New Criterion of Aromaticity and Implications for the (4*n* + 2)π Rule

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A new criterion of aromaticity for cyclic π-conjugated compounds is proposed on the basis of CiLC (CI/LMO/CASSCF) analysis founded on ab initio molecular orbital methods. The new criterion states that the all bonds should have equivalent electronic structures and the difference between weights for the singlet coupling and polarization terms (from CiLC analysis) should be small. The $(4n + 2)\pi$ rule of aromaticity for cyclic π-conjugated compounds is reexamined using this new criterion. The criterion is applied to C_nH_n structures with D_{nh} ($n = 4$, 6, 8, and 10) symmetries and their equilibrium structures, and it is demonstrated that the proposed criterion reasonably explains the $(4n + 2)\pi$ rule. An index of deviation from the aromaticity (IDA) is also defined to compare the aromaticity of ring-unit compounds.

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. Although this concept was introduced in 1865,[1] a precise or generally well-established definition has yet to be presented. 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, giving rise to the $(4n + 2)\pi$ rule in Hückel molecular orbital (HMO) theory.[2] Although the definition of aromaticity on the basis of HMO theory can be readily understood, the treatment of complex compounds such as nonplanar molecules remains difficult. Aromaticity has also been treated magnetically,[3−5] and Schleyer et al.[6] proposed the nucleus-independent chemical shift (NICS) as an index of aromaticity. 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.[7,8]

Recently, I presented a new criterion[8,9] of aromaticity for benzene-like molecules with six-membered rings on the basis of a CiLC method in reference to ab initio molecular orbital (MO) calculations. The CiLC method is a combination of configuration interaction (CI), localized molecular orbital (LMO), and complete active space self-consistent field (CASSCF) analysis. From the CiLC analysis of the aromaticity of six compounds (C_6H_6, Si_6H_6, B_6, Al_6, N_6, and P_6) with six-membered rings, a new criterion of aromaticity for six-membered rings was defined, taken as the degree of equality of electronic structures for each of the bonds in the six-membered ring and by the narrowness of the gap between the weights of the singlet coupling and polarization terms for each bond.

In this study, the criterion of aromaticity for six-membered rings is extended to cyclic C_nH_n ($n = 4$, 6, 8, and 10) compounds, and the $(4n + 2)\pi$ rule is reexamined. A new index of aromaticity for ring-unit compounds—the index of deviation from aromaticity (IDA)—is also proposed.

2. Computational Methods and Models

To study the $(4n + 2)\pi$ rule of aromaticity, four compounds (C_nH_n; $n = 4$, 6, 8, and 10) were treated here. It is well known that the structures of C_4H_4 and C_8H_8 exhibit bond alternation outside the $(4n + 2)\pi$ rule, and it is considered that compounds with such bond alternation do not satisfy the criterion of "equivalent electronic structures for each bond" in terms of geometrical parameters. Therefore, the stable and aromatic structures with equivalent bond lengths for all bonds are treated here. Aromatic structures were determined by geometry optimization including D_{nh} ($n = 4$, 6, 8, and 10 for C_nH_n) symmetry. All stationary points of the geometries were determined with analytical calculated energy gradients using the CASSCF method[10] with the 6-31G(d) basis set.[11] For CASSCF calculations, all active spaces corresponding to valence π and π^* orbitals were included, and all configurations in active spaces were generated.

CiLC analysis was used with the 6-31G(d) basis set to interpret the aromaticity. This procedure has been used by us for reaction mechanism analyses[12−24] and aromaticity analyses,[8,9] and the details of the method can be found in previous papers.[8,9,12−28] Briefly, the CASSCF calculation was carried out to obtain a starting set of orbitals for the localization procedure. Boys localization[29] 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 the relative weights in the atomic orbital-like wave functions. Because CI configurations obtained at the determinant level include redundancy in spin configurations (reverse configurations of α and β), the weight (or square) of the CI coefficient of one spin function of the configuration with the redundancy was added to that of the other after the CI procedure. The total energy calculated by the CI procedure corresponds well to that obtained from the CASSCF calculation. CiLC calculations and geometry optimization of $C_{10}H_{10}$ compounds were performed using the GAMESS software package.[30] Other

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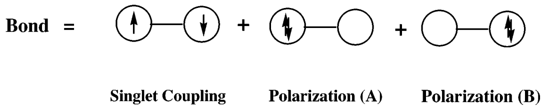
geometry optimization calculations were carried out using Gaussian 98.[31]

3. Results and Discussion

3.1. Aromaticity of Benzene. In the notation of the valence bond-like model, the electronic structures of a π bond by the CiLC method were presented as one singlet coupling term and two polarization terms (Scheme 1).

SCHEME 1



From a comparison of the electronic structures for each C−C bond of the aromatic and Kekule structures of benzene molecules by CiLC analysis, as shown in the previous paper, the criterion of aromaticity was redefined according to whether the following conditions are satisfied: (1) the weights of each of the singlet coupling and polarization terms are equal for all bonds, and (2) 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,[32] and the second corresponds to the π-resonance stabilization energy. In this paper, the $(4n + 2)\pi$ rule is reexamined with respect to the second criterion, assuming that the first condition is satisfied (i.e., all C−C bonds in the compound are of equal length). The aromaticity of the Kekule and aromatic structures of benzene based on CiLC analysis presented in previous papers[8,12,33] is outlined here briefly for comparison with the present results.

The weights of the CI coefficients by CiLC calculations for the Kekule (D_{3h}) and aromatic (D_{6h}) structures of benzene are shown in Figure 1. The Kekule structure of benzene with D_{3h} symmetry is as described in the previous paper.[8,12] Small values (<0.001) of the weights for both structures were neglected. Some of the configurations with large CI coefficients are displayed in Scheme 2, in which dotted lines denote triplet coupling (antibonding) between orbitals and ellipses denote ionic coupling (polarization). The weight of configuration 1, the reference state, is the largest, but configuration 1 has total symmetry for the electronic state and consequently yields at the same weights for all bonds. Configurations 2-4 and 31-33 are considered to involve the interaction of singlet coupling in each C−C bond, and configurations 5-10 and 25-30 are associated with the polarization terms for each C−C bond. Accordingly, configuration sets {2, 5, 6}, {3, 7, 8}, {4, 9, 10}, {31, 25, 26}, {32, 27, 28}, and {33, 29, 30} correspond to the overall bonding for each C−C bond. According to the definition of the singlet coupling and polarization terms for each bond, the values for the optimized geometries with some symmetrical restrictions for all compounds treated here are listed in Table 1. Benzene with D_{6h} symmetry satisfies the first criterion of aromaticity: equivalent electronic structures for all bonds. For the second criterion, the difference between the weights of the singlet coupling and polarization terms at the geometry with the equilibrium C−C bond length is only 0.001. This small difference satisfies the second criterion of aromaticity. In contrast, the Kekule-type benzene with D_{3h} symmetry does not satisfy both criteria of aromaticity. To show the relationship between the singlet coupling and polarization terms, the weights for the variation of C−C bond lengths of benzene with D_{6h} symmetry are illustrated in Figure 2. The crossing point for the weights of the singlet coupling and polarization terms occurs at a bond length of 1.36−1.37 Å, which is close to the equilibrium C−C distance of the CASSCF optimized geometry of benzene (D_{6h}). It is considered that the structure with the equilibrium C-C distance at the crossing point for the weights of the singlet coupling and polarization terms have large resonance energy as benzene.

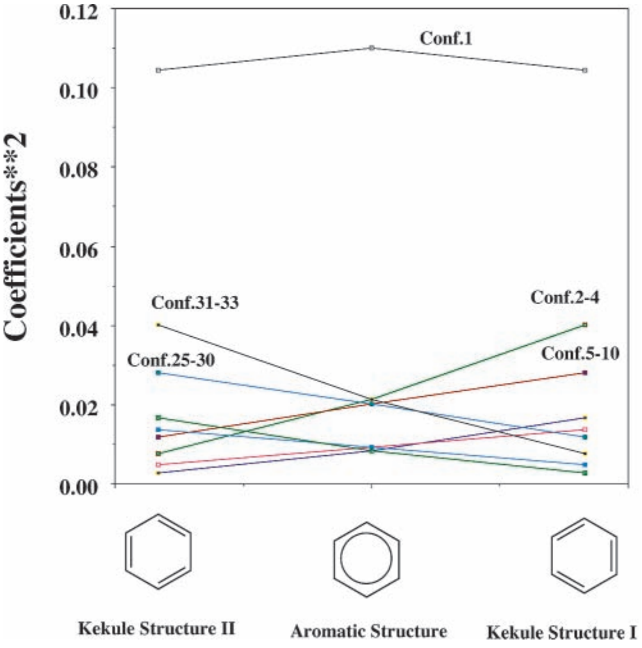
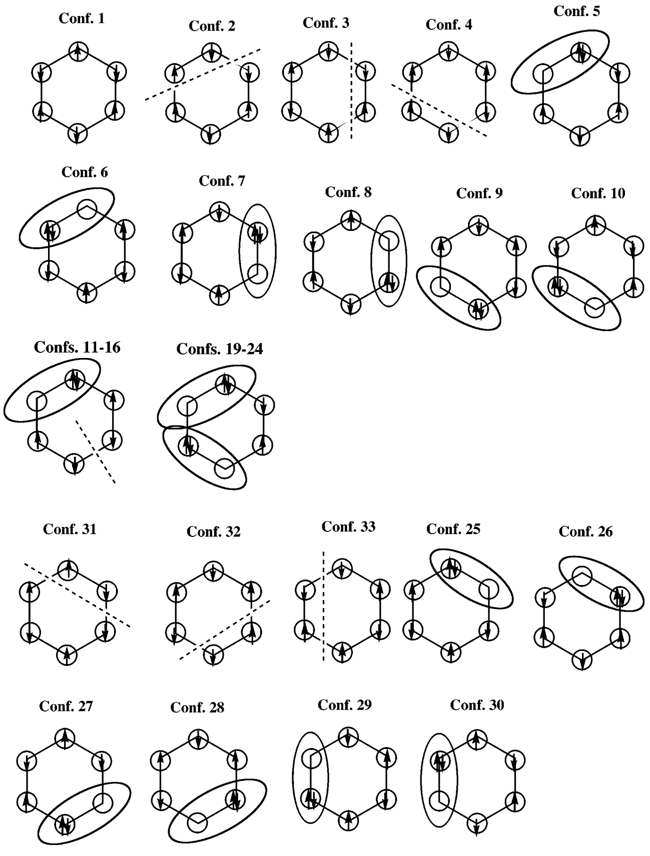


Figure 1. Weights of CI coefficients for aromatic and Kekule structures by the CiLC calculation. Coefficients**2 means the weight (square) of the CI coefficient.

SCHEME 2



3.2. Cyclobutadiene (C_4H_4). It is well known that the stable structure of cyclobutadiene has D_{2h} symmetry (Kekule). From

TABLE 1: Weights of Singlet Coupling and Polarization Terms and Total Weights for Each Bond

compound	C−C bond length (Å)	singlet coupling	polarization (A)	polarization (B)	total
C_4H_4 (D_{4h})	1.443	0.1033	0.0451	0.0451	
		(0.0516)*[a]			0.1418
C_4H_4 (D_{2h})	1.353	0.2330	0.0947	0.0947	
		(0.1165)*[a]			0.3060
	1.546	0.0045	0.0044	0.0044	
		(0.0022)*[a]			0.0111
C_6H_6 (D_{6h})	1.396	0.0213	0.0202	0.0202	0.0617
C_6H_6 (D_{3h})	1.338	0.0402	0.0281	0.0281	0.0964
	1.469	0.0077	0.0118	0.0118	0.0312
C_8H_8 (D_{8h})	1.408	0.0125	0.0108	0.0108	0.0341
C_8H_8 (D_{4h})	1.351	0.0123	0.0130	0.0130	0.0494
	1.472	0.0011	0.0029	0.0029	0.0069
C_8H_8 (D_{2d})	1.344	0.0273	0.0128	0.0128	0.0528
(boat)	1.480	0.0001	0.0008	0.0008	0.0018
$C_{10}H_{10}$ ($D_{10}h$)	1.403	0.0038	0.0038	0.0038	0.0113
$C_{10}H_{10}$ (C_2)	1.490	0.0000	0.0000	0.0000	0.0000
(twist type)	1.347	0.0109	0.0048	0.0048	0.0205
	1.487	0.0001	0.0004	0.0003	0.0008
	1.350	0.0098	0.0047	0.0046	0.0191
	1.477	0.0000	0.0002	0.0003	0.0006
	1.344	0.0102	0.0045	0.0045	0.0192
$C_{10}H_{10}$ (C_2)	1.355	0.0104	0.0049	0.0049	0.0202
(naphthalene-like)	1.485	0.0001	0.0003	0.0005	0.0009
	1.347	0.0105	0.0050	0.0044	0.0199
	1.479	0.0001	0.0003	0.0005	0.0008
	1.353	0.0098	0.0046	0.0050	0.0194
	1.486	0.0002	0.0006	0.0006	0.0014
$C_{10}H_{10}$ (C_s)	1.383	0.0040	0.0038	0.0041	0.0118
(heart)	1.395	0.0037	0.0034	0.0040	0.0111
	1.407	0.0038	0.0034	0.0041	0.0113
	1.417	0.0040	0.0036	0.0040	0.0116
	1.428	0.0038	0.0036	0.0037	0.0111

[a] Weight of modified singlet coupling term.

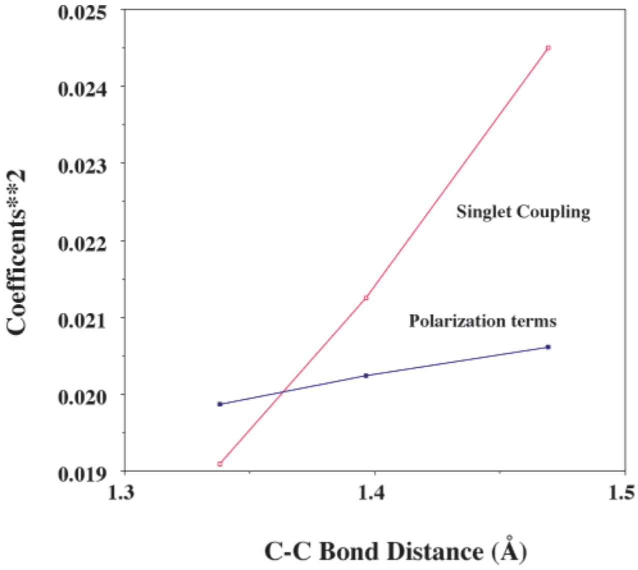


Figure 2. Weights of singlet coupling and polarization terms for the variation of C−C bond lengths of benzene with D_{6h} symmetry by the CiLC calculation. Coefficients**2 means the weight (square) of CI the coefficient.

the weights of the singlet coupling and polarization terms of cyclobutadiene with D_{2h} symmetry in Table 1, the first criterion of aromaticity is not satisfied. The non- (or anti-) aromaticity of cyclobutadiene is indicated only in the first criterion, which relates closely to the geometrical parameters (i.e., bond alternation) in this case. However, the $(4n + 2)\pi$ rule, introduced from HMO theory, does not account for geometrical parameters. Therefore, the aromaticity of cyclobutadiene according to the proposed criterion was further investigated without bond alternation. To study the second criterion of aromaticity, I optimized the geometry of cyclobutadiene under the restriction of D_{4h} symmetry (aromatic type) by CASSCF. The calculated C−C bond length was 1.443 Å. The weights of the singlet coupling and polarization terms for the variation of the C−C bond length of cyclobutadiene with D_{4h} symmetry are shown in Figure 3, and the configurations of the singlet coupling and polarization terms are shown in Scheme 3. For the singlet coupling term, it can be considered that one singlet coupling term includes the singlet coupling terms of two bonds. Namely, the upper configuration of the singlet coupling in Scheme 3 includes the singlet coupling terms for both C−C bonds of the upper part and of the lower part. Therefore, the weights of singlet coupling terms in Figure 3 were divided by 2 to evaluate each C−C bond. The results (green line) of this modification for the singlet coupling term are also shown. The crossing point of the modified singlet coupling and polarization terms occurs at a C−C bond length of about 1.33 Å, which is shorter by 0.11 Å than the equilibrium C−C bond length (1.443 Å). The difference between the modified singlet coupling and polarization terms at the equilibrium C−C bond length is about 0.007, which is 7

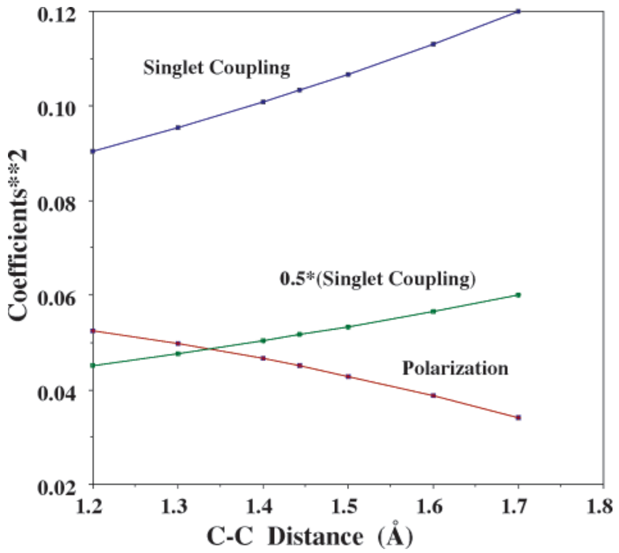


Figure 3. Weights of singlet coupling and polarization terms for the variation of the C−C bond length of cyclobutadiene with D_{4h} symmetry by the CiLC calculation. Coefficients**2 means the weight (square) of the CI coefficient.

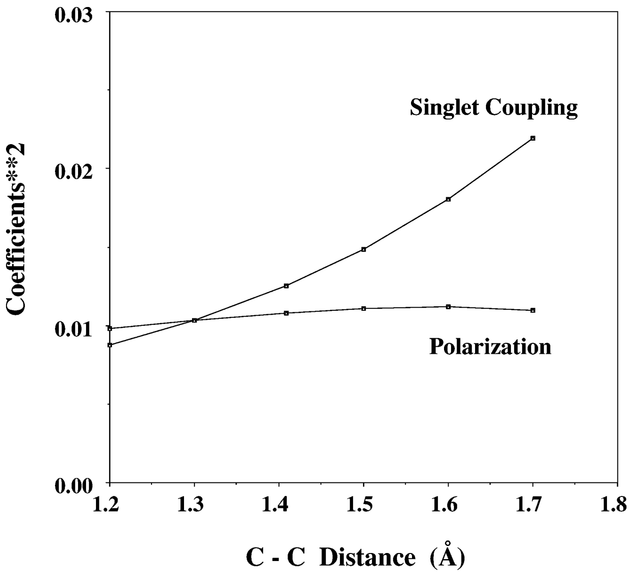


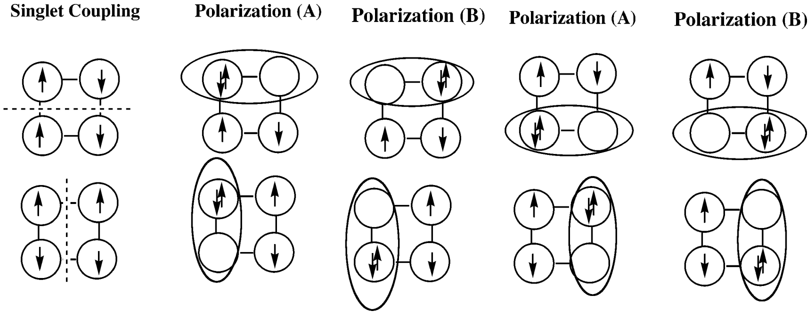
Figure 4. Weights of singlet coupling and polarization terms for the variation of the C−C bond length of C_8H_8 with D_{8h} symmetry by the CiLC calculation. Coefficients**2 means the weight (square) of the CI coefficient.

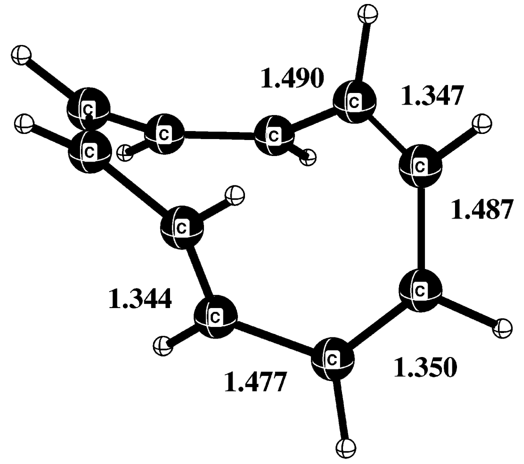
times larger than that (0.001) of benzene. This large difference indicates the anti-aromaticity of cyclobutadiene.

3.3. [8]Annulene (C_8H_8). A recent high-level ab initio calculation[34] revealed the most stable D_{2d} boat-type structures for cyclooctatetraene and [8]annulene. The electronic states for the D_{8h} (aromatic), D_{4h} (Kekule), and D_{2d} (boat) symmetries of [8]annulene were optimized by the CASSCF(8,8)/6-31G(d) calculation. The calculated relative energies for D_{8h} and D_{4h} were 16.7 and 10.4 kcal/mol above that of D_{2d}, respectively. The weights of the singlet coupling and polarization terms for each bond are also listed in Table 1. The structures with D_{4h} and D_{2d} symmetries exhibit bond alternation for each C−C bond, and the weights of the singlet coupling and polarization terms for theses bonds differ significantly. The second criterion of aromaticity was examined by treating the geometry of [8]annulene with D_{8h} symmetry. The weights of the singlet coupling and polarization terms for the variation of the C−C bond length in the D_{8h} structure are shown in Figure 4. From the Figure, the crossing point of the singlet coupling and polarization terms occurs at a C−C bond length of about 1.3 Å, which is shorter by about 0.11 Å than the equilibrium C−C bond length. The large difference between the weights of the singlet coupling and polarization terms indicates the low stabilization energy of π resonance. This corresponds to the estimation of anti-aromaticity from the $(4n + 2)\pi$ rule on the basis of HMO theory.

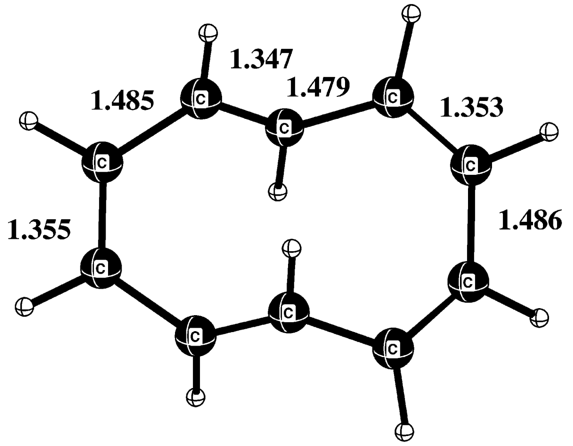
3.4. [10]Annulene ($C_{10}H_{10}$). In 1994, Schaefer and co-workers[35] presented the lowest-energy structure of [10]annulene as a boat shape with alternating single and double bonds by ab initio MO calculations. However, results in 1998 by Allinger et al.[36] suggest that only the high-order correlated methods will be able to predict correctly whether *E*,*Z*,*Z*,*Z*,*Z*-[10] annulene is more stable in the C_2 (twist) or C_s (heart) -type conformations. More recently, Schaefer and co-workers[37] presented the most stable twist-type structure with C_2 symmetry by CCSD(T). It was also shown that the energy difference between the twist-type and naphthalene-like structures with C_2 symmetry is only 1.40 kcal/mol and that the heart type with C_s symmetry is 4.24 kcal/mol higher in energy than the twist type. In this study, four structures (planar D_{10h}, twist-type C_2, naphthalene-like C_2, and heart-type C_s) were optimized by the CASSCF(10,10)/6-31G(d) calculation. Three structures of twist-type C_2, naphthalene-like C_2, and heart-type C_s are shown in Figure 5. The weights of the singlet coupling and polarization terms for each bond of the four types are listed in Table 1. The bond lengths of the twist-type and naphthalene-like structures exhibit bond alternation, and the weights of the singlet coupling and polarization terms for these bonds are also very different. Therefore, the twist-type and naphthalene-like structures do not satisfy the first criterion of aromaticity. The C−C bonds of the heart-type structure change from 1.383 to 1.428 Å for the neighboring bonds as shown in the Figure. To study the $(4n + 2)\pi$ rule for the C_nH_n series, the weights of the singlet coupling and polarization terms for the variation of the C−C bond length of the D_{10h} structure are shown in Figure 6. The most interesting point is the crossing point of the weights of the singlet coupling

SCHEME 3

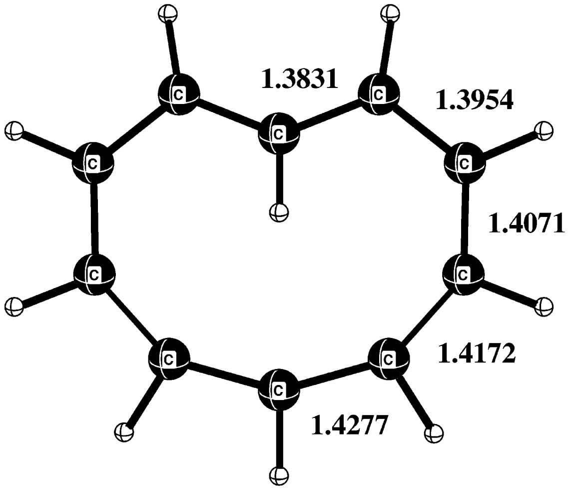




Twist type structure with C_2 symmetry



Naphthalene-like structure with C_2 symmetry



Heart type structure with C_s symmetry

Figure 5. Stationary point geometries for $C_{10}H_{10}$ by CASSCF(10,10)/6-31G(d).

and polarization terms. The C−C bond length at the crossing point is almost equal to the equilibrium C−C bond length in $C_{10}H_{10}$ with D_{10h} symmetry. This means that the difference between the weights of the singlet coupling and polarization terms, the second criterion of aromaticity, is almost zero. These results also show that the proposed criterion of aromaticity corresponds to the $(4n + 2)\pi$ rule on the basis of HMO theory.

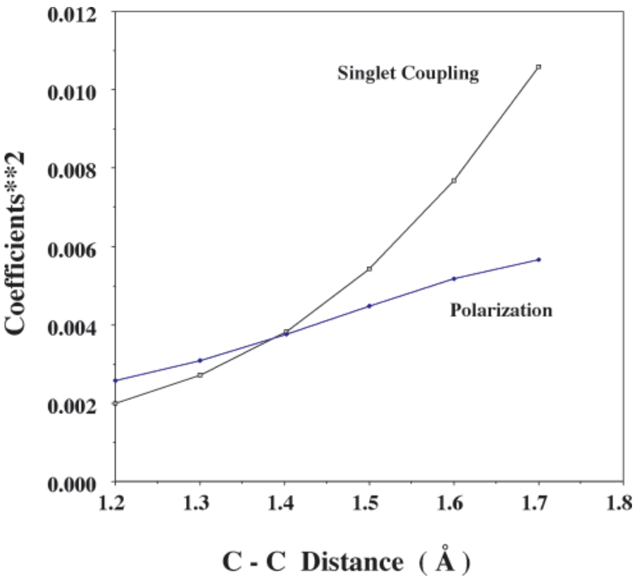


Figure 6. Weights of singlet coupling and polarization terms for the variation of the C−C bond length of $C_{10}H_{10}$ with D_{10h} symmetry by the CiLC calculation. Coefficients**2 means the weight (square) of the CI coefficient.

3.5. Index of Deviation from Aromaticity for a Ring Unit. As shown in the previous sections, the criterion of aromaticity with respect to the singlet coupling and polarization terms for each bond by CiLC analysis is also applicable to C_nH_n-type compounds. Here, the criterion is extended to ring units.

From the two criteria of aromaticity, the index of deviation from the aromaticity (IDA) for an n-cyclic ring can be defined as follows.

$$\mathrm{IDA} = D_s + D_p + G_{sp} \tag{1}$$

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

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

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

S_i is weight of the singlet coupling term for the ith 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 ith 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 1. 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 term. The values of IDA for the compounds treated here are listed along with D_s, D_p, and G_{sp} in Table 2. For comparison with the $(4n + 2)\pi$ rule, which does not account for geometrical parameters, the compounds with D_{nh} symmetry for an n-ring are also shown. The IDA values for C_6H_6 (D_{6h}) and $C_{10}H_{10}$ (D_{10h}) are much

TABLE 2: Index of Deviation from Aromaticity (IDA) for C_nH_n Molecules

molecules	D_s	D_p	G_{sp}	IDA
C_4H_4 (D_{4h})	0.0	0.0	0.1272	0.1272
C_4H_4 (D_{2h})	0.9621	0.9111	0.5738	2.4470
C_6H_6 (D_{6h})	0.0	0.0	0.0474	0.0474
C_6H_6 (D_{3h})	0.6800	0.4101	0.4175	1.5076
C_8H_8 (D_{8h})	0.0	0.0	0.1375	0.1375
C_8H_8 (D_{4h})	0.9103	0.6361	1.0415	2.5878
C_8H_8 (D_{2d}:boat)	0.9922	0.8769	3.7037	5.5729
$C_{10}H_{10}$ ($D_{10}h$)	0.0	0.0	0.0225	0.0225
$C_{10}H_{10}$ (C_2) (twist type)	0.9929	0.8931	7.3124	9.1984
$C_{10}H_{10}$ (C_2) (naphthalen-like)	0.9845	0.8334	2.7106	4.5285
$C_{10}H_{10}$(C_s) (heart type)	0.0269	0.0577	0.0607	0.1453

smaller than those for C_4H_4 (D_{4h}) and C_8H_8 (D_{8h}), whereas for the Kekule structures the IDA for C_6H_6 (D_{3h}) is smaller than that of both C_4H_4 (D_{2h}) and C_8H_8 (D_{4h}). This means that the IDA does reflect the geometrical parameters alone. In the four structures of $C_{10}H_{10}$, the IDA of the twist type is the largest, indicating that the twist-type structure with the lowest energy has strong bond-alternation character (bond localization). Bond alternation for the twist-type structure can be predicted from a detailed investigation of the geometrical parameters.

4. Conclusions

The electronic states of C_nH_n ($n = 4$, 6, 8, and 10) were studied by CiLC analysis on the basis of ab initio MO theory. The CilC analysis characterizes the aromaticity, as given by the $(4n + 2)\pi$ rule from HMO theory in terms of the difference between the weights of the singlet coupling and polarization terms. The two requisites proposed as a new criterion of aromaticity on the basis of CiLC analysis are as follows: (1) the electronic structures of each bond must be equal (equal weights of the respective terms for all bonds), and (2) the difference between the weights of the singlet coupling and polarization terms must be small. To study the correspondence to the $(4n + 2)\pi$ rule (not including geometrical information), criterion 1 was assumed (i.e., C_nH_n with D_{nh} symmetry). As pointed out in the previous paper, the second criterion corresponds to the bond-stabilization energy and reasonably explains the $(4n + 2)\pi$ rule. To allow a comparison of aromaticity on the basis of the ring unit, the index of deviation from aromaticity (IDA) was defined and demonstrated to be useful for this comparison. In the previous papers,[8,9] the aromaticity of benzenes annelated to small rings and heterocyclic compounds with six-membered rings was explained by the criterion based on the CiLC analysis. To support the criterion of aromaticity, the application of IDA to other compounds such as heterocycles and fused rings will be reported separately.

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