An efficient algorithm for generating all Kekulé patterns of a generalized benzenoid system*

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An algorithm for generating all Kekulé patterns of a benzenoid system was given by Jiang [1]. However, for a generalized benzenoid system, this problem is more complex. In this paper, we give an efficient algorithm for generating all Kekulé patterns of a generalized benzenoid system by the generalized directed tree structure [2] of the set of Kekulé patterns of a generalized benzenoid system.

1. Introduction

It is well known that the number $K(B)$ of Kekulé patterns of a benzenoid system B is closely related to the stability of the π-electronic system corresponding to B. By using the conceptual framework of the valence bond method, some resonance theoretical models have been formulated [3–13]. In ref. [3], Clar was the first to establish the aromatic sextet theory, based on mutually resonant sextets (hexagons). Later, Hosoya and Yamaguchi [4] introduced the sextet polynomial for enumeration of Clar's sextets. It was found that there exists a one-to-one correspondence between Kekulé patterns and sextet patterns of a benzenoid system. In recent years, the one-to-one correspondence has been rigorously proved [2,14–16]. In ref. [9], Randić introduced the concept of conjugated cycles (circuits). Enumeration of conjugated cycles has led to expressions for the resonant energies of polycyclic conjugated hydrocarbons, to the generalization of the Hückel rule to polycyclic conjugated systems, etc. [9–12]. Furthermore, Gutman and Randić [13] extended the enumeration of conjugated cycles to include disjoint conjugated cycles. It was shown that for any Kekulé pattern of a benzenoid system B, the number of groups of disjoint conjugated cycles of B is always $K(B) - 1$. The reciprocal relation between Kekulé patterns and conjugated cycles enables one to determine $K(B)$ from a Kekulé pattern and the corresponding conjugate cycles of it, and even to determine all Kekulé patterns. Alternatively, one can find all groups of disjoint conjugated cycles of a Kekulé pattern K_i by taking the symmetric difference of K_i and each of the other Kekulé patterns. However, for large conjugated systems, it is more difficult to find all the

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groups of disjoint conjugated cycles, and enumeration of all the Kekulé patterns is less arbitrary. It was pointed out by Gutman and Randić [13] that the interest in Kekulé patterns had brought also new schemes for their enumeration. Although some efficient algorithms for finding a Kekulé pattern of a Kekuléan benzenoid system or a generalized benzenoid system have been published [17–19], it is still difficult to find all Kekulé patterns of a (generalized) Kekuléan benzenoid system. On the other hand, many scientists [4,20–24] have shown interest in the mathematical structures of the set of Kekulé patterns of a benzenoid system. In ref. [24], Ohkami et al. proved the directed tree structure of the set of Kekulé patterns of a cata-condensed benzenoid system; they also believed that the same property exists in peri-condensed benzenoid systems. Later, this property was proved by Chen [25]. Based on the directed tree structure of the set of Kekulé patterns of a Kekuléan benzenoid system B, Jiang [1] established an efficient algorithm for generating all Kekulé patterns of B systematically.

For a generalized Kekuléan benzenoid system B, the set of Kekulé patterns of B possesses a directed forest structure [25]. This brings about some essential difficulty in generating all Kekulé patterns of B using Jiang's algorithm, since it is difficult to find all roots of a directed forest structure.

Recently, by introducing some new concepts, the present authors [2] generalized the above results to obtain the generalized directed tree structure of the set of Kekulé patterns of a generalized benzenoid system. Based on this result, we give a new efficient algorithm for generating all Kekulé patterns of a generalized Kekuléan benzenoid system.

2. Some related results

We first give some necessary definitions. For convenience, a generalized benzenoid system or a benzenoid system (simply, a GBS or a BS) is always placed on a plane so that a pair of edges of each hexagon is parallel to the vertical line.

DEFINITION 2.1

A GBS B is a 2-connected subgraph on the hexagonal lattice. A ring of B is the boundary of an interior face of B.

Generally, B may have some rings with length greater than six which are called holes of B (see fig. 1). In particular, if B has no holes, it is also a benzenoid system.

DEFINITION 2.2

For a Kekulé pattern K_i of a GBS B, a K_i-alternating cycle is right (left) if the extreme right (left) vertical edge of it is a K_i-double bond. A right (left) K_i-

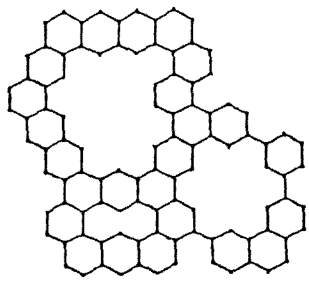

Fig. 1.

alternating cycle C of B is said to be a generalized proper (improper) sextet, or simply proper (improper) g-sextet, if it is minimal in the sense that there is no other right (left) K_i-alternating cycle whose interior is contained in the interior of C. In particular, if a proper (improper) g-sextet C is a ring of B, it is also called a proper (improper) ring, and if C is a hexagon of B, it is a proper (improper) sextet (see fig. 2).

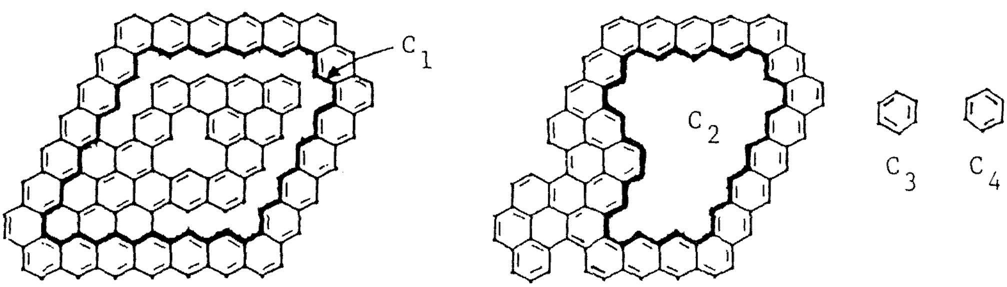

Fig. 2. C_1: a proper g-sextet; C_2: a proper ring; $C_3(C_4)$: a proper (improper) sextet.

DEFINITION 2.3

A simultaneous rotation of all the proper g-sextets (rings; sextets) in a given Kekulé pattern K_i of a GBS B into left K_i-alternating cycles (improper rings; improper sextets) to give another Kekulé pattern K_j of B is called a proper g-sextet (ring; sextet) rotation. We denote it as $K_j = R_g(K_i)$, or $K_i \xrightarrow{R_g} K_j$ ($K_j = R_r(K_i)$, or $K_i \xrightarrow{R_r} K_j$; $K_j = R(K_i)$, or $K_i \xrightarrow{R} K_j$) (see fig. 3).

DEFINITION 2.4

The g-sextet (ring; sextet) rotation graph $R_g(B)$ ($R_r(B)$; $R(B)$) of a GBS B is a directed graph whose vertex set is the set of Kekulé patterns of B and there is an arc from a vertex K_i to another vertex K_j if and only if $R_g(K_i) = K_j$ ($R_r(K_i) = K_j$; $R(K_i) = K_j$).

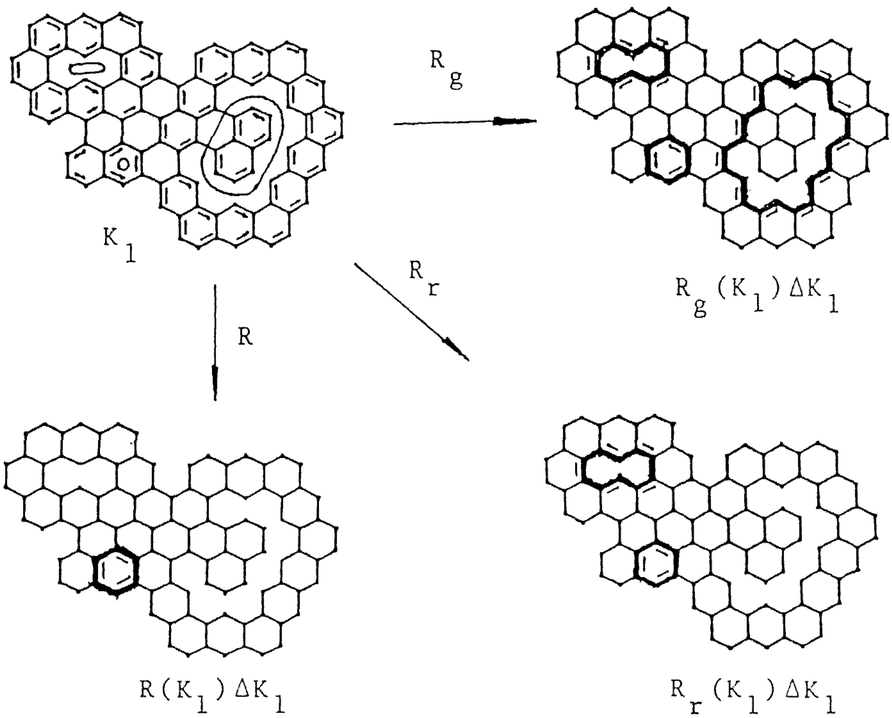

Fig. 3. In the Kekulé patterns $R_g(K_1)$, $R_r(K_1)$ and $R(K_1)$, only the double bonds which are distinctly other than those in K_1 are drawn.

DEFINITION 2.5

A root Kekulé pattern of a GBS B is the Kekulé pattern with no proper sextet. A generalized root Kekulé pattern of a GBS B is the Kekulé pattern with no proper g-sextet, denoted by a g-root Kekulé pattern.

In ref. [25], Chen proved that if B is a BS, then $R(B)$ is a directed tree, and the root of $R(B)$ corresponds to the unique root Kekulé pattern of B. However, if B is a GBS which is not a BS, then $R(B)$ is a directed forest with roots more than one, and in the general case, $R_r(B)$ is also a directed forest.

Recently, the following theorems were proved by the present authors [2].

THEOREM 2.6 [2]

Let C be a proper (improper) g-sextet of a Kekulé pattern of a GBS B. Then either C is a hexagon or in C there is a ring with length greater than six, i.e. a hole.

THEOREM 2.7 [2]

For any Kekuléan GBS B, there is exactly one g-root Kekulé pattern.

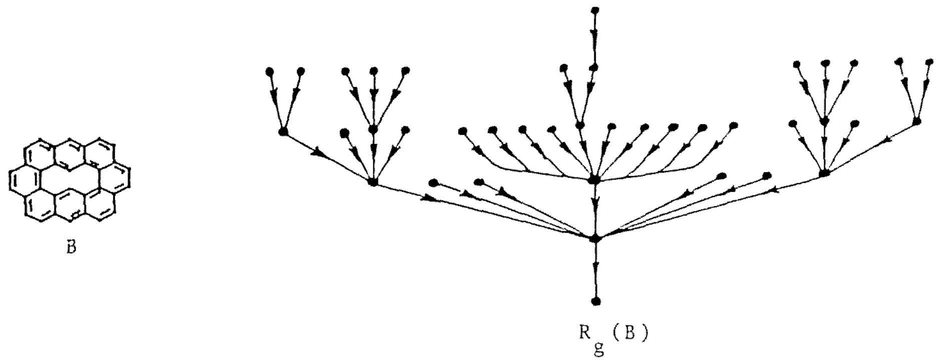

Fig. 4. A GBS B and the g-sextet rotation graph $R_g(B)$ of B.

THEOREM 2.8 [2]

Let B be a Kekuléan GBS. Then the g-sextet rotation graph $R_g(B)$ is a directed tree. Moreover, the root of $R_g(B)$ corresponds to the unique g-root Kekulé pattern of B (see fig. 4).

It is easy to see from theorem 2.6 that the concept of a proper (improper) g-sextet is a natural and reasonable generalization of that of a proper (improper) sextet. Hence, all the characters concerning proper (improper) g-sextets and the g-sextet rotation graph of a GBS will naturally include those of proper (improper) sextets and the sextet rotation graph of a BS.

3. An efficient algorithm for generating all Kekulé patterns of a GBS

Based on the generalized directed tree structure of the set of Kekulé patterns of a GBS B, we can design an algorithm similar to that of Jiang. However, it is much more difficult to find a proper (improper) g-sextet of a GBS than to find a proper (improper) sextet of a BS. We have to explore this new way further.

THEOREM 3.1

Let C be a proper (improper) g-sextet of a Kekulé pattern K_i of a GBS B. Then, if C is neither a hexagon nor a hole, all the edges with one end vertex on C and the other in the interior of C are fixed single bonds.

Proof

Since C is a K_i-alternating cycle that is neither a hexagon nor a hole, in B there is an edge e with one end vertex v on C and the other in the interior of C which is a K_i-single bond. Suppose that e is not a fixed single bond. Then there is a Kekulé pattern K_j such that e is a K_j-double bond. Thus, in the symmetric difference $K_i \Delta K_j$, there is a $K_i(K_j)$-alternating cycle C^* containing the edge e. Let $\upsilon e \ldots \upsilon'$ be a $K_i(K_j)$-alternating path on C^* which has only the end vertices υ and υ' on C. Let e^* be a K_i-double bond with an end vertex being υ. Then the segment $\upsilon e \ldots \upsilon'$ on C^* and $\upsilon e^* \ldots \upsilon'$ on C form a right (left) K_i-alternating cycle of B whose interior is contained in the interior of C, contradicting that C is a proper (improper) g-sextet of K_i of B (see fig. 5).

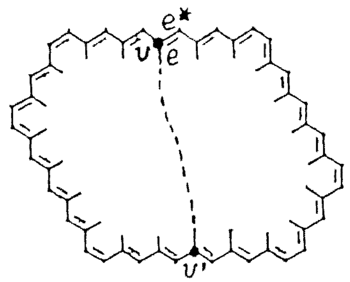

Fig. 5.

Theorem 3.1 implies the following corollaries.

COROLLARY 3.2

Let B be a GBS with no fixed bond. Then any proper or improper g-sextet of B is either a hexagon or a hole.

COROLLARY 3.3

Let B be a GBS with no fixed bond. Then $R_g(B) \cong R_r(B)$.

The above theorems and corollaries mean that, for finding proper (improper) g-sextets of a GBS with no fixed bond, we need only to recognize proper (improper) rings, and it is as easy as to recognize proper (improper) sextets. This enables us to establish an efficient algorithm for generating all Kekulé patterns of a GBS with no fixed bond.

DEFINITION 3.4

Let B be a GBS with no fixed bond, and K a Kekulé pattern of B. A set $S_i(K)$ of improper rings of K is said to be a proper ring covering of K if each of the proper rings of K has at least an edge in common with some ring in $S_i(K)$ (see fig. 6).

DEFINITION 3.5

A simultaneous rotation of all improper rings in a proper ring covering of a Kekuléan pattern K_j of a GBS B with no fixed bond into proper rings to give another

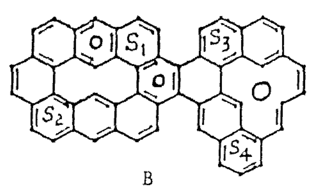

Fig. 6. The Kekulé pattern K of B has three proper rings (indicated by 0) and six proper ring coverings, where $S_1(K) = \{s_1, s_3\}$, $S_2(K) = \{s_1, s_4\}$, $S_3(K) = \{s_1, s_3, s_4\}$, $S_4(K) = \{s_1, s_2, s_3\}$, $S_5(K) = \{s_1, s_2, s_4\}$, $S_6(K) = \{s_1, s_2, s_3, s_4\}$.

Kekulé pattern K_i is called a proper ring covering rotation of K_j, denoted by $\overline{R}_r(K_j) = K_i$ or $K_j \xrightarrow{\overline{R}_r} K_i$.

THEOREM 3.6

Let K_j be a Kekulé pattern of a GBS with no fixed bond. Then there exists a Kekulé pattern K_i of B such that $R_r(K_i) = K_j$ if and only if there is a proper ring covering of K_j such that $\overline{R}_r(K_j) = K_i$.

Proof

Suppose that there is a Kekulé pattern K_i of B such that $R_r(K_i) = K_j$, and S_i is the set of all the proper rings of K_i. Then any proper ring s of K_j must have an edge in common with a ring in S_i. Otherwise, s would also be a proper ring of K_i, a contradiction. Hence, S_i is a proper ring covering K_j which satisfies that $\overline{R}_r(K_j) = K_i$.

Conversely, assume that there is a proper ring covering $S_i(K_j)$ of K_j such that $\overline{R}_r(K_j) = K_i$. Then all the proper rings of K_j are not proper rings of K_i since each of them has an edge in common with some ring in $S_i(K_j)$. Thus, $S_i(K_j)$ is just the set of all the proper rings of K_i, and $R_r(K_i) = K_j$.

ALGORITHM 3.7

Let B be a Kekuléan GBS with no fixed bond.

Step 1: Find a Kekulé pattern of B by the Hungarian algorithm, and then find the g-root Kekulé pattern K_0 of B by repeating the proper ring rotations. Let $K_B(i)$ be the set of the Kekulé patterns of distance i to K_0 in $R_r(B)$. Set $i = 0$.

Step 2: For every Kekulé pattern K_j in $K_B(i)$, search all the proper ring coverings of K_j and generate all the Kekulé patterns in the set $\{\overline{R}_r(K_j)\}$ by proper ring coverings of K_j. Set $\{\overline{R}_r(K_j)\} \subset K_B(i+1)$.

Step 3: If $K_B(i+1) = \varnothing$, all Kekulé patterns have been generated, then stop. Otherwise, set $i + 1 \to i$, and go to step 2.

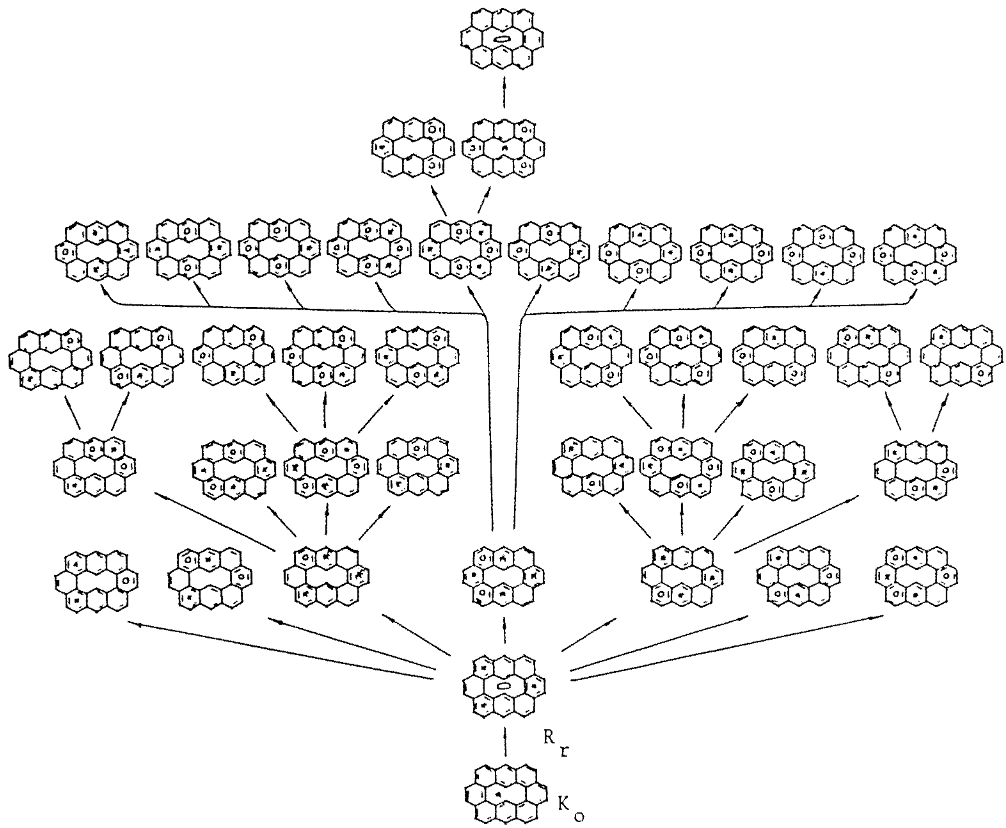

Fig. 7. Generation of all Kekulé patterns of a GBS B with no fixed bonds by proper ring covering rotations from the g-root Kekulé pattern K. Here, the rings marked o are proper rings, while the starred rings are improper.

An example of using this algorithm to generate all the Kekulé patterns of a GBS B is shown in fig. 7.

For a GBS B with fixed bonds, that is, an essentially disconnected GBS, after deleting from B all fixed single bonds and the vertices of all fixed double bonds, the resultant graph consists of some connected components, called effective units, each of which is a GBS with no fixed bond. Clearly, any Kekulé pattern of B consists of all the fixed double bonds of B together with a Kekulé pattern of every effective unit. Hence, we can establish the following algorithm for generating all Kekulé patterns of an essentially disconnected GBS.

ALGORITHM 3.8

Let B be an essentially disconnected GBS with effective units $B_1, B_2, \ldots, B_n$, and E_0 the set of fixed double bonds of B.

Step 1: Apply algorithm 3.7 to generate all Kekulé patterns of B_i, for $i = 1, 2, \ldots, n$.

Step 2: Generate all Kekulé patterns of B by taking every element in $K_{B_1} \times K_{B_2} \times \ldots \times K_{B_n}$ together with E_0.

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