36.7 kcal/mol) of *c*(Z)c-hexatriene at the MRMP level. The activation energy barrier is also much lower than that (35.3 kcal/mol) of vinylallene. The difference between the activation energies of the cyclic reactions of (Z)-1,2,4,6-heptatetraene and vinylallene probably cause from the difference of geometrical strain energies. In fact, while

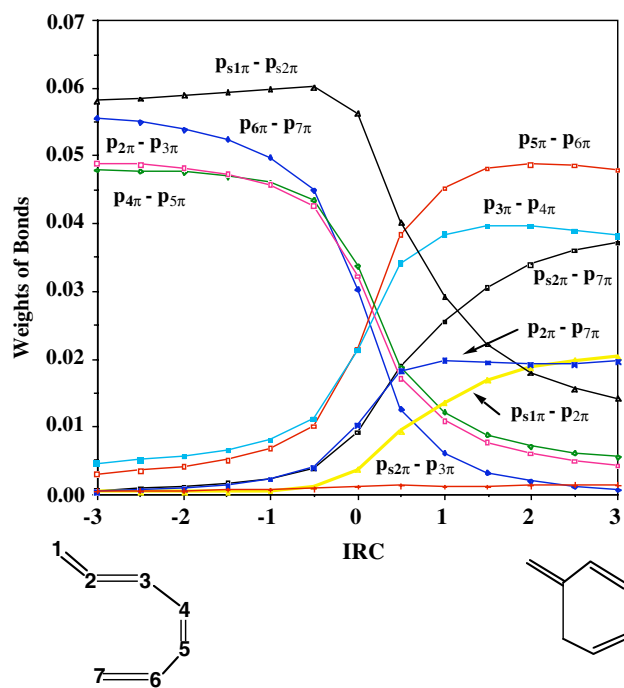


Fig. 2 Weights of some orbital interactions by CiLC analysis along the IRC pathway of electrocyclic reaction of (Z)-1,2,4,6-heptatetraene

the heat of reactions from (Z)-1,2,4,6-heptatetraene to the product is -39 kcal/mol , that from vinylallene is -2 kcal/mol .

3.2 (2Z)-2,4,5-hexatriene-1-imine

The stationary point geometries for [1,5]-electrocyclic reactions of (2Z)-2,4,5-hexatriene-1-imine are shown in Fig. 3. For the analogues reactions of (Z)-1,2,4,6-heptatetraene, two types of (2Z)-2,4,5-hexatriene-1-imine were studied. One is a *trans*-type of imine part ($\text{HN}_1\text{C}_6\text{C}_5$) and the other is a *cis*-type. The former is the inward direction for the lone pair orbital

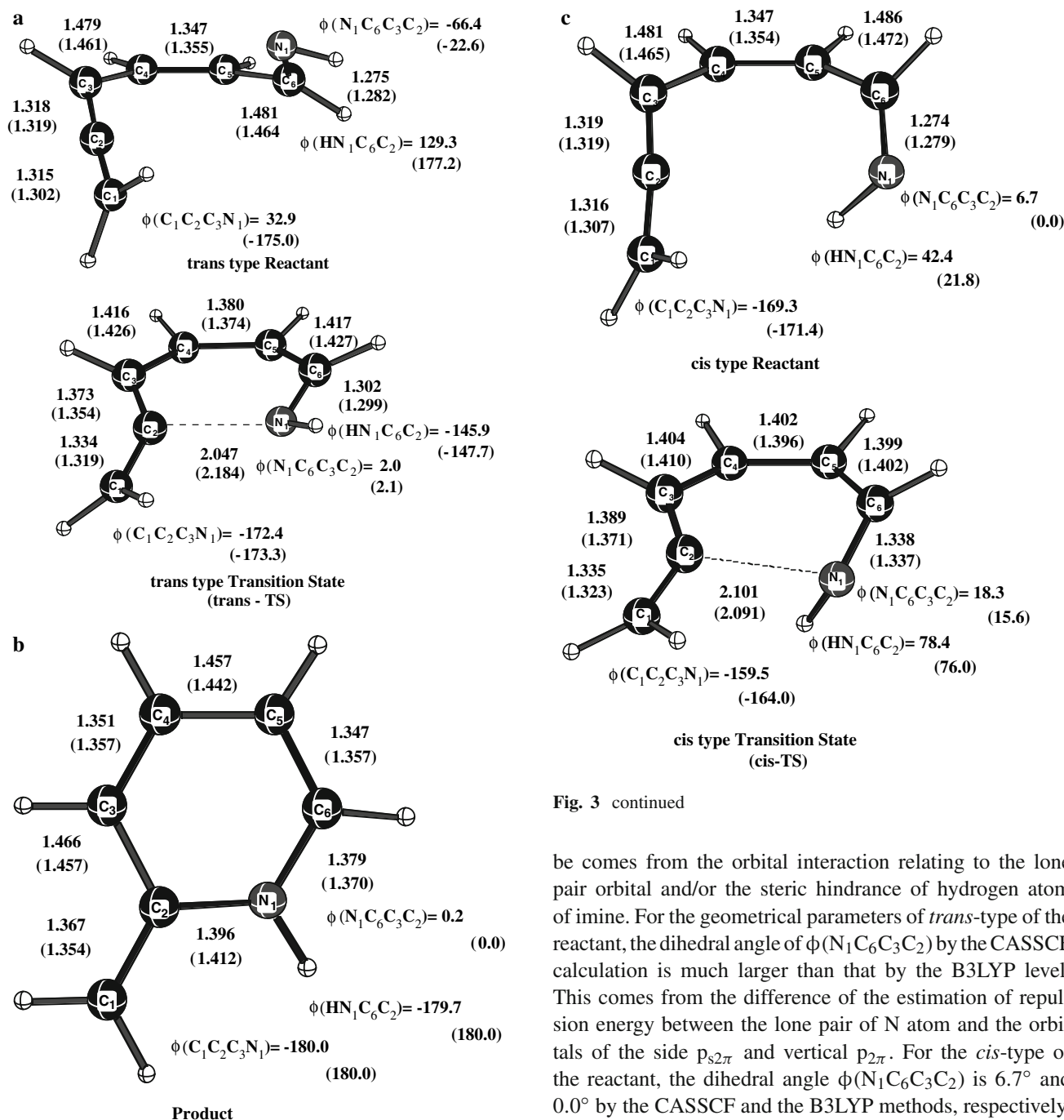


Fig. 3 Stationary point geometries (in angstroms and degrees) for electrocyclic reaction of (2Z)-2,4,5-hexatriene-1-imine at the CASSCF/6-31G(d) and the B3LYP/6-31G(d) levels. The B3LYP values are indicated in parentheses

tal of nitrogen and the latter is the outward direction. The lone pair orbital of the *trans*-type is involved in the reaction, while that of the *cis*-type does not. The *trans*-type is about 1 kcal/mol higher in energy than the *cis*-type. For the transition state, the *trans*-type is about 10 kcal/mol lower in energy than the *cis*-type. This energy difference of 10 kcal/mol may

Fig. 3 continued

be comes from the orbital interaction relating to the lone pair orbital and/or the steric hindrance of hydrogen atom of imine. For the geometrical parameters of *trans*-type of the reactant, the dihedral angle of $\phi(N_1C_6C_3C_2)$ by the CASSCF calculation is much larger than that by the B3LYP level. This comes from the difference of the estimation of repulsion energy between the lone pair of N atom and the orbitals of the side $p_{s2\pi}$ and vertical $p_{2\pi}$. For the *cis*-type of the reactant, the dihedral angle $\phi(N_1C_6C_3C_2)$ is 6.7° and 0.0° by the CASSCF and the B3LYP methods, respectively. For the transition state, the dihedral angle of $\phi(N_1C_6C_3C_2)$ of *trans*-TS is 2.0° , and is obviously different from that of (Z)-1,2,4,6-heptatetraene. On the other hand, the dihedral angle of $\phi(N_1C_6C_3C_2)$ of *cis*-TS is 18.3° , and is about 3° smaller than that of (Z)-1,2,4,6-heptatetraene. Consequently, the cyclization mechanism of the *cis*-type of (2Z)-2,4,5-hexatriene-1-imine is probably similar to that of (Z)-1,2,4,6-heptatetraene. But the cyclization mechanism of the *trans*-type of (2Z)-2,4,5-hexatriene-1-imine is different from that of (Z)-1,2,4,6-heptatetraene. The activation energy barrier of *trans*-type is only 5.4 kcal/mol at the MRMP level, and is about 3 kcal/mol lower than that of (Z)-1,2,4,6-heptatetraene.

The activation energy barrier of the *cis*-type is 14.3 kcal/mol and is higher by 5.7 kcal/mol than that of (*Z*)-1,2,4,6-heptatetraene.

The weights of the orbital interactions by the CiLC analysis along the IRC pathways at the B3LYP level for the cyclic reactions of the *trans*-type and the *cis*-type of (*Z*)-2,4,5-hexatriene-1-imine were shown in Figs. 4 and 5. In the figures, 8D-Refer and 9D-Refer mean the weights of the reference configurations of double electrons occupied in $p_{N\pi}$ and $p_{sN\pi}$, respectively. The weights of other orbital interactions, the singlet coupling term and the polarization terms, were calculated on the basis of configurations of 8D-Refer and 9D-Refer. From Fig. 4, the weight of 9D-Refer decreases from the reactant side through the transition state. This means the $p_{sN\pi}$ (lone pair) orbital is extremely concerned in the reaction. The π bonds of $p_{2\pi}-p_{3\pi}$, $p_{4\pi}-p_{5\pi}$, $p_{6\pi}-p_{N\pi}$, and $p_{6\pi}-p_{sN\pi}$ decrease from the reactant side to the product side and the π bonds of $p_{5\pi}-p_{6\pi}$ and $p_{3\pi}-p_{4\pi}$ increase from near the transition state to the product side. The crossing points of the increasing π orbital group and the decreasing π orbital group along the IRC pathway for the *trans*-type is later than that for (*Z*)-1,2,4,6-heptatetraene. Although the crossing point of the side-vertical $p_{s1\pi}-p_{2\pi}$ and the side-side $p_{s1\pi}-p_{s2\pi}$ of the cyclic reaction of (*Z*)-1,2,4,6-heptatetraene is about -2 bohr \times amu^{1/2} of the IRC pathway, that of the *trans*-type of (*Z*)-2,4,5-hexatriene-1-imine is much far from the transition state to the product side. The weight of the orbital interaction of the $p_{sN\pi}-p_{2\pi}$ is largest in the σ bond formations between C₂ and N atoms at near the transition state. The second larg-

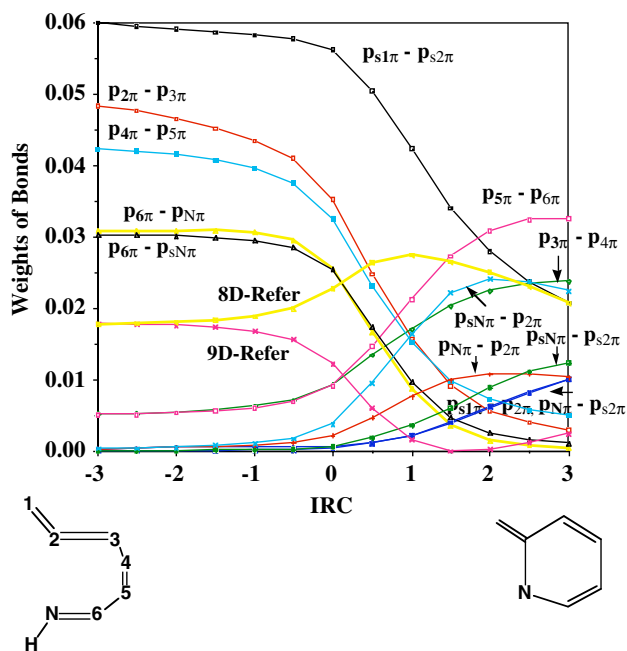


Fig. 4 Weights of some orbital interactions by CiLC analysis along the IRC pathway of electrocyclic reaction of the *trans*-type (*Z*)-2,4,5-hexatriene-1-imin

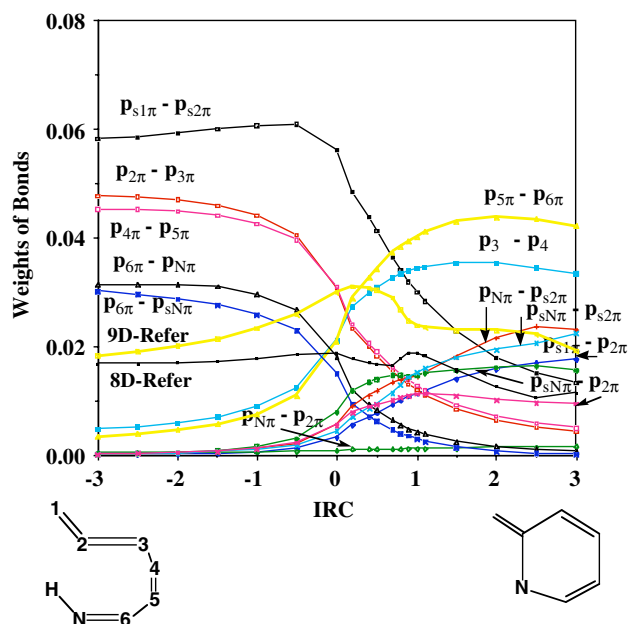


Fig. 5 Weights of some orbital interactions by CiLC analysis along the IRC pathway of electrocyclic reaction of the *cis*-type (*Z*)-2,4,5-hexatriene-1-imin

est weight is the orbital interaction of $p_{N\pi}-p_{2\pi}$. Namely, the vertical π orbital $p_{2\pi}$ for the cyclic reaction of the *trans*-type (*Z*)-4,5,6-hexatriene-1-imine relates much than the side π orbital of $p_{s2\pi}$ at near the transition state. This orbital interaction of allene part is very different from the reaction of (*Z*)-1,2,4,6-heptatetraene. Namely the vertical and side π orbitals of C₂ atom of (*Z*)-1,2,4,6-heptatetraene interact almost equal weights with the π orbital of C₇ atom at near the transition state and the vertical π orbital ($p_{2\pi}$) of C₂ atom of the *trans*-type (*Z*)-2,4,5-hexatriene-1-imine interacts much more than the side π orbital ($p_{s2\pi}$) with the orbitals of N atom. The large interaction of $p_{2\pi}$ with the orbital of N atom corresponds to the small dihedral angle (2.0°) of $\phi(N_1C_6C_3C_2)$ at the transition state. This also corresponds to the position of crossing parts of the side-side $p_{s1\pi}-p_{s2\pi}$ and the side-vertical $p_{s1\pi}-p_{2\pi}$ as described above.

For the cyclic reaction of the *cis*-type of (*Z*)-2,4,5-hexatriene-1-imine, the weights of π orbital interactions of $p_{2\pi}-p_{3\pi}$, $p_{4\pi}-p_{5\pi}$, $p_{6\pi}-p_{N\pi}$, and $p_{6\pi}-p_{sN\pi}$ decrease from the reactant side to the product side and those of $p_{3\pi}-p_{4\pi}$ and $p_{5\pi}-p_{6\pi}$ increase from the reactant side to the product side. The crossing point of the increasing π orbital group and the decreasing π orbital group is almost at near the transition state, and is similar to that for (*Z*)-1,2,4,6-heptatetraene. For σ bond formation between C₂ and N atoms, the weight of the vertical-vertical $p_{N\pi}-p_{2\pi}$ interaction is a little larger than the other interactions as the vertical-side $p_{N\pi}-p_{s2\pi}$, the side-vertical $p_{sN\pi}-p_{2\pi}$, and the side-side $p_{sN\pi}-p_{s2\pi}$ at near the transition state. The weights of the interactions of the vertical-side $p_{N\pi}-p_{s2\pi}$, the side-vertical $p_{sN\pi}-p_{2\pi}$, and the

side-side $p_{sN\pi}$ – $p_{s2\pi}$ are almost the same at near the transition state. Therefore, the cyclic reaction of the *cis*-type is similar to that of (Z)-1,2,4,6-heptatetraene.

4 Conclusion

The potential energy surfaces of the electrocyclic reactions of (Z)-1,2,4,6-heptatetraene and (2Z)-2,4,5-hexatriene-1-imine were calculated by the ab initio CASSCF and the density functional methods. The energy barrier of the transition state of the electrocyclic reaction of (Z)-1,2,4,6-heptatetraene is extremely low (8.58 kcal/mol). The energy barrier height is lower by 28.12 kcal/mol than that of *cZc*-hexa-1,3,5-triene and 26.67 kcal/mol lower than that of vinylallene. The low energy barrier of the transition state of (Z)-1,2,4,6-heptatetraene arises from the aromaticity at the transition state. Namely, the orthogonality between the side π orbital ($p_{s1\pi}$) and the vertical π orbital ($p_{2\pi}$) collapsed at near the transition state. Then the electrocyclic reaction system occurs also through two-type six-electron six-orbital systems of $p_{7\pi}$ – $p_{2\pi}$ – $p_{3\pi}$ – $p_{4\pi}$ – $p_{5\pi}$ – $p_{6\pi}$ and $p_{7\pi}$ – $p_{s2\pi}$ – $p_{3\pi}$ – $p_{4\pi}$ – $p_{5\pi}$ – $p_{6\pi}$ and an eight-electron eight-orbital system of $p_{7\pi}$ – $p_{s2\pi}$ – $p_{s1\pi}$ – $p_{2\pi}$ – $p_{3\pi}$ – $p_{4\pi}$ – $p_{5\pi}$ – $p_{6\pi}$. This orbital interaction mechanism along the IRC pathway was explained by the CiLC analysis.

For the electrocyclic reaction of (2Z)-2,4,5-hexatriene-1-imine, the two-type reactions of the *trans*-type and the *cis*-type of H–N–C–C part were studied. The energy barrier height at the transition state of the electrocyclic mechanism of the *trans*-type is 5.40 kcal/mol above the *trans*-type (2Z)-2,4,5-hexatriene-1-imine, and is lower by 8.89 kcal/mol than that of the *cis*-type. For the *trans*-type, the orbital interaction of $p_{sN\pi}$ – $p_{2\pi}$ is dominant to the σ bond formation of C₂ and N atoms at the transition state, because the $p_{sN\pi}$ (lone pair) overhangs to the direction of C₂ atom. For the *cis*-type, the weight of the orbital interaction of $p_{N\pi}$ – $p_{2\pi}$ is a little larger than others at near the transition state. The reaction mechanism of the *cis*-type is similar to that of (Z)-1,2,4,6-heptatetraene.

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