A Simple Method for Estimating the Superaromatic Stabilization Energy of a Super-Ring Molecule

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A simple graph-theoretical method is proposed for readily estimating the degree of extra stabilization due to macrocyclic conjugation (superaromaticity). This method is based theoretically on the concept of circuit resonance energy previously defined for cyclic π systems. We confirmed that kekulene and related super-ring molecules are essentially nonsuperaromatic, with very small superaromatic stabilization energies.

1. Introduction

Superaromaticity represents extra stabilization due to macrocyclic conjugation in super-ring molecules, such as kekulene and carbon nanotubes.[1−10] It constitutes part of the aromaticity that arises from cyclic conjugation. In 1991, Cioslowski et al. estimated the superconjugative energy component for kekulene and reached the conclusion that this super-ring molecule is slightly superaromatic.[1] They employed the semiempirical additive nodal increments (ANI) concept to assess the π energy of the superaromaticity-free reference structure. We have since discussed superaromaticity by applying our graph-theoretical way of thinking to many super-ring molecules but could not find appreciably superaromatic molecules.[2−9] Jiao et al. also noted that the lack of significant equalization of the CC bond lengths, the extra stabilization energy, the extra magnetic susceptibility exaltation and anisotropy, and the nucleus-independent chemical shift (NICS) values show that kekulene is not superaromatic.[10]

Our graph theory of aromaticity and ring-current diamagnetism[11−27] has been used for exploring energetic and magnetic properties of cyclic π systems consistently. In this theory, circuit resonance energy (CRE) is a key quantity that connects energetic and magnetic scales of aromaticity, which represents a contribution of each cyclic path or circuit in a polycyclic π system to the aromatic stabilization energy (ASE).[23−27] Main magnetic quantities can be formulated exactly in terms of CREs. For polycyclic aromatic hydrocarbons and heterocycles, the sum of CREs for all possible circuits represents a kind of ASE.[23−27] Bond resonance energy (BRE) represents the contribution of a given π bond to aromaticity.[21,22] Recently, we found that BRE can also be reproduced well using CREs.[27] In this paper, we show that the superaromatic stabilization energy (SSE) for a super-ring π system can likewise be formulated accurately in terms of CREs and propose a new simple method for assessing the SSE on this basis.

2. Theoretical Background for the Present Study

We first survey our graph theory briefly. It is a graph-theoretical variant[13−27] of Hückel−London theory.[28,29] This theory allows a partitioning of the ring-current diamagnetic susceptibility for a polycyclic π-system exactly into individual circuit contributions. Here, circuits stand for all possible cyclic or closed paths that can be chosen from a cyclic π system.[30] Topological resonance energy (TRE), defined within the same theoretical framework, has been used as a typical energetic criterion of aromaticity.[11,12,17]

Circuit Resonance Energy. We beforehand evaluate the A_i values for all possible circuits in carbocyclic π systems[14,23−26]

$$A_{\mathrm{i}} = 4\sum_{j}^{\mathrm{occ}} \frac{P_{\mathrm{G-r}_i}(X_j)}{P'_{\mathrm{G}}(X_j)} \qquad (1)$$

where r_i refers to a set of conjugated atoms and π-bonds that constitute the ith circuit c_i; G-r_i is the subsystem of G, obtained by deleting r_i from G; $P_{\mathrm{G}}(X)$ and $P_{\mathrm{G-r}_i}(X)$ are the characteristic polynomials for G and G-r_i, respectively; X_j is the jth largest zero of $P_{\mathrm{G}}(X)$; a prime added to $P_{\mathrm{G}}(X)$ indicates a first derivative with respect to X; and j runs over all occupied π molecular orbitals. If there are degenerate π molecular orbitals and/or heteroatoms, eq 1 must be replaced by others.[14,15,18,19]

The A_i value is interpretable as an energy gain or loss due to cyclic conjugation along the ith circuit and so is termed the circuit resonance energy (CRE) for the circuit.[23,25] Magnetic resonance energy (MRE) is defined as the sum of CREs over all circuits. MRE means a TRE-like aromatic stabilization energy (ASE) derived from the magnetic response of the π system.[23−26] For many polycyclic aromatic hydrocarbons and heterocycles, there is an excellent correlation between MRE and TRE.

Ring-Current Magnetic Susceptibility. When an external magnetic field, H, is oriented perpendicular to the plane of G, the ring-current diamagnetic susceptibility, χ_{G}, is then given in the form[14−20]

$$\chi_{\mathrm{G}} = 4.5\chi_0 \sum_{i}^{\mathrm{G}} A_i\left(\frac{S_i}{S_0}\right)^2 \qquad (2)$$

where χ_0 is the ring-current susceptibility of benzene; S_i and S_0 are the areas of c_i and the benzene ring, respectively. Positive and negative A_i values represent diamagnetic and paramagnetic contributions, respectively. χ_{G} agrees exactly with the value calculated using conventional Hückel−London theory.[28,29,31] Thus, χ_{G} can be evaluated additively with respect to individual circuits. The contribution of the ith circuit to χ_{G}, that is, the circuit current susceptibility, is then given as[14−19]

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$$\chi_i = 4.5\chi_0 A_i \left(\frac{S_i}{S_0}\right)^2 \tag{3}$$

Circuit Current. A π-electron current induced in each circuit may be called a circuit current. According to general electromagnetism, magnetization, M, due to a loop current, I, induced by a magnetic field, H, is given by IS, where S is the area enclosed by the loop.[32] Since $M = \chi H$, I can be equated formally with $\chi H/S$, and the circuit current susceptibility for the ith circuit, χ_i, must correspond to the induction of a π-electron current in the circuit, the intensity of which is given by[19,20]

$$I_\mathrm{i} = 4.5 I_0 A_\mathrm{i} \frac{S_i}{S_0} \tag{4}$$

where I_0 is the intensity of a current induced in the benzene ring. Positive and negative A_i values indicate diatropicity and paratropicity, respectively. Equation 4 indicates that the intensity of a circuit current is proportional not only to the CRE but also to the area of the circuit. In this context, Haddon noted in 1979 that the intensity of the ring current induced in an aromatic annulene is proportional not only to the ASE but also to the area of the ring.[33,34] A π current density map for an entire π system is obtained by superposing all of the circuit currents.[23−25]

Superaromatic Stabilization Energy. In 1995, we proposed a general graph-theoretical method for assessing the degree of superaromaticity in super-ring molecules, such as **1**−**7** in Figure 1.[6] Let us consider the kekulene π system (**1**) as an example. We change two pairs of resonance integrals in the kekulene secular determinant into the imaginary numbers[6]

$$\beta_{1,2} = \mathrm{i}\beta \qquad \beta_{2,1} = -\mathrm{i}\beta$$
$$\beta_{20,21} = \mathrm{i}\beta \qquad \beta_{21,20} = -\mathrm{i}\beta \tag{5}$$

where β is the standard resonance integral for CC π bonds. For the numbering of carbon atoms in **1**, see Figure 2. The two pairs of resonance integrals must belong to the same ring. Of course, there are many other ways of choosing two pairs of resonance integrals. By solving the modified secular equation, we obtain a total π-binding energy for the superaromaticity-free reference structure, which lacks in extra stabilization energy due to superaromaticity (i.e., SSE). The SSE for **1** is then calculated by reference to this total π-binding energy.[6] SSE defined in this manner will be referred to as t-SSE, where t indicates a topologically defined quantity. For the physical meaning of this definition, see ref 6.

3. New Method for Estimating Superaromatic Stabilization Energy

Many circuits can be chosen from a polycyclic super-ring π system with an inner cavity. As illustrated in Figure 3, they can be classified into two groups, the circuits not enclosing the inner cavity and those enclosing the inner cavity.[2,6] The former and the latter circuits may be denoted by type-I and -II circuits, respectively. The A_i values for type-I circuits can be evaluated rather easily because there are not so many. There are 132 type-I circuits in kekulene (**1**). In contrast, as many as 4096 type-II circuits can be chosen from the kekulene π system. Type-II circuits are the origin of superaromaticity in a super-ring π system.[2,6] However, it is not easy to choose all type-II circuits from a large super-ring molecule. This is why we propose a new method for calculating the sum of A_i values for all type-II circuits.

We deform the kekulene π system artificially into **1a** in Figure 2. This polygonal prismatic structure is topologically identical to the original kekulene π system. The top view of this prismatic π system **1a** is shown as **1b**, which is monocyclic (polygonal) in appearance. Suppose that all CC bonds that shape the inner cavity are located on the xy plane and that they are drawn as straight lines. As can be seen from the top view, **1a** is designed in such a manner that each of the upper carbon atom has the same xy coordinates as those of one of the carbon atoms shaping the inner cavity. In addition, all π bonds other than those located along the inner perimeter must also come above the inner perimeter. In other words, all conjugated atoms and all π bonds in **1a** are formally arranged on the surface of a polygonal prism. Therefore, the projection of polygonal prismatic kekulene onto the xy plane is simply polygonal in shape.

An external magnetic field is then oriented perpendicularly to the xy plane formed by the inner cavity (i.e., parallel with the z axis). Under such experimental conditions, π-electron currents would not be induced in type-I circuits because the projections of these circuits onto the xy plane have no areas. In contrast, all type-II circuits will sustain diamagnetic or paramagnetic π currents. The projections of all of these circuits onto the xy plane have the same areas as the inner cavity. Therefore, the intensity of a π current induced in each type-II circuit must be proportional simply to the A_i value. The sum of A_i values for all type-II circuits then is equal to the intensity of the overall π current induced along the super-ring, divided by 4.5 times the cavity area. Here and hereafter, the area of the cavity is given in units of the area of the benzene ring (S_0).

The intensities of bond currents in planar and prismatic kekulene molecules can be calculated easily using any variant of the Hückel−London method.[35−37] By bond currents, we mean π-electron currents flowing through individual π bonds. Only the connectivity of conjugated atoms and their xy coordinates are necessary to calculate ring currents. Steiner et al. noted that the Hückel−London method reproduces well the ab initio π-current density in kekulene.[38] The intensities of bond currents thus obtained for deformed kekulene (**1a**) are listed in Table 1. In fact, type-II circuits contribute much less to aromaticity than type-I ones. This is simply because type-II circuits have large areas. In general, larger circuits contribute less to aromaticity.[39]

We found that the prismatic kekulene π system sustains very weak diamagnetic currents both along the inner and outer perimeters. Thus, bond currents flow counterclockwise along the inner and outer perimeters. Note that apparent paramagnetic and diamagnetic currents are induced along the inner and outer perimeters of planar kekulene, respectively.[2] An overall π current with an intensity of 0.109299 I_0 circulates around the prismatic macrocycle **1a**, which, however, amounts only to 10% of the π current induced in benzene. This current intensity was calculated as a $I_{2\rightarrow1} + I_{21\rightarrow20}$ or $I_{3\rightarrow2} + I_{22\rightarrow21}$ in Table 1. If this current intensity is divided by 4.5 times the cavity area, the sum of CREs for all type-II circuits in kekulene will be obtained. This quantity can be interpreted as an SSE because it represents the stabilization due to all type-II circuits. This kind of SSE will be referred to as m-SSE, which means a magnetically defined SSE-like quantity.

The m-SSE for kekulene is calculated to be $0.00347|\beta|$, which must be equal to the sum of CREs for 4096 type-I circuits. This value is quite reasonable considering that it is very close in magnitude to the t-SSE of $0.00348|\beta|$.[6] Prismatic kekulene has a ring-current diamagnetic susceptibility of $0.765089\chi_0$. The same value for m-SSE ($0.00347|\beta|$) can be obtained by dividing this susceptibility value first by 4.5 and then by the cavity area

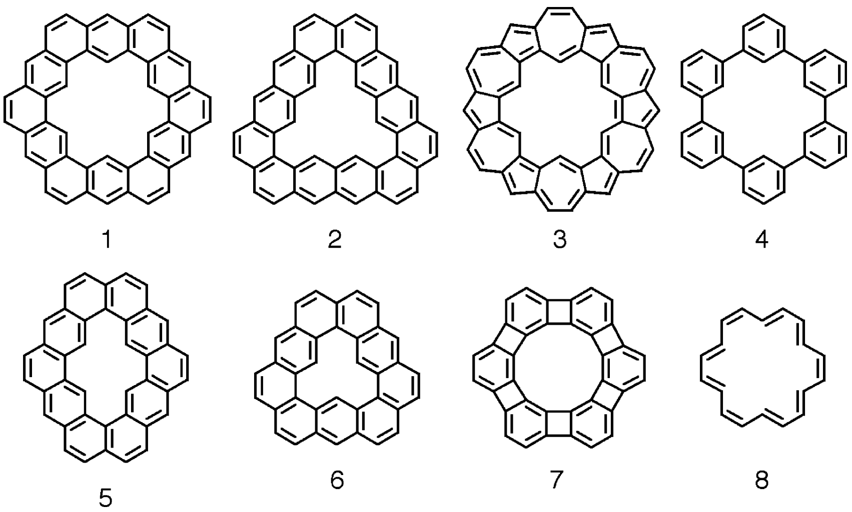

Figure 1. Super-ring molecules (**1**−**7**) and [18]annulene (**8**).

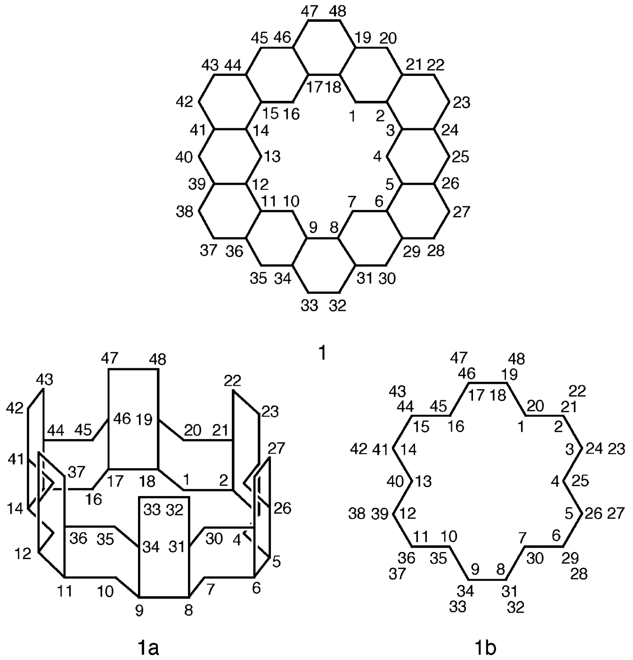

Figure 2. Planar kekulene (**1**) and polygonal prismatic kekulene (**1a**,**1b**).

squared. This *m*-SSE is very small as compared with the TRE (1.569|β|) for **1**. Thus, kekulene is essentially nonsuperaromatic. The inner perimeter in **1** is identical in shape to aromatic [18]-annulene (**8**). The *m*-SSE amounts to only 4% of the TRE for **8** (0.08766|β|), although there are many [$4n + 2$] site type-II conjugated circuits[40] in **1**.

The present approach to superaromaticity can, in principle, be applied to all super-ring π systems other than carbon nanotube with an infinite π system. The *m*-SSEs thus obtained for kekulene (**1**) and related hydrocarbons (**2**−**7**) are listed in Table 2. It is noteworthy that, for all of these super-ring species, *m*-SSE is very close to *t*-SSE. For kekulene, *m*- and *t*-SSEs are 0.00347 and 0.00348|β|, respectively. As suggested previously,[16] MRE may be interpreted mathematically as an approximate TRE. However, we have regarded this quantity as an exact ASE, derived from the magnetic response of a super-ring molecule.[23,25] In the same sense, we regard *m*-SSE as an exact ASE, derived from the magnetic response of a super-ring molecule, although it can be interpreted as an approximate *t*-SSE.

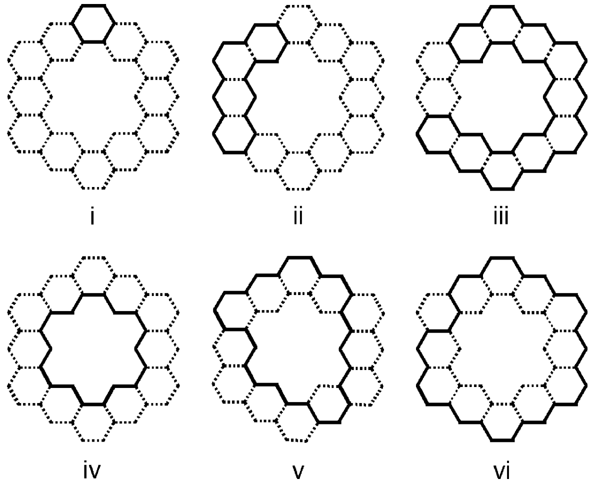

Figure 3. Examples of type-I (**i**−**iii**) and type-II (**iv**−**vi**) circuits in kekulene (**1**).

TABLE 1: Bond Currents in Planar and Prismatic Kekulene π Systems

π bond	bond current/I_0 (planar structure)	bond current/I_0 (polygonal prism)
2 → 1	−1.169	0.064424
3 → 2	−0.808	0.060629
21 → 2	0.361	0.003796
22 → 21	0.998	0.048670
21 → 20	1.359	0.044874

TABLE 2: Superaromatic Stabilization Energies (SSEs) of Typical Super-Ring Molecules

species	*m*-SSE/|β|	*t*-SSE/|β|	TRE/|β|
kekulene (**1**)	0.00347	0.00348	1.569
triangular kekulene (**2**)	0.00277	0.00278	1.428
azulenoid kekulene (**3**)	0.00504	0.00489	0.601
hexa-*m*-phenylene (**4**)	0.00000	0.00000	1.397
[10]coronaphene (**5**)	0.00952	0.00960	1.321
[9]coronaphene (**6**)	−0.01450	−0.01433	1.162
antikekulene (**7**)	−0.03901	−0.03750	−0.710

Triangular kekulene (**2**), azulenoid kekulene (**3**), and [10]-coronaphene (**5**) share essentially the same features of superaromaticity. Although all of these hydrocarbons are formally [$4n + 2$]annulene-within-[$4n' + 2$]annulene molecules, they are marginally superaromatic. Hexa-*m*-phenylene (**4**) is an ideal nonsuperaromatic species, which corresponds to the fact that CC bonds connecting adjacent benzene rings are formal single ones. Therefore, there are no type-II conjugated circuits[40] in **4**. The inner perimeters of [9]coronaphene (**6**) and antikekulene (**7**) are identical to antiaromatic [12]annulene; the outer ones are identical to [24]annulene. These [4*n*]annulene-within-[4*n*′]-annulene macrocycles have marginally negative *m*-SSEs and marginally negative *t*-SSEs. Thus, the conjugated subsystem along the inner perimeter seems to be the determinant of superaromaticity. It may be noteworthy that [9]coronaphene (**6**) is marginally antisuperaromatic, although the entire π system is highly aromatic with a large positive TRE. Antikekulene (**7**) is highly antiaromatic with a large negative TRE.

4. Concluding Remarks

CRE is a key quantity that links energetic and magnetic criteria of aromaticity. Typical energetic and magnetic properties can be formulated exactly or approximately in terms of CREs.[23−27] Therefore, it is necessary to evaluate CREs for all circuits in order to interpret energetic and magnetic measures of aromaticity consistently. However, it has not been easy to evaluate the CREs for type-II circuits in super-ring molecules because many such circuits can be chosen from them. The present approach to superaromaticity enabled us to obtain the sum of CREs for thousands of type-II circuits by a single calculation of ring currents. This approach does not require any knowledge of circuits in the π system. We can now very easily obtain the SSE for any super-ring molecule. This approach may also be found useful to solving some problems of aromatic chemistry in the future.

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