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New Criterion on the Aromaticity of Six-Membered Rings

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The aromaticity of six-membered rings with six π electrons was studied by CiLC (CI/LMO/CASSCF) analysis on the basis of ab initio molecular orbital methods. The aromaticity was defined for equivalent electronic states for each bond and the gap between the weights of the singlet coupling and polarization terms. These weights were calculated for the aromatic structure (D_{6h}) of C_6H_6, Si_6H_6, B_6, Al_6, N_6, and P_6, and it was revealed that the aromaticity is closely related to the electronegativity of the composed atoms. The definition of aromaticity employed here corresponds to resonance concepts.

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. Aromaticity has been defined as the difference between π-electron resonance energies of a noncyclic π-conjugated compound and the cyclic π-conjugated compound, giving rise to the $4n + 2$ rule in Huckel molecular orbital (HMO) theory.[1] The definition of aromaticity on the basis of HMO theory can be readily understood; however, the treatment of complex compounds such as nonplaner molecules remains difficult. Aromaticity has also been treated magnetically,[2−4] and Scheyer et al.[5] proposed the nucleus-independent chemical shift (NICS) as an index of aromaticity. The values of the NICS are adequate for classification of aromaticity and anti-aromaticity, but measurement is intensive. Furthermore, magnetic properties such as NICS cannot be used to distinguish between Kekule benzenes and aromatic benzenes. In fact, the NICS of Kekule benzene (D_{3h} with C−C bond distance fixed at 1.350 and 1.449 Å, corresponding to the central distances in 1,3,5-hexatriene) is only 0.8 ppm less than that for D_{6h} benzene itself (−9.7).[6]

Recently, our group characterized the aromaticity of benzene by a CiLC method on the basis of ab initio molecular orbital (MO) calculations.[7] The CiLC method is a combination of configuration interaction (CI), localized molecular orbital (LMO), and complete active space self-consistent field (CASSCF) analyses. From the analysis of the aromaticity of benzene, CiLC calculation along the intrinsic reaction coordinate (CiLC-IRC) revealed that the transition state of the Diels−Alder reaction between butadiene and ethylene is, indeed, aromatic. Our definition for benzene aromaticity is based on whether all bonds in the six-membered ring have equivalent electronic states. In this study, we examine the applicability of this definition and test its generality by investigating the aromaticity of six compounds (C_6H_6, Si_6H_6, B_6, Al_6, N_6, P_6) by CiLC analysis based on our proposed criterion.

2. Computational Methods and Models

Aromaticity is discussed here with respect to both the aromatic structure and the Kekule structure of six-membered ring compounds. Aromatic structures were determined by geometry optimization including D_{6h} symmetry based on analytically calculated energy gradients using a CASSCF method[8] with the 6-31G(d) basis set.[9] For CASSCF calculation, six active spaces corresponding to three π and π* orbitals for six-membered ring compounds were included, and all configurations in active spaces were generated. Cyclotriene Kekule structures were examined, with the double bond distance obtained from the equilibrium bond distance of the diatomic compound including a π bond and the single bond distance obtained from that of the diatomic compound including a twisted-π bond.

Aromaticity was interpreted through a CI localized molecular orbital (LMO) CASSCF analysis carried out according to a method described in detail elsewhere.[7,10−21] In this process, the CASSCF calculation was performed to obtain a starting set of orbitals for the subsequent Boys localization procedure.[22] The calculated localized orbitals were very atomic in nature, and appear as p_π orbitals on an atom. Using the localized MOs as a basis, a full CI simulation with determinant level was performed to generate electronic structures and relative weights in the atomic orbital-like wave functions. As the CI configurations obtained with determinant level include redundancy in spin configurations (reverse configurations of α and β), after the CI procedure, the weight (or square) of the CI coefficient of the side of the configuration with the redundancy was added to that of the other side. The total energy as calculated by the CI procedure corresponded well to that by CASSCF calculation, and the relative weights of the electronic states of different CI configurations are expected to indicate the electronic state of the bond. This procedure is referred to as the CiLC method.

Calculations for the CiLC method were performed using the GAMESS software package.[23] Other calculations were carried out using Gaussian98.[24]

3. Results and Discussion

3.1. Electronic Structure of π Bond. The electronic state of the π bond was examined on the basis of a valence bond-like picture by analyzing the variation in the C−C bond distance of the π bond of ethylene by the CiLC method. The weights of the CI coefficients with respect to the C−C bond distance are shown in Figure 1. In the notation of the valence bond-like model, the electronic state of the π bond is represented by three electronic configurations: one singlet coupling and two polarization terms (Scheme 1).

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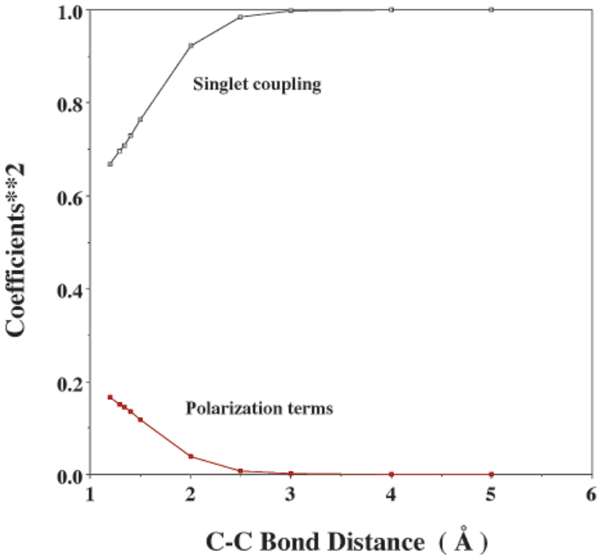
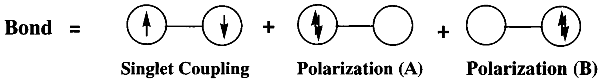


Figure 1. Weights of CI coefficients of singlet coupling and polarization terms for ethylene by CiLC calculation.

SCHEME 1



The weights of singlet coupling terms decrease with decreasing C−C bond distance, whereas the weights of the polarization terms increase. A decrease in the C−C bond distance contributes to π resonance stabilization because of the increasing overlap between p_π orbitals. Such π resonance stabilization is indicated by a narrowing of the gap between the weights of singlet coupling and polarization terms. The relationship between π resonance stabilization and the gap between the weights of singlet coupling and polarization terms can be extended to the definition of aromaticity.

The differences between the Kekule and aromatic structures of benzene were presented in a previous paper.[7] Those results are outlined here briefly for comparison with the present results.

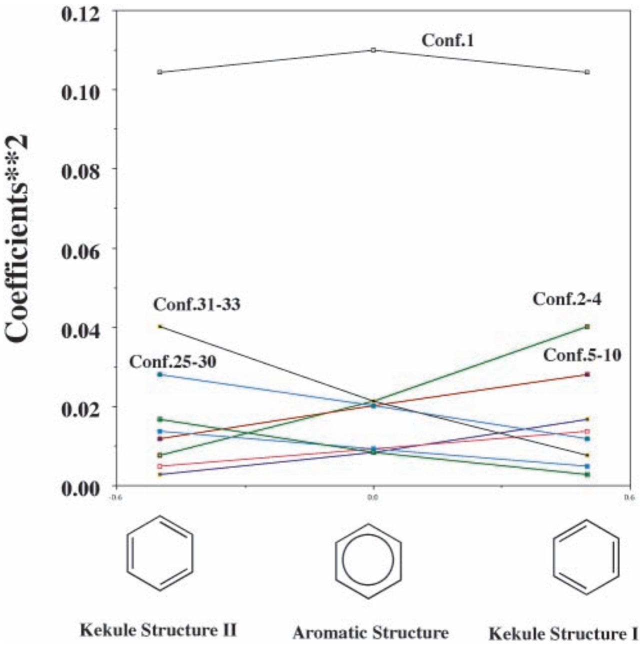


Figure 2. Weights of CI coefficients for aromatic and Kekule structures by CiLC calculation.

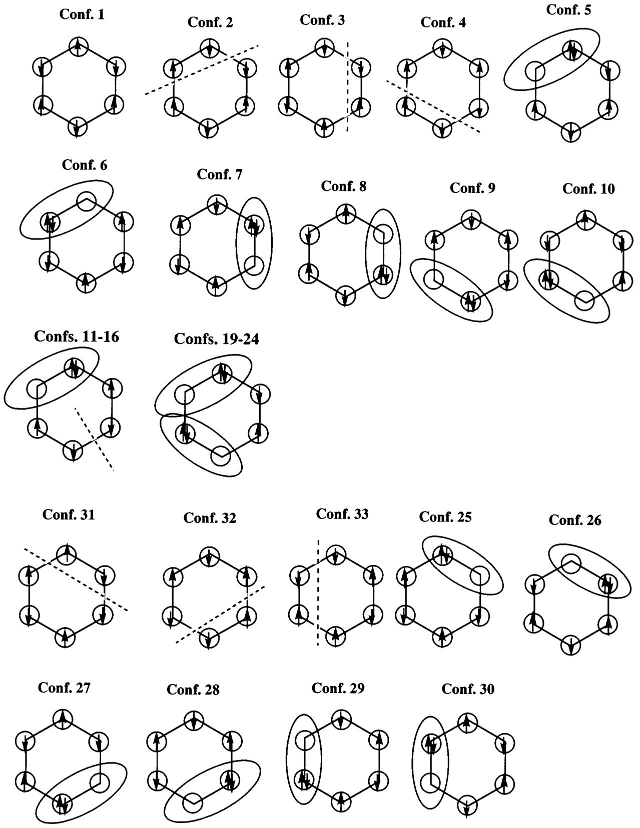


Figure 3. Selected electronic configurations of benzene for CiLC analysis. Dotted lines denote triplet coupling (antibonding) between orbitals, and ellipses denote ionic coupling.

The weights of the CI coefficients for the Kekule and aromatic structures of benzene as determined by the CiLC method are shown in Figure 2. Small values (<0.001) for both structures were neglected. Some of the configurations with larger CI coefficients are displayed in Figure 3. The weight of configuration 1, the reference state, is virtually identical in the Kekule and aromatic structures. Configuration 1 has total symmetry for the electronic structure, and does not affect the variation of a bond. Configurations 2−4 are considered to involve the interaction of singlet coupling in the double bonds of Kekule structure I and configurations 5−10 are associated with the polarization terms for the double bonds of Kekule structure I. The set of the one term of configurations 2−4 and the two associated terms of configurations 5−10 may therefore represent overall bonding for one double bond of Kekule structure I, that is, configuration sets {2,5,6}, {3,7,8}, and {4,9,10}. Similarly, sets of the one term of configurations 31−33 and the two associated terms of configurations 25−30 could describe the single bond of Kekule structure I. The weights of configurations 2−10 in Kekule structure I are higher than those of configurations 25−33, corresponding to the double bonds and single bonds in the Kekule structure. The weights of coefficients of Kekule structure I for configurations 2−4 and for configurations 5−10 therefore correspond to those for configurations 31−33 and 25−30 for the aromatic structure, respectively. This indicates the equilibrium electronic state for the π bonds of the six-membered ring (benzene). The gap between the weights of singlet coupling and polarization in the aromatic structure is extremely narrow, considered to represent the π resonance stabilization characteristic of the aromaticity of benzene.

3.2. Hexasilabenzene. It is known that the chair structure is the most stable structure for hexasilabenzene and that the aromatic or Kekule structures are less stable.[25,26] Therefore, it

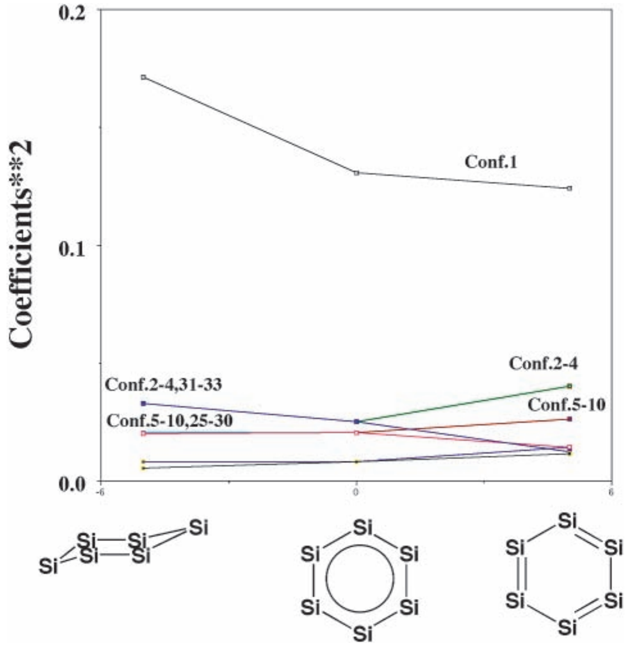


Figure 4. Weights of CI coefficients for Kekule, aromatic, and chair structures of hexasilabenzene by CiLC calculation.

is interesting to compare the electronic structure of chair-type hexasilabenzene with the aromatic and Kekule structures. The weights of CI coefficients for the aromatic, Kekule, and chair-type structures of hexasilabenzene determined by the CiLC method are shown in Figure 4. The electronic states for the aromatic and Kekule structures are similar to those of the benzene molecule. In the Kekule structure, the difference between the electronic states of the single and double bonds of Si−Si is remarkable. All singlet coupling (configurations 2−4 and 31−33) and polarization (configurations 5−10 and 25−30) terms for the Si−Si bonds have the same weights in the aromatic structure, respectively, as shown in the case of benzene. The gap between the weights of the singlet coupling and polarization terms in the aromatic structure is larger than for benzene. As shown for ethylene, the gap may correspond to π bond stabilization. Therefore, it is considered that the different gaps for hexasilabenzene and benzene relates to the level of aromaticity.

CiLC analysis was performed to determine the variation in bond distances for the aromatic structures (D_{6h}) of benzene and hexasilabenzene. The variations in the gap between the weights of the singlet coupling and polarization terms for the C−C bond distance of benzene and the Si−Si bond distance of hexasilabenzene are shown in Figures 5 and 6. The crossing points of the singlet coupling and the polarization terms occur at about 1.36 Å for the C−C bond of benzene and at 2.05 Å for the Si−Si bond of hexasilabenzene. The C−C bond distance at the crossing point for benzene is about 0.02 Å longer than the equilibrium C−C bond distance (1.338 Å) of ethylene and 0.04 Å shorter than that (1.396 Å) of benzene (D_{6h}). The Si−Si bond distance at the crossing point for hexasilabenzene is about 0.11 Å shorter than the equilibrium Si−Si bond distance (2.162 Å) of disilaethylene. This C−C bond distance at the crossing point for benzene is nearly equal to the equilibrium C−C bond distance of the aromatic benzene (D_{6h}), which has considerable π stabilization energy. However, the Si−Si bond distance at the crossing point for hexasilabenzene is overly short, preventing formation of the D_{6h} structure due to nuclear repulsion. The bond distance at the crossing point therefore reveals the difference in aromaticity of benzene and hexasilabenzene. The lower aromaticity of hexasilabenzene may lead to the chair structure.

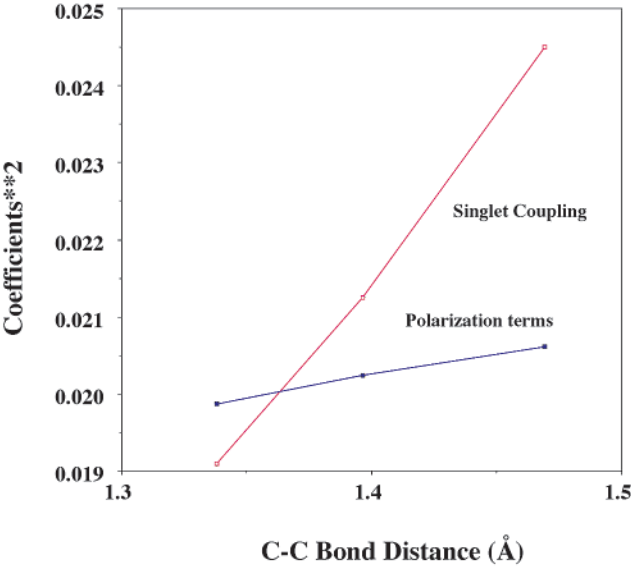


Figure 5. Weights of CI coefficients of singlet coupling and polarization terms for benzene with D_{6h} symmetry by CiLC calculation.

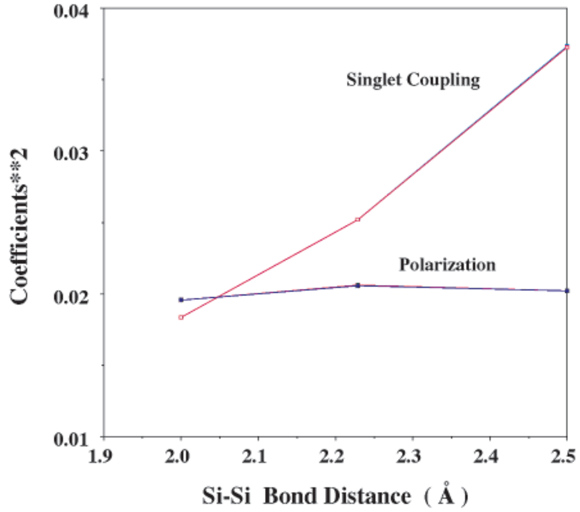


Figure 6. Weights of CI coefficients of singlet coupling and polarization terms for hexasilabenzene with D_{6h} symmetry by CiLC calculation.

For the chair-type hexasilabenzene, the weights of the singlet coupling terms are almost the same for each of the Si−Si bonds, as are the weights of the polarization terms. Therefore, all the Si−Si bonds in the chair-type hexasilabenzene have the same π bond stabilization energy. However, the aromaticity of the chair-type configuration may be lower than for D_{6h}, as indicated by the different gaps between the weights of the singlet coupling and polarization terms.

3.3. Six-Membered Rings. To compare the aromaticity of more general six-membered ring compounds involving six π electrons, CiLC calculation was performed for aromatic C_6H_6, Si_6H_6, B_6, Al_6, N_6, and P_6. The weights of the singlet coupling and polarization terms for these compounds are shown in Figure 7. The aromaticity of these compounds can be inferred from the gap between the weights of the singlet coupling and polarization terms. Two important points can be seen in this figure. Rings composed of second-row elements (B, C, and N) tend to be more aromatic than rings of third-row elements (Si, Al, and P) in each group atom of the periodic table. Furthermore,

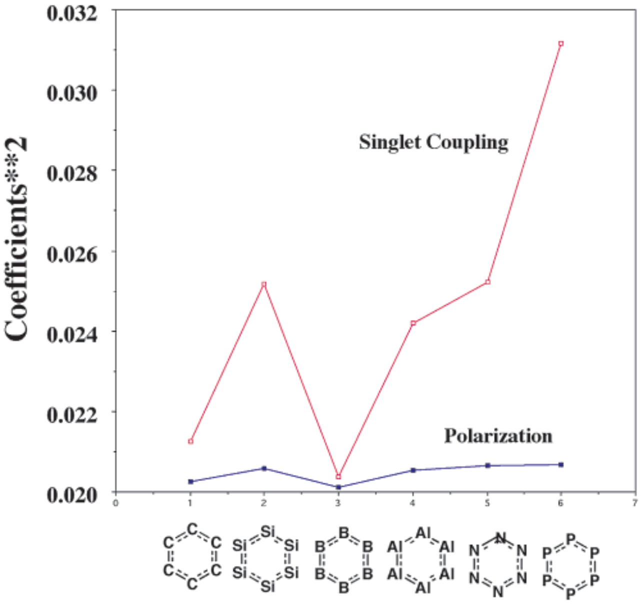


Figure 7. Weights of CI coefficients of singlet coupling and polarization terms for six-membered rings with D_{6h} symmetry by CiLC calculation.

rings composed of elements with weaker electronegativity in the same row tend to be more aromatic than those composed of elements with stronger negativity. The relationship between the electronegativity of the base element and the aromaticity of the ring corresponds to the concepts of resonance, in which the electrons of atoms with strong electronegativity localize near the atom and electrons of atoms with weak electronegativity distribute in the interatomic region. The resonance for the interatomic region also corresponds to the overlap between orbitals.

Therefore, the aromaticity determined by the gap between the weights of the singlet coupling and polarization terms calculated by the CiLC method is closely related to resonance in six-membered rings.

4. Conclusion

The aromaticity of six-membered ring compounds was studied by CiLC analysis on the basis of ab initio molecular orbital methods. The aromaticity determined by CiLC analysis was defined as the degree of equality of electronic state 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. For the aromatic structure (D_{6h} symmetry), the difference between the aromaticity of benzene and hexasilabenzene can be seen directly from the location of the crossing point between the singlet coupling and the polarization terms of the C−C and Si−Si bonds. The crossing point for benzene is located near the equilibrium C−C bond distance of benzene, whereas the crossing point for hexasilabenzene is located at a distance shorter than the Si−Si bond distance of disilaehylene. The aromaticity of six aromatic (D_{6h}) compounds (C_6H_6, Si_6H_6, B_6, Al_6, N_6, and P_6) was also investigated. The six-membered ring compounds composed of second-row elements tend to have more aromatic character than those composed of third-row elements in each group atoms, and within each row, compounds composed from elements with weak electronegativity exhibit more aromatic character. The relationship between the electronegativity and aromaticity corresponds to the concepts of resonance.

The criterion of aromaticity based on CiLC analysis is related closely to resonance concepts and is appropriate for the general concept of aromaticity. This criterion of aromaticity is expected to be extendable to more general problems such as transition states including heterogeneous compounds in chemical reactions.

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