

Theoretical Study on the Aromaticity of Transition States in Pericyclic Reactions

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Received: October 20, 2005; In Final Form: March 12, 2006

The aromaticity of transition states in pericyclic reactions such as electrocyclic reactions, cycloaddition reactions, and sigmatropic shifts was studied by the IDA (index of deviation from aromaticity) on the basis of a CASSCF wave function. The aromaticity defined by the IDA classified the allowed and forbidden transition states of pericyclic reactions treated here. The order of the aromaticity levels corresponds to that of the energy barriers of some reactions. The difference between the aromaticity defined by the IDA and that by the magnetic properties as a NICS is also discussed.

1. Introduction

Of all the theoretical concepts that constitute the rational basis of modern organic chemistry, the concept of aromaticity is one of the most general but at the same time one of the most vaguely defined. Because aromaticity is not an observable quantity and is not directly measurable, it must be defined by convention. Generally, aromaticity has been defined as the difference between π -electron resonance energies of a noncyclic π -conjugated compound and a cyclic π -conjugated compound. Although the definition of aromaticity on the basis of π -electron resonance energy can be readily understood and is useful for the discussion of stabilization energy, the treatment of complex compounds such as nonplanar molecules remains difficult. Aromaticity has also been treated magnetically,^{1–3} and the nucleus-independent chemical shift (NICS) as an index of aromaticity was proposed.⁴ The values of the NICS are adequate for the classification of aromaticity and anti-aromaticity, but measurements of the order for some compounds are not adequate as shown in previous papers.^{5,6}

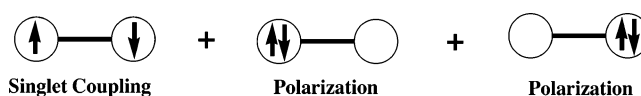
Recently, I have presented a new index⁷ of aromaticity, IDA (index of deviation from aromaticity), for a ring-unit of compounds on the basis of a CiLC method in reference to ab initio molecular orbital calculations. The CiLC method^{8–10} is a combination of configuration interaction (CI), localized molecular orbital (LMO), and complete active space self-consistent field (CASSCF) analysis. The criterion^{6,11} of aromaticity with IDA was defined as the deviation of equality for the electronic structure of each bond in the ring-compound and by the narrowness of the gap between the weights of the singlet coupling and polarization terms for each bond. The IDA can treat not only planar compounds but also nonplanar compounds.

In this paper, we focus our attention on the aromaticity by the IDA for the forbidden and allowed transition states of pericyclic reactions. To rationalize the fact that the forbidden reaction has a much higher activation barrier than the allowed reaction, it has been suggested that the transition states of a forbidden reaction have less aromatic character.

2. Computational Methods and an Aromatic Model

The geometries and the frequencies of all stationary points treated here were determined with analytical calculated energy gradients using the CASSCF method¹² with 6-31G(d) basis set.¹³

SCHEME 1



For CASSCF calculations, all active spaces corresponding to valence π , π^* , σ , and σ^* orbitals relating to each reaction were included, and all configurations in active spaces were generated.

The CiLC calculations were used to interpret the aromaticity. This procedure has been used by us for reaction mechanism analyses^{14–27} and aromaticity analyses,^{6,7,11} and the details of the method can be found in previous papers.^{6,9–11,14–27} Briefly, the CASSCF calculation was carried out to obtain a starting set of orbitals for the localization procedure. Boys localization²⁸ was then applied to give localized orbitals with a highly atomic nature. Using the localized MOs as a basis, a full CI at the determinant level was used to generate electronic structures and to evaluate the relative weights of configurations in the atomic orbital-like wave functions. The total energy calculated by the CI procedure corresponds well to that obtained from the CASSCF calculation. In the notation of the valence bond-like model, the electronic structures of a bond on the basis of CiLC calculation were present roughly as one singlet coupling term and two polarization terms (Scheme 1). In the scheme, a circle indicates an atomic-like orbital obtained by the localization process in the CiLC calculations. The representation with three terms (one singlet coupling and two polarization terms) for a bond has been successful to explain the bond formation and bond extinction along a chemical reaction path, and also used for the index of aromaticity.

The criterion of aromaticity was defined according to the following conditions on the basis of the CiLC calculations: (A) each weight of the singlet coupling and polarization terms is equal for all bonds and (B) the difference between the weights of the singlet coupling and polarization terms for each bond is small. The first criterion corresponds to the aromaticity of bond length equalization and the second corresponds to the resonance stabilization energy. From the two criterion of aromaticity, the index of deviation from aromaticity (IDA) for an n -cyclic ring can be defined in eqs 1–4.

$$IDA = D_s + D_p + G_{sp} \quad (1)$$

$$D_s = \frac{\left(\sum_{i=1}^n \frac{|S_i - S_{av}|}{S_{av}} \right)}{n} \quad (2)$$

$$D_p = \frac{\left(\sum_{i=1}^n \frac{|PA_i - P_{av}| + |PB_i - P_{av}|}{2P_{av}} \right)}{n} \quad (3)$$

$$G_{sp} = \frac{\left(\sum_{i=1}^n \frac{|S_i - PA_i| + |S_i - PB_i|}{2S_i} \right)}{n} \quad (4)$$

S_i is the weight of the singlet coupling term for the i -th bond, S_{av} is the average of the weights of the singlet coupling terms for all bonds, PA_i and PB_i are the weights of the polarization terms for the i -th bond, P_{av} is the average of the weights of the polarization terms for all bonds, and n is the number of bonds in the ring.

Here, D_s and D_p are the ratios of deviation from the average weights of the singlet coupling and polarization terms, respectively, and they correspond to the requirement of criterion A. The term G_{sp} denotes the average ratio of the difference between the weights of the singlet coupling and polarization terms on the basis of the average singlet coupling.

The CiLC calculations were performed using the GAMESS software package,²⁹ and the others were carried out using Gaussian98.³⁰

3. Results and Discussion

3.1. Electrocyclic Reactions. It is well-known that the electrocyclic reactions for polyene occur through the conrotatory path or the disrotatory path, which corresponds to the symmetry allowed and forbidden reactions from the definition of the orbital symmetry rules such as the Woodward–Hoffmann rule³¹ and the frontier orbital theory.³² The concept of the orbital symmetry rules may be related to the aromaticity for the reaction mechanisms. To study the relationship of the symmetry allowed or forbidden reactions and the aromaticity by the IDA, the geometries and the IDA values of conrotatory (C_2 symmetry) and disrotatory (C_s symmetry) transition states for three electrocyclic reactions (butadiene,^{33–37} 1,3,5-hexatriene,^{19,35,38,39} and 1,3,5,7-octatetraene^{35,36,40}) were calculated and shown in Figure 1. Although the transition state with the C_s symmetry for the electrocyclic reaction of butadiene is not a real transition state (has two negative eigenvalues for the force constant matrix), the others are real transition states. The IDA value of the transition state with the C_2 symmetry of butadiene is less than one-half of that with the C_s symmetry. This corresponds to the reactivity (activation energy barrier heights) of both symmetry allowed and symmetry forbidden reactions of butadiene.

For hexatriene and octatetraene, the IDA value of the transition state with the C_s symmetry of 1,3,5-hexatriene is smaller than that with the C_2 symmetry, and the IDA value of the transition state with the C_2 symmetry of 1,3,5,7-octatetraene is also smaller than that with the C_s symmetry. Consequently the symmetry allowed transition state is more aromatic than the symmetry forbidden one.

For the above three polyenes, the order of the IDA values of the symmetry allowed transition states is that of butadiene > hexatriene > octatetraene. The activation energy barriers for

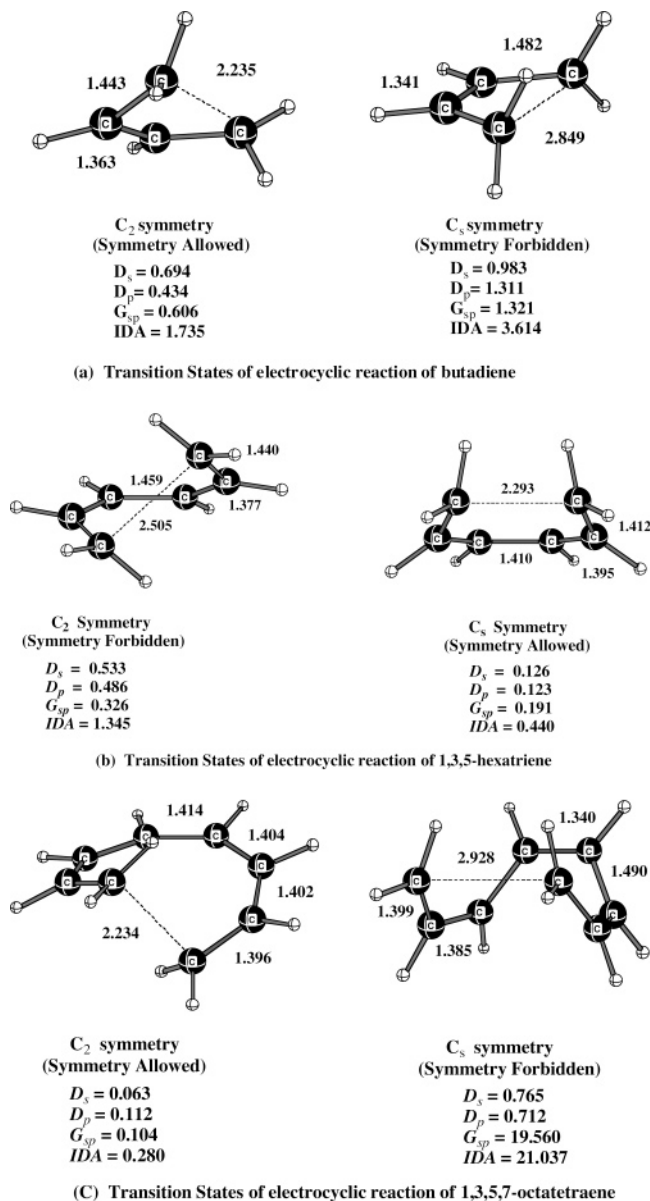


Figure 1. Transition state geometries and their IDA values for electrocyclic reactions.

the symmetry allowed transition states are 52.6 kcal/mol for butadiene, 36.8 kcal/mol for hexatriene, and 21.4 kcal/mol for octatetraene at the CASSCF/6-31G(d) calculation level. Thus, the order of the activation energy barrier height of the symmetry allowed transition states of the three polyenes corresponds to the order of their IDA values. On the other hand, the NICS values⁴¹ of the symmetry allowed transition states of butadiene, hexatriene, and octatetraene are -12.3 , -25.4 , and -6.6 to -12.3 , respectively. Thus, the NICS values show that the symmetry allowed transition state of hexatriene is the most aromatic of the three polyenes. The aromaticity of the NICS, which results from the magnetic property, may not reflect the stabilization energy.

3.2. Diels–Alder Reaction of Butadiene with Ethylene. The Diels–Alder reaction 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.^{14,35,36,42–54} The proposed mechanisms are the concerted, the stepwise diradical, and stepwise zwitterion processes. Recent ab initio studies showed that the cycloaddition of butadiene with ethylene, which is the prototype of the pericyclic [4 + 2] cycloaddition reaction,

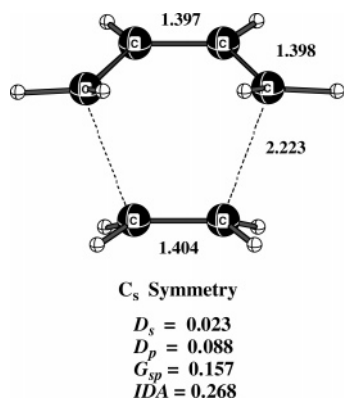
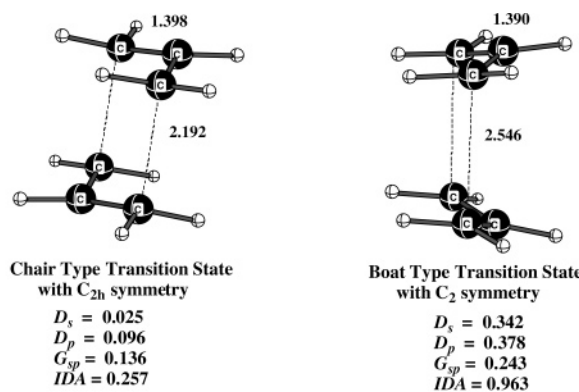


Figure 2. Transition state geometry and the IDA value for the Diels–Alder reaction of butadiene with ethylene.

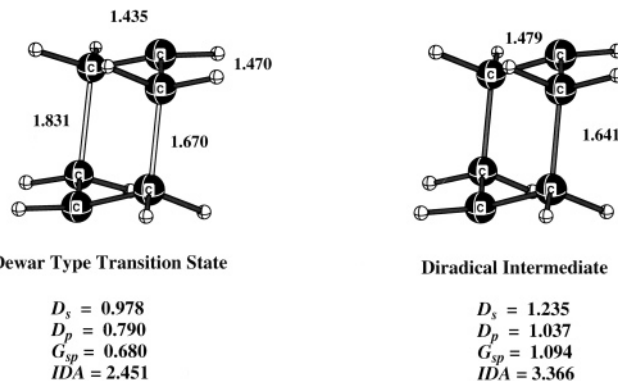
occurs through the concerted mechanism with a C_s symmetrical transition structure. The aromaticity of the transition state structure has been also discussed with some theoretical treatments.^{19,44} The transition state structure and the IDA value for the Diels–Alder reaction of butadiene with ethylene are shown in Figure 2. The IDA value of the transition state is a little larger than that (IDA value = 0.047) of benzene. This means the transition state has an aromatic stabilization character with “the unstable transition state structure”, although the reaction requires a high activation energy. In other words, the activation energy of the reaction is the result that added the stabilization of aromatic property to the unstable energy of the transition state. Although the transition state is less aromatic than benzene, it has a strong aromatic nature. From comparison of the aromaticity of the transition state and benzene, the results of the IDA are reasonable. However, the NICS value⁴¹ of the transition state is about between -21.4 and -27.2 , and it is indicated from the NICS value that the transition state is much more aromatic than benzene (NICS = -9.7).⁵ It cannot be considered that the NICS values are adequate for the aromaticity from the point of view of resonance stabilization energy. From the geometrical parameters of the transition state, the largest difference among the C–C bond lengths of the ethylene part and butadiene part is only 0.007 Å. This may correspond to the fact that the total value of D_s and D_p is less than one-half of the IDA value. The aromaticity for the geometrical points of view also corresponds to the results of the IDA.

3.3. Sigmatropic Reactions.

3.3.1. Cope Rearrangements. The reaction mechanism of the Cope rearrangement has been controversial. Theoretically, three types of transition states^{55–64} were observed in the Cope rearrangement of 1,5-hexadiene: a concerted chair type with the C_{2h} symmetry, a concerted boat type with the C₂ symmetry, and an asymmetric Dewar type transition state leading to diradical tight-chain intermediate species. The concerted transition states should be more aromatic than the asymmetric Dewar type and the diradical intermediate. The geometries of these transition states, the intermediate and their IDA values are also indicated in Figure 3. The concerted chair type is the most aromatic one among three transition states and a diradical intermediate from their IDA values, and the aromaticity is comparable to that of the transition state of the Diels–Alder reaction of butadiene with ethylene as shown in the previous section. The concerted boat type transition state has less aromatic nature than the chair type. This may be understood from the geometrical parameters of the chair type and boat type transition states. Namely the C–C bond length of allyl part of the boat type transition state is shorter by 0.08 Å than that of the chair type, and the C–C bond length between allyl parts of the boat

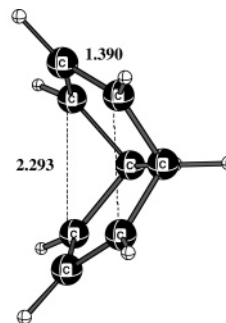


(a) Concerted type Transition States of the Cope Rearrangement of 1,5-hexadiene



(b) Dewar type Transition States and Diradical Intermediate

Figure 3. Transition state and intermediate geometries and their IDA values for the Cope rearrangement of 1,5-hexadiene.



Transition State with C₂ symmetry

$D_s = 0.348$
 $D_p = 0.438$
 $G_{sp} = 0.256$
 $IDA = 1.042$

Figure 4. Transition state geometry and the IDA value for the Cope rearrangement of semibullvalene.

type is about 0.354 Å longer than that of the chair type. Therefore, the boat type transition state may have the character of a diyl (singlet diradical) type transition state. The diradical intermediate has large IDA values, and naturally it indicates much less aromaticity.

It is known that the Cope rearrangement of semibullvalene has a low energy barrier of only 4.8–5.2 kcal/mol.^{65,66} The transition state of semibullvalene can be considered as the boat type model of the Cope rearrangement of 1,5-hexadiene. Then, the aromaticity of the transition state for the rearrangement of semibullvalene is interesting in comparison with the aromaticity of the Cope rearrangement of 1,5-hexadiene. The transition state geometry and the IDA value of semibullvalene are shown in Figure 4. The C–C bond lengths of allyl part of the transition

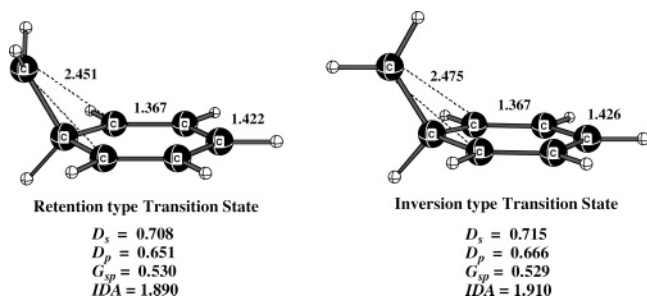
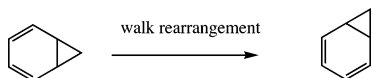


Figure 5. Retention type and inversion type transition states and their IDA values for a [1,5]-carbon shift.

state for the rearrangement of semibullvalene is similar to that of the boat type transition state of 1,5-hexadiene, and the C–C bond length at the reacting point of semibullvalene is shorter by 0.253 Å than that of the boat type and about 0.101 Å longer than that of the chair type. However the transition state of semibullvalene is a little less aromatic than the boat type from their IDA values. This may cause from the difference of the overlap between p_π orbitals of the terminal carbon atoms of allyl part because of the geometry restriction with bridged atoms between allyl parts of semibullvalene.

3.3.2. [1,5]-Sigmatropic Shift.

[1,5]-Sigmatropic Carbon Shift. The [1,5]-sigmatropic carbon shift is an example of the orbital symmetry rules for pericyclic process, potentially involving a six-electron aromatic transition state. The [1,5]-sigmatropic shift of norcaradiene is an example of a walk rearrangement, in which a substituted methylene “walks” around the perimeter of an aromatic ring. For the walk rearrangement, there are two reaction paths.^{67–72} One is the



concerted process of the alkyl shift and occurs with retention of configuration at the migrating carbon, [1r,5s] rearrangement. The other is the inversion reaction path and occurs with inversion of configuration at the migrating carbon atom, [1i,5s]. Both transition state structures for the [1r,5s] process and the [1i,5s] process and their aromaticity values of the IDA are shown in Figure 5. Both retention and inversion transition states have large IDA values. Accordingly, both structures are not an aromatic transition state. Houk and co-workers⁶⁸ indicated that both transition structures have strong diradical character as shown by ab initio MO methods. This corresponds to the large IDA values for both transition states. The difference of the IDA values for both transition states is only 0.02 and may correspond to their activation barriers. Namely, the energy barrier of the retention transition state is only 0.3 kcal/mol higher than that of the inversion transition state at the CASSCF calculation and 0.5 kcal/mol lower than that by the CASPT2N level. As shown above, the IDA can be reflected in the electronic states as diradical and the stabilization energies corresponding to activation energy.

[1,5]-Sigmatropic Hydrogen Shift. There are two types of reaction paths for the [1,5]-hydrogen shift of 1,3-pentadiene from the orbital symmetry rules. One is a symmetry allowed process with the C_s symmetry and the other is a forbidden process with the C_2 symmetry. Most of the theoretical treatments in previous studies^{35,73–76} presented the energy barrier for the allowed process. We compared the aromaticity of the allowed and forbidden transition states. The transition state geometries of the [1,5]-hydrogen shift of 1,3-pentadiene and the aromaticity

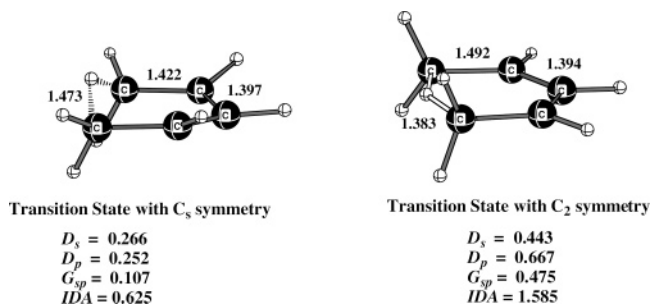


Figure 6. Transition state geometries and their IDA values for the [1,5]-hydrogen shift of 1,3-pentadiene.

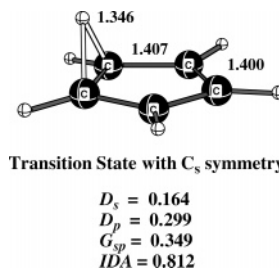


Figure 7. Transition state geometry and the IDA value for the [1,5]-hydrogen shift of 1,3-cyclopentadiene.

values of the IDA are shown in Figure 6. Although the transition state with the C_s symmetry has one negative eigenvalue for the force constant matrix, that with the C_2 symmetry has two negative eigenvalues. Therefore, the transition state with the C_s symmetry is the real transition state and the other is not. The transition state with the C_s symmetry is about 29 kcal/mol lower by energy than that with the C_2 symmetry at the CASSCF/6-31G(d) level. From comparison of the C–C bond lengths, the transition state structure with the C_s symmetry is more aromatic than that with the C_2 symmetry. Namely the difference of two C–C bond lengths in the frame bonds (except for the reacting points of the C–H–C) of the transition state with C_s symmetry is 0.025 Å, and that with the C_2 symmetry is 0.098 Å. The IDA value of the transition state with the C_s symmetry is a little larger than that of the transition state with the C_s symmetry of the electrocyclic reaction of 1,3,5-hexatriene including six π -electrons. The transition state with the C_2 symmetry has a large IDA value of about 1.6 and is not aromatic.

In comparison with the aromaticity of the transition state of 1,3-pentadiene, the transition state of the [1,5]-hydrogen shift of 1,3-cyclopentadiene^{73,77} was also calculated, and the geometrical parameters and the IDA value are shown in Figure 7. From geometrical parameters of the C–C bond lengths, the transition state of cyclopentadiene looks more aromatic than that of pentadiene with the C_s symmetry. Namely the difference of the two C–C bond lengths of the transition state with C_s symmetry of pentadiene is 0.025 Å and that of cyclopentadiene is 0.007 Å. However, the IDA value of the transition state with C_s symmetry of pentadiene is smaller than that of cyclopentadiene. This means the transition state with C_s symmetry of pentadiene is more aromatic than the transition state of cyclopentadiene. The order of the aromaticity by the IDA values for the transition state with C_s symmetry of pentadiene and for the transition state of cyclopentadiene corresponds to that of the magnetic aromaticity as defined by NICS values⁴¹ (NICS = –16.6 for the transition state with the C_s symmetry of pentadiene and NICS = –14.8 for the transition state of cyclopentadiene).

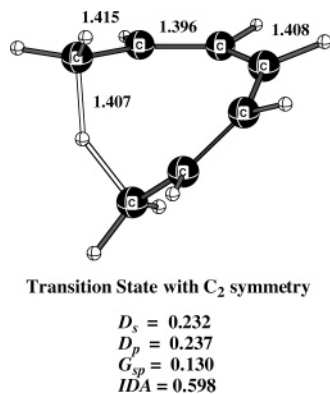


Figure 8. Transition state geometry and the IDA value for the [1,7]-hydrogen shift of 1,3,5-heptatriene.

3.3.3. [1,7]-Sigmatropic Hydrogen Shift of 1,3,5-Heptatriene. While [1,5]-sigmatropic hydrogen shift in pentadiene and/or cyclopentadiene is a thermally favored suprafacial isomerization involving six electrons, the eight-electron [1,7]-hydrogen shift is an antarafacial sigmatropic rearrangement with a Möbius topology. Experimentally and theoretically,^{35,78,79} it is known that the activation energy barrier height of a [1,7]-hydrogen shift of 1,3,5-heptatriene is lower than those of a [1,5]-hydrogen shift for cyclopentadiene and 1,3-pentadiene.

We now provide a detailed theoretical analysis of the [1,7]-hydrogen shift of 1,3,5-heptatriene. The transition state geometries and the aromaticity value of the IDA for the [1,7]-hydrogen shift of 1,3,5-heptatriene are shown in Figure 8. The transition state structure can be termed aromatic from the C–C bond lengths. Namely the largest difference of C–C bond lengths at the transition state is 0.019 Å. Thus, the geometrical criterion of aromaticity is fulfilled. In comparison with the geometrical parameters (C–C bond lengths) of transition states of 1,3,5-heptatriene and 1,3-pentadiene with the C_s symmetry, the [1,7]-hydrogen shift transition state is more aromatic than that of the [1,5]-hydrogen shift transition state. The IDA value of the transition state structure of [1,7]-hydrogen shift is 0.598 and is less than the IDA values for the [1,5]-hydrogen shift as described in the previous section. The order of the aromaticity by the IDA for the transition states of [1,7]-hydrogen shift and [1,5]-hydrogen shift corresponds to that by the geometrical aromaticity. The order of the aromaticity for both transition states corresponds also to that of their activation energy barrier height.⁷⁹ On the other hand, the NICS value (-14.0)⁴¹ of the transition state structure of the [1,7]-hydrogen shift indicates less aromaticity than that (-16.6) of the transition state structure of the [1,5]-hydrogen shift.

4. Conclusions

The aromaticity of the transition state structures for pericyclic reactions was studied with the IDA values. The pericyclic reactions treated here are the electrocyclic reactions, the Diels–Alder reaction, and the sigmatropic reactions. For the electrocyclic reactions of three polyenes (butadiene, hexatriene, and octatetraene), the transition states of the symmetry allowed process are more aromatic than those of the symmetry forbidden process. The transition states of the Diels–Alder reaction of butadiene with ethylene and the Cope rearrangement of the chair type concerted transition state of hexadiene indicate almost the same aromaticity level, while the boat type transition state of the Cope rearrangement of hexadiene has low aromaticity, equivalent to that of semibullvalene. As expected, the diradical intermediate and the Dewar type transition state leading to a

diradical intermediate have large values of the IDA, and the results are reasonable.

Two transition states (retention and inversion types) of [1,5]-sigmatropic carbon shift reactions have almost the same values of the IDA, and this may correspond to almost the same activation energy barriers. On the other hand, for the [1,5]-hydrogen shift, the transition state with the C_s symmetry of 1,3-pentadiene has a smaller IDA value than that with the C_2 symmetry. For the aromaticity of the transition states of 1,3-pentadiene and cyclopentadiene, the geometrical parameters (C–C bond lengths) of the transition state of cyclopentadiene indicate more aromaticity than that of the transition state with the C_s symmetry of 1,3-pentadiene, but the IDA value for the cyclopentadiene is larger than that for 1,3-pentadiene. Consequently, from the point of view of electronic states, the transition state with the C_s symmetry of 1,3-pentadiene is more aromatic than that of cyclopentadiene. This also agrees with the magnetic aromaticity by the NICS values. For the Möbius type reaction, the transition state with the C_2 symmetry of the [1,7]-sigmatropic hydrogen shift of 1,3,5-heptatriene has a little smaller IDA value than that of the [1,5]-hydrogen shift with the C_s symmetry of 1,3-pentadiene. As the above results indicate, the IDA value characterized the nature of the transition states and is one of the useful tools for the classification of reactions.

Acknowledgment. This research was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan. Computer time was made available by the Computer Center of the Institute for Molecular Science.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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