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Topological properties of KHF-graphs and a proof of a one-to-one correspondence between Kekulé and sextet patterns of KHF-graphs

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In this paper, the definition of a super sextet is given, the concept of a KHF-graph is proposed, and some of the topological property theorems of KHF-graphs are developed using a similar method as [1]. And so Ohkami-Hosoya conjecture [2] is proved rigorously.

Key words: KHF-graph—Kekulé pattern—Sextet pattern—Super sextet—Conjugated circuit

1. Introduction

CAS (Clar aromatic sextet) theory [3] is an interesting topological theory of benzenoid hydrocarbons. Because it is believed to have an acceptable quantum chemical justification [4–7], this theory has recently attracted some attention. The following conjecture plays a key role [2]:

Ohkami-Hosoya conjecture. For any benzenoid hydrocarbons (polyhex graph [18]) G, which has at least one Kekulé structure (or Kekulé pattern), there exists a one-to-one correspondence between Kekulé and sextet patterns.

In [1], we have investigated this problem, the concept of generalized sextet patterns, and proved the one-to-one correspondence between Kekulé and generalized sextet patterns. However, it is not the one-to-one correspondence in the same sense as in the Ohkami-Hosoya conjecture, since our concept of a generalized sextet pattern is different from their concept of a sextet pattern. In the present paper, the definition of a super sextet is given, some of the topological property theorems of KHF-graphs are developed, and the Ohkami–Hosoya conjecture is proved.

2. KHF-graphs and some of their topological properties

First of all, we give the following definitions:

KHF-graph. If a finite connected graph on the hexagonal lattice (honeycomb lattice) has at least one decomposition into 1-factors [9, 10] (or at least a Kekulé pattern [2]), then this connected graph is called a honeycomb fragment graph with Kekulé pattern (a Kekulé honeycomb fragment graph, simply a KHF graph). In Fig. 1, a, c, e, f and g are KHF-graphs, but b and d are not. Although b and d are honeycomb fragments, they haven't any Kekulé pattern.

Localized bond. In all Kekulé Patterns of a KHF-graph, a bond is maintained (either a single or double), then it is called a localized bond [11].

Obviously, in a KHF-graph, an edge starting from an end-vertex (i.e. a vertex of degree one) must have a localized bond. If all the bonds in a KHF-graph are localized, such a KHF-graph is trivial (see Fig. 1a) in our discussion. From now on, without loss of generality, we only consider KHF-graphs in which not all bonds are localized, unless otherwise stated.

Basic circuit. If within a circuit of a KHF-graph there aren't any other circuits, then this circuit is called a basic circuit. Obviously, the number of edges of any basic circuit is even. In Fig. 1e, there are two basic circuits and in Fig. 1f, there are fourteen basic circuits.

Conjugated circuit. In a given Kekulé pattern of a KHF-graph, if a circuit with h edges has a set of $h/2$ conjugated double bonds then this circuit is called a conjugated circuit. If the extreme right vertical edge of a conjugated circuit is a double bond edge, then this circuit is called a right conjugated circuit, otherwise, it is called a left one.

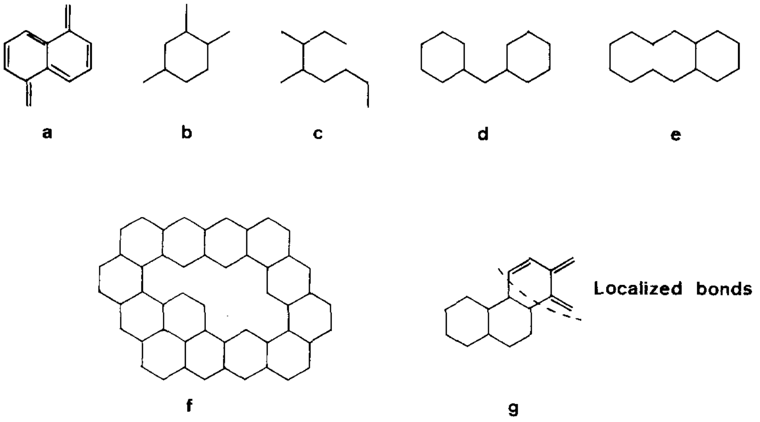

Fig. 1. KHF and non-KHF graphs

Theorem 1. *In any Kekulé pattern of a* KHF-*graph without vertices of degree one, there is at least one basic circuit which is a conjugated circuit.*

Proof. By using Euler's formula about connected planar graphs, for any KHF-graph G, we have [9,10,12]

$$|E| = |V| - 1 + f, \qquad (f \geq 0) \tag{1}$$

where $|V|$ is the number of vertices of the KHF-graph G, $|E|$ is the number of its edges, and f is the number of its basic circuits. If a basic circuit in the KHF-graph isn't a conjugated circuit, the number of single-bond edges on this basic circuit must be at least two plus that of the double-bond edges.

Obviously, every edge of a KHF-graph belongs to at most two basic circuits. If none of the basic circuits in the KHF-graph is conjugated, then

$$E_s - E_d \geq f, \tag{2}$$

where E_s is the number of single-bond edges in the KHF-graph, and E_d is that of double-bond edges.

From (1) and (2),

$$E_s - E_d \geq |E| - |V| + 1. \tag{3}$$

Since

$$|E| - E_s = E_d,$$

and

$$2E_d = |V|,$$

(3) becomes

$$0 \geq 1 \tag{4}$$

From this contradiction, Theorem 1 is proved. Q.E.D.

Theorem 2. *For any* KHF-*graph G (without vertices of degree one), there is one and only one Kekulé pattern in which all the conjugated circuits are right (left).*

Proof. From Theorem 1, in a given Kekulé pattern of G, there exists at least one conjugated circuit. If some of the conjugated circuits are left ones, on one of these left conjugated circuits changes the single-bonds into the double-bonds and vice versa. As a result,

(a) the vertical double-bond edges on this circuit shift right;
(b) this circuit becomes a right conjugated circuit.

In the transformed Kekulé pattern, if there are still left conjugated circuits, choose one of them and proceed with the interchange of single and double bonds again.

Because of the finiteness of the KHF-graph, it is impossible that the shift process in (a) is infinite. Finally, we can obtain a Kekulé pattern of G, in which all the conjugated circuits are right ones. Now, let us prove the uniqueness of the result. Assume that there are two different Kekulé patterns of G, in which all the conjugated circuits are right ones. Denote the two patterns by K_1 and K_2, respectively.

Let the two patterns overlap completely. Delete the coincident double-bond edges (together with their endpoints). In the residual subgraph, every vertex must be an endpoint of a double-bond edge of K_1, and be also an endpoint of a double-bond edge of K_2. But these two edges can't be coincident with each other. Thus, if a_1 is a vertex of the residual subgraph, and $\overline{a_1a_2}$ is a double-bond edge of K_1, then $\overline{a_2a_3}$ is a double-bond edge of K_2 (a_3 is not coincident with a_1), $\overline{a_3a_4}$ is a double-bond edge of K_1 (a_4 is not coincident with a_2), and so on. Obviously, $a_1, a_3, a_4, \ldots$ also belong to the residual subgraph.

Finally, an edge $\overline{a_{m-1}a_m}$ must be a double-bond edge of K_1, and $\overline{a_ma_1}$ a double-bond edge of K_2, otherwise it would be contradictory to the finiteness of KHF-graph. Thus, the circuit $a_1a_2a_3a_4 \cdots a_{m-1}a_ma_1$ is a conjugated circuit either in K_1 or in K_2. But in K_1 and K_2, the arrangements of the double-bonds on the circuit are different from each other. Obviously, in one of the two patterns, there exists a left conjugated circuit. This is contradictory to the assumption on K_1 and K_2. Hence, K_1 is identical with K_2. This proves Theorem 2.

For some KHF-graphs with vertices of degree one, their Kekulé patterns may contain neither right conjugated circuits nor left ones, provided all the bonds in these KHF-graphs are localized.

As a consequence of Theorem 2, the following statement is valid.

Consequence. For any KHF-graph, with or without vertices of degree one, there is one and only one Kekulé pattern which doesn't contain any left (or right) conjugated circuits.

3. Definition of a super sextet and one-to-one correspondence between Kekulé and sextet patterns

We start with some definitions.

Proper sextet [2]. A right conjugated six-membered circuit is called a proper sextet.

If two right conjugated circuits haven't any common edges, then the two right conjugated circuits are separated from each other.

In Fig. 2a, there are two right conjugated circuits 1, 2, 3, 4, 5, 10, 1 and 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 1. Since they have some common edges, they are not separated from each other.

Using the following program, step by step, among the numerous right conjugated circuits of a given Kekulé pattern, we can find a special set of separated right conjugated circuits, called a set of s-separated right conjugated circuits.

Step 1. Let all the right conjugated basic circuits (including all the proper sextets) be s-separated right conjugated circuits.

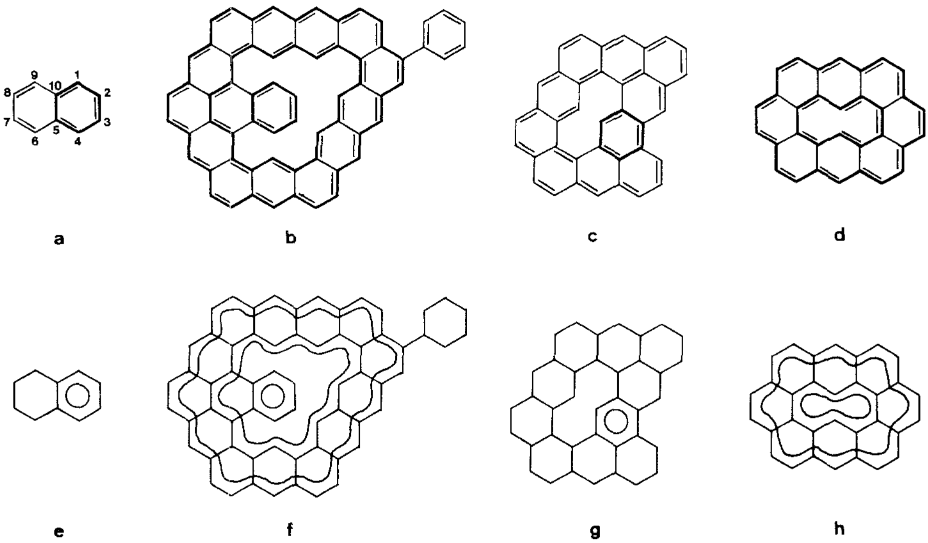

Fig. 2. *S*-separated right conjugated circuits and sextet patterns

Step 2. In addition to the preceding determined s-separated right conjugated circuits, another right conjugated circuit is also a s-separated right conjugated circuit if it is separated from all the preceding determined s-separated right conjugated circuits, and within it there exist no other right conjugated circuits which are separated from all the preceding determined s-separated right conjugated circuits.

Step 3. In the given Kekulé pattern, if there are still some other right conjugated circuits which are separated from the preceding determined s-separated right conjugated circuits, reapply step 2 until we find a unique complete set of s-separated right conjugated circuits.

In Fig. 2a–d, the set of s-separated right conjugated circuits are marked with bold line.

Definition of a proper super sextet. A s-separated right conjugated circuit with more than six vertices is called a proper super sextet. If in a proper super sextet, we draw a closed curve and delete all the double-bonds, we obtain a super sextet [2].

Definition of sextet pattern. For a given Kekulé pattern of a KHF-graph, in each proper sextet, draw a circle (i.e. transform all the proper sextets into aromatic sextets [2]), in each proper super sextet, draw a closed curve, and delete all the double-bonds of this Kekulé pattern. Thus, we can obtain a sextet pattern, which corresponds to the given Kekulé pattern.

For example, the sextet patterns corresponding to Fig. 2a–d are shown in Fig. 2*e*–*h*, respectively.

Theorem 3. *For any given orientation of any* KHF-*graph G, there exists a one-to-one correspondence between Kekulé and sextet patterns*

Proof. From the definition of a sextet pattern, for any Kekulé pattern of G there exists one corresponding sextet pattern. Conversely, for a sextet pattern of a given KHF-graph, we can prove that there is one and only one Kekulé pattern corresponding to the sextet pattern. In this given sextet pattern, transform all the circles and the other closed curves into the proper sextets and the proper super sextets (i.e. a complete set of s-separated right conjugated circuits). What remains can't contain any other s-separated right conjugated circuits. Furthermore, there can't exist any right conjugated circuits in the remainder. (If they existed, they would be separated from all the s-separated right conjugated circuits, and so there would exist s-separated right conjugated circuits in the remainder.) According to the consequence of Theorem 2, the Kekulé pattern of the remainder must be unique. Thus, Theorem 3 holds.

Specifically, in the case of benzenoid hydrocarbons, the above proof becomes the proof of the Ohkami–Hosoya conjecture.

4. Discussion

In this paper, we define "super sextet". It seemed to be one of the most significant open problems on the topological theory of benzenoid systems [13-15]. Our definition of sextet pattern agrees with that of other authors' [2, 8] in the case of cata-condensed and peri-condensed benzenoid systems. But our definition includes the case of corona-condensed benzenoid system [16, 17], and other more general systems. Hence it is not only compatible with other authors' work [2, 3, 8, 13-15], but also more advantageous.

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