Theoretical Studies on the Structures and the Aromaticity for Condensed Cyclobutadienoids Series: The Combination of Kekulé Structures

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The structures and aromaticity of a series of condensed cyclobutadienoids were investigated by ab initio molecular orbital and density functional methods. A boat-type structure was found to be the most stable for all cyclobutadienoids except butalene, and the structures could also be predicted from a simple combination of asymmetric Kekulé structures. There were found to be three types of stable structure for cyclobutadienoids ($C_{2n}H_4$). In the case of $2n = 6m$ ($m = 1, 2, ...$), the structure consists of a succession of six-membered π-resonance ring units, while for $2n - 4 = 6m$, the structure is an assembly of six-membered π-resonance ring units with two "double-bonds" in the center or at the ends of the structure. In all other cases, the structures are of symmetric Kekulé type. The aromaticity for each ring was obtained on the basis of the index of deviation from aromaticity. Although all compounds examined here (except for butalene) showed anti- or nonaromatic nature in the whole molecule, the six-membered ring units in some molecules had an aromatic nature similar to that of butalene.

1. Introduction

Cyclobutadiene is a typical antiaromatic (nonaromatic) compound and is a highly reactive molecule. In 1965, Pettit and co-workers[1] first prepared cyclobutadiene as a highly reactive intermediate by oxidation of an iron tricarbonyl complex. Dewar and co-workers[2] theoretically verified the antiaromaticity of cyclobutadiene by a perturbation (P) method using Hückel molecular orbital (MO) approximation. They also studied the aromaticity of butalene and bicyclobutadienylene by the PMO method and found that butalene was more aromatic (less antiaromatic) than cyclobutadiene and bicyclobutadienylene. Butalene is known as an isomer of *p*-benzynes, and the reaction between these has been studied experimentally and theoretically. Cyclobutadiene, butalene, and bicyclobutadienylene are envisaged as an antiaromatic series. Vollhardt and co-workers[3,4] synthesized cobalt metal complexes with substituted cyclobutadiene, butalene, and bicyclobutadienylene. Thus, these polycyclic benzenoid hydrocarbons have played an important part in the development of the theory of π-electron rings. With an interest in the aromaticity of butalene and the related compounds, Warner and Jones[5] studied the structures and magnetic properties of the condensed cyclobutadienoid series (butalene, bicyclobutadienylene, and dicyclobutalene) using the density functional method (BLYP) and concluded that butalene had an aromatic nature while bicyclobutadienylene had a nonaromatic and nonantiaromatic nature. However, the aromaticity or antiaromaticity of the larger members of the condensed cyclobutadienoid series is unknown. The aromaticity and structures of these compounds are interesting from the point of view of π-electronic theory for polycyclic compounds, fullerenes, and nanotubes.

Although the concept of aromaticity was introduced in 1865,[6] a precise or generally well-established definition has yet to be presented. Generally, aromaticity has been defined as the π-electron resonance energy of a cyclic π-conjugated compound. Although the definition of aromaticity on the basis of HMO theory[7] can be readily understood, treatment of complex compounds such as nonplanar molecules remains difficult. Aromaticity has also been treated magnetically,[8−10] and as a nucleus-independent chemical shift (NICS);[11] a harmonic oscillator model (HOMA)[12] and a para-delocalization index (PAI) have also been proposed.[13] Among the proposed indexes of aromaticity, the NICS has been used in many studies. The values of the NICS may be adequate for classification of aromaticity and antiaromaticity, but measurements of order for some compounds are not adequate, as shown in previous studies.[14−16] Bultinck and co-workers[17] also showed that NICS values did not reveal the individual aromatic nature of specific rings in polycyclic aromatic hydrocarbons. Therefore, in order to evaluate the order of π-electron resonance energies, we proposed in previous papers an index of deviation from aromaticity (IDA) for whole molecules and/or ring units.[18,19] The value of the IDA corresponds[16] to the π-electron resonance energy.

In this paper, the geometries and aromaticity values of the condensed cyclobutadienoid series are investigated by ab initio MO and density functional methods. The stationary point structures of the series are also predicted by a simple selected combination of Kekulé structures.

2. Computational Methods

Molecular geometries were obtained by ab initio CASSCF[20] and CCSD(T)[21,22] MO methods, and the B3LYP density functional method[23,24] with a 6-31G(d) basis set.[25] For CASSCF calculations, all active spaces corresponding to valence π and π^* orbitals were included, and all configurations in active spaces were generated.

CiLC (CI/LMO/CASSCF) calculations were carried out to interpret aromaticity; the details of this method can be found in previous papers.[26−28] The electronic structures of bonds on the basis of CiLC calculations were presented 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. A

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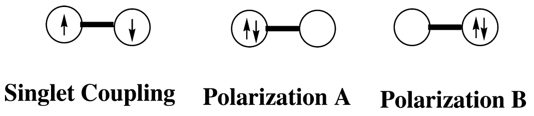
SCHEME 1



representation with three terms (one singlet coupling and two polarization terms) for a bond was used for the index of aromaticity.

The criterion of aromaticity was defined[18,29,30] according to the following conditions on the basis of the CiLC calculations: (A) the weights of the singlet coupling and polarization terms are 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 aromaticity in terms of bond length equalization, while the second corresponds to resonance stabilization energy. From these two criteria of aromaticity, the IDA for an *n*-cyclic ring can be defined as shown in eq 1.

$$\mathrm{IDA} = D_{\mathrm{s}} + D_{\mathrm{p}} + G_{\mathrm{sp}} \tag{1}$$

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 the polarization terms on the basis of average singlet coupling. Therefore, a small IDA value indicates an aromatic nature, while a large value indicates a non- or antiaromatic nature. The IDA can be evaluated not only for a whole molecule but also for a ring unit within a molecule.

The CiLC calculations were performed using the GAMESS software package,[31] and other calculations were carried out using the Gaussian03 program.[32]

3. Results and Discussion

3.1. Cyclobutadiene and Butalene. The geometrical parameters of cyclobutadiene and butalene, obtained by the B3LYP, CASSCF, and CCSD(T) methods, are shown in Figure 1. The relative energies for each molecule, from the lowest energy geometry, and the whole-molecule IDA values for $C_{2n}H_4$ ($n = 2-5$) are listed in Table 1. All IDA values were calculated using CASSCF optimized geometries, except for the values in parentheses, which were calculated using B3LYP optimized geometries. It is well-known that cyclobutadiene has an antiaromatic (less aromatic) nature and that its geometry is rectangular. The IDA of cyclobutadiene (**1−1**) is large (2.037) and is in the antiaromatic (nonaromatic) region.

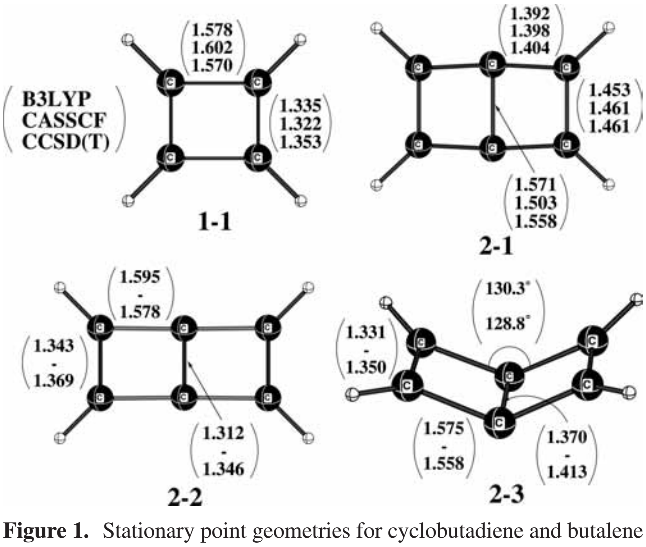


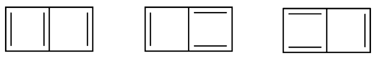
Figure 1. Stationary point geometries for cyclobutadiene and butalene by the B3LYP, CASSCF, and CCSD(T) methods.

TABLE 1: Relative Energies (kcal/mol) of $C_{2n}H_4$ ($n = 2-5$), from the Lowest Energy, and IDA Values[a]

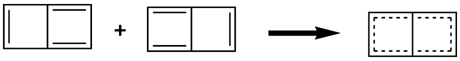
compounds			methods			
	structure	symmetry	B3LYP	CASSCF	CCSD(T)	IDA
C_4H_4	1−1	D_{2h}	0.0	0.0	0.0	2.037
C_6H_4	2−1	D_{2h}	0.0	0.0	0.0	0.865
	2−2	D_{2h}	67.7		55.6	(2.306)
	2−3	C_{2v}	43.7		31.6	(2.768)
C_8H_4	3−1	D_{2h}	1.2	10.2	5.4	1.959
	3−2	C_{2v}	0.0	0.0	0.0	2.899
	3−3	C_{2h}	64.2		52.9	(3.446)
	3−4	D_{2h}	57.0		53.9	(2.191)
	3−5	C_{2h}		70.0		3.529
$C_{10}H_4$	4−1	D_{2h}	8.2	18.7	16.4	2.148
	4−2	C_{2h}		17.3		2.038
	4−3	D_{2h}	16.1	23.9	21.4	2.019
	4−4	C_{2v}	0.0	0.0	0.0	2.687

[a] The IDA values in parentheses were calculated using B3LYP optimized geometry.

For butalene (**2−1**), three types of Kekulé structure can be drawn: **I**, **II**, and **III**. However, from the point of view of bond distances, the geometries obtained by three methods (B3LYP, CASSCF, and CCSD(T)) can be considered as a resonance structure between **II** and **III**, with **I** not included. Stationary point geometries corresponding to the asymmetric structures **II** or **III** could not be obtained by any of these computational methods. We will use the terms "asymmetric structures" and "symmetric structures" based on the symmetry of the σ_v plane (including the central C−C bond in the case of butalene); **I** is symmetric, while **II** and **III** are asymmetric. For the relationship between **II** and **III**, we use the term "anti-symmetric". The geometric parameters of butalene were previously calculated at the GVB level by Ohta and Shima,[33] and the results obtained were similar to ours (**2−1**). The IDA values for two rings in butalene (a four-membered ring and a six-membered ring) were obtained: that of the four-membered ring is 1.995, which is a little less than that of cyclobutadiene but still large, while that of the six-membered ring is 0.865, which indicates considerable aromaticity. It is considered that the aromaticity (stabilization energy) of the six-membered ring works to the exclusion of Kekulé structure **I** (double bond in the center and single bonds in the horizontal bonds) for the calculated geometry of butalene. In other words, **2−1** does not include the symmetric Kekulé structure **I** but is composed of a combination of the asymmetric Kekulé structures **II** and **III**. Structure **IV** may be obtained from the overlap between **II** and **III**, with treatment only of π bonds. To normalize π bonds in a structure, the structure **IV** is included a half weight of each π bond for **II** and **III**. So, the dashed line of the structure **IV** indicates a half π bond. The π-bond structure of **IV** corresponds to that of benzene.



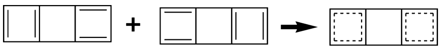
I **II** **III**



II + **III** → **IV**

The stationary point geometries corresponding to Kekulé structure **I** were obtained as **2−2** and **2−3** (Figure 1) by the B3LYP and CCSD(T) methods. Both geometries have one negative eigenvalue for the force-constant matrices. The geometry **2−2** collapses to **2−3** upon geometry optimization along the eigenvector of the negative eigenvalue, and that of **2−3** collapses to **2−1** along the eigenvector of the eigenvalue. The geometries of **2−2** and **2−3** are much more unstable (by 67.7 and 43.7 kcal/mol by the B3LYP method, and 55.6 and 31.6 kcal/mol by the CCSD(T) method, respectively) than that of **2−1**. The IDA values for the four-membered rings of **2−2** and **2−3** are 1.939 and 2.286, respectively, while those of the six-membered rings are 2.306 and 2.768, respectively. Thus, the IDA values of **2−2** and **2−3** indicate a non- or antiaromatic nature.

3.2. C_8H_4. The stationary point geometries of the polybutadienoids C_8H_4 are shown in Figure 2. There are a total of five Kekulé structures for C_8H_4, including three symmetric and two asymmetric structures, and these are also shown in Figure 3. For the structures with D_{2h} symmetry, two geometries (**3−1** and **3−4**) were obtained by the theoretical calculations, which correspond to the symmetric Kekulé structures **II** and **III**, respectively, from the point of view of C−C bond distances. Although **3−1** was obtained by three methods (B3LYP, CASSCF, and CCSD(T)), **3−4** could not be obtained by the CASSCF method. The geometry **3−1** is about 47 kcal/mol more stable than that of **3−4** at the CCSD(T) calculation level. The **3−1** and **3−4** structures, which have D_{2h} symmetry, each have one negative eigenvalue for their force-constant matrices. Geometry optimization along the eigenvectors of the negative eigenvalues gave two stationary point structures, **3−2** and **3−5**, respectively, from **3−1** and **3−4**. As shown in the previous section, the geometries (**2−2** and **2−3**) corresponding to the symmetric Kekulé structure **I** of butalene are less stable (about 68 kcal/mol using B3LYP (56 kcal/mol by the CCSD(T)) higher in energy) than the lowest geometry (**2−1**) of butalene. A geometry with D_{2h} symmetry corresponding to the symmetric Kekulé structure **I** could not be obtained for C_8H_4 by any computational methods; however, a chair-type geometry (**3−3**) with C_{2v} symmetry corresponding to the symmetric Kekulé structure **I** was obtained by the B3LYP and CCSD(T) methods. Only **3−2** was obtained by all three methods; this is the most stable geometry. The structures **3−3**, **3−4**, and **3−5** are less stable (by 50 to 70 kcal/mol) than **3−2**, but **3−1** is only a few kcal/mol higher in energy than **3−2**. The structure **3−2** shows a nature more typical of Kekulé-type **II** than **3−1**; namely, the double bond units in **II** are shorter in **3−2** than in **3−1**, while the single bonds are longer. We could not find asymmetric stationary point geometries **IV** or **V** or a symmetric structure consisting of a combination of asymmetric Kekulé structures **IV** and **V**, as in the case of butalene. The structure of the combination of asymmetric Kekulé structures **IV** and **V** is shown in the following:



IV + **V** → **VI**

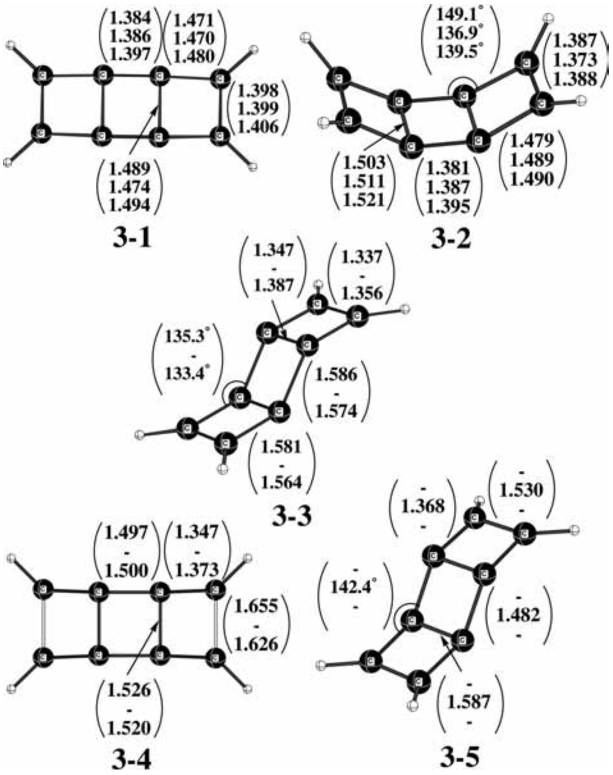


Figure 2. Stationary point geometries for C_8H_4 by the B3LYP, CASSCF, and CCSD(T) methods.

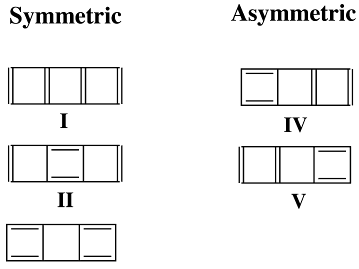


Figure 3. Kekulé structures of C_8H_4.

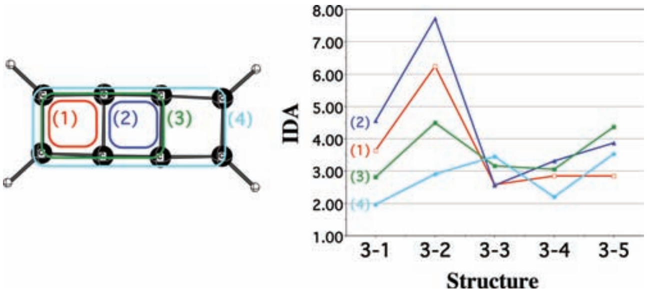


Figure 4. IDA values for each ring unit in the stationary point geometries of C_8H_4.

Structure **VI** resembles a combination of two square-type cyclobutadienes; consequently, it is considered to be unstable. As the geometry of cyclobutadiene with D_{4h} symmetry is 6.4 kcal/mol more unstable than with D_{2h} symmetry (by CASSCF calculations), **VI** may be about 13 kcal/mol more unstable than **IV** or **V**.

The IDA values for the calculated geometries of C_8H_4 are shown in Figure 4. The IDA values for the ring units in all geometries are greater than 2, which means that all of the rings are nonaromatic or antiaromatic when compared with the IDA value of cyclobutadiene (2.04). This corresponds to the stationary point geometries obtained; the structures are of symmetric

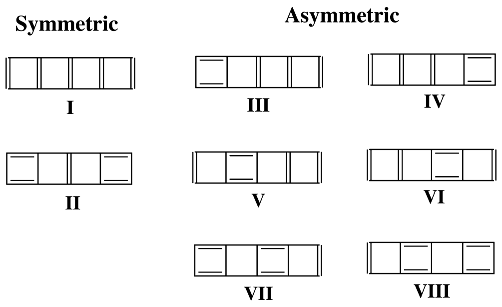
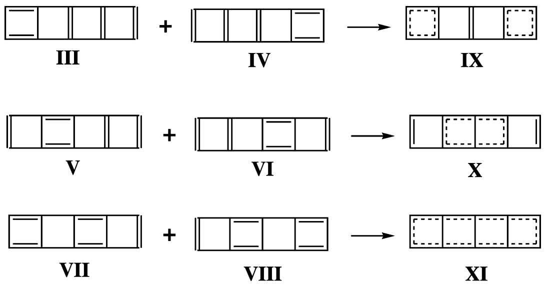


Figure 5. Kekulé structures of $C_{10}H_4$.

SCHEME 2



Kekulé type, and a six-membered π-resonance structure, as in the case of butalene, is not included in all of them. The range of IDA values for the rings of **3−1** and **3−2** is wider than that for **3−3**, **3−4**, and **3−5**, which indicates that the structures of **3−3**, **3−4**, and **3−5** are typical Kekulé structures. In fact, the difference between the longest and the shortest bond lengths for **3−3**, **3−4**, and **3−5** is much greater than that for **3−1** and **3−2**.

3.3. $C_{10}H_4$. For the polybutadienoids represented by the formula $C_{10}H_4$, there are eight Kekulé structures, including two symmetric and six asymmetric structures. These Kekulé structures and the stationary point geometries obtained by the three methods are shown in Figure 5 and Figure 6, respectively. A stationary point geometry corresponding to the symmetric Kekulé structure **I**, which corresponds to **2−3** for C_6H_4 and **3−3** for C_8H_4, could not be found. The relative energies of the lowest energy geometries of **2−3** and **3−3** are 43.7 and 64.2 kcal/mol by the B3LYTP method (31.6 and 52.9 kcal/mol by the CCSD(T) method), respectively. The lowest energy geometries of C_6H_4 and C_8H_4 are of aromatic type, with six-membered π-resonance, and nonaromatic Kekulé type, respectively. Thus, the larger molecule of this type has the larger relative energy. Accordingly, it may be concluded that the stationary point geometry corresponding to **I** for $C_{10}H_4$ probably has a large relative energy, greater than that of the lowest energy geometry. The stationary point structure **4−1**, corresponding to the symmetric Kekulé structure **II**, was obtained by three methods. The geometry **4−1** has two negative eigenvalues for the force-constant matrix. From geometry optimization with movement along the eigenvectors of the negative eigenvalues, the geometry **4−2** was obtained by the CASSCF method. The geometry **4−2** is the real minimal and is only 1.4 kcal/mol more stable than that of **4−1**.

We could not find stationary point geometries corresponding to the asymmetric Kekulé structures **III−VIII** by any computational methods. Combinations of these asymmetric Kekulé structures are shown in Scheme 2; the combinations of two asymmetric Kekulé structures are chosen from structures that are antisymmetric with respect to each other, because other combinations do not produce a symmetric structure.

The structure **IX**, composed from a combination of **III** and **IV**, has a cyclobutadiene-type unit at both ends; accordingly, the structure is probably unstable, and a stationary point geometry could not be found by any computational methods. The structure **X**, composed from a combination of **V** and **VI**, includes a six-membered π-resonance ring, with a “double-bond” at both ends of the structure, and the corresponding geometry **4−3** was obtained by three computational methods.

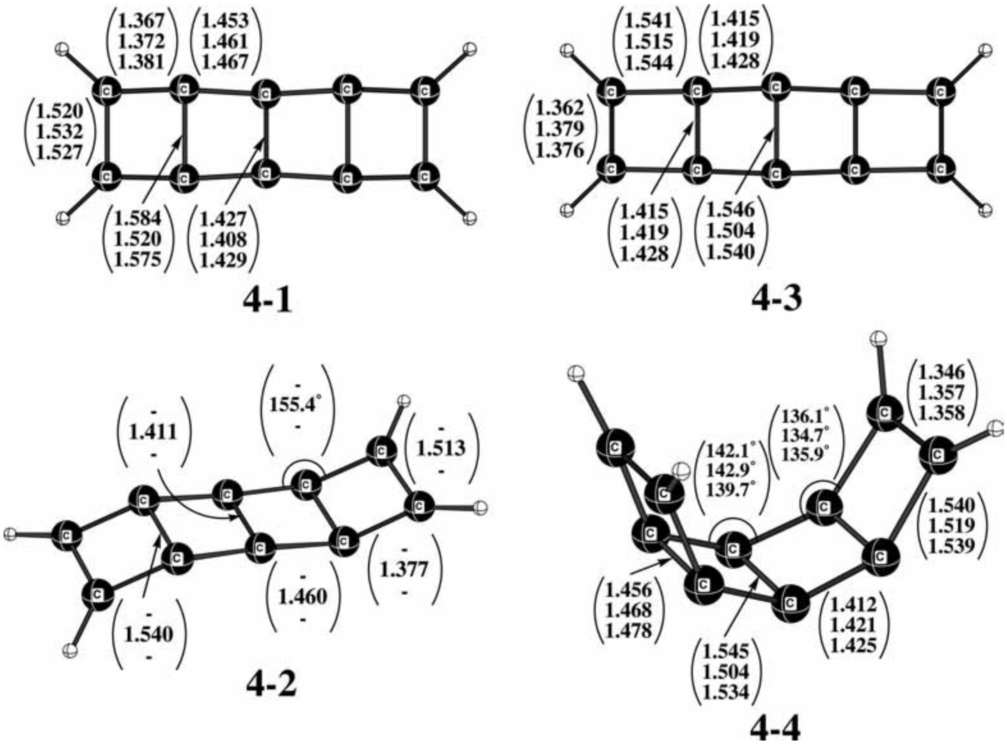


Figure 6. Stationary point geometries for $C_{10}H_4$ by the B3LYP, CASSCF, and CCSD(T) methods.

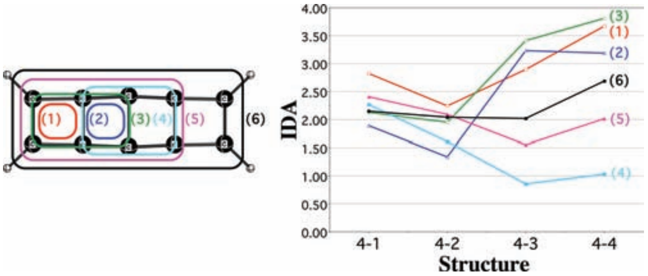


Figure 7. IDA values for each ring unit in the stationary point geometries of $C_{10}H_4$.

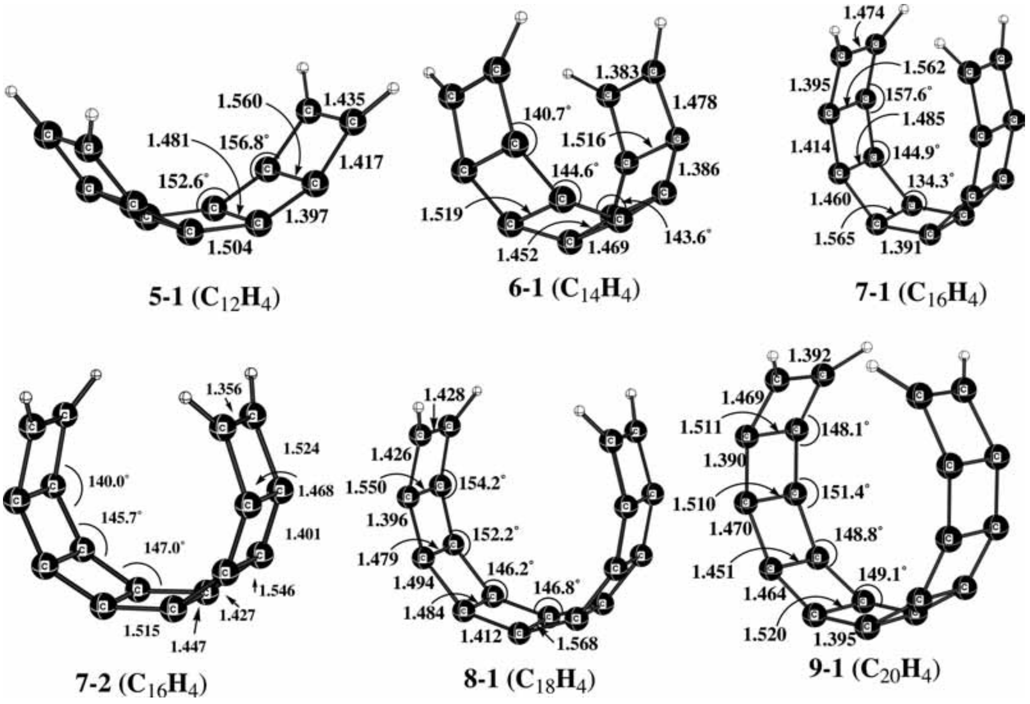
Here, "double-bond" in the structure **X** means a strong double bond. In fact, the bond lengths at both ends of **4−3** are very short, 1.36 Å by the B3LYP method, and the C−C bonds of the six-membered ring in the center are about 1.42 Å, which corresponds to the bond length found in benzene. The geometry **4−3** has one negative eigenvalue for the force-constant matrix. From geometry optimization along the eigenvector of the negative eigenvalue, the geometry **4−4** was obtained by all three methods. This is the most stable geometry, with a six-membered π-resonance ring similar to that of benzene in the center. The structure **XI**, composed from a combination of **VII** and **VIII**, is a 10 membered π ring, which is predicted from the Hückel rule to be a stable aromatic structure. However, this stationary point geometry could not be found by any computational methods. This is probably due to the strain energy of the 10 membered ring, as shown in a previous paper.[18]

The IDA values for the calculated geometries of $C_{10}H_4$ are shown in Figure 7. The IDA values for each ring structure in **4−1** and **4−2** are over a narrow range of about 1, while the IDA values for those of **4−3** and **4−4** are in a wider range of around 3. This means that the structures of **4−3** and **4−4** contain local aromaticity, while those of **4−1** and **4−2** are typical Kekulé structures. The six-membered rings in the center of **4−3** and **4−4** have small IDA values of 0.855 and 1.030, corresponding to that of butalene (0.865). However, the IDA values of the four-membered rings are much greater than that of cyclobutadiene, which indicates nonaromaticity. The range of IDA values for the ring units of **4−4** is wider than that for **4−3**. Although the IDA value of the six-membered ring in the center of **4−4** is a little larger than that of **4−3**, the IDA values of the four-membered rings at the two ends of **4−4** are much greater than those for **4−3**. This means that the variation from planar to arc-shaped structure is based on stabilization due to strong terminal double bonds without much loss of aromaticity (and thus stability) in the central six-membered ring. The IDA value of the 10 membered ring does not change much for any of the structures. This corresponds to the nonexistence of aromatic compounds with 10 π electrons.

3.4. $C_{2n}H_4$. On the basis of the results obtained in the previous sections, the lowest energy geometry for $C_{2n}H_4$ (n = 2, 3, 4, and 5) can be obtained by all three computational methods used here. The geometrical parameters obtained by the three methods are qualitatively the same, and the wave function is dominated by the main determinant with coefficient $C_0 > 0.9-0.8$).[34] The lowest energy geometries of $C_{2n}H_4$ (n = 6, 7, 8, 9, and 10) were calculated by the B3LYP method, and the results are shown in Figure 8. All structures obtained here are boat-type with C_{2v} symmetry.

The geometry (**5−1**) obtained for $C_{12}H_4$ comprises two terminal six-membered π-resonance units. There are 13 Kekulé structures for $C_{12}H_4$, including 5 symmetric and 8 asymmetric structures, and these structures, along with combinations of the asymmetric Kekulé structures, are shown in Figure 9. The structure **XVII**, which is a combination of **XII** and **XIII**, appears to be the most stable because of the inclusion of two six-membered π-resonance rings. This combination structure corresponds to the stationary point geometry **5−1** obtained by the B3LYP calculation method.

The calculated geometry (**6−1**) for $C_{14}H_4$ appears similar to a symmetrical Kekulé type on the basis of a comparison of the bond distances of adjoining C−C bonds. There are 21 Kekulé structures for $C_{14}H_4$, including three symmetric and 18 asymmetric structures, and these structures, along with combinations



5-1 ($C_{12}H_4$) **6-1** ($C_{14}H_4$) **7-1** ($C_{16}H_4$)

7-2 ($C_{16}H_4$) **8-1** ($C_{18}H_4$) **9-1** ($C_{20}H_4$)

Figure 8. Stationary point geometries for $C_{2n}H_4$ (n = 6, 7, 8, 9, and 10) by the B3LYP method.

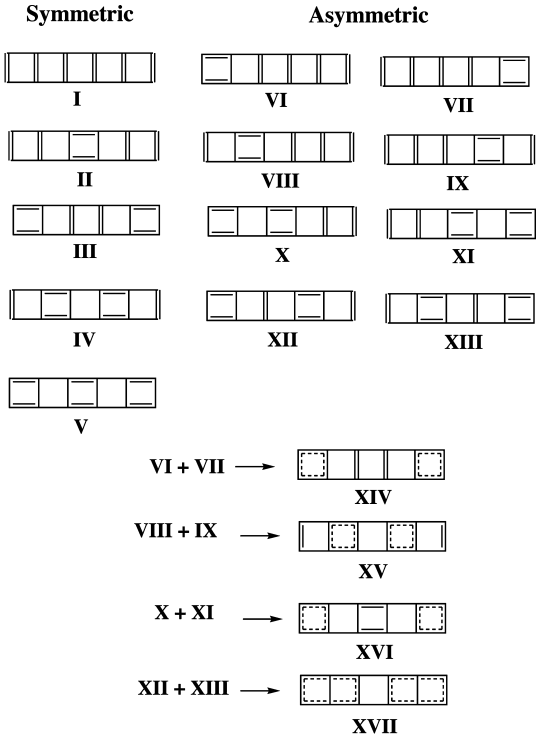
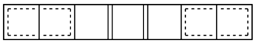


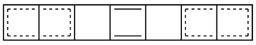
Figure 9. Kekulé structures of $C_{12}H_4$.

of the asymmetric Kekulé structures, are shown in Figure 10. The possible stable structures are symmetric structure **III** and combination structure **XXVIII**, which is a combination of **XVI** and **XVII**. Structure **XXVIII** contains a six-membered π-resonance ring at both ends and appears to be stable. However, the "double-bond" in the central vertical bond probably results in strong strain energies for the four-membered rings on both sides. Therefore, the symmetric Kekulé-type structure **III** is the likely structure for $C_{14}H_4$ and corresponds to the calculated geometry **6−1**.

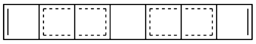
For $C_{16}H_4$, the conceivable stable structures from combinations of asymmetric Kekulé structures may be considered as the three structures shown below, which include two six-membered π-resonance rings and two "double-bonds". In the first structure, the two double-type bonds are the central vertical bonds, while in the second, they are the central horizontal bonds, and in the third, they are the terminal vertical bonds. Double-type bonds at the central vertical bond result in strain for the four-membered rings in the center and at both sides; consequently, the combination structure **I** is probably unstable. Although the combination structure **II** also includes double-type bonds at the center of the structure, the bonds are horizontal and thus avoid producing strain. The third structure **III** includes two terminal "double-bonds", but the strain energy for the four-membered ring of **III** is probably less than that in structure **I**.



I



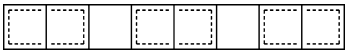
II



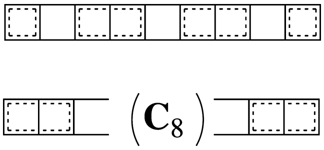
III

We obtained two stable structures, **II** and **III** (**7−1** and **7−2**); in **7−1**, the central horizontal C−C bonds are the shortest (1.391 Å) among all C−C bonds, while in **7−2**, the terminal C−C bonds are also among the shortest (1.356 Å). The energy of **7−1** is only 0.23 kcal/mol lower (more stable) than that of **7−2**.

The most stable structure of $C_{18}H_4$, from a combination of the asymmetric Kekulé structures, is that shown in below which contains three six-membered rings. The calculated geometry **8−1** corresponds reasonably to the predicted structure:



From a combination of asymmetric Kekulé structures for $C_{20}H_4$, two possible structures were obtained, as shown in the following:



Both structures contain six-membered π-resonance ring units. Since one of them contains two terminal four-membered rings similar to cyclobutadiene, it may be unstable. The other structure includes two six-membered π-resonance rings as the terminal units and a C_8 series in the center. In the structure of C_8H_4, the stable structure is not a combination of asymmetric Kekulé structures but is of symmetric Kekulé type. Therefore, the stable structure of $C_{20}H_4$ can be considered as a symmetric Kekulé structure and corresponds to the geometry **9−1** obtained by the B3LYP method.

4. Conclusions

The structures and electronic states of condensed cyclobutadienoids $C_{2n}H_4$ ($n = 2-10$) were investigated by ab initio MO (CASSCF and CCSD(T)) and density functional (B3LYP) methods. All Kekulé structures of the condensed cyclobutadienoids were classified as either symmetric or asymmetric type, and combinations were constructed from the overlap of two asymmetric Kekulé structures that were antisymmetric with respect to each other.

Cyclobutadiene is a typical Kekulé structure, which has a rectangular shape due to antiaromatic π resonance energy. The square structure of cyclobutadiene is about 6 kcal/mol higher in energy than the rectangular one. The resonance term (G_{sp}) of the IDA for square cyclobutadiene is about 0.139 greater than that for the rectangular structure, which means that the square structure is less aromatic than the rectangular one. For butalene, the stable structure is of benzene-type, with a six-membered π-electronic ring, which can be predicted by combining asymmetric Kekulé structures. The lowest energy geometry of C_8H_4 corresponds to the symmetric Kekulé structure because the combination of asymmetric Kekulé structures predicts only unstable structures. For $C_{10}H_4$, we can predict a combination of asymmetric Kekulé structures to be the most stable, and the predicted structure corresponds to that obtained by theoretical calculations.

The most stable structures for $C_{2n}H_4$ ($n = 2-5$) can be obtained by all of the theoretical methods used here; consequently, the structures for $C_{2n}H_4$ ($n = 6-10$) were also obtained by the B3LYP method. The most stable structure of $C_{12}H_4$

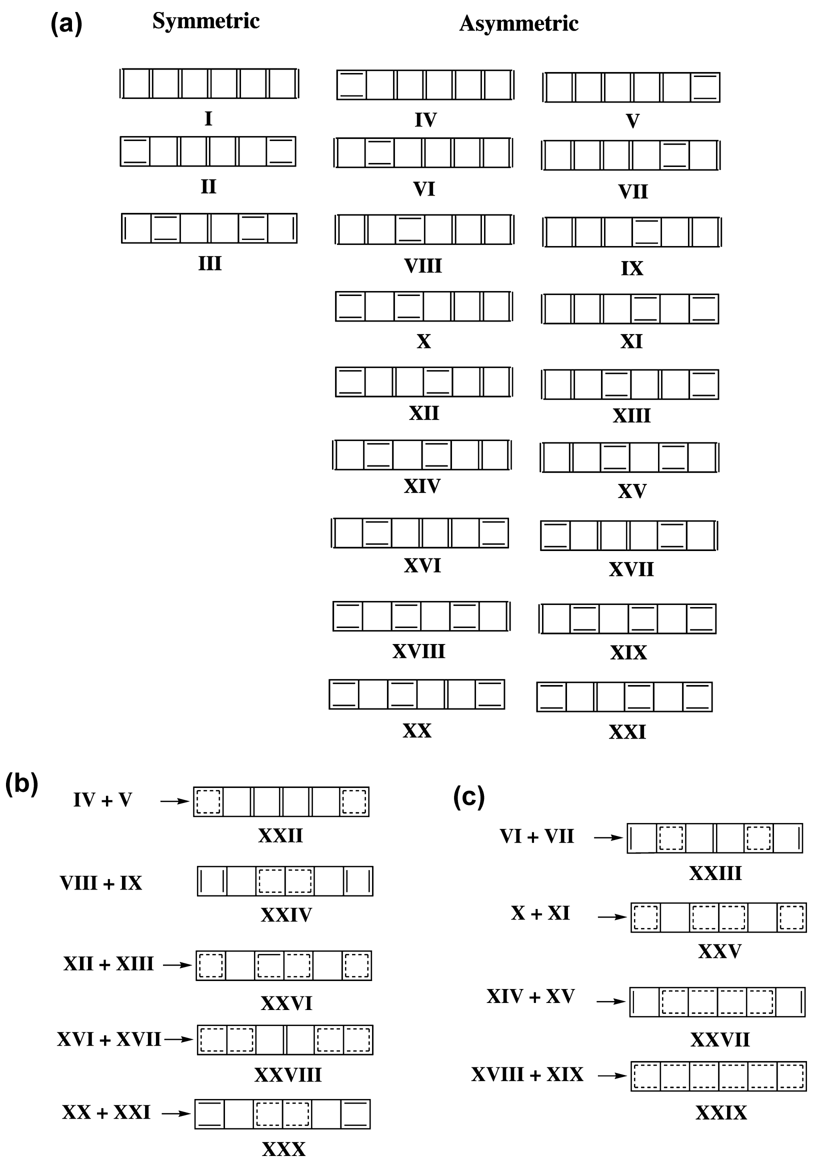
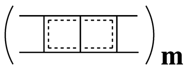


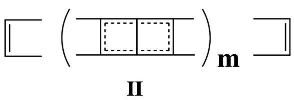
Figure 10. Kekulé structures and combination structure of $C_{14}H_4$.

includes two terminal six-membered π-resonance rings; this can also be predicted from a combination of asymmetric Kekulé structures. For $C_{14}H_4$, a structure with two terminal six-membered π-resonance rings is predicted from a combination of asymmetric Kekulé structures; however, the predicted structure includes “double-bonds” at the central vertical bonds. Accordingly, the structure becomes a symmetric Kekulé structure, which corresponds to the geometry obtained by the theoretical method. For $C_{16}H_4$ and $C_{18}H_4$, the most stable structures can be also predicted from combinations of asymmetric Kekulé structures and correspond to the geometries obtained by theoretical calculations. For $C_{20}H_4$, the most stable structure can be predicted as the symmetric Kekulé type and corresponds to the geometry obtained by the theoretical calculations.

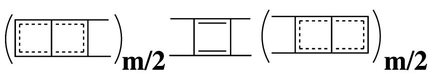
Thus, by combining asymmetric Kekulé structures, we can predict the most stable structure for each cyclobutadienoid. All of the stable structures for the condensed cyclobutadienoids ($C_{2n}H_4$) can be classified into three types. If $2n$ is a multiple of 6, the structure will consist of a succession of 6 membered π-resonance units (**I**). If $2n - 4$ is a multiple of 6, the structure will be an assembly of 6 membered π-resonance ring units with 2 “double-bonds” (**II** or **III**). In the other cases, the structure will be of symmetric Kekulé type.



I



II



III

The IDA values of the cyclobutadienoids were also estimated. The whole-molecule values for all cyclobutadienoids except butalene showed anti- or nonaromaticity; however, the IDA values of the six-membered π-resonance ring units predicted by combining asymmetric Kekulé structures for some molecules indicated an aromatic nature.

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Supporting Information Available: Geometry data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Watts, L.; Fitzpatrick, J. D.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 3253.

(2) Dewar, M. J. S.; Kohn, M. C.; Trinajstic, N. *J. Am. Chem. Soc.* **1971**, *93*, 3437.

(3) Fritch, J. R.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1978**, *100*, 3643.

(4) Fritch, J. R.; Vollhardt, K. P. C. *Organometallics* **1982**, *1*, 590.

(5) Warner, P. M.; Jones, G. B. *J. Am. Chem. Soc.* **2001**, *123*, 10322.

(6) Kekulé, A. *Bull. Soc. Chim. Fr. (Paris)* **1865**, *3*, 98.

(7) Dewar, M. J. S. *The Molecular Orbital Theory of Organic Chemistry*; McGraw-Hill: New York, 1969.

(8) Minkin, V. I.; Glukhovtsev, M. N.; Simin, B. Y. *Aromaticity and Antiaromaticity*; Wiley: New York, 1994.

(9) Garratt, P. J. *Aromaticity*; Wiley: New York, 1986.

(10) Eluidge, J. A.; Jackman, L. M. *J. Chem. Soc.* **1961**, 859.

(11) Schleyer, P.v.R.; Freeman, P.; Jiao, H.; Goldfuss, B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 337.

(12) Kruszewski, J.; Krygowski, T. M. *Tetrahedron Lett.* **1972**, 3839.

(13) Poater, J.; Fradera, X.; Duran, M.; Solá, M. *Chem.—Eur. J.* **2003**, *9*, 400.

(14) Schleyer, P.v.R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N.J.R.v.E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(15) Sakai, S. *J. Phys. Chem. A* **2002**, *106*, 10370.

(16) Sakai, S. *J. Mol. Str. (THEOCHEM)* **2005**, *715*, 101.

(17) Fias, S.; Damme, S. V.; Bultinck, P. J. *Comput. Chem.* **2008**, *29*, 358.

(18) Sakai, S. *J. Phys. Chem. A* **2003**, *107*, 9422.

(19) Sakai, S. *J. Phys. Chem. A* **2006**, *110*, 6339.

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

(21) Purvis, G. D.; Bartlett, R. *J. Chem. Phys.* **1982**, *76*, 1910.

(22) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Headgordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(23) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(25) Hariharan, P. C.; Pople, J. A. *Theo. Chim. Acta* **1973**, *28*, 231.

(26) Sakai, S. *J. Mol. Struc(THEOCHEM)* **1999**, *461*−*462*, 283.

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

(28) Sakai, S. *J. Phys. Chem. A* **2000**, *104*, 922.

(29) Sakai, S. *J. Phys. Chem. A* **2002**, *106*, 10370.

(30) Sakai, S. *J. Phys. Chem. A* **2002**, *106*, 11526.

(31) Schmidt, M. W.; Buldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gorgon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S.; Windus, T. L.; Dupuis, M.; Montgomerry, J. A. *J. Comput. Chem.* **1993**, *14*, 1347. Gordon, M. S.; Schmidt, M. W. *“Theory and Applications of Compoutational Chemistry; the first forty years”*; Dykstra, C.E.,Frenking, G., Kim, K. S., Scuseria, G. E., Eds.; Elsevier: Amsterdam, 2005; pp 1167−1189.

(32) Frisch, K. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheseman, J. R.; Montgomery, J. A,; Vreven, Jr. T.; 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.

(33) Ohta, K.; Shima, T. *Chem. Phys. Lett.* **1994**, *217*, 7.

(34) The difference between the coefficents C_0 of the main configuration of CASSCF for the arc and planer structures of $C_{10}H_4$ molecule is 0.03. Consequently, it is considered that the wave function stability due to the bent structure is not much.

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