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Theoretical studies of the structures and local aromaticity of conjugated polycyclic hydrocarbons using three aromatic indices

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ABSTRACT

The structures and local aromaticity of some conjugated polycyclic hydrocarbons (from the butadienoid, acene, and phenylene series) are studied using ab initio MO and density functional methods. The aromaticities of the molecules are estimated using three indices: the nucleus-independent chemical shift (NICS), the harmonic oscillator model of aromaticity (HOMA), and the index of deviation from aromaticity (IDA). Assessment of the relationships between the structures and the aromatic indices shows that the IDA values correspond best to the characteristics of the conjugated polycyclic hydrocarbon structures.

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1. Introduction

The term 'aromaticity' is one of the popular and important concepts in organic chemistry. However, the definition of aromaticity is not clear, and various criteria [1], including energetic, geometric, and magnetic parameters, have been used to account for this concept. Aromaticity has generally been defined as the difference between the π-electron resonance energies of a cyclic non-π-conjugated compound and a cyclic π-conjugated compound. This had been introduced as the $(4n + 2)\pi$ rule of the Hückel molecular orbital (HMO) theory [2]. Although the definition of aromaticity in the HMO theory is readily understandable, the treatment of complex compounds, such as non-planar molecules, remains difficult. Schleyer et al. [3–5] proposed a nucleus-independent chemical shift (NICS) as an aromaticity index on the basis of magnetic properties, and this index has been used in many studies. The NICS values may be adequate for classifying aromaticity and antiaromaticity, but their actual values are inadequate for putting some chemicals into an appropriate order, as shown in Ref. [6]. Bultinck et al. [7] stated that NICS values did not indicate the individual aromatic natures of specific rings in polycyclic aromatic hydrocarbons, and Stanger [8] showed that the relative aromaticities of each ring in a polycyclic system (i.e., the local aromaticities) could not be estimated using NICS. Krygowski et al. [9,10] proposed a harmonic oscillator model of aromaticity (HOMA) as an aromaticity index, and this is calculated from data on the bond length elongations and alternations that accompany the development of aromatic characteristics. However, the HOMA index is difficult to use for complex compounds such as non-planar molecules and/or non-hydrocarbons.

Therefore, we have formerly proposed an index of deviation from aromaticity (IDA) to assess the order of π-electron resonance energies for whole molecules and/or ring units [11,12]. The IDA value corresponds [6] to the π-electron resonance energy. Estimation of the aromaticity of a whole ring and/or a local ring unit in polycyclic conjugated molecules using these aromatic indices is, therefore, a challenging problem for defining aromaticity.

We have investigated in the present study the relationship between the geometric parameters and aromaticity of polycyclic hydrocarbons using ab initio MO and density functional methods. We have also tested the aromaticity models with different types of structure, including four- and six-membered ring compounds, and compounds with both four- and six-membered rings. For four-membered ring, it has been shown [13,14] that some compounds have a local aromatic nature and others have only Kekulé structure. Six-membered ring compounds indicate local aromatic nature at either the center or the side rings. Since bicyclo[1,2:4,5]butadienobenzene, in which four- and six-membered rings are combined, has two stable structures and is interesting issue, the three aromatic indices, NICS, HOMA, and IDA, are compared and discussed on the aromaticity of these compounds.

2. Computational methods

Molecular geometries were determined by analytically calculating energy gradients using CCSD(T) [15,16], CASSCF [17], and B3LYP methods [18,19] with 6-31G(d) basis sets [20]. For the CASSCF calculations, all active spaces corresponding to valence π and π* orbitals were included, and all configurations in active spaces were generated. The calculations of the NICS(1) were performed using the gauge-including atomic orbital method [21] with B3LYP/6-31G(d), the calculation points being located 1.0 Å above the center of the molecular ring and/or the bonds.

The HOMA method is based on the normalized deviation of a given bond length (R_i) from the optimal aromatic value

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(R_{opt} = 1.388 Å) so that the aromaticity index is calculated using the expression

$$\mathrm{HOMA} = 1 - (\alpha/n)\sum (R_{\mathrm{opt}} - R_i)^2, \quad (1)$$

where n is the number of bonds used in the summation, and α is the normalization coefficient required to make HOMA equal to 1.00 for an ideal aromatic molecule with all bond lengths equal to R_{opt} and HOMA to equal to 0 for hypothetical Kekulé structures with the same C–C bond lengths as acyclic 1,3-butadiene.

The IDA is calculated to describe the localization of electrons using the CiLC (CI/LMO/CASSCF) [22–26] method and CASSCF wavefunctions. The CiLC method gives the singlet coupling term and polarization terms for the electronic states of a bond, as shown in Figure 1.

For the IDA, the aromaticity criterion is based on two points: (a) electronic equalization of each bond in a ring unit and (b) large stabilization for the ring. The latter corresponds to the nature of the covalent bond for all bonds of the ring unit. These criteria are determined according to the following conditions using the CiLC calculations: (A) each weight for 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. Criterion (A) corresponds to the aromaticity for the electronic state equalization of bonds being similar to the bond length equalization [27], while (B) corresponds to the resonance stabilization energy. Using these criteria, the IDA for an n-cyclic ring can be defined using the following Eqs. (2)–(5).

$$\mathrm{IDA} = D_{\mathrm{s}} + D_{\mathrm{p}} + G_{\mathrm{sp}} \quad (2)$$

$$D_{\mathrm{s}} = \left(\sum_{i=1}^{n} |(S_i - S_{\mathrm{av}})/S_{\mathrm{av}}|\right)/n \quad (3)$$

$$D_{\mathrm{p}} = \left(\sum_{i=1}^{n} (|PA_i - P_{\mathrm{av}}| + |PB_i - P_{\mathrm{av}}|)/2P_{\mathrm{av}}\right)/n \quad (4)$$

$$G_{\mathrm{sp}} = \left(\sum_{i=1}^{n} (|S_i - PA_i| + |S_i - PB_i|)/2S_i\right)/n \quad (5)$$

S_i is the 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. 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). G_{sp} is the average ratio of the difference between the weights of the singlet coupling and polarization terms based on the singlet coupling. Therefore, the IDA value vanishes for an ideal aromatic ring, and those for e.g. benzene, Kekulé-type benzene, and cyclobutadiene using the CASSCF/6-31G(d) level are 0.047, 1.508, and 2.037, respectively.

The optimized structures from the CASSCF MO method are used in the IDA calculations, and the NICS and HOMA calculations are performed using B3LYP optimized geometries. The IDA calculations are also performed using the GAMESS software package [28,29] and our own program, and other calculations are carried out using the GAUSSIAN03 program [30].

3. Results and discussion

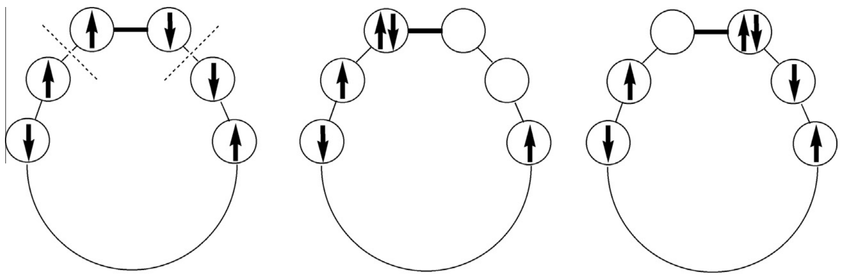
Butalene, bicyclobutadienylene, anthracene, phenanthrene, and benzo [1,2:4,5] dicyclobutene molecules are assessed, and their stationary point geometry parameters are shown in Figure 2. The IDA and HOMA values are calculated for rings A and B and for the whole molecule, and their NICS values are calculated at each point, from 1 to 4, shown in Scheme 1, because the IDA and HOMA values, shown in Table 1, can be used as aromaticity indices for each ring unit, and the NICS values listed in Table 2 can be used at specific locations in the whole molecule.

3.1. Polybutadienoids

The C–C bond lengths for butalene and bicyclobutadienylene geometries are similar when calculated using the B3LYP, CASSCF, and CCSD(T) methods. The C–C bond length at the center of the whole ring is calculated to exceed 1.5 Å and thus can be viewed as a single bond. The surrounding C–C bond lengths in the ring are clearly shorter. Butalene appears to have six π electrons in its resonance structure, which can be explained using the combination method of asymmetric Kekulé structures (CMAK) as proposed in Ref. [13]. The electronic structure of butalene, assessed from its geometry, corresponds to its IDA aromaticity index with the four-membered ring on one side of butalene having a large IDA value and non-aromatic, and the IDA value for the six-membered ring (whole outside ring) in this molecule showing aromaticity.

The HOMA values for butalene do not correspond to its electronic state, assessed from its geometrical parameters; their HOMA values indicate that the four- and six-membered ring should both be non-aromatic (or antiaromatic). The NICS method cannot give values for specific rings, but the values are obtained at the three points shown in Scheme 1, and all NICS values indicate aromaticity; higher degrees of aromaticity at points 1 and 3 than at point 2 imply that the NICS values above the bond indicate higher aromaticity than those above the ring center.

Although a bent structure of bicyclobutadienylene with C_{2v} symmetry is the most stable, the planar structure with D_{2h} symmetry has been chosen for our calculations to clarify the origin of peculiarities of the NICS method. This molecule appears to have a typical Kekulé structure with bond alternation, but the molecule



Singlet Coupling Polarization A Polarization B

Figure 1. Singlet coupling and polarization terms for electronic state of a bond.

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