January, 1993] © *1993 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*,**66**, *57—60(1993)* 57

General Graph Theory of Superaromaticity

Jun-ichi Aihara
Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422

(Received August 7, 1992)

A conjugated super-ring molecule with a cavity inside may exhibit superaromaticity, i.e., extra thermodynamic stabilization due to the super-ring structure. General graph theory of superaromaticity was developed so as to analyze superaromatic character of all kinds of conjugated super-ring molecules. Typical conjugated super-ring molecules, such as kekulene, azulenoid kekulene, anti-kekulene, octadecabenzokekulene, hexa-*m*-phenylene, and hexabenz[18]annulene, were predicted to be essentially non-superaromatic.

Aromaticity or aromatic stabilization stems from cyclic conjugation of π electrons.[1—4] Large polycyclic conjugated systems such as **1**—**6** comprise not only many rings but also a super-ring formed by these rings (Chart 1). If such a macrocyclic structure gives rise to extra thermodynamic stabilization, they might be classified as superaromatic species.[5,6] One of the most studied super-ring molecules is kekulene (**1**).[5—13] In 1991 Cioslowski and co-workers carried out elaborate ab initio molecular orbital calculations of this molecule, and discussed the possibility of superaromaticity.[5] We then devised simple graph theory for analyzing the degree of superaromaticity in this molecule.[6] Our analysis clarified that **1** is highly aromatic but not superaromatic in character. In this paper we further develop our graph theory of superaromaticity so as to analyze the degree of superaromaticity in all kinds of conjugated super-ring systems. Hückel molecular orbital (HMO) theory in used in its simplest form.

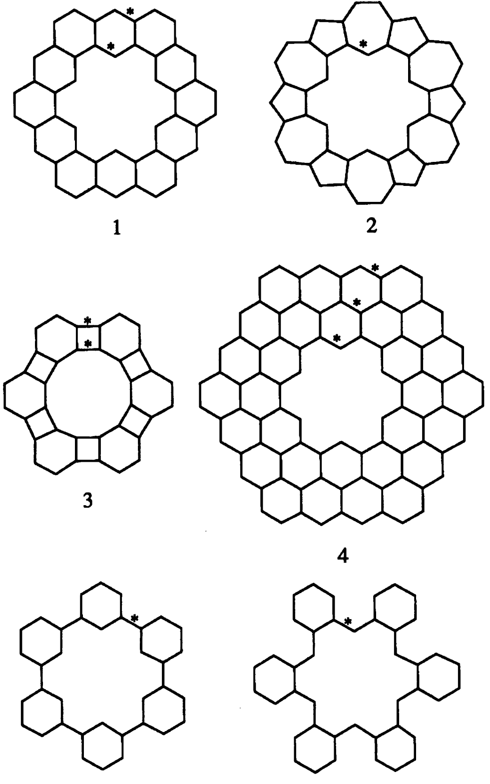

1 2 3 4 5 6

Chart 1.

Results and Discussion

Among typical conjugated super-ring molecules are kekulene (**1**),[5—13] azulenoid kekulene (**2**),[14] anti-kekulene (**3**),[15,16] octadecabenzokekulene (**4**), hexa-*m*-phenylene (**5**),[17] and hexabenz[18]annulene (**6**). So far two of them (**1** and **5**) have been prepared,[9—12,17] but others have not. Since these super-ring molecules consist of many rings, numerous cyclic paths can be chosen from the conjugated systems. These paths are termed ring components or circuits in chemical graph theory.[1—3] The coefficients in the HMO characteristic polynomial can be obtained by enumerating disjoint π bonds and circuits according to the Sachs theorem.[1—3]

There always are two different types of circuits in conjugated super-ring molecules.[6] Type-I circuits are those enclosing one or more fused rings, while type-II circuits are those with a cavity inside. For example, there are 132 type-I and 4096 type-II circuits in **1**—**3**. In a previous paper[6] we illustrated type-I and type-II circuits in **1**. Almost innumerable circuits can be chosen from **4**. Typical four circuits in this molecule are shown in Fig. 1, where A and B are type-I circuits, and where C and D are type-II circuits. Note that the latter two circuits have a cavity inside but that A and B do not.

The topological resonance energy (TRE) represents the aromaticity of a cyclic conjugated molecule.[1—4] All circuits in the molecule are responsible for the TRE. The percent resonance energy (%RE) is used to predict the degree of aromaticity,[6] which is defined as 100 times the TRE divided by the total π-electron energy of the graph-theoretically defined polyene reference. The TREs and %REs calculated for **1**—**6** are summarized in Table 1. Polycyclic benzenoid systems **1** and **5** are highly aromatic with large %REs, whereas **2** and **6** are moderately aromatic with smaller %REs. Another benzenoid molecule **4** is too large to evaluate the TRE, but must be as aromatic as **1** and **5**. In contrast, **3** is antiaromatic with a negative %RE.

We previously pointed out that type-II circuits are responsible for superaromaticity because they differentiate superaromatic molecules from others.[6] Superaro-

Table 1. Topological Resonance Energies (TREs) and Superaromatic Stabilization Energies (SSEs)

Species	Total π-electron energy/β	TRE/$\lvert\beta\rvert$	%RE	SSE/$\lvert\beta\rvert$
Kekulene (**1**)	68.6102	1.569	2.340	0.0035
	68.6032	1.562	2.330	−0.0035
Azulenoid kekulene (**2**)	67.4548	0.601	0.899	0.0047
	67.4454	0.591	0.885	−0.0047
Anti-kekulene (**3**)	51.3705	−0.710	−1.364	−0.0362
	51.4428	−0.638	−1.225	0.0362
Octadecabenzokekulene (**4**)	132.5133	—	—	0.0951
	132.3231	—	—	−0.0951
Hexa-*m*-phenylene (**5**)	50.2948	1.397	2.857	0.0000
	50.2948	1.397	2.857	0.0000
Hexabenz[18]annulene (**6**)	57.2679	0.880	1.561	0.1066
	57.0547	0.667	1.183	−0.1066

maticity is interpretable as extra thermodynamic stabilization arising from type-II circuits. It follows that a conjugated super-ring molecule is superaromatic if type-II circuits contribute appreciably to the TRE. The overall aromaticity of the molecule then consists of local aromaticity due to type-I circuits and superaromaticity due to type-II circuits. Our concept of superaromaticity is based on this way of reasoning.

In order to estimate the degree of superaromaticity, we define a so-called Möbius-like isomer (Y) for every conjugated super-ring molecule (X). Some π bonds must beforehand be chosen from X, in such a manner that every type-II circuit passes $2n+1$ of these bonds. Y is then defined as a hypothetical molecule, obtained by changing the sign of the resonance integral ($\beta \rightarrow -\beta$) for these particular π bonds. Every π bond with a resonance integral of $-\beta$ is identical with a twisted π bond because $-\beta$ represents the resonance integral for a π bond twisted by 180°.[18] Möbius-like isomers for **1**—**6** are obtained by reversing the sign of the resonance integral for the π bonds denoted by $*$ in their respective structural formulas. Many other Möbius-like isomers can be designed for each molecule, but all have the same total π-electron energy. It should be noted that Möbius-like isomers can be defined for any large or complicated super-ring molecule.

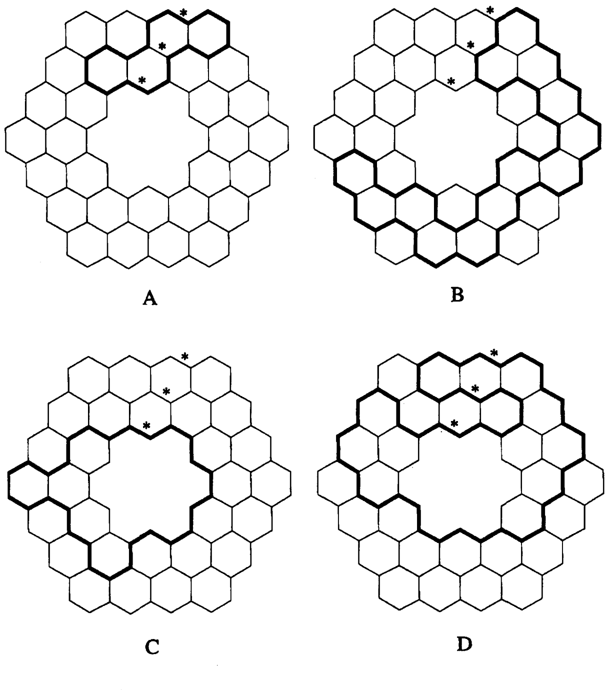


Fig. 1. Typical circuits in octabenzokekulene (**4**).

The total π-electron energies of X and Y are calculated in the usual way. Formally, they are functions of all possible circuits in the molecule.[19,20] It is known that the Hückel $4n+2$ rule is operative for individual even-membered circuits in X.[19] All $(4n+2)$-membered circuits lower the total π-electron energy, whereas all $4n$-membered ones raise it. In this sense, $(4n+2)$- and $4n$-membered circuits in X are aromatic and antiaromatic, respectively. This rule applies to most of neutral conjugated systems not containing twisted π bonds.[19,21,22] The TRE represents aromatic character of all circuits collectively.

Circuits in Y lie in a somewhat different situations. As shown in Fig. 1, type-I circuits in Y pass none or an even number of twisted π bonds. Therefore, this type of circuits in X retain their aromatic character in Y. However, all type-II circuits in Y pass an odd number of twisted π bonds. These circuits are physically identical with singly twisted Möbius rings. The reverse of the Hückel $4n+2$ rule is operative for these Möbius circuits.[21,22] Aromatic and antiaromatic type-II circuits in X become antiaromatic and aromatic in Y, respectively.[21,22] Therefore, the energy difference between X and Y can be attributed to the change in aromaticity of all type-II circuits.

Let the superaromatic stabilization energy (SSE) be a stabilization energy due to superaromaticity. It constitutes part of the TRE. The sign of the SSE will be changed on going from X to Y because aromaticities of all type-II circuits are reversed. Then, if X is superaromatic at all, Y must be superantiaromatic to a similar degree. The energy difference between X and Y represents the difference in SSE between X and Y. Therefore, the SSE of X must be about half the energy difference between X and Y.[6] If Y is destabilized relative to X, a plus sign is given to the SSE value. The SSEs thus calculated for **1**—**6** are also listed in Table 1.

By definition, a superaromatic molecule is a molecule with an appreciably large positive SSE. Unfortunately, all molecules studied were found to have very small positive or negative SSEs. The total π-electron energy of every molecule turned out to be very close to that of the Möbius-like isomer. It is true that twisting some π bonds in **1**—**6** makedly changes the energies of individual π-electron molecular orbitals, but the total π-electron energy is changed to a much lesser extent. These molecules should be regarded as essentially non-superaromatic species.

It is interesting to see that **5** has almost no SSE. The SSE increases in the order: $\mathbf{1}<\mathbf{2}<\mathbf{4}$. This order apparently reflects the increase in the number of type-II circuits. However, the SSE of **4** is still very small compared with the total π-electron energy. For **1**—**5**, the SSE is less than 0.072% of the total π-electron energy. The SSE of **6** is relatively large, amounting to 0.186% of the total π-electron energy. The SSEs of **1** and **2** are comparable in magnitude to each other although the TREs are not. While **1**, **2**, and **4**—**6** are predicted to be slightly superaromatic with positive SSEs, **3** is predicted to be slightly superantiaromatic with a negative SSE. Thus, **3** is not only an antiaromatic but also slightly superantiaromatic species.

Super-rings in **5** and **6** are not the ones formed by circularly condensed rings. The former molecule (**5**) consists of six isolated benzene rings connected with each other by essential single π bonds. Since six aromatic sextets[8,23] can be chosen simultaneously from **5**, this molecule may be viewed as a cluster of six benzene molecules. This interpretation is fairly consistent with the fact that the TRE of **5** is 5.1 times that of benzene. On the other hand, all possible Kekulé structures for **6** consist of three benzene rings and three *o*-xylylene moieties, so only three aromatic sextets can be chosen simultaneously from this molecule. The TRE of **6** is only 3.2 times that of benzene, but the SSE is the largest of the molecules studied. Therefore, this molecule should be regarded not as a superaromatic species but as a derivative of [18]annulene.

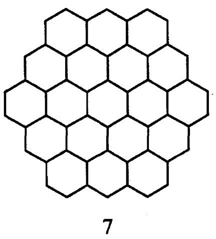
Randić's concept of conjugated circuits[24,25] is useful for rationalizing the above results systematically. If one or more Kekulé structures can be written for the subsystem of a cyclic conjugated system, obtained by deleting a given circuit from it, this very circuit is called a conjugated circuit. Not a few conjugated circuits can be chosen from **1**—**6**. For example, circuits A and D in Fig. 1 are type-I and type-II conjugated circuits in **4**, respectively. According to Randić,[24,25] relatively small conjugated circuits are primarily responsible for aromaticity.

Relatively small type-II conjugated circuits are then thought to play a significant role in enhancing superaromaticity. Various type-II conjugated circuits can be chosen from **1**, **2**, and **4**—**6**, but all are large with eighteen or more vertices. The lack of relatively small type-II conjugated circuits is consistent with the very small SSEs for these molecules. No type-II conjugated circuits can be chosen from **5**. This justifies the negligibly small SSE of **5**. In **3** the smallest type-II conjugated circuit is the twelve-membered one along the inner periphery. This antiaromatic circuit must be the main origin of superantiaromaticity in this molecule.

Concluding Remarks

The present graph theory of superaromaticity can be applied to any conjugated super-ring molecules. However, all molecules studied were found to be essentially non-superaromatic, regular conjugated hydrocarbons with type-I conjugated circuits as the main origin of aromaticity. In principle, it must be difficult to design highly superaromatic molecules because the presence of small type-II conjugated circuits is not compatible with the super-ring structure with a large cavity inside.

In 1954 Platt suggested that in polycyclic conjugated systems the peripheral subsystem plays an important role in aromatic stabilization of the molecule.[26] It is evident that his idea is not applicable to the above molecules. Inner and outer peripheries in **1**—**4** constitute type-II circuits, but contribute little to the overall aromaticity. The present study strongly suggests that even in such species as dodecabenzocoronene (**7**) and graphite (**8**) relatively large circuits do not contribute much to the overall aromaticity of the molecule (Chart 2).


7

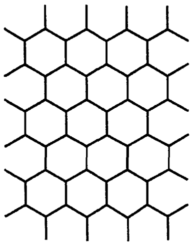

8

Chart 2.

This work was supported by the Grant-in-Aid for Scientific Research on Priority Area "Theory of Chemical Reactions" from the Ministry of Education, Science and Culture. All calculations were carried out at the Information Processing Center, Shizuoka University.

References

1) J. Aihara, *J. Am. Chem. Soc.*, **98**, 2750 (1976).

2) M. Milun, I. Gutman, and N. Trinajstić, *J. Am. Chem. Soc.*, **99**, 1692 (1977).

3) A. Graovac, I. Gutman, and N. Trinajstić, "Topological Approach to the Chemistry of Conjugated Molecules," Springer, Heidelberg (1977).

4) J. Aihara, *Sci. Am.*, **266** (3), 62 (1992).

5) J. Cioslowski, P. B. O'Connor, and E. D. Fleischmann, *J. Am. Chem. Soc.*, **113**, 1086 (1991).

6) J. Aihara, *J. Am. Chem. Soc.*, **114**, 865 (1992).

7) G. Ege and H. Vogler, *Theor. Chim. Acta*, **26**, 55 (1972).

8) J. Aihara, *Bull. Chem. Soc. Jpn.*, **49**, 1429 (1976).

9) F. Diederich and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, **17**, 372 (1978).

10) C. Krieger, F. Diederich, D. Schweitzer, and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, **18**, 699 (1979).

11) H. A. Staab and F. Diederich, *Chem. Ber.*, **116**, 3487 (1983).

12) H. A. Staab, F. Diederich, C. Krieger, and D. Schweitzer, *Chem. Ber.*, **116**, 3504 (1983).

13) H. Vogler, *J. Mol. Struct.* (*Theochem*), **122**, 333 (1985).

14) B. A. Hess, Jr., and L. J. Schaad, *J. Org. Chem.*, **36**, 3418 (1971).

15) R. Diercks and K. P. C. Vollhardt, *Angew. Chem., Int. Ed. Engl.*, **25**, 266 (1986).

16) N. Trinajstić, T. G. Schmalz, T. P. Živković, S. Nikolić, G. E. Hite, D. J. Klein, and W. A. Seitz, *New J. Chem.*, **15**, 27 (1991).

17) H. A. Staab and F. Binning, *Tetrahedron Lett.*, **1964**, 319.

18) E. Heilbronner, *Tetrahedron Lett.*, **1964**, 1923.

19) H. Hosoya, K. Hosoi, and I. Gutman, *Theor. Chim. Acta*, **38**, 37 (1975).

20) J. Aihara, *J. Org. Chem.*, **41**, 2488 (1976).

21) N. Mizoguchi, *J. Phys. Chem.*, **92**, 2754 (1988).

22) N. Mizoguchi, *Chem. Phys. Lett.*, **158**, 383 (1989).

23) E. Clar, "The Aromatic Sextet," Wiley, London (1972).

24) M. Randić, *Chem. Phys. Lett.*, **38**, 68 (1976).

25) M. Randić, *J. Am. Chem. Soc.*, **99**, 444 (1977).

26) J. R. Platt, *J. Chem. Phys.*, **22**, 144 (1954).