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Is Superaromaticity a Fact or an Artifact? The Kekulene Problem

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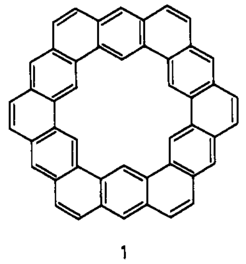
Abstract: If a cyclic array of benzene rings in kekulene brings about extra thermodynamic stabilization, this molecule may be classified as a superaromatic species. A simple but decisive method for determining whether kekulene is superaromatic or not was devised. This method is based on the graph-theoretical analysis of the total π-electron energies of true kekulene and hypothetical superantiaromatic kekulene. Kekulene was found to be essentially non-superaromatic with a vanishingly small superaromatic stabilization energy (ca. $0.0035|\beta|$), and that aromaticity stems primarily from relatively small ($4n + 2$)-membered conjugated circuits. Other graph-theoretical approaches support this interpretation. Superaromatic ring currents, i.e., additional ring currents caused by a cyclic array of the benzene rings, were evaluated for the first time.

Greenish-yellow kekulene (**1**) was prepared in 1978 by Diederich and Staab.[1-4] This molecule is often called superbenzene on account of its planar cyclic conjugation and D_{6h} symmetry. Its electronic structure has long been investigated extensively.[5-14] Kekulene can be viewed as a closed cycle of angularly annellated benzene rings and also as a combination of two interacting [$4n + 2$]annulenes. As early as 1972, Ege and Vogler pointed out that kekulene cannot be treated as a pair of macrocyclic annulenes.[7] We subsequently showed that a formulation employing Clar's sextet notation (**1a**)[15] is the best representation of the actual bonding situation in kekulene.[8] Molecular geometry and proton chemical shifts are not consistent with annulenoid structures (**1b**).[2-4,7,10-14]



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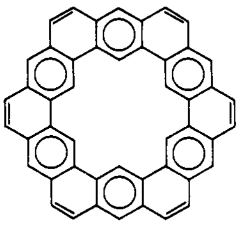
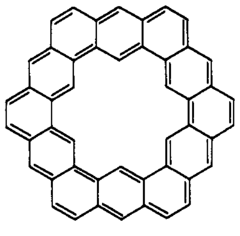


1a



1b

However, whether or not a cyclic annellation of benzene rings in kekulene gives rise to extra thermodynamic stability has been an open question.[8,9,14] Cioslowski and co-workers recently carried out elaborate ab initio molecular orbital calculations on kekulene.[14] They noted that kekulene has a larger thermodynamic stability than expected from localized structures of small benzenoid hydrocarbons. This kind of stabilization energy may be referred to as a superaromatic stabilization energy. Cioslowski and coworkers[14] defined superaromaticity as thermodynamic stabilization due to macrocyclic conjugation along the cyclic array of benzene rings. If kekulene is fully superaromatic in this sense, it must be treated not only as a benzenoid but also as a kind of annulenoid species.

In general, aromaticity arises from cyclic conjugation of π electrons.[16-23] All possible cyclic paths in a conjugated system are responsible for aromaticity.[20-23] These cyclic paths are termed ring components or circuits in chemical graph theory.[23] Among the circuits in kekulene, those surrounding the inner cavity must be responsible for superaromaticity. If so, to what extent do these circuits contribute to the stability or aromaticity of kekulene? In this paper, we apply some graph-theoretical methods to kekulene and related polycyclic aromatic hydrocarbons (PAHs) to elucidate the superaromaticity of kekulene. One of the methods employed enables us to detect the degree of superaromaticity with very high sensitivity.

Theory

Topological resonance energies (TREs) of PAHs were calculated by the original method developed by us.[20-23] The degree of aromaticity was estimated by evaluating the percent resonance cenergy (% RE),[24] which is 100 times the TRE, divided by the total π-electron energy of the graph-theoretically-defined polyene reference. Circuit resonance energies (CREs) were calculated by the method devised by us.[22,25-27] They were formerly called ring resonance energies.[22] Partition of ring currents among the individual circuits was made by use of the graph-theoretical formulas derived by us.[28-32] Hückel molecular orbital (HMO) theory was used in these calculations. The Dewar resonance energy (DRE) of

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(1) Systematic name: 15,23:16,22-dimethenobenzo[12-*a*:4,5-*a'*]dipentaphene.
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kekulene was calculated by the semiempirical Dewar–de Llano procedure.[33]

Results and Discussion

Additive Nodal Increments. Cioslowski's ANI model[14,34,35] provides a basis for initiating discussion on the superaromaticity of kekulene. In 1985 he classified benzene rings in polycyclic aromatic hydrocarbons (PAHs) into several types and found that isonodal benzenoid hydrocarbons (i.e., hydrocarbons with an equal number of benzene rings of each type) have very similar total π-electron energies.[34,35] The total π-electron energy (E_π) of any linearly annellated benzenoid hydrocarbon is then approximated by

$$E_{\mathrm{ANI}} = n_1E_1 + n_2E_2 + n_3E_3 \qquad (1)$$

where n_i and E_i (i = 1, 2, 3) are the numbers and the energy increments for three types of benzene rings concerned. This approach to molecular π-electron energy is called the additive nodal increments (ANI) model.

Three types of benzene rings appear in eq 1. Type 1 benzene rings are those flanked by one benzene ring, such as edge rings in anthracene and phenanthrene. Type 2 benzene rings are those flanked by two benzene rings, in such a manner that the centers of the three rings form an angle of 180°. Finally, type 3 benzene rings are those flanked by two benzene rings, in such a manner that the centers of the three rings form an angle of 120°. Type 2 and type 3 rings are exemplified by the central rings in anthracene and phenanthrene, respectively. Cioslowski's values for E_1, E_2, and E_3 are 6.84532β, 5.65185β, and 5.75130β, respectively.[34,35] These values reproduce the total π-electron energy (E_π) with a mean error less than 0.1% for 1030 PAHs. The total π-electron energies of PAHs are to a large degree additive.

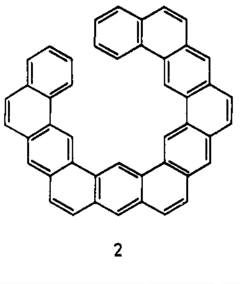
Now, eq 1 is applicable to kekulene. For this PAH having six type 2 and six type 3 benzene rings, we have

$$E_{\mathrm{ANI}} = 6E_2 + 6E_3 = 68.4189\beta \qquad (2)$$

Here, one comment must be made on E_{ANI}. It is true that for common PAHs the E_{ANI} value represents the total π-electron energy.[34,35] However, kekulene is not a common PAH, in that it may be a superaromatic species with a large inner cavity.[14] We must note that E_1, E_2, and E_3 are free from superconjugation or macrocyclic conjugation around the inner cavity since they were estimated from superconjugation-free PAHs. Since eqs 1 and 2 consist of such superconjugation-free energy terms, the E_{ANI} value given by eq 2 must represent the total π-electron energy of a "superconjugation-free" reference for kekulene.[14]

The total π-electron energy (E_π) of kekulene is calculated to be 68.6102β, which is lower than the superconjugation-free reference energy (E_{ANI}) by 0.1913$|\beta|$. If we adopt Cioslowski's way of reasoning,[14] this energy difference can be interpreted as a "superaromatic" stabilization energy, indicating that kekulene is appreciably superaromatic. Cioslowski and co-workers reported that the superaromatic stabilization energy of kekulene is 25.4 kcal/mol at the HF/6-31G** level.[14] Thus, not only ab initio but also HMO calculations apparently support the presence of superaromaticitiy in kekulene.

PAHs **2** and **3** are open kekulene analogues. PAH **3** contains exactly the same number of benzene rings as kekulene, whereas PAH **2** has one-less benzene ring. Although superconjugation is not possible for these PAHs, E_{ANI} calculated for each is again significantly larger than the total π-electron energy. PAH **2** has E_{ANI} larger by 0.1285$|\beta|$ than the total π-electron energy, and PAH **3** has E_{ANI} larger by 0.1345$|\beta|$ than the total π-electron energy. These energy differences cannot be interpreted as superaromatic stabilization energies. They represent the accumulation of errors in the energy increments since PAHs **2** and **3** are very large in size.



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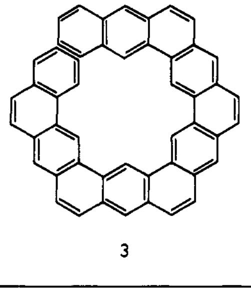

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Table I. Some Stability Indexes for Kekulene and Related PAHs

species	E_π/β	E_{ANI}/β	$(E_\pi - E_{\mathrm{ANI}})/\beta$	TRE/$\lvert\beta\rvert$	% RE
1	68.6102	68.4189	0.1913	1.569	2.340
2	65.1830	65.0545	0.1285	1.590	2.500
3	70.8409	70.7064	0.1345	1.689	2.443

Large errors found in E_{ANI} values oblige us to reconsider the validity of the "superaromatic" stabilization energy calculated for kekulene (0.1913$|\beta|$). It must also contain a large error. However, this stabilization energy is somewhat large as compared to the difference between the total π-electron energy and E_{ANI} for PAHs **2** and **3**, so there is a possibility that part of it is due to the superaromaticity of kekulene. Anyhow, the ANI model is not very appropriate to confirming the presence of superaromaticity in kekulene. Relevant numerical values are summarized in Table I.

Conjugated Circuits. Many cyclic paths can be chosen from the conjugated system of a PAH. They constitute ring components or circuits appearing in the Sachs theorem.[23] Aromaticity and diamagnetic susceptibility exaltation are associated with all these circuits.[20–23,25,29–32] If one or more Kekulé structures can be written for the subsystem of a conjugated system, obtained by deleting a given circuit from the system, the very circuit is called a conjugated circuit. According to Randić,[19] all ($4n$ + 2)-membered conjugated circuits lower the energy of the conjugated system, whereas all $4n$-membered conjugated circuits raise it.

Circuits in kekulene can be classified into the following two types. The first type of circuits are those enclosing one or more consecutive benzene rings. These circuits will be referred to as type I circuits. The second type of circuits are those surrounding the inner cavity of the molecule and will be referred to as type II circuits. One can choose 132 type I and 4096 type II circuits from the kekulene conjugated system. Circuits a–f in Figure 1 exemplify type I circuits, while circuits g–j are examples of type II circuits.

Superaromaticity of kekulene is attributable to the presence of type II circuits because these circuits are related straightforwardly to the macrocyclic structure. All conjugated circuits in kekulene and PAHs **2** and **3** are the ($4n$ + 2)-membered ones. Since all type II conjugated circuits in kekulene are necessarily the ($4n$ + 2)-membered ones, we might say that this molecule is more or less superaromatic in nature.

Herndon[16,17] and Randić[18,19] noted that relatively small conjugated circuits, such as six- and ten-membered ones, are the main source of aromaticity and that the Dewar resonance energy (DRE)[33,36] can be expressed in terms of these conjugated circuits. Randić showed that conjugated circuits with more than 18 vertices are not necessary to reproduce the DRE. The DRE of kekulene was estimated to be 145.8 kcal/mol by Randić's conjugated circuits method. This value is in good agreement with the DRE calculated for this molecule (141.4 kcal/mol).

The smallest type II conjugated circuit in kekulene is an 18-membered one chosen along the inner periphery. All the other type II circuits are larger than this one. Therefore, the smallest type II conjugated circuit alone must contribute appreciably to superaromaticity. In other words, this circuit must be the only source of the superaromatic stabilization energy in kekulene. However, by means of Randić's conjugated circuits method,[18,19] the superaromatic stabilization energy arising from this circuit was estimated to be vanishingly small (0.02 kcal/mol). Therefore, it seems very likely that kekulene is never highly superaromatic.

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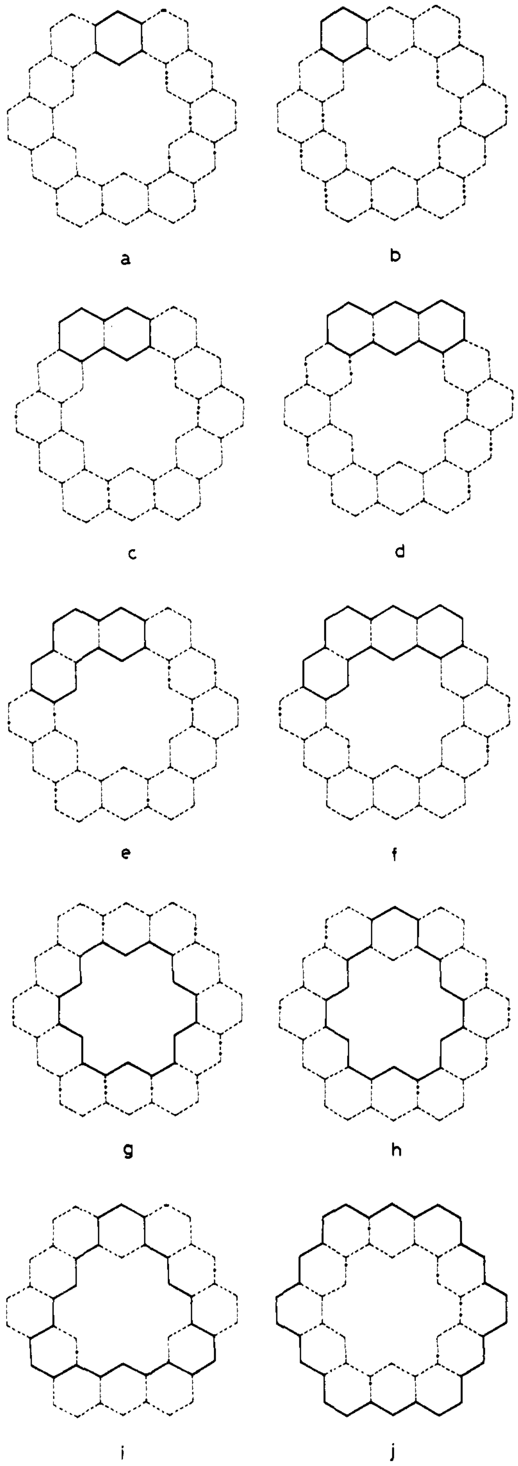

Figure 1. Typical circuits in kekulene.

Topological Resonance Energy. The topological resonance energy (TRE) has been used as an excellent index for assessing the degree of aromaticity, above all, for benzenoid hydrocarbons.[20-24] As listed in Table I, kekulene has a large TRE of $1.569|\beta|$. Therefore, there is no doubt about regarding this molecule as an aromatic species. Open kekulene analogues **2** and **3** are also highly aromatic with large positive TREs. However, it is worth mentioning that kekulene has a slightly smaller % RE than **2** and **3** although the latter two PAHs are not superaromatic in nature. This fact indicates that kekulene is slightly less aromatic than nonsuperaromatic PAHs **2** and **3**. There is no appreciable indication of superaromaticity in the TRE of kekulene. Thus, TREs never support the presence of high superaromaticity in kekulene.

Table II. CREs of Typical Circuits in Kekulene

circuit	CRE/$|\beta|$	circuit	CRE/$|\beta|$
a	0.1400	f	0.0125
b	0.0829	g	0.0036
c	0.0446	h	−0.0002
d	0.0157	i	−0.0000
e	0.0327	j	0.0017

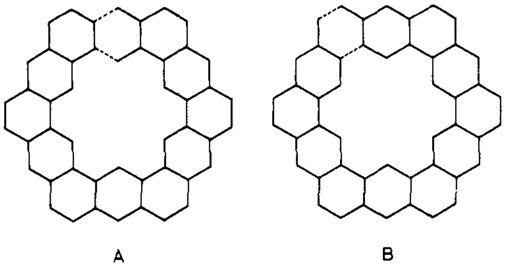

Figure 2. Two examples of superantiaromatic kekulene (A and B). Dashed lines denote π bonds with a resonance integral of $-\beta$.

Circuit Resonance Energies. The circuit resonance energy (CRE) is an approximate measure of the contribution of each circuit to the overall aromaticity.[22,25-27] In general, $(4n + 2)$-membered circuits have positive CREs, whereas $4n$-membered circuits have negative CREs.[22] Therefore, $(4n + 2)$- and $4n$-membered circuits can be referred to as aromatic and antiaromatic circuits, respectively. All aromatic circuits contribute to the increase in the overall TRE. All antiaromatic circuits in kekulene contribute to the decrease in the overall TRE. Hosoya and coworkers justified such a relationship between circuits and π-electron energy by analyzing the coefficients of the characteristic polynomial.[37] The CREs of typical circuits in kekulene are listed in Table II.

There are many conjugated circuits in kekulene. In general, smaller conjugated circuits have much larger positive or negative CREs. All nonconjugated circuits have very small positive or negative CREs. Type II circuits in kekulene, which are the source of superaromaticity, are all large with very small positive or negative CREs. We can say again that type I conjugated circuits are the main source of aromaticity in kekulene and that superaromaticity must contribute modestly to the overall aromaticity. All aspects of CREs fully conform to Randić's concept of conjugated circuits.[18,19] Circuits h and i in Figure 1 are not conjugated circuits, having negligibly small negative CREs.

Superantiaromatic Kekulene. Decisive evidence for the lack of superaromaticity in kekulene is given simply by calculating the total π-electron energy of superantiaromatic kekulene. Here, superantiaromatic kekulene is a hypothetical molecule, obtained by changing the sign of the resonance integral for two of the CC bonds in kekulene. These two bonds must not be chosen arbitrarily. One bond must be located at the outer periphery and the other bond at the inner periphery. Furthermore, both must belong to the same benzene ring. There are many ways to choose two bonds which meet these requisites, two of which are shown in Figure 2. The total π-electron energies of these superantiaromatic kekulenes are the same.

Type I circuits in superantiaromatic kekulene pass no or two bonds with a resonance integral of $-\beta$. For these circuits, the product of all resonance integrals around a circuit is equal to that around the corresponding circuit in true kekulene. Therefore, the CRE of any type I circuit remains unchanged on going from true to superantiaromatic kekulene. On the contrary, all type II circuits in superantiaromatic kekulene pass one of the bonds with a resonance integral of $-\beta$. For these circuits, the product of all resonance integrals around the circuit has the same absolute value as that around the corresponding circuit in true kekulene, but has an opposite sign. Then, the CRE of any type II circuit in superantiaromatic kekulene has a different sign and magnitude from that of the corresponding circuit in true kekulene.

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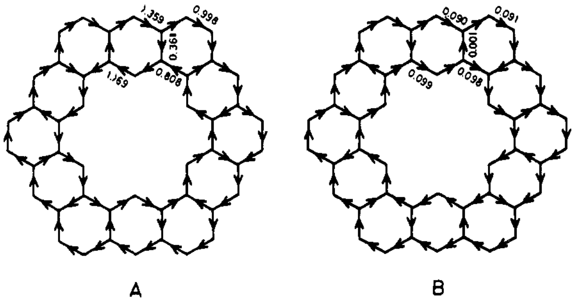

Figure 3. Overall (A) and superaromatic (B) ring currents induced in kekulene. The intensity of the current induced in benzene under the same conditions is set equal to unity. Clockwise currents indicate diatropicity.

The total π-electron energy of each molecule reflects the aromaticity of all circuits collectively. All type I circuits in kekulene retain their aromatic character in superantiaromatic kekulene. However, aromatic and antiaromatic type II circuits in kekulene become antiaromatic and aromatic in superantiaromatic kekulene, respectively. Therefore, the energy difference between true and superantiaromatic kekulenes is attributable to the change in aromaticity of type II circuits.

It is now evident that the sign of the superaromatic stabilization energy is changed on going from true to superantiaromatic kekulene. If true kekulene has a positive superaromatic stabilization energy at all, superantiaromatic kekulene must have a negative superaromatic stabilization energy. This is the reason why such conjugated systems as shown in Figure 2 are referred to as superantiaromatic kekulenes.

The total π-electron energy of superantiaromatic kekulene can be obtained in the usual way. We found that superantiaromatic kekulene has almost the same total π-electron energy as true kekulene. The former species is more unstable only by $0.0070|\beta|$. This energy difference represents the difference between the positive superaromatic stabilization energy of true kekulene and the negative superaromatic stabilization energy of superantiaromatic kekulene. It is clear from this that kekulene has a positive superaromatic resonance energy.

The stabilization energy due to superaromaticity is approximately equal to half the energy difference between true and superantiaromatic species. The superaromatic stabilization energy estimated for kekulene is only $0.0035|\beta|$. This is a vanishingly small energy value, indicating that the contribution of all type II circuits to the TRE is vanishingly small. Compare this with the TRE of $1.569|\beta|$, which corresponds to the DRE of 141.4 kcal/mol. We should say more appropriately that kekulene is essentially nonsuperaromatic because its superaromatic stabilization energy is negligibly small. This definite result is fully consistent with other analyses described above.

Superaromatic Ring Currents. Ring currents can be partitioned exactly into parts associated with individual circuits.[29-32] When kekulene is placed in the external magnetic field, all type I and type II circuits contribute to the induction of ring currents. Diamagnetic currents are induced in all $(4n + 2)$-membered circuits, whereas paramagnetic currents are induced in all $4n$-membered circuits.[31] The overall ring current passing each bond is given by summing up the currents over all circuits passing the very bond. The ring current distribution in kekulene is shown in Figure 3. Directions of ring currents are defined in such a manner that diamagnetic ring currents are induced clockwise.

The currents due to superconjugation may be referred to as superaromatic ring currents. The superaromatic ring current passing a given bond is given by summing up the induced currents over all type II circuits passing the bond. The superaromatic ring currents induced in kekulene are also shown in Figure 3. It is interesting to see that the superaromatic ring currents are induced clockwise both along the inner and outer peripheries. In view of the direction of superaromatic ring currents, kekulene is superaromatic but not superantiaromatic in nature.

Diederich and others took the peculiar downfield shift of the inner protons in kekulene as a strong experimental argument against the dominance of annulenoid ring currents in the macrocyclic system and in favor of a strong coupling between the inner and outer perimeters according to the benzenoid formulation (**1b**).[2-4] Very small superaromatic ring currents shown in Figure 3 support this viewpoint.

We previously showed that the current induced in a given circuit is expressed approximately as a product of the circuit area and a kind of CRE for the circuit.[28] As seen from Figure 3, type II circuits contribute much less to the overall ring currents than type I circuits although the former circuits have very large areas. Superaromatic ring currents amount to less than 10% of the overall ring currents. Considering that the circuit areas concerned are very large, fairly small superaromatic ring currents do not conform to a significant contribution of type II circuits to aromaticity or superaromaticity.

Concluding Remarks

Graph-theoretical analyses have clarified that superconjugation resulting from the cyclic array of benzene rings does not yield appreciable superaromatic energetic effects. Decisive evidence for the lack of superaromaticity in kekulene was given simply by calculating the energy difference between true kekulene and superantiaromatic kekulene. The total π-electron energy of true kekulene is very close to that of superantiaromatic kekulene. This fact indicates that true kekulene is never highly superaromatic and that superantiaromatic kekulene is never highly superantiaromatic. This approach is general and applicable to any macrocyclic conjugated system with an inner cavity.

The idea that kekulene consits of two weakly interacting annulenes is presumably based on the unproven assumption that the Hückel $4n + 2$ rule is applicable to polycyclic conjugated systems. However, this assumption is wrong in many cases. Organic chemists have long favored Platt's perimeter model,[38] but it cannot be justified theoretically. It is clear that this model is not consistent with the concept of conjugated circuits.[16-19] We previously proved that the Hückel $4n + 2$ rule in principle holds for monocyclic conjugated systems only.[39] Thus, there is no reason to believe that annulenoid conjugation contributes much to the thermodynamic stability of kekulene. Kekulene is a regular benzenoid hydrocarbon in all aspects.

Registry No. 1, 15123-47-4; **2**, 137626-77-8; **3**, 137626-78-9.

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