k-Resonant Benzenoid Systems and *k*-Cycle Resonant Graphs†

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A benzenoid system (or hexagonal system) H is said to be k-resonant if, for $1 \leq t \leq k$, any t disjoint hexagons of H are mutually resonant; that is, there is a Kekule structure (or perfect matching) K of H such that each of the k hexagons is an K-alternating hexagon. A connected graph G is said to be k-cycle resonant if, for $1 \leq t \leq k$, any t disjoint cycles in G are mutually resonant. The concept of k-resonant benzenoid systems is closely related to Clar's aromatic sextet theory, and the concept of k-cycle resonant graphs is a natural generalization of k-resonant benzenoid systems. Some necessary and sufficient conditions for a benzenoid system (respectively a graph) to be k-resonant (respectively k-cycle resonant) have been established. In this paper, we will give a survey on investigations of k-resonant benzenoid systems and k-cycle resonant graphs.

1. INTRODUCTION

In the topological theory of benzenoid hydrocarbons, a benzenoid system (or hexagonal system) denotes the carbon atom skeleton graph of a benzenoid hydrocarbon, which is a two-connected plane graph whose every interior face is bounded by a regular hexagon. A Kekule structure K of a benzenoid system H corresponds to a perfect matching (1-factor) of H. An edge in H is said to be a K-double bond if it belongs to K, otherwise a K-single bond. An edge in H is said to be a fixed double (respectively, single) bond if it belongs to (respectively does not belong to) every Kekule structure of H. A benzenoid system is said to be normal if it contains no fixed bond. A cycle (or circuit) C in H is said to be *conjugated* or *resonant* if there is a Kekule structure K of H such that C is a K-alternating cycle. In conjugated circuit model,[1−12] conjugated circuits with different sizes have different resonant energies. If the size of a conjugated circuit is equal to $4n + 2$, then the smaller n is, the larger the resonant energy is. So the conjugated hexagon has the largest energy. On the other hand, from a purely empirical standpoint, Clar found that various electronic properties of polycyclic aromatic hydrocarbons can be predicted by appropriately defining an aromatic sextet for their Kekule structures.[13−23] According to Clar's aromatic sextet theory, a *Clar formula* of a benzenoid system is a set of mutually resonant sextets with the maximum cardinal number, where sextets mean resonant hexagons and a set of mutually resonant sextets means a set of disjoint hexagons for which there is a Kekule structure K so that all of the disjoint hexagons are K-alternating hexagons. The number of sextets in a Clar formula of G is called the Clar number of G. For a benzenoid system H with Clar number c, Clar formulas of H may not be unique, and, for $1 \leq k \leq c$, any k-disjoint hexagons of H are not certainly mutually resonant. Figure 1 shows a benzenoid system H with Clar number 5, which has two Clar formulas, and the hexagon s is not resonant.

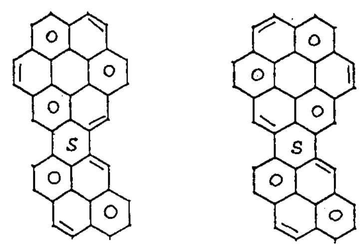

Figure 1. Benzenoid system H with Clar number 5 and with two Clar formulas.

An interesting problem arises: under what conditions are any k disjoint hexagons of a benzenoid system H mutually resonant?

If a benzenoid system H satisfies such a property, that is, for a positive integer k and $1 \leq t \leq k$, with any t disjoint hexagons of H being mutually resonant, it is said to be k-resonant or k-coverable.

1-Resonant benzenoid systems were first investigated by Zhang and Chen.[24] Some necessary and sufficient conditions for a benzenoid system to be 1-resonant were given. Later Zhang and Zheng[25] gave a similar characterization for 1-resonant generalized benzenoid systems, where a generalized benzenoid system is a 2-connected subgraph of a benzenoid system, which may have some holes (see Figure 2). Zheng[26] further gave some pretty results for k-resonant benzenoid systems with $k \geq 2$.

The concept of k-cycle resonant graphs was first introduced by Guo and Zhang, which is a natural generalization of the concept of k-resonant benzenoid systems. Some properties and necessary and sufficient conditions of k-cycle resonant graphs were also given.

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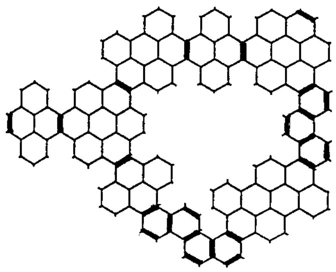

Figure 2. *k*-coverable generalized benzenoid system with $k \geq 3$.

In this paper, we will give a survey and review on investigations of *k*-resonant benzenoid systems and *k*-cycle resonant graphs.

2. *K*-RESONANT (OR *K*-COVERABLE) BENZENOID SYSTEMS

A *cover* of H is a set of disjoint hexagons of H such that after deleting all the vertexes on these hexagons, the remainder of H has a Kekule structure or is empty. A maximum cover of H is a cover with maximum cardinal number, which is also called a Clar formula. In other words, a cover of H is a set of mutually resonant hexagons of H, and a maximum cover is a set of mutually resonant hexagons with the maximum cardinal number.

Definition 1. For a positive integer k, a benzenoid system H is said to be *k*-resonant or *k*-coverable if, for $1 \leq t \leq k$, any t disjoint hexagons of H form a cover of H.

For 1-coverable benzenoid systems, Zhang and Chen gave the following theorem.

Theorem 1.[24] Let H be an hexagonal system. Then each hexagon of H covers H iff either (1) H contains no fixed bond or (2) there exists a perfect matching M of H such that the contour of H is an *M*-alternating cycle.

A generalized benzenoid system G is said to be complete if each edge of G is contained on a hexagon. For a complete generalized benzenoid system H, Zhang and Zheng[25] gave a similar necessary and sufficient condition for H to be *k*-resonant.

Theorem 2.[25] Every hexagon of a completely generalized hexagonal system H is resonant if and only if the boundaries of the infinite face and nonhexagon faces of H are resonant.

A sufficient condition for a benzenoid system to be 2-resonant was given by Zheng.[26]

Theorem 3.[26] A benzenoid system H is 2-resonant if H is 1-resonant and any pair of two disjoint hexagons of H with at least one boundary hexagon are mutually resonant.

In a draft of a book,[27] the above sufficient condition is improved as the following theorem.

Theorem 4.[27] A benzenoid system H is 2-coverable if and only if H is 1-coverable and any two disjoint side hexagons of H form a cover of H.

A complete characterization of $k(\geq 3)$-resonant benzenoid systems was given by Zheng.[26]

Theorem 5.[26] A benzenoid system is $k(\geq 3)$-resonant if and only if it is 3-resonant.

Zheng defined three *k*-resonant bricks as shown in Figure 3. If a benzenoid system H can be constructed from the three bricks by affixing them in heavy edges, H is said to have a $k-r$-brick decomposition (see Figure 3). A series of lemmas in ref 26 imply the following theorem.

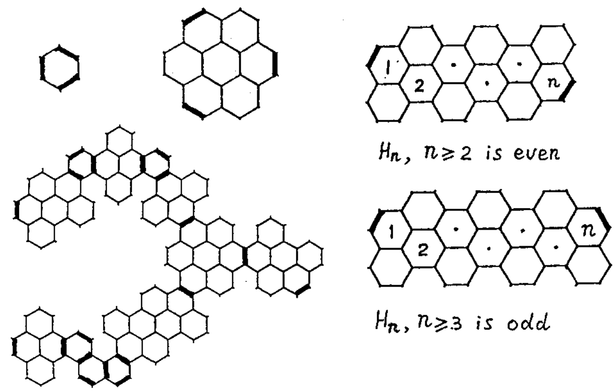

Figure 3. Three *k*-resonant bricks and the *k*-resonant-brick decomposition of a *k*-resonant benzenoid system.

Theorem 6.[26] A benzenoid system H is $k(\geq 3)$-resonant if and only if H has a $(k - r)$-brick decomposition.

Chen and Guo[28] proved that the results of theorems 5 and 6 are also valid for generalized benzenoid systems (see Figure 2).

3. *K*-CYCLE RESONANT GRAPHS

After investigations of *k*-resonant benzenoid systems got great advance, Guo and Zhang began to consider whether the concept of *k*-resonant benzenoid systems can be generalized to general cases. Hence a new concept of *k*-cycle resonant graphs was introduced in ref 29.

Definition 2.[29] A graph G is said to be *k*-cycle resonant or *k*-cycle extendable if G contains at least k (≥ 1) disjoint cycles and, for $1 \leq t \leq k$, any t disjoint cycles in G are mutually resonant; that is, there is a Kekule structure K of G such that the t disjoint cycles are *K*-alternating cycles.

The following theorems were given in ref 29.

Theorem 7.[29] Let G be a *k*-cycle resonant graph. Then

(1) G is bipartite.

(2) For $1 \leq t \leq k$ and any t disjoint cycles $C_1, C_2, ..., C_t$ in G, $G - \cup_{i=1}^{t} C_i$ contains no odd component.

(3) Any two 2-connected components in G have no common vertex.

Theorem 8.[29] Let G be a *k*-cycle resonant graph. Then G is elementary or 1-extendable if and only if G is 2-connected.

Theorem 7 conditions 1 and 2 give some necessary conditions for a graph to be *k*-cycle resonant. It was proved that the necessary conditions are also sufficient.

Theorem 9.[29] A connected graph with at least k disjoint cycles is *k*-cycle resonant if and only if G is bipartite and, for $1 \leq t \leq k$ and any t disjoint cycles $C_1, C_2, ..., C_t$ in G, $G - \cup_{i=1}^{t} C_i$ contains no odd component.

From theorem 7 condition 3 and theorem 8, it is not difficult to see that the following theorem 10 holds.

Theorem 10.[30] Let G be a *k*-cycle resonant graph. Then, (i) for a 2-connected component G' of G with the maximum number k^* of disjoint cycles, if $k^* \leq k$, G' is k^*-cycle resonant, otherwise G' is *k*-cycle resonant; (ii) the forest induced by all the vertexes of G not in any 2-connected component of G has a perfect matching.

The above theorems imply that a non-2-connected *k*-cycle resonant graph with $k \geq 3$ can be constructed from some disjoint 2-connected k^*(or k)-cycle resonant graphs and a forest with perfect matching by adding some edges between

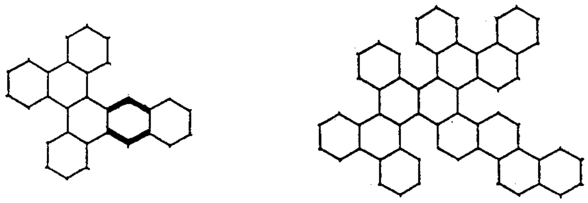
(1) (2)

Figure 4. (1) 1-Cycle resonant hexagonal system with two chains of even length. (2) k^*-Cycle resonant benzenoid system.

the 2-connected graphs and the forest so that the resultant graph is connected and the added edges are cut edges. Hence we need only to consider 2-connected k-cycle resonant graphs. However, in general cases, the construction of 2-connected k-cycle resonant graphs is still an open problem.

4. PLANAR K-CYCLE RESONANT GRAPHS

The necessary and sufficient conditions in theorem 9 is simple and formally graceful. However, when it is used to determine whether or not a graph is k-cycle resonant, one needs to check any t disjoint cycles. It is obviously tedious. This is why we need to find new, simpler, necessary, and sufficient conditions for planar graphs to be k-cycle resonant.

For a class of planar graphs, k-cycle resonant hexagonal systems, we obtained the following theorems.

A path P in a graph G is said to be a **chain** if all internal vertexes of P are of degree 2 in G and the degree of any end vertex of P is not equal to 2 in G. A hexagonal system is said to a catacondensed hexagonal system if any vertex of it lies on the boundary.

Theorem 11.[29] A hexagonal system H is 1-cycle resonant if and only if H is a catacondensed hexagonal system.

Theorem 12.[29] A hexagonal system H is 2-cycle resonant if and only if (1) H contains at least two disjoint cycles and (2) H is a catacondensed hexagonal system with no chain of even length.

Theorem 13.[29] Let H be a 2-cycle resonant hexagonal system, and let k^* be the maximum number of disjoint cycles in H. Then H is k^*-cycle resonant.

Theorem 14.[29] A hexagonal system H with $k^* \geq 2$ is k^*-cycle resonant if and only if H is a catacondensed hexagonal system with no chain of even length, where k^* is the maximum number of disjoint cycles in H.

Figure 4(1) shows a 1-cycle resonant hexagonal system, which is not 2-cycle resonant because it has two chains of length 2. Figure 4(2) shows a $k(\geq 2)$-cycle resonant hexagonal system. It was pointed out in ref 29 that, in the hexagonal systems with h hexagons obtained from a same parent hexagonal system with $h - 1$ hexagons, k^*-cycle resonant hexagonal systems have greater resonance energies than 1-cycle resonant hexagonal systems; also 1-cycle resonant hexagonal systems have greater resonance energies than hexagonal systems not being 1-cycle resonant, where k^* is the maximum number of disjoint hexagons of a hexagonal system.

For general planar k-cycle resonant graphs, their characterization is more difficult. Recently, we just finished a manuscript on planar k-cycle resonant graphs with $k = 1,2$, which has been submitted to *Discrete Applied Mathematics*.[30] In that paper, some new necessary and sufficient conditions for a graph to be planar 1-cycle resonant graphs or planar 2-cycle resonant graphs are established.

Before stating these results, we need to give some terminology and notations

Let G be a connected graph, and H a subgraph of G. A vertex in H is said to be an *attachment vertex* of H if it is incident with an edge in $G - E(H)$. The set of all attachment vertexes of H is denoted by $V_A(H)$. A bridge B of H in G is either an edge in $G - E(H)$ with two end vertexes being in H, or a subgraph of G induced by all the edges in a connected component B' of $G - V(H)$ together with all the edges with an end vertex in B' and the other in H. The vertexes in $V(B) \cap V(H)$ are also attachment vertexes of B to H. A bridge with k attachment vertexes is called a *k-bridge.*

The attachment vertexes of a k-bridge B of a cycle C in G divide C into k edge-disjoint paths, called the segments of B. Two bridges of C avoid one another if all the attachment vertexes of one bridge lie in a single segment of the other bridge; otherwise they overlap. Two bridges B and B^* of C are skewed if there are four distinct vertexes on C, in the cyclic order u, u^*, v, v^*, such that u and v are attachment vertexes of B and u^* and v^* are attachment vertexes of B^*.

For a bipartite graph G, we always color vertexes of G white and black so that any two adjacent vertexes have different colors.

We first gave several equivalent propositions.

Theorem 15.[30] Let G be a 2-connected bipartite planar graph. Then the following statements are equivalent:

(i) G is 1-cycle resonant.

(ii) For any cycle C in G, $G - V(C)$ has no odd component.

(iii) For any cycle C in G, any bridge of C has exactly two attachment vertexes which have different colors.

(iv) For any cycle C in G, any two bridges of C avoid one another. Moreover, for any 2-connected subgraph B of G with exactly two attachment vertexes, the attachment vertexes of B have different colors.

From the above theorem, we can give the following necessary and sufficient conditions for a graph to be planar 1-cycle resonant.

Theorem 16.[30] A 2-connected graph G is planar 1-cycle resonant if and only if G is bipartite and either (i) for any cycle C in G, any bridge of C has exactly two attachment vertexes which have different colors or (ii) for any cycle C in G, any two bridges of C avoid one another; moreover, for any 2-connected subgraph B of G with exactly two attachment vertexes, the attachment vertexes of B have different colors.

A vertex u of a graph G is said to be *cycle-related* to another vertex v of G if u is contained in a 2-connected block of G, and any cycle containing u must also contain v. If v is also cycle-related to u, then u and v are *mutually cycle-related.*

Property 1.[30] If a vertex u of a connected graph G is cycle-related to another vertex v of G, then u and v belong to the same 2-connected block B in G and all the edges in $B-v$ incident with u are cut edges of $G-v$.

For a chain P in a graph G, let $V_I(P)$ denote the set of internal vertexes of P. For a subgraph B of G, let $\bar{B}$ denote the subgraph of G induced by $E(G)\backslash E(B)$. The necessary and sufficient conditions for a planar graph to be 2-cycle resonant were also given in ref 30.

Theorem 17.[30] A 2-connected graph G is planar 2-cycle resonant if and only if, (i) G is planar 1-cycle resonant; (ii) for a chain P with even length and end vertexes v_1 and v_2, $G-V_I(P)$ has exactly two blocks, each of which is 2-connected, and v_1 and v_2 are cycle-related to the common vertex of the two blocks; (iii) for a chain P with odd length and end vertexes v_1 and v_2 such that $G-V_I(P)$ is not 2-connected, either (a) $G-V_I(P)$ has exactly three blocks, each of which is 2-connected, and each of v_1 and v_2 is cycle-related to the other attachment vertex of the block containing it, and the attachment vertexes of the third block are mutually cycle-related in the third block, or (b) any two 2-connected blocks of $G-V_I(P)$ are disjoint; (iv) for a 2-connected subgraph B_1 of G with exactly two attachment vertexes, if $\bar{B}_1$ is not 2-connected and every block of $\bar{B}_1$ is 2-connected, then $\bar{B}_1$ has exactly three blocks, say B_2,B_3,B_4, and the attachment vertexes of each of B_1,B_2,B_3,B_4 are mutually cycle-related in the block.

Based on the above necessary and sufficient conditions, an efficient algorithm for determining whether a 2-connected graph to be planar 1-cycle resonant or 2-cycle resonant can be developed.

k-Cycle resonant hexagonal systems are a special class of planar *k*-cycle resonant graphs, the construction of which was completely characterized in ref 29. For general planar *k*-cycle resonant graphs, their construction is more complex. Further investigations are needed.

5. CONCLUSION

Investigations of *k*-resonant benzenoid systems and *k*-cycle resonant graphs have obtained great advance. The above many results are very interesting. For example, the coefficients of the sextet polynomial of a $k(\geq 3)$-coverable benzenoid system H can be obtained by enumerations of any $i(\geq 1)$ disjoint hexagons in H. The two classes of graphs not only have a strong chemistry background but are also important topics in matching theorem. In the investigation of matching theory, Lovasz et al.[31−39] introduced and investigated elementary graphs, 1-extendable graphs, and *n*-extendable graphs, etc. A graph G is said to be *n*-extendable if any *n* independent edges of G are contained in a perfect matching of G. We can similarly call *k*-cycle resonant graphs as *k*-cycle extendable graphs and call *k*-coverable benzenoid systems as *k*-hexagon extendable benzenoid systems. The above investigations are also a new advance of matching theory research. There are still some open problems for further investigations.

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