

Algebraic Kekulé Structures of Benzenoid Hydrocarbons[†]Ivan Gutman,[‡] Damir Vukičević,[§] Ante Graovac,^{*,§,||} and Milan Randić[⊥]

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An algebraic Kekulé structure of a benzenoid hydrocarbon is obtained from an ordinary Kekulé structure by inscribing into each hexagon the number of π -electrons which (according to this Kekulé structure) belong to this hexagon. We show that in the case of catafusenes, there is a one-to-one correspondence between ordinary and algebraic Kekulé structures. On the other hand, in the case of perifusenes, one algebraic Kekulé structure may correspond to several ordinary Kekulé structures.

INTRODUCTION

One of the present authors¹ conceived recently the so-called “algebraic Kekulé structures” of benzenoid hydrocarbons. These are obtained from the ordinary Kekulé structures by inscribing into each hexagon the number of π -electrons which (according to the Kekulé structure considered) belong to this hexagon. Double bonds shared by two hexagons are assumed to contribute one π -electron to each hexagon; other double bonds are viewed as contributing both of their π -electrons to the hexagon in which they lie.

A self-explanatory example, illustrating the construction of an algebraic Kekulé structure, is given in Figure 1.

To distinguish between ordinary and algebraic Kekulé structures, in ref 1 the former were referred to as “geometric Kekulé structures”. Here we adopt the same terminology.

Whereas the geometric Kekulé structures reflect the traditional, somewhat naive, way of thinking of organic chemists,² the algebraic ones are more abstract, shedding some light on the peculiar features of the π -electron distribution in benzenoid hydrocarbons,³ and might be preferred in theoretical considerations.⁴ With regards to coding and any kind of computer-aided processing, the algebraic Kekulé structures have an obvious advantage over their geometric counterparts. In view of this, it is of primary interest to establish the actual relation between them, with hope that this relation is bijective (one-to-one). If so, then it would be legitimate to deal with, analyze, and process algebraic Kekulé structures instead of the old-fashioned geometric ones.

The paper¹ is concerned with benzenoid hydrocarbons. Therefore also the present considerations are restricted to benzenoid hydrocarbons. However, it would be of obvious interest to extend the concept of algebraic Kekulé structures

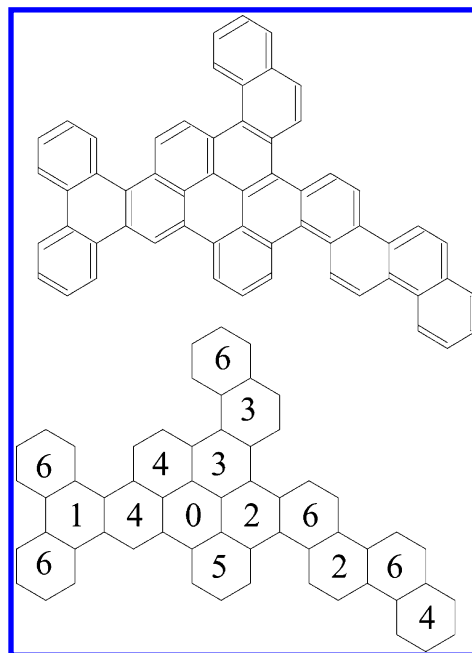


Figure 1. An example illustrating the construction of the algebraic Kekulé structure. In this example, the π -electron counts associated with hexagons take all possible values from 0 up to 6.

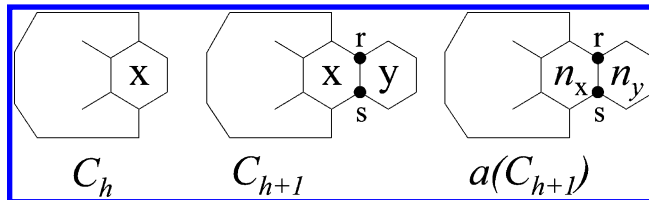


Figure 2. Any catafusene C_{h+1} with $h + 1$ hexagons can be obtained from some catafusene C_h with h hexagons, by attaching (via the edge rs) to the hexagon X a new (terminal) hexagon Y .

to other classes of polycyclic aromatic compounds, such as benzenoids with holes (coronoids), phenylenes, fullerenes, etc. Some work in this direction has already been done by one of the present authors.⁵

In this work we show that a one-to-one correspondence between geometric and algebraic Kekulé structures exists in

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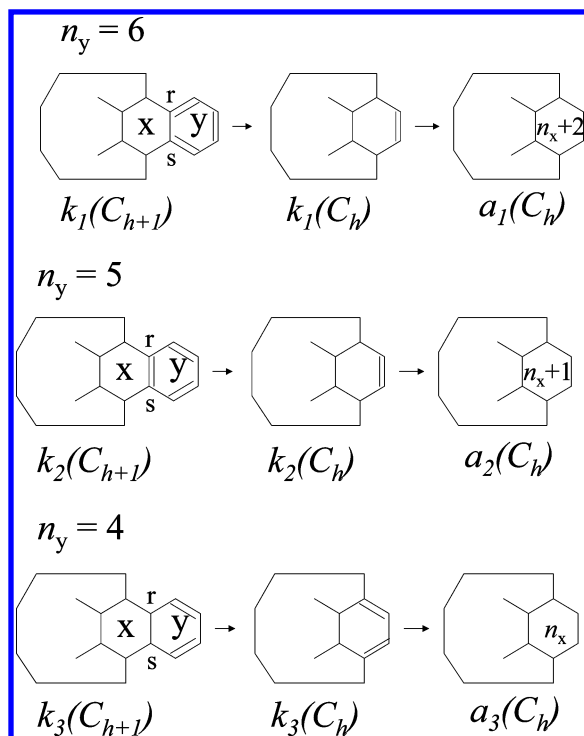


Figure 3. The three cases that may occur with regard to the number n_y of π -electrons in the hexagon Y of the catafusene C_{h+1} and their consequences.

the case of catafusenes but is violated in the case of (some) perifusenes.

A benzenoid hydrocarbon is said to be a catafusene^{6,7} (or a catacondensed benzenoid system³) if no three of its hexagons have a carbon atom in common. Otherwise it is a perifusene^{6,7} (or a pericondensed benzenoid system³).

KEKULE STRUCTURES OF CATAFUSENES

All catafusenes possess Kekulé structures. In particular, a catafusene with h hexagons has at least $h + 1$ Kekulé structures.⁸

Theorem 1a. There exists a one-to-one correspondence between the geometric and algebraic Kekulé structures of any catafusene with at least 2 hexagons.

Bearing in mind the way in which algebraic Kekulé structures are constructed, we see that any geometric Kekulé structure leads to a unique algebraic Kekulé structure. Therefore we need only to show that from two different geometric Kekulé structures we always obtain two different algebraic Kekulé structures. Thus we reformulate Theorem 1a as follows:

Theorem 1b. From any algebraic Kekulé structure of any catafusene a unique geometric Kekulé structure can be reconstructed.

Proof. We demonstrate the validity of Theorem 1b by induction on the number h of hexagons.

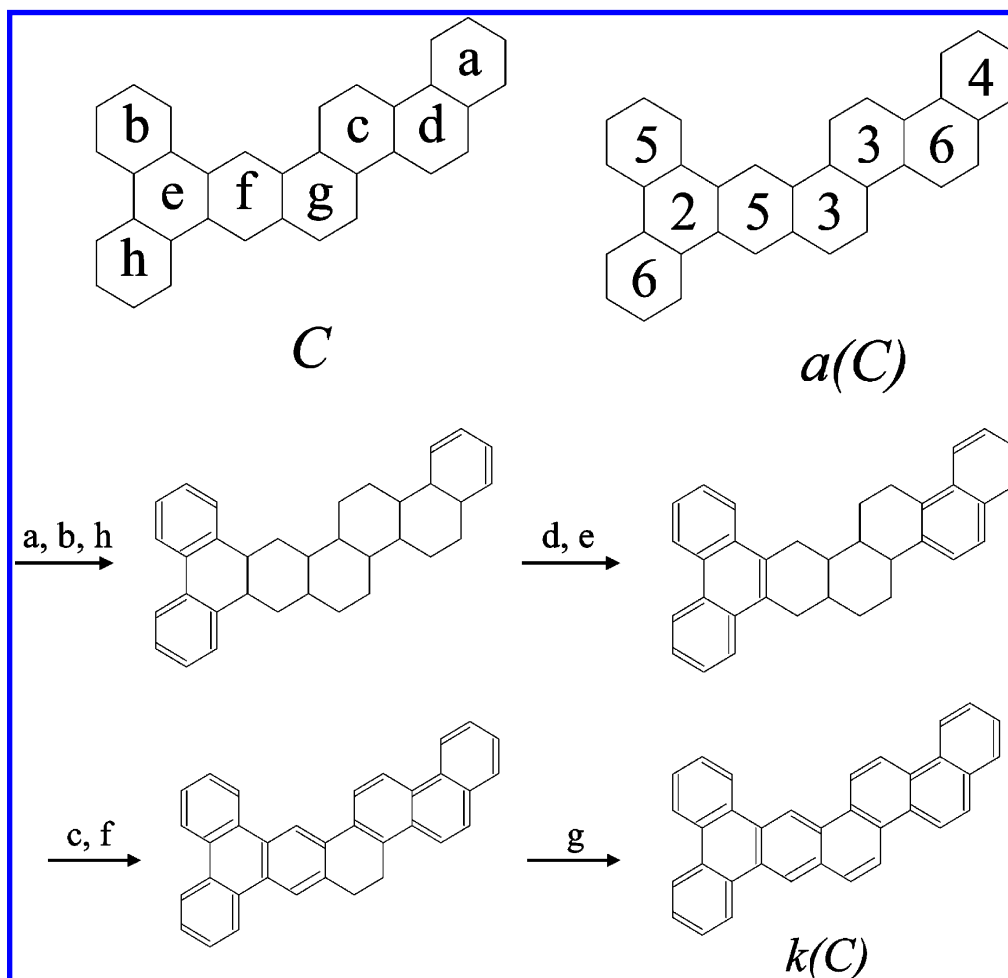


Figure 4. A catafusene C , its algebraic Kekulé structure $a(C)$, and the way in which its geometric Kekulé structure $k(C)$ is reconstructed. The hexagons of C are labeled by a, b, c, \dots, h ; the labels above the arrows indicate the hexagons in which the positions of the double bonds are currently determined.

Step 1. By direct checking it is easily verified that the statement of Theorem 1b holds for $h = 2$ (naphthalene) and $h = 3$ (anthracene and phenanthrene).⁹

Step 2. We assume that the statement of Theorem 1b is true for all catacondensed benzenoids with h hexagons. The proof will be completed if from this assumption we deduce the validity of Theorem 1b for all catafusenes with $h + 1$ hexagons.

Step 3. A hexagon of a benzenoid system is said to be terminal if it has only one neighboring hexagon. Every catafusene has at least two terminal hexagons. Therefore, a catafusene C_{h+1} with $h + 1$ hexagons can be viewed as being obtained from some catafusene C_h with h hexagons, by adding to it a new terminal hexagon. This construction is illustrated in Figure 2.

Consider now an algebraic Kekulé structure $a(C_{h+1})$ of the catafusene C_{h+1} . Let n_X and n_Y be the counts of the π -electrons associated with the hexagons X and Y , see Figure 2. Because the hexagon Y is terminal, n_Y may assume only three values $n_Y = 6$, $n_Y = 5$, and $n_Y = 4$. In all three cases, in the respective geometric Kekulé structures $k_1(C_{h+1})$, $k_2(C_{h+1})$, and $k_3(C_{h+1})$, the positions of the double bonds in the hexagon Y are uniquely determined, see Figure 3.

For $i = 1, 2, 3$, the double bonds in the geometric Kekulé structures $k_i(C_h)$ are arranged in the same manner as in $k_i(C_{h+1})$, see Figure 3. Exceptionally, but consistently, in $k_1(C_h)$ the bond rs is set to be double. Consequently, the geometric Kekulé structures $k_i(C_h)$ correspond to the algebraic Kekulé structures $a_i(C_h)$, $i = 1, 2, 3$. If the positions of all double bonds in $k_i(C_h)$ can be reconstructed from $a_i(C_h)$, then also the positions of all double bonds in $k_i(C_{h+1})$ are determined.

According to the inductive assumption (Step 2), $a_i(C_h)$ uniquely determines $k_i(C_h)$. Therefore $a_i(C_{h+1})$ uniquely determines $k_i(C_{h+1})$, for $i = 1, 2, 3$.

This proves Theorem 1b, which in turn implies the validity of Theorem 1a.

It is now easy to design an algorithm for reconstructing the geometric Kekulé structure from the algebraic one:

Determine the positions of the double bonds in the terminal hexagons, and then do this in the hexagons next to the terminal, etc. Usually very few steps are required, until the positions of all double bonds are determined.

An example of the application of the above algorithm is shown in Figure 4.

KEKULE STRUCTURES OF PERIFUSENES

In the proof of Theorem 1b we have used the fact that each catafusene possesses a terminal hexagon, and that by deleting a terminal hexagon from a catafusene with $h + 1$ hexagons we arrive at a catafusene with h hexagons. Such an argument is not applicable in the case of perifusenes, and Theorems 1a and 1b cannot be extended to them.

In fact, there exist many perifusenes in which two or more geometric Kekulé structures correspond to the same algebraic Kekulé structure. Two such examples are shown in Figure 5. These are the smallest symmetric and the smallest nonsymmetric examples of this kind.

We can prove a somewhat stronger result.

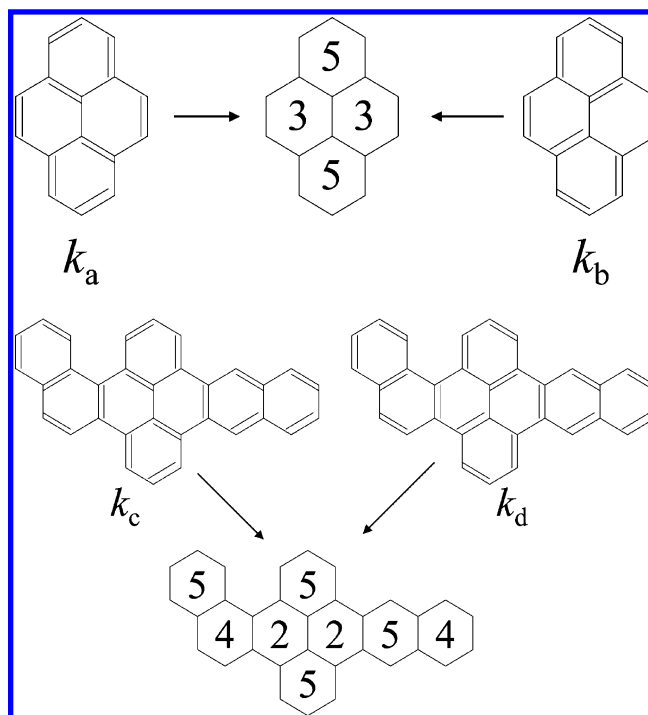


Figure 5. Perifusenes in which two distinct geometric Kekulé structures correspond to the same algebraic Kekulé structure. In the case of pyrene, the Kekulé structures k_a and k_b are symmetry-equivalent. In the case of tribenzo[*a,fg,ts*]pentacene, there is no symmetry-based relation between the Kekulé structures k_c and k_d .

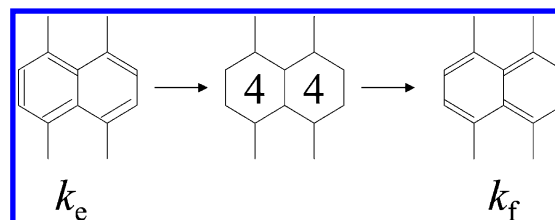


Figure 6. A structural detail needed for the proof of Theorem 2.

Theorem 2. For any positive integer N there exist perifusenes, such that at least N of their geometric Kekulé structures correspond to the same algebraic Kekulé structure.

Proof. It is sufficient to note that whenever a benzenoid system possesses a structural detail shown in Figure 6, then two of its geometric Kekulé structures are mapped onto the same algebraic Kekulé structure. In the benzenoid system with p such naphthalene fragments, at least 2^p geometric Kekulé structures pertain to the same algebraic Kekulé structure.

CONCLUDING REMARKS

Our analysis has shown that the concept of algebraic Kekulé structures could be used only for catafusenes, for which these contain precisely the same structural information as the ordinary “geometric” Kekulé structures. Which of the two types of Kekulé structures one will use is a matter of personal preference. However, for computer-aided studies the algebraic variant has evident advantages.

In the case of perifusenes, an algebraic Kekulé structure may contain less information than its geometric counterpart, and the usage of the former should be done with due caution.

REFERENCES AND NOTES

- (1) Randic, M. Algebraic Kekulé Formulas for Benzenoid Hydrocarbons. To be published.
- (2) Cyvin, S. J.; Gutman, I. *Kekulé Structures in Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, 1988.
- (3) Gutman, I.; Cyvin, S. J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer-Verlag: Berlin, 1989.
- (4) Randic, M. Aromaticity of Polycyclic Conjugated Hydrocarbons. *Chem. Rev.* **2003**, *103*, 3449–3606.
- (5) Randic, M.; Balaban, A. T. Polycyclic Aromatic Compounds. Submitted for publication. Randic, M.; Balaban, A. T. *J. Chem. Inf. Comput. Sci.* In press. Balaban, A. T.; Randic, M. Work in preparation.
- (6) Balaban, A. T. Enumeration of Catafusenes, Diamondoid Hydrocarbons, and Staggered Alkane C-Rotames. *MATCH Commun. Math. Chem.* **1976**, *2*, 51–61.
- (7) Bonchev, D.; Balaban, A. T. Topological Centric Coding and Nomenclature of Polycyclic Hydrocarbons. I. Condensed Benzenoid Systems (Polyhexes, Fusenes). *J. Chem. Inf. Comput. Sci.* **1981**, *21*, 223–229.
- (8) Gutman, I. On Kekulé Structure Count of Cata-condensed Benzenoid Hydrocarbons. *MATCH Commun. Math. Chem.* **1982**, *13*, 173–181.
- (9) Note that Theorem 1 does not hold for benzene ($h = 1$) which one should not be worried about as benzene is not a catacondensed system and represents a class by itself.

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