Advances of Clar's Aromatic Sextet Theory and Randić's Conjugated Circuit Model

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Abstract: Clar's aromatic sextet theory provides a good means to describe the aromaticity of benzenoid hydrocarbons, which was mainly based on experimental observations. Clar defined sextet pattern and Clar number of benzenoid hydrocarbons, and he observed that for isomeric benzenoid hydrocarbons, when Clar number increases the absorption bands shift to shorter wavelength, and the stability of these isomers also increases. Motivated by Clar's aromatic sextet theory, three types of polynomials (sextet polynomial, Clar polynomial, and Clar covering polynomial) were defined, and Randić's conjugated circuit model was also established. In this survey we attempt to review some advances on Clar's aromatic sextet theory and Randić's conjugated circuit model in the past two decades. New applications of these polynomials to fullerenes, and calculation methods of linear independent and minimal conjugated circuit polynomials of benzenoid hydrocarbons are also presented.

Keywords: Sextet polynomial, Clar polynomial, Clar covering polynomial, Linearly independent and minimal conjugated circuit polynomial, k-Resonance, Benzenoid hydrocarbon, Fullerene.

1. INTRODUCTION

The aromaticity reflects extra stability of certain types of conjugated systems due to the nature of molecular orbitals. The resonance energy, calculated from experimental measurements, denotes the energy gain or loss due to the interaction between Kekulé structures, and represents the extra stability of the conjugated system. There have been distinct approaches developed to estimate the resonance energy. To deal with the problem in semiempirical valence-bond view, different VB based models (see [1] for details) were built successively and hierarchically, following Pauling and Wheland [2]. Among these models, Clar's aromatic sextet theory is mainly based on experimental observations, which describes the aromaticity of benzenoid hydrocarbons. In this survey we attempt to review some advances on Clar's aromatic sextet theory and Randić's conjugated circuit model for polyhexes (i.e., benzenoid hydrocarbons (benzenoid systems)), and coronoid hydrocarbons (coronoid systems), as well as fullerenes.

We first discuss three polynomials on the aromaticity of polyhexes. Then we extend the discussions to investigate the stability of fullerenes.

The sources of Clar's aromatic sextet theory seem to be the paper of chemists Armit and Robinson [3] and the work of physical chemist Hückel [4-6]. The important role of 6-membered conjugated cycles among 4k+2 conjugated cycles may also have inspired Clar's aromatic sextet theory, sextet polynomial, Clar polynomial, and Clar cover polynomial. In Clar's aromatic sextet theory, delocalized electrons in a 6-conjugated cycle are denoted by a circle, and as stated in Gutman [7] a Clar structure (Clar formula) consisting of circles satisfies the following three rules:

(a) Circles are never drawn in adjacent hexagons,
(b) The remainder of the polyhex obtained by the deletion of the vertices of the hexagons that possess circles must be empty or have a Kekulé structure, and
c) As many circles as possible are drawn subject to the constraints (a) and (b).

If we draw some circles with only the constraints (a) and (b), we obtain a generalized Clar structure (or sextet pattern).

Clar observed that for isomeric benzenoid hydrocarbons when the number of the circles of Clar structures (called Clar number) increases, the absorption bands shift to shorter wavelength, and the stability of the isomers also increases. In his book [8], Clar provided many examples to support his observation and built Clar's aromatic sextet theory. Recently, topographical features of the molecular electrostatic potential of a series of polycyclic aromatic benzenoid hydrocarbons have been analyzed at B3LYP/6-31+G(d,p) and MP2/6-31+G(d,p) levels. The theoretical results fully support Clar's aromatic sextet theory [9].

In the study of Clar's aromatic sextet theory, the first task is to determine the Clar number.

For small benzenoid hydrocarbons we can easily find a Clar structure by pen and paper. The Clar structures of some large benzenoid hydrocarbons are exemplified in Fig. (1).
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Fig. (1). Clar formulas of some classes of benzenoid systems, possessing \( x \) aromatic sextets.

Hansen and Zheng [17, 18] computed the Clar number of a benzenoid hydrocarbon by the integer linear programming and conjectured that the linear programming relaxation was sufficient for the general case. The conjecture has been proved by Abeledo and Atkinson in [19].

A further problem is whether we can refine the idea of Clar number. A reasonable assumption is that all generalized Clar structures contribute to the resonance energy. From this point of view, Hosoya and Yamaguchi defined the sextet polynomial [20]. Another reasonable assumption is that the maximal generalized Clar structures (which are not a proper subset of another generalized Clar structure) contribute the most to the resonance energy. From this point of view, El-Basil and Randić defined the Clar polynomial [21].

Inspired by Clar structure, we reasonably thought that, for the resonance energy of a benzenoid hydrocarbon, besides the aromatic 6-circuits all double bounds should also be considered. This motivated us to define the Clar cover of a benzenoid hydrocarbon and the counting polynomial, Clar covering polynomial [22].

The conjugated circuit model, a resonance-theoretic model, was introduced by Randić [23-25] in 1976 for the study of aromaticity and conjugation in polycyclic conjugated systems. It considers contributions of not only 6-membered rings but also all \((4k + 2)\)-membered conjugated circuits, as well as negative contributions of \(4k\)-membered conjugated circuits to the resonance energy. The model was motivated from an empirical point of view elaborating the Clar aromatic sextet theory [8]. The conjugated-circuit model has also a firm quantum mechanical basis [1, 26, 27]. It can be derived rigorously from the Pauling-Wheland resonance theory [28-31] via a Simpson-Herndon model Hamiltonian [32-34]. The conjugated circuit model can be applied to more general cases. For example, Manoharana et al. [35] investigated the stability of fullerenes predicted by the topological resonance energy (TRE) model and the conjugated circuit model, and Babić and Trinajstić [36] reported the resonance energies (REs) of several fullerenes with 4-membered rings and their isomers with only 5- and 6-membered rings, using the conjugated circuit model and the TRE model.

Here we consider only the conjugated circuit model for benzenoid hydrocarbons. The linear independent and minimal conjugated circuit polynomials (\( \text{LMCC} \) polynomials) are defined explicitly, and a recursive method and analytical expressions for calculation of \( \text{LMCC} \) polynomials are discussed.

Finally we mention some results on \( k \)-resonance (\( k \)-cycle resonance) in polyhexes, open end nanotubes, toroidal polyhexes, Klein-bottle polyhexes, and fullerenes as well.

2. Sextet Polynomial

Let \( G \) denote a benzenoid system. A generalized Clar structure (sextet pattern) of \( G \) is a set of disjoint hexagons of \( G \), in each hexagon of which a circle is drawn, such that the deletion of the vertices of such hexagons together with their incident edges results in a graph with a perfect matching or an empty graph. To count sextet patterns of a benzenoid hydrocarbon \( G \), Hosoya and Yamaguchi [20] defined the sextet polynomial \( B_c(x) \) as follows.

\[
B_c(x) = \sum_{i=0}^{C(G)} r(G,i)x^i, \tag{1}
\]

where \( r(G,i) \) is the number of sextet patterns of \( G \) with \( i \) hexagons (or generalized Clar structures with \( i \) cycles), and \( C(G) \) is Clar number, the maximum size of sextet patterns. The concepts of sextet pattern and Clar number have been naturally extended to polycyclic conjugated hydrocarbons, such as coronoid systems, carbon nanotubes, and fullerenes, etc.

The sextet polynomial has some interesting mathematical properties. Hosoya and Yamaguchi [20], and Ohkami and Hosoya [37] found that there is a one-to-one correspondence between the sextet patterns and the Kekulé structures for a catacondensed benzenoid hydrocarbon \( G \), i.e.
$B_G(1) = K(G)$,  \hfill (2)

where $K(G)$ denotes the number of Kekulé structures of $G$. They conjectured that for any benzenoid hydrocarbon (polyhex graph) which has at least one Kekulé pattern, there exists a one-to-one correspondence between Kekulé structures and sextet patterns. Two proofs of the conjecture were given by He and He [38], and by Ohkami [39]. But the proofs are not complete and have some errors. Zhang and Guo [40, 41] gave an explicit definition of super sextets of generalized polyhexes and a new proof of the Ohkami-Hosoya conjecture.

Zhang and Chen [42] showed that each hexagon of a benzenoid system $B$ forms a sextet pattern, i.e., $r(B,1)$ is equal to the number of hexagons of $B$, if and only if $B$ is normal. The similar results hold for normal coronoid systems [43] and plane elementary bipartite graphs [44].

The sextet polynomial can be formally differentiated with respect to $x$ as $B'_G(x) = \frac{d}{dx} B_G(x)$, where the derivative can be expressed as the sum of sextet polynomials of some subgraphs of $G$.

**Theorem 2.1** [45] Let $G$ be a benzenoid system. Then

$$B'_G(x) = \sum_{h} B_{G-h}(x),$$ \hfill (3)

where the summation goes over all hexagons $h$ of $G$ and $G-h$ denotes the subgraph obtained from $G$ by deleting hexagon $h$ with incident edges and vertices.

Randić [46] pointed out that the quotient $\frac{B'_G(1)}{B_G(1)}$ can be regarded as a measure of the total aromaticity of a benzenoid $G$. In the following subsections we introduce some mathematical properties and chemical applications of sextet polynomials in various chemical graphs.

### 2.1. Benzenoid Chains and Cyclo-Polyphenacenes

How to compute the sextet polynomial for a benzenoid hydrocarbon? This is a problem of importance. It is well known that there are recurrence relations for computing almost all polynomials with applications in chemistry such as the characteristic polynomial, the independent polynomial and the matching polynomial of a graph. In [47], Gutman et al. gave a method of recurrence to compute the sextet polynomials for cata-condensed benzenoids. Gutman [48] found that for any benzenoid chain (unbranched cata-condensed benzenoid hydrocarbon) there is a bijection between its generalized Clar structures and $s$-matchings of the corresponding Gutman (caterpillar) tree.

Recall that in graph theory, a caterpillar tree is a tree in which the removal of all its pendant vertices (vertices of degree 1) results in a path. In other words, let $v_{i+1}v_i\cdots v_1$ be a path. If we join each of $v_i$ vertices to a vertex $v_i$ by an edge, $i=1,2,\cdots$, then a caterpillar tree is obtained.

For a benzenoid chain $B$, its corresponding Gutman tree is defined by the following construction: For the kink hexagons and the end hexagons of $B$, represent each of them by an edge. Then join these edges successively to obtain a path. If $B$ contains $n_1$ (linear annulated) hexagons between the hexagons corresponding to the successive edges $v_{i+1}v_i$ and $v_{i}v_{i+1}$, then we add $n_1$ new vertices and join each of them to $v_i$ by an edge (see Fig. 2 for an example). Gutman [48] and El-Basil [49] proved the following result.

![Fig. (2)](image)

**Theorem 2.2** [48, 49] Let $B$ be a benzenoid chain and $G$ its corresponding Gutman tree. Then $r(B,k) = m(G,k)$, where $r(B,k)$ is the number of sextet patterns of $B$ with $k$ hexagons and $m(G,k)$ is the number of $k$-matchings of $G$.

Considering the contribution of Clar structure to the resonance energy, we introduce a quasi-order on benzenoid hydrocarbon isomers to compare their resonance energy. For two benzenoid isomers $B_i$ and $B_j$, if $r(B_i,k) \geq r(B_j,k)$ for $k = 0,1,2,\ldots$, then we say $B_i$ is $s$-greater than $B_j$ and write $B_i > B_j$. If both $B_i > B_j$ and $B_j > B_i$ hold, then $B_i$ and $B_j$ are said to be $s$-equivalent. If neither $B_i > B_j$ nor $B_j > B_i$ holds, then $B_i$ and $B_j$ are incomparable. Clearly, two $s$-equivalent benzenoid chains may have the same sextet polynomial but need not be isomorphic. Based on the number of $k$-matchings of a graph, we can define a similar quasi-order ($m$-greater) for graphs with the same number of vertices. If for two graphs $G_i$ and $G_j$, $m(G_i,k) \geq m(G_j,k)$, where $m(G,k)$ is the number of $k$-matchings of $G$, then we say $G_i$ is $m$-greater than $G_j$ and write $G_i > G_j$ [50]. By Theorem 2.2 we have:

**Theorem 2.3** [51] Let $B_i$ and $B_j$ be two benzenoid chains with the same number of hexagons and $G_i$ and $G_j$ are the Gutman trees of $B_i$ and $B_j$, respectively. Then $B_i > B_j$ if and only if $G_i > G_j$.

Using Theorems 2.2 and 2.3 we can determine the extreme benzenoid chains with respect to their Clar aromatic
sextets. In [51], it is showed that the minimal benzenoid chain is a linear chain, and the last four minimal benzenoid chains are also determined. On the other hand, the maximal benzenoid chains are $k'$-cycle resonant benzenoid chains (the benzenoid chains whose hexagons are all kinks except the first and last one) and the second ones are the benzenoid chains whose hexagons are all kinks except the first and last two. Note that [51] contains an error in describing the second maximal benzenoid chains.

Similar to [51] concerning the ordering for benzenoid chains, the authors also consider the ordering of cyclo-polyphenacenes (including the special case of primitive coronoids). The cyclo-polyphenacenes can be obtained from a chain of hexagons by identifying one edge of an end hexagon with an edge of the other end hexagon so that each hexagon is adjacent to exactly two hexagons. We can compute the sextet polynomial of cyclo-polyphenacenes recurrently with the help of matching polynomial. For isomeric cyclo-polyphenacenes, we introduce a quasi-order to compare their resonance energy. For this aim, we need to define the generalized crown corresponding to a cyclo-polyphenacene. Recall that a generalized crown is a graph in which the removal of all its end vertices (vertices of degree 1) results in a cycle. In other words, let $v_i v_2 \cdots v_n v_1$ be a cycle. If we join each of $m_i$ new vertices by an edge to the vertices $v_j$, for $i=1,2,\ldots,n$, then a generalized crown is obtained. For a cyclo-polyphenacene $B$, we can define a corresponding generalized crown (as illustrated in Fig. 3) and prove the following theorem.

**Theorem 2.4** [52] Let $B$ be a cyclo-polyphenacene and $G$ be its corresponding generalized crown. Then the number of sextet patterns of $B$ having precisely $i$ hexagons is equal to the number of $i$-matchings of $G$ for any non-negative integer $i$.

Theorem 2.4 was used to solve "Hosoya's mystery" [53, 54] concerning the coincidence between the characteristic polynomial of a cycle and the polynomial of Kekulé structure count of a prime coronoid. For details, the reader is referred to [55].

With the help of matching polynomial, Theorem 2.4 can be also used to compute sextet polynomials of cyclo-polyphenacenes. Some examples were given in [52]. Similar to the case of benzenoid chains, the ordering of cyclo-polyphenacenes can also be set up. Then we have

**Theorem 2.5** [51] Let $B_1$ and $B_2$ be two cyclo-polyphenacenes with the same number of hexagons, with $G_1$ and $G_2$ their corresponding generalized crowns, respectively. Then $G_1 \succ G_2$ (strictly) if and only if $B_1 \succ B_2$ (strictly).

Theorem 2.4 reduces the ordering problem of cyclo-polyphenacenes (with fixed number of Clar structures) to the ordering problem of the number of $i$-matchings of general crowns. Using Theorems 2.4 and 2.5, and some old results in [50], the authors of [51] determined the minimal, second minimal to seventh minimal cyclo-polyphenacenes with respect to the number of Clar's sextets. They also determined the maximal and second maximal family of cyclo-polyphenacenes with respect to their number of Clar structures. For details, the reader is referred to [51].

2.2. Resonant Patterns and Kekulé Structures - Alternant Case

The one-to-one correspondence between the sextet patterns and Kekulé structures was first revealed for thin benzenoids by Hosoya and Yamaguchi as follows.

**Theorem 2.6** [20] For a catacondensed benzenoid system $H$, $B_H(1) = K(H)$.

For the coronene $G$ (see Fig. 4), its sextet polynomial $B_G(x) = 1 + 7x + 9x^2 + 2x^3$. So $B_G(1) = 19 < K(G) = 20$. In fact the coronene is the critical forbidden subgraph for the above relation (2). This can be expressed in the following theorem obtained by Zhang and Chen [56], which was reproven later in a novel approach [57]. A subgraph $H$ of a graph $G$ is called nice if $G - V(H)$ either has a perfect matching or is empty.

**Theorem 2.7** [56] For a hexagonal system $H$ with perfect matchings, $B_H(1) \leq K(H)$, and equality holds if and only if $H$ contains no coronene as its nice subgraph.

By introducing super rings in sextet patterns of a benzenoid system, a general one-to-one correspondence between sextet patterns and Kekulé patterns can be established (see [40, 41]). For example, the exterior boundary of coronene as a super ring is added to the central hexagon to produce a new sextet pattern.

For the general alternant case -- plane bipartite graphs $G$ with perfect matchings, Gutman [58] and John [59]...
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independently defined resonant polynomials and cell polynomials to be count polynomials of resonant patterns. They extend sextet polynomials of benzenoid systems, by replacing hexagons of a sextet pattern with even inner faces. Let \( r(G) \) denote the number of resonant patterns of \( G \). John et al. [60] obtained Theorem 2.8; and a refined result -- Theorem 2.9 was obtained in [61, 62].

**Theorem 2.8** [60] For a plane bipartite graph \( G \), \( r(G) \leq K(G) \).

**Theorem 2.9** [62, Theorem 3.2.1] Let \( G \) be a 2-connected plane bipartite graph with perfect matchings. Then \( r(G) \leq K(G) \), and equality holds if and only if there do not exist disjoint cycles \( R \) and \( C \) such that (a) \( R \) is a facial boundary lying in the interior of \( C \) and (b) \( C \cup R \) is a nice subgraph of \( G \).

### 2.3. Resonant Patterns and Kekulé Structures - Non-Alternant Case

From the above subsection, we see that the correspondence between resonant patterns and Kekulé patterns relies strongly on the existence of the root perfect matching of a plane bipartite graph [63, 64]. This is not suitable for the non-alternant case (non-bipartite plane graphs).

By applying a novel approach, mathematical induction and the principle of inclusion and exclusion in combinatorics, Zhang and He [65] showed that for any plane graphs, the number of perfect matchings is not less than the number of resonant patterns. This generalizes the corresponding results in benzenoid systems and plane bipartite graphs. Applications to fullerenes (planar cubic graphs with only pentagonal and hexagonal faces) were also discussed.

For example, the resonant patterns of corannulene (Fig. 5) are as follows:

\[ \mathcal{O}, \{C_1\}, \{C_2\}, \{C_3\}, \{C_4\}, \{C_5\}, \{C_6\}, \{C_7\}, \{C_8\}, \{C_9\}, \{C_{10}\}, \{C_{11}\}, \{C_{12}\}. \]

Hence

\[ B_{\text{corannulene}}(x) = 1 + 5x + 5x^2. \]

It is computed [66] that \( K(\text{corannulene}) = 11 \). That is, \( r(\text{corannulene}) = K(\text{corannulene}) = 11 \).

Fig. (5). Corannulene.

For the well-known fullerene--icosahedron \( C_{60} \) (Fig. 6 (left)), El-Basil [67] first found that its Clar number equals 8. Since it has the Fries structure so that each hexagon is alternating, any set of disjoint hexagons always forms a sextet pattern. Based upon this, Shiu et al. [68] computed the sextet polynomial of \( C_{60} \) as

\[ B_{C_{60}}(x) = 5x^5 + 320x^5 + 1240x^5 + 1912x^5 + 1510x^5 + 660x^5 + 160x^5 + 20x + 1. \]

Ye et al. [69] showed that every hexagon of a fullerene is resonant, determined all the other eight 3-resonant fullerenes (i.e. every set of at most three disjoint hexagons forms a sextet pattern) and proved that any independent hexagons of a 3-resonant fullerene graph form a sextet pattern. So the sextet polynomials of the other eight 3-resonant fullerene graphs are computed by counting sets of disjoint hexagonal faces (see [69] for details).

For such 3-resonant fullerene graphs \( F \), we can confirm that the \( B_F(1) < K(F) \). In general, Zhang and He showed the following result.

**Theorem 2.10** [65] For any plane graph \( G \), \( r(G) \leq K(G) \).

For all fullerene graphs, Sereni and Stehlík [70] proved the following result, which was conjectured earlier by Zhang and He in [65].

**Theorem 2.11** [70] For every fullerene graph \( F \), \( B_F(1) < K(F) \).

### 2.4. Stability Indicators

For benzenoid hydrocarbons, both the Clar number and Kekulé count can measure their stabilities. However, Austin et al. [71] constructed 20 distinct fullerene isomers of \( C_{60} \) whose Kekulé counts surpass the Kekulé count (12500) of icosahedral \( C_{60} \). So, the maximality of Kekulé counts of fullerene isomers may not correspond to the highest stability. Zhang et al. [72] turned to investigating a significant role of the Clar numbers of fullerenes in their stabilities. Zhang and Ye [73] obtained the sharp upper bound for the Clar number of fullerenes as follows.

**Theorem 2.12** [73] Let \( F_n \) be a fullerene with \( n \) vertices. Then \( c(F_n) \leq \left\lfloor \frac{n-12}{6} \right\rfloor \).

They also showed that there are infinite many fullerene graphs whose Clar number can achieve this upper bound.
including $C_{60}$ and $C_{70}$, and zigzag and armchair carbon nanotubes as well; Theorem 2.12 shows that none of fullerene graphs are "all-benzenoids" [74, 75]. Combining theorem 2.12 and some construction of Clar formula of fullerenes, they found that the experimentally characterized $C_{60}$, $C_{70}$, $C_{76}$, $C_{84}$; $22D_2$ (IV) and $C_{84}$; $23D_{2d}$ (II) attain the maximum Clar number among their fullerene isomers.

Ye and Zhang [76] have rigorously proved that exactly 18 fullerenes with 60 atoms (including the icosahedral $C_{60}$) achieve the maximum Clar number 8. A comparison shows that none of these 18 fullerenes belongs to the collection of the 20 fullerene isomers with Kekulé counts surpassing 12500 in [71]. That is, the Clar numbers of these 20 fullerene isomers are all less than 8. Hence, a combination of Clar number and Kekulé count as a stability predictor distinguishes uniquely the icosahedral $C_{60}$ from its all 1812 fullerene isomers.

Furthermore, W. Sun and F. Wang in Lanzhou University have computed the sextet polynomials of all fullerene isomers of $C_{60}$ and $C_{70}$. It is known that $C_{60}$ and $C_{70}$ have 1812 and 8149 fullerene isomers, respectively [77]. From their computational results we can see that $C_{60}$ (60:1812) is a unique fullerene isomer of $C_{60}$ with the maximum number of sextet patterns 5828, and the isomer 60:1809 has the second maximum number of sextet patterns 3970. So $C_{60}$ (60:1812) has a much larger sextet pattern count than the isomer 60:1809. Similarly, the experimentally characterized 70:8149 is a unique fullerene isomer of $C_{70}$ with the maximum sextet pattern count 18714, and 70:7106 has the second maximum sextet pattern count 17463. Such partial computational results are listed in Table 1.

How to compute Clar numbers of fullerenes is an interesting problem in both mathematics and theoretical chemistry. Up to this date, an effective general way has not been found for this problem. It is worthwhile to seek appropriate combinations of Clar numbers with other invariants as stability predictors of fullerenes.

3. CLAR COVERING POLYNOMIALS

The definition for a sextet pattern of a generalized benzenoid system $B$ was slightly modified in [22]. We add a Kekulé structure of $H-Q$ to a sextet pattern $Q$ to get a vertex-cover of $B$, and we call such a vertex-cover a Clar cover of a (generalized) benzenoid system $B$. In other words, a spanning subgraph $C$ of $B$ is said to be a Clar cover of $B$ if each of its components is either a hexagon or an edge. Then the Clar covering polynomial of $B$ is defined as:

$$\zeta(x) = \zeta(B, x) = \sum_{i=0}^{z(B,i)x^i},$$  \hspace{3cm} (4)

where $z(B,i)$ denotes the number of Clar covers of $B$ having precisely $i$ hexagons (refer to [22, 78-81]).

This polynomial was used to conveniently compare topological indices of some types of benzenoid isomers [80]. It is also called "Zhang-Zhang polynomial" in a series of papers due to Gutman $et al.$ [82-88].

Table 1. The First, Second and Third Maximum $B_f(1)$ Fullerene Isomers of $C_{60}$ and $C_{70}$

<table>
<thead>
<tr>
<th>Isomers $F$</th>
<th>Sextet polynomial $B_f(x)$</th>
<th>$B_f(1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60:1804</td>
<td>$x8 + 48x7 + 377x6 + 934x5 + 1061x4 + 588x3 + 157x2 + 20x + 1$</td>
<td>3187</td>
</tr>
<tr>
<td>60:1809</td>
<td>$x8 + 98x7 + 594x6 + 1250x5 + 1232x4 + 616x3 + 158x2 + 20x + 1$</td>
<td>3970</td>
</tr>
<tr>
<td>60:1812</td>
<td>$5x8 + 320x7 + 1240x6 + 1912x5 + 1510x4 + 660x3 + 160x2 + 20x + 1$</td>
<td>5828</td>
</tr>
<tr>
<td>70:7716</td>
<td>$3x9 + 303x8 + 1871x7 + 4478x6 + 5435x5 + 3613x4 + 1307x3 + 253x2 + 25x + 1$</td>
<td>17289</td>
</tr>
<tr>
<td>70:7106</td>
<td>$20x9 + 343x8 + 1902x7 + 4500x6 + 5474x5 + 3634x4 + 1311x3 + 253x2 + 25x + 1$</td>
<td>17463</td>
</tr>
<tr>
<td>70:8149</td>
<td>$25x9 + 375x8 + 2065x7 + 4715x6 + 5958x5 + 3940x4 + 1355x3 + 255x2 + 25x + 1$</td>
<td>18714</td>
</tr>
</tbody>
</table>
3.1. Basic Properties

We first introduce some basic properties of Clar covering polynomial of a generalized benzenoid system $B$.

**Theorem 3.1** [22] Let $B$ be a benzenoid system. Then we have the following properties for the Clar covering polynomial of $B$:

1. $\zeta(B,0) = K(B)$,
2. the degree of the polynomial $\zeta(B,x)$ is $C(B)$, the Clar number of $B$,
3. the coefficient of the highest degree term, $z(B,C(B))$ equals the number of Clar formulas of $B$,
4. $z(B,1) = h(B)$, the first Herndon number.

The Clar covering polynomial closely relates to the sextet polynomial via a transformation of polynomials.

**Fig. (7).** Modes of proper sextet and improper sextet.

Let $B$ be a benzenoid system with a perfect matching (Kekulé structure or 1-factor) $M$. A conjugated (or alternating) hexagon of $B$ is called a proper sextet if the extreme right vertical edge belongs to $M$; an improper sextet otherwise, as illustrated in Fig. (7). Use $a(i)$ to denote the number of perfect matchings of $B$ which contains precisely $i$ proper sextets for $0 \leq i \leq C(B)$. Then we have

$$\sum_{i=0}^{C(B)} a(B,i) = K(B), \quad a(B,i) > 0 \text{ for all } 0 \leq i \leq C(B), \text{ and } a(B,0) = 1.$$ Further, these $a(B,i)$ become the coefficients of a new polynomial expression for the Clar covering polynomial in variable $(x+1)$.

**Theorem 3.2** [79] Let $B$ be a benzenoid system with a perfect matching. Then $\zeta(B,x)$ can be expressed in the following form:

$$\zeta(B,x) = \sum_{i=0}^{C(B)} z(B,i)x^i = \sum_{i=0}^{C(B)} a(B,i)(x+1)^i.$$ 

**Fig. (8).** Modes of hexagons $s_1$ and $s_2$ in a benzenoid system for some reduced procedures.

Via such a transformation, we can establish a relation with the sextet polynomial as follows.

**Theorem 3.3** [79] Let $B$ be a benzenoid system with a perfect matching. For all $0 \leq i \leq C(B)$, $a(B,i) \geq r(B,i)$ and all the equalities hold if and only if $B$ has no coronene $C$ (see Fig. 4) as its nice subgraph.

**Corollary 3.4** [79] Let $B$ be a benzenoid system with a perfect matching. Then

$$\sum_{i=0}^{C(B)} a(B,i)x^i$$ is the sextet polynomial of $B$ if and only if $B$ has no coronene as its nice subgraph.

For other interesting properties, the reader is referred to [79].

In general, the polynomial $\sum_{i=0}^{C(B)} a(B,i)x^i$ can be viewed as the revised sextet polynomial of $B$ which counts sextet patterns with super rings.

3.2. Computation Approach

Compared with the sextet polynomial, the Clar covering polynomial of a benzenoid system has one advantage in computation: it has general recurrence relations. This enables one to compute some significant topological indices of benzenoid systems as mentioned in Theorem 3.1 by some recurrence procedures.

**Theorem 3.6** [22] Let $B$ be a generalized benzenoid system. Let $s_1$ and $s_2$ be two hexagons of $B$ having a common edge $e = xy$ (see Fig. 8 (left)). Then

$$\zeta(B,x) = \prod_{i=1}^{k} \zeta(B_i,x).$$

**Theorem 3.7** [22] Let $B$ be a generalized benzenoid system. Let $xy$ be an edge of a hexagon $s$ of $B$ which lies on the periphery of $B$ (see Fig. 8 (middle)). Then

$$\zeta(B) = w\zeta(B - s) + \zeta(B - xy) + \zeta(B - x - y),$$

where $B - s$ denotes the subgraph obtained from $B$ by deleting all vertices of $s$ together with incident edges.

**Theorem 3.8** [22] Let $B$ be a generalized benzenoid system. Let $xy$ be an edge of a hexagon $s$ of $B$ which lies on the periphery of $B$ (see Fig. 8 (middle)). Then

$$\zeta(B) = w\zeta(B - s) + \zeta(B - x - y) + \zeta(B - xy).$$
Theorem 3.8 [22] Let \( X_1 \) and \( X_2 \) be two Kekuléan benzenoid systems which contain hexagons \( s_1 \) and \( s_2 \), respectively, as indicated in Fig. 8 (right) (or one of them be \( K_2 \)). Let \( X_1 : X_2 \) be a benzenoid system obtained by gluing \( X_1 \) and \( X_2 \) only along an edge \( xy \) of \( s_1 \) and \( s_2 \). Then the Clar covering polynomial of \( X_1 : X_2 \) is

\[
\zeta(X_1 : X_2) = \zeta(X_1)\zeta(X_2) + \zeta(X_1)\zeta(X_2) - \zeta(X_1)\zeta(X_2)
\]

where \( X_i = X_i - x - y \) for \( i = 1 \) or \( 2 \).

Corollary 3.4 and Theorem 3.8 can be used to derive a recurrence relation for sextet polynomial of cata-condensed benzenoid systems as follows.

Corollary 3.9 [62, Corollary 5.2.11] Let \( X_2 \) be a catacondensed benzenoid system. Then

\[
B_{m,x_2}(x) = mxB_{x_2}(x) + B_{x_2}(x),
\]

where \( L_m \) denotes the linear benzenoid chain of \( m \) hexagons.

Clar covering polynomials have been computed for of some types of benzenoid and coronoid systems, such as benzenoid chains [22], parallelogram [62], multiple linear hexagonal chains [88], cyclo-polyphenacenes [89], and so on [90, 91].

3.3. Applications to Resonance Energy

Each of the quantities mentioned in points (1)-(4) of Theorem 3.1 was shown to relate to some kinds of the resonance energy. It is reasonable to expect that the Clar covering polynomial will also be somehow connected with the resonance energy.

Zhang et al. [78] established an approximation model of DRE with Clar covering polynomial of benzenoid hydrocarbons:

\[
RE = \alpha \sum_{i=0}^{C(B)} z(B,i)\varepsilon_i + \beta.
\]

For condensed aromatic hydrocarbons with Clar number \( \leq 4 \), the parameters \( \alpha \) and \( \beta \) and weights \( \varepsilon_i (1 \leq i \leq 4) \) in the above Eq. (5), we determined \( \varepsilon_1 = 1 \), \( \varepsilon_2 = 0.18, \varepsilon_3 = 0.14 \) and \( \varepsilon_4 = 27.33 \), \( \alpha = 1.940 \) and \( \beta = 0.0113 \). The correlation coefficient is 0.9971 and the mean error is 0.014.

Gutman et al. [82] found good linear correlations between TRE and \( \ln \zeta(x) \) for fixed values of \( x \) lying in the interval \([0, 2]\) as,

\[
RE = a\ln\zeta(x) + b,
\]

where \( a \) and \( b \) are constants. The special case of the above approximation (6) for \( x = 0 \) is the usual approximation of resonance energy via Kekulé count:

\[
RE = a_0 \ln K.
\]

In fact, the correlation coefficient \( R \) attains a maximum, and the average relative error attains a minimum, for some \( x \) that considerably differs from zero. The unexpected finding is that the optimal value of \( x \) is always remarkably close to unity. There is no statistically significant difference between the accuracy of the approximation for optimal \( x \) and for \( x = 1 \). This leads to the conclusion that \( \zeta(1) \) is a quantity of some importance in the Clar theory of benzenoid molecules.

Further studies of Gutman et al. [83, 86] revealed certain hitherto concealed properties of resonance energies of benzenoid molecules, and their dependence on Kekulé- and Clar-structure-based parameters.

3.4. An Extension to Fullerenes

Similarly to the sextet polynomial, the Clar covering polynomial can be naturally extended to fullerene graphs. We also checked its role in the stability of fullerenes.

W. Sun and F. Wang also computed the Clar covering polynomials of all fullerene isomers of \( C_{60} \) and \( C_{70} \). Their computation results show that \( C_{60} \) (60:1812) achieves the maximum \( \zeta(1) = 250967 \), and the isomer 60:1809 has the second maximum \( \zeta(1) = 158829 \). These are consistent with their sextet pattern counts. For \( C_{70} \), fullerene isomers 70:8149, 70:7716 and 70:7106 have the first, second and third maximum \( \zeta(1) \), which are 1305863, 1289527 and

<table>
<thead>
<tr>
<th>Isomers</th>
<th>Clar covering polynomial ( \zeta(x) )</th>
<th>( \zeta(1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>60:288</td>
<td>( 2x^6 + 82x^6 + 1082x^6 + 7168x^6 + 24956x^6 + 46144x^6 + 42862x^6 + 15745 )</td>
<td>138041</td>
</tr>
<tr>
<td>60:1809</td>
<td>( x^8 + 106x^6 + 696x^4 + 20972x^4 + 38968x^4 + 46156x^4 + 33092x^4 + 11230 )</td>
<td>158829</td>
</tr>
<tr>
<td>60:1812</td>
<td>( 5x^6 + 360x^4 + 16352x^2 + 42000x^2 + 66900x + 67650x^2 + 41580x + 12500 )</td>
<td>250967</td>
</tr>
<tr>
<td>70:7106</td>
<td>( 20x^6 + 523x^6 + 5474x^6 + 30727x^6 + 104690x^6 + 230671x^6 + 337496x^6 + 324001x^6 + 188633x^6 + 51068 )</td>
<td>1273303</td>
</tr>
<tr>
<td>70:7716</td>
<td>( 3x^6 + 335x^6 + 4569x^6 + 28288x^6 + 101911x^6 + 229711x^6 + 342961x^6 + 333691x^6 + 195714x^6 + 53064 )</td>
<td>1289527</td>
</tr>
<tr>
<td>70:8149</td>
<td>( 25x^6 + 600x^6 + 5965x^6 + 31970x^6 + 106065x^6 + 233215x^6 + 345490x^6 + 335385x^6 + 194980x^6 + 52168 )</td>
<td>1305863</td>
</tr>
</tbody>
</table>
1273303, respectively (see Table 2). We can see that the fullerene isomers 60:1812 and 70:8149 retain the maximum values in both sextet pattern count and Clar cover count among their fullerene isomers. However, the isomers 70:7716 and 70:7106 have the near among their fullerene isomers. However, the isomers values in both sextet pattern count and Clar cover count fullerene isomers 60:1812 and 70:8149 retain the maximum which corrects the error in [67].

We now discuss an index $cc(B)$ related to Clar polynomial of a benzenoid system $B$. Let $cc(B)$ denote the number of Clar covers without alternating hexagons. Then $\xi(1, B) \leq cc(B)$.

The sextet rotation, transforming all proper sextets of a Kekulé structure of a benzenoid system $B$ into improper sextets, results in a directed tree on the set of Kekulé structures of $B$ with one root, denoted by $R(B)$. Let $nl(B)$ denote the number of non-leaves in $R(B)$.

**Theorem 4.3** [57] Let $B$ be a benzenoid system with a perfect matching. Then $cc(B) = nl(B)$.

**Theorem 4.4** [57] If a benzenoid system $B$ has a perfect matching and contains no coronene as its nice subgraph, then $\xi(B,1) = cc(B)$.

If all Clar covers without alternating hexagons in a benzenoid system are identical to their Clar structures, i.e. $\xi(B,1) = cc(B)$, we can obtain the Clar polynomial by enumerating Clar covers without alternating hexagons. In fact, the converse of Theorem 4.4 does not hold. For example, $\xi(\text{coronene}, 1) = cc(\text{coronene})$. So we can easily obtain the Clar polynomial of coronene as $\xi(\text{coronene}, x) = 2x^3 + 3x^2 + 2x$, which, of course, agrees with the earlier result of Ref. [94]. In fact many benzenoid systems $B$ that contain coronene as its nice subgraph with $\xi(B,1) = cc(B)$, have been constructed. For more details, the reader is referred to [57].

5. LINEARLY INDEPENDENT AND MINIMAL CONJUGATED CIRCUIT POLYNOMIALS OF BENZENOID HYDROCARBONS

5.1. Introduction

The conjugated circuit model is a resonance-theoretic model, which was introduced by Randić in 1976 for the study of aromaticity and conjugation in polycyclic conjugated systems. Enumeration of conjugated circuits led to expressions for the resonance energy of polycyclic conjugated hydrocarbons [96]. In recent years, various investigations on the conjugated-circuit model have been made [96-104], such as quantum-mechanical and computational aspects of the conjugated-circuit model, the selection of the optimum parameters of the conjugated-circuit model, and comparison between the conjugated-circuit model and several other models for computing the resonance energies of benzenoid hydrocarbons.

In [105], Guo and Randić gave a strict definition of linearly independent and minimal conjugated circuits and $LM$ -conjugated circuit polynomials as follows.

**Definition 5.1** [105]. A set $S$ of linearly independent and minimal conjugated circuits of a Kekulé structure $K$, of a benzenoid hydrocarbon $B$ consists of a maximum number of linearly independent circuits of $B$ in which every circuit
is a conjugated circuit of \( K_n \), and has the minimum length. Denote a circuit of size \( 4n+2 \) in \( S \) by \( R_s \), and the summation expression of \( S \) by
\[
R(K_i) = \sum_{R_i \in S} R_i = \sum_{i=1,2,\ldots} r_i(K_i) R_i, \quad \text{where} \quad r_i(K_i) = \text{the number of the circuits of size } 4n+2 \text{ in } S.
\]
The summation expression of all sets of \( LM \)-conjugated circuits of all Kekulé structures of \( B \) is denoted by
\[
R(B) = R = \sum_{i} R(K_i) = \sum_{i=1,2,\ldots} r_i R_i, \quad \text{where} \quad r_i = \sum_i r_i(K_i).
\]

The summation expression \( R(B) \) of \( LM \)-conjugated circuits of \( B \) is called \( LM \)-C-expressions or the \( LM \)-conjugated circuit polynomial (simply the LMCC-polynomial) of \( B \), which is a polynomial of degree one with multi-variants and may also be denoted by a sequence of numbers \( (r_1, r_2, r_3, \ldots, r_n, \ldots) \), called the LMCC-code of \( B \).

The \( LM \)-conjugated circuit polynomials of benzenoid hydrocarbons play a central role in the conjugated-circuit model, because the resonance energy \( RE(B) \) of a benzenoid hydrocarbon \( B \) is simply equal to \( R(B)/K(B) \). Here \( K(B) \) is the number of Kekulé structures of \( B \). The \( LM \)-conjugated circuit polynomials had been also applied to calculate generalized bond orders of polycyclic conjugated hydrocarbons [106]. Thus the calculation of the \( LM \)-conjugated circuit polynomials of benzenoid hydrocarbons becomes a fundamental problem on the conjugated-circuit model.

However, for a general case, the enumeration of \( LM \)-conjugated circuits of benzenoid hydrocarbons requires to construct all Kekulé structures and then to find a set of \( LM \)-conjugated circuits for every Kekulé structure. When the size of a molecule increases, the number of Kekulé structures increases fast, and hence enumerating \( LM \)-conjugated circuits by this method becomes tedious.

Guo and Randić [105] investigated the properties and the construction of minimal conjugated circuits of benzenoid hydrocarbons, and gave the necessary and sufficient condition for a set of conjugated circuits of a benzenoid hydrocarbon to be linearly independent and minimal. Furthermore, they established some recursive relations for calculating the \( LM \)-conjugated circuit polynomials of several classes of benzenoid hydrocarbons, so that the \( LMCC \)-polynomials of the several classes of benzenoid hydrocarbons can be directly obtained from the \( LMCC \)-polynomials and the Kekulé structure counts of their subgraphs. Guo and Randić [107] extended the recursive formulae for calculating \( LMCC \)-polynomials for both catacondensed benzenoid hydrocarbons and some families of structurally related pericondensed benzenoid hydrocarbons. There are still some classes of benzenoid hydrocarbons whose \( LMCC \)-polynomials cannot be obtained by the above recursive method. For general cases, Guo, Randić, and Klein [108] further gave an analytical expression for the count of \( LM \)-conjugated circuits of \( B \) which is based on the counts of Kekulé structures of selected subgraphs of \( B \).

By using the method, the \( LMCC \)-polynomials of any benzenoid hydrocarbon can be obtained.

A benzenoid hydrocarbon \( BH \) is a 2-connected plane graph whose every interior face is bounded by a regular hexagon. A connected subgraph of a \( BH \) is said to be a \( BH \)-fragment \( (BHF) \). A 2-connected \( BHF \) is said to be a generalized \( BH \) \( (GBH) \). Let \( B \) be a \( BH \) or \( GBH \). A bond of \( B \) is said to be a fixed bond if it appears always as a double bond in every Kekulé structure, or always as a single bond. If \( B \) contains no fixed bond, then \( B \) is said to be normal; otherwise \( B \) is said to be essentially disconnected.

A normal component \( B_i \) of \( B \) is a maximal subgraph of \( B \) with no fixed bond (possibly, \( B_i = B \), that is, \( B \) is normal).

All normal components of \( B \) are denoted by \( B_i \). The boundary of an interior face of a \( BH \) or \( BH \)-fragment \( B \) is called a ring of \( B \).

**Definition 5.2** [105]. Let \( s \) be a ring (i.e. a hexagon) of a benzenoid hydrocarbon \( B \), and \( K_s \) a Kekulé structure of \( B \). A conjugated circuit \( C \) of \( K_s \) \( (\text{simply, a } K_s \text{-conjugated circuit } C \) \) is said to be a minimal conjugated circuit of the ring \( s \) if the interior of \( C \) contains the interior of \( s \) and \( C \) has the minimum length. We also say that a \( K_s \)-conjugated circuit \( C \) of \( B \) is minimal if there is a ring \( s \) in \( B \) such that \( C \) is a minimal conjugated circuit of \( s \) (see Fig. 9).

**Theorem 5.1** [105]. Let \( K_s \) be a Kekulé structure of a benzenoid hydrocarbon \( B \), and let \( C \) be a minimal conjugated circuit of a ring \( s \) of \( B \). Then \( B[C] \) is one of

![Fig. 9](image_url)
the BHs shown in Fig. (9), and the $K_i$ double bonds in $B[C]$ are uniquely determined.

**Theorem 5.2** [105]. Let $K_i$ be a Kekulé structure of a benzenoid hydrocarbon $B$. A set $S = \{C_1, C_2, C_3, \ldots, C_j\}$ of $K_i$-conjugated circuits of $B$ is a set of $LM$-conjugated circuits of $K_i$ if and only if for any ring $s_j$ in all normal components $B'$ of $B$ there is exactly one circuit $C$ in $S$ such that $C_j$ is a minimal $K_i$-conjugated circuit of $s_j$.

### 5.2. Recursive Method for Computing $LM$-Conjugated Circuit Polynomials of Benzenoid Hydrocarbons

Theorem 5.2 establishes the theoretical basis of the partition of the $LMC$-expression of $B$ into the $LMC$-expressions of rings of $B$. The $LMC$-expression of a ring $s$ in $B$, denoted by $R_i(B)$, is determined by taking the summation expression of the minimal conjugated circuits of $s$, one for every Kekulé structure of $B$, and $R(B) = \sum R_i(B)$. $R_i(B)$ may also be denoted by a sequence of numbers (ring code) $(r_1(s), r_2(s), \ldots, r_j(s), \ldots)$, where $r_i(s)$ is the coefficient of the term $R_i(s)$ in $R_i(B)$.

Theorem 5.2 also enables us to establish some recursive relations for enumeration of $LMC$-conjugated circuits of $B$.

**Definition 5.3** [105]. For an edge $e = uv$ of a benzenoid hydrocarbon $B$, let $B_e (B_u)$ denote the labeled graph of $B$ for which the edge $e$ is labeled as double (single) bond, and $B_e (B_u)$ may be thought as the normal components of $B - e$. $B_e$ and $B_u$ may be regarded as the normal components of $B$ such that $e$ is in fact a fixed double (single) bond in $B_e$ ($B_u$). The subgraph of $B_e$ ($B_u$) induced by the hexagons in $B_e$ ($B_u$) which are not in $B_e$ ($B_u$) is denoted by $B_{e'}$ ($B_{u'}$). The contribution of all rings in $B_{e'}$ ($B_{u'}$) to $R(B_e)$ ($R(B_u)$) is denoted by $R'(B_e)$ ($R'(B_u)$), and the contribution of all rings in $B_{e'}$ ($B_{u'}$) to $R(B_u)$ ($R(B_u)$) is denoted by $R'(B_u)$ ($R'(B_u)$).

Clearly, $R(B_e)$ and $R(B_u)$ are just the $LMC$-expressions of all the Kekulé structures of $B$ containing and not containing the edge $e$, respectively. Thus $R(B) = R'(B_u) + R'(B_u) + R'(B_u) + R'(B_u)

The above expressions give some partitions of $LMC$-conjugated circuits of $B$, so that we can obtain $R(B)$ from its all parts. However, we need to further reduce them to $LMC$-expressions of subgraphs of $B$.

**Theorem 5.3** [105]. Let $B_1, B_2, \ldots, B_t$ be $t$ mutually disjoint $BH$ s, or $BH$-fragments, and $B = B_1 \cup B_2 \cup \ldots \cup B_t$. Then $R(B) = R(B_1) + R(B_2) + \ldots + R(B_t)$.

**Theorem 5.4** [105]. Let $B_1, B_2, \ldots, B_t$ be the normal components of an essentially disconnected $BH$ or a $BH$-fragment $B$. Then $R(B) = R(B') = \sum R_i(B_i)$.

**Theorem 5.5** [105]. Let $B$ be a $BH$ which contains no crown (see Fig. 10 (1)) as its subgraph. Then for any edge $e = uv$ of $B$, each of the $LM$-conjugated circuits of $B'$ ($B_u$) is also a minimal in $B_e$ ($B_u$).

**Theorem 5.6** [105]. Let $B$ be a normal $BH$, which contains no crown as its subgraph. Then, for any edge $e$ of $B$, $R(B_e) = R'(B_u) + R(B_u)$, $R(B_u) = R'(B_u) + R(B_u)$.

**Theorem 5.7** [105]. Let $e$ be an edge on the boundary of a benzenoid hydrocarbon $B$, and let $S_p(B_e)$ ($S_q(B_e)$) be...
the set of rings in \( B_e \) \((B'_e)\). Let \( C_s(B_e) \) \((C_s(B'_e))\) denote the set of minimal conjugated circuits of a ring \( s \) in \( B_e \) \((B'_e)\). Then for \( s \in S(B_e) \), \( R_s(B_e) = \sum_{C \in C_s(B_e)} K(B - C)R_{C_{(C_{2})}} \), for \( s \in S(B'_e) \), \( R_s(B'_e) = \sum_{C \in C_s(B'_e)} K(B - C)R_{C_{(C_{2})}} \), where \( |C| \) denotes the length of \( C \), \( K(B - C) \) is the number of Kekulé structures of \( B - C \).

**Definition 5.4** [105]. Let \( e \) be an edge on the boundary of a benzenoid hydrocarbon \( B \). If \( B \) and \( e \) satisfy one of the following conditions: (1) \( B \) contains no crown (see Fig. 10 (1)) as its subgraph; (2) \( B \) contains a local structure as shown in Fig. 10 (2), and \( e \) is the marked edge; (3) \( B \) contains a local structure as shown in Fig. 10 (3), and \( e \) is the marked edge; then \( e \) is said to be a recursive edge of \( B \).

**Theorem 5.8** [105]. Let \( B \) be a \( BH \) which contains a recursive edge \( e \) on the boundary of \( B \). Then

\[
R(B) = R(B') + R(B'_e) + R'(B_e) + R(B_e) + \frac{1.8}{2} \sum_{s \in S(B_e)} \sum_{C \in C_s(B_e)} K(B - C)R_{C_{(C_{2})}}
\]

2.3 \( cm + \frac{1.8}{2} \sum_{s \in S(B_e)} \sum_{C \in C_s(B'_e)} K(B - C)R_{C_{(C_{2})}} \).

**Definition 5.5** [105]. Let \( C \) be a minimal conjugated circuit of a ring \( s \) of a benzenoid hydrocarbon \( B \), and let \( s' \) be a hexagon of \( B \) for which \( s \) and the interior of \( s' \) is contained in the exterior of \( C \). If \( C' = C \setminus s' \) \((\text{the symmetry difference of edge sets of } C \text{ and } s') \) is also a minimal conjugated circuit of \( s \), then we say \( C' \) is obtained from \( C \) by an extension and \( s' \) is an extendible hexagon of \( C \). For a ring \( s \) in \( B'_e \), a minimal conjugated circuit \( C \) of \( s \) in \( B'_e \) is said to be minimum if \( C \) has the smallest length and \( B[C] \) contains a smallest number of hexagons.

**Theorem 5.9** [105]. Let \( e \) be a recursive edge of a benzenoid hydrocarbon \( B \), and let \( s \) be a ring in \( B'_e \). Let \( C \) be a minimal conjugated circuit of \( s \) in \( B_e \), which is not minimum. Then \( C \) can be obtained from another minimal conjugated circuit of \( s \) in \( B_e \) by an extension.

**Procedure 5.1** [105]. Let \( e \) be a recursive edge of a benzenoid hydrocarbon \( B \), and \( s \) a ring in \( B_e \). Let \( C' \) be a unique minimum conjugated circuit of \( s \) in \( B_e \).

1. Set \( S_0 = \{ C' \}, S_e = S_0 \).
2. For every minimal conjugated circuit \( C_i \) in \( S_i \), find all extendible hexagons of \( C_i \), extend \( C_i \) to new minimal conjugated circuits, and set them to \( S_{i+1} \).
3. If \( S_{i+1} = \emptyset \), then go to (4). Otherwise set \( i+1 \rightarrow i \) and go to (2).
4. Set \( C_i(B_e) = \bigcup_{j=1}^{i} S_j \), \( C_i(B'_e) = \bigcup_{j=1}^{i} S_j \).

Fig. (11). An example for application of procedure 1.
An example of application of Procedure 5.1 is shown in Fig. 11.

5.3. $LM\text{-Conjugated Circuit Polynomials in Catacondensed Benzenoid Hydrocarbons}$

In a general case, a catacondensed benzenoid hydrocarbon (cata-$BH$) $B$ has the construction shown in Fig. (12), where $B_1, B_2, \ldots, B_n$ are subgraphs of $B$, each of which is a cata-$BH$. Particularly, if $n_2 = n_3 = 0$, $B$ becomes a straight cata-$BH$.

**Theorem 5.10** [107]. Let $B = B_o(n)$ denote the straight cata-$BH$ with $n$ hexagons (see Fig. (13a)). Then $R(B) = 2\sum_{i=1}^{n}(n+1-i)R_i$.

**Theorem 5.11** [107]. Let $B$ be a cata-$BH$ shown in Fig. (12). Then

$$R(B) = R(B_j) + (n_j - 1)(K(B_j)R(B_j) + K(B_j)R(B_j)) + 2K(B_j)K(B_j)\sum_{i=1}^{n-j}(n-i)R_i +$$

$$+ \sum_{j=2}^{n}R_j + \sum_{i=1}^{n-j}R_i + \sum_{j=1}^{n-j}R_j + \sum_{i=1}^{n-j}R_i +$$

$$+ \sum_{j=1}^{n-j}R_j + \sum_{i=1}^{n-j}R_i + \sum_{j=1}^{n-j}R_j + \sum_{i=1}^{n-j}R_i +$$

$$+ \sum_{j=1}^{n-j}R_j + \sum_{i=1}^{n-j}R_i + \sum_{j=1}^{n-j}R_j + \sum_{i=1}^{n-j}R_i +$$

where, if $n_2 = 0$ ($n_3 = 0$), then $K(B_j) = 1$ for $j = 2, 4, 5$ ($j = 3, 6, 7$), $K(B_j) = 0$ for $j = 8, 9, 10, 11, 12, 13, 14, 15$, and

$$\sum_{i=1}^{n_j}R_i + \sum_{i=1}^{n_j}R_i + \sum_{i=1}^{n_j}R_i + \sum_{i=1}^{n_j}R_i +$$

**Corollary 5.1** [107]. Let $B = B_i(m_1, m_2, \ldots, m_i)$ denote an unbranched cata-$BH$ as shown in Fig. (14). Then

$$R(B) = m_1R(B_j) + R(B_j) + \sum_{i=1}^{n_j}[2K(B_j)(m_i - i) + K(B_j)]R_i + 2(K(B_j))$$

$$+ \sum_{i=1}^{n_j}R_i + \sum_{i=1}^{n_j}R_i + \sum_{i=1}^{n_j}R_i +$$

$$+ \sum_{i=1}^{n_j}R_i + \sum_{i=1}^{n_j}R_i +$$

where, if $m_2 = 0$ ($m_3 = 0$), then $K(B_j) = 1$ for $j = 2, 3$ ($j = 3, 4$) and $K(B_j) = 0$ for $j \geq 4$ ($j \geq 5$).

By Theorem 5.10 and Corollary 5.1, we can easily obtain the following calculation formulae for enumerating the $LM\text{-conjugated circuits of the cata-$BH$s in Fig. (13)}$.

**Corollary 5.2** [107]. Let $B_i(n), n \geq 2$, be the cata-$BH$ shown in Fig. (13b). Then

$$R(B_i(n)) = (6n - 2)R_i + 4(n - 1)R_i + \sum_{i=1}^{n}(4n - 3 - 4i)R_i + 3R_{i+1}.$$  

**Corollary 5.3** [107]. Let $B_i(n), n \geq 1$, be the cata-$BH$ shown in Fig. (13c). Then

$$R(B_i(n)) = 4(4n + 1)R_i + 8nR_i + 4(2n - 3 - 2i)R_i + 6R_{i+1} + 2R_{i+2}.$$  

**Corollary 5.4** [107]. Let $B_i(n), n \geq 2$, be the cata-$BH$ shown in Fig. (13d). Then

$$R(B_i(n)) = 2(8n - 3)R_i + 2(4n - 5)R_i +$$

$$+ \sum_{i=1}^{n}(8n - 5 - 8i)R_i + 3R_{i+1} + R_{i+2}.$$  

**Corollary 5.5** [107]. Let $B_i(n), n \geq 1$, be the cata-$BH$ shown in Fig. (13e). Then

$$R(B_i(n)) = 96nR_i + 8R_i + 8\sum_{i=1}^{n}(4n - 5 - 4i)R_i + 26R_{i+1} + 12R_{i+2} + 2R_{i+3}.$$  

**Corollary 5.6** [107]. Let $B_i(n), n \geq 3$, be the cata-$BH$ shown in Fig. (13f). Then

$$R(B_i(n)) = \sum_{i=1}^{n}R_i \left(2F_{i-1}R_i + 2F_{i-2}R_i + F_{i-3}R_i \right),$$  

where $F_i = F_{i-1} + F_{i-2}$ is Fibonacci’s number, $F_0 = F_1 = 1$ and $F_i = 0$ for $i \leq -1$.

Concerning more general cases, we give the following examples.

**Corollary 5.7** [107]. Let $B_i(m_1, m_2)$ be an unbranched cata-$BH$ (see Fig. 14). Then

$$R(B_i(m_1, m_2)) = \sum_{i=1}^{m_1}[2(m_1 + 1)(m_i - i) + 1]R_i + 2$$

$$+ \sum_{i=1}^{m_1}m_1(m_1 + 1 - i)R_i + 4cm + \sum_{i=1}^{m_1}m_iR_i +$$

$$+ \sum_{i=1}^{m_1}R_i - R_i + 2R_{m_1+1}.$$  

**Corollary 5.8** [107]. Let $B_i(m_1, m_2, m_3)$ be an unbranched cata-$BH$ (see Fig. 14). Then

**Fig. (12). The construction of a catacondensed benzenoid hydrocarbon.**
$R(B_n^{(m_1, m_2, m_3)})$

$= \sum_{i=1}^{m_1} \{2[m_2(m_3+1)+1](m_3-i) + (m_3+1)\} R_i$

$+ \sum_{i=1}^{m_2} [2m_2(m_1+1)(m_1-i) + m_1 + 2m_1 + 2] R_i + 2$

$\sum_{i=1}^{m_3} [(m_3+1-i)(m_2m_1+1) + m_1] R_i$

$+ (m_3+1) \sum_{i=2}^{m_1} \sum_{j=0}^{m_2} R_{i+j} + m_1 \sum_{i=2}^{m_2} \sum_{j=0}^{m_3} R_{i+j} +$

$\sum_{i=m_1+2}^{m_1+m_2} R_i + \sum_{i=m_1+m_2+1}^{m_1+m_2+m_3} R_i$

$+ m_1 \sum_{i=m_1+m_2+1}^{m_1+m_2+m_3} R_i -(m_1+m_3+1) R_i + (m_3+1)$

$R_{m_1} + 2R_{m_1+1} + 2m_1 R_{m_2+1} + R_{m_2+m_3+1}$. 

Fig. (13). Some families of benzenoid hydrocarbons.

Fig. (14). An unbranched catacondensed benzenoid hydrocarbon B.
We first give the recursive formulae for enumeration of but omit the operation processes.

**Corollary 5.9** [107]. Let \( B_j(n_1, n_2, n_3) \) denote the cata-\( \text{BH} \) shown in Fig. (15). Then

\[
\begin{align*}
R(B_j(n_1, n_2, n_3)) & = \sum_{i=1}^{n_1} [2(n_1 + 1)(n_i + 1)(n_i - i + 1)] R_i + \sum_{i=1}^{n_1} \left[ \sum_{j=0}^{n_1-1} \sum_{k=0}^{n_1-1} R_{i+j+k} \right] R_i \\
& + \sum_{i=2}^{n_1} \sum_{j=i}^{n_1-1} R_{i+j} + \frac{n_1}{2} \sum_{j=1}^{n_1-1} R_{i+j} + \frac{n_1}{2} \sum_{j=1}^{n_1-1} R_{n_1+j} \\
& + \sum_{i=1}^{n_1} \sum_{j=1}^{n_1} R_{n_1+j} - 2R_i + R_{n_1} + R_{n_1+1} + R_{n_1+2}.
\end{align*}
\]

### 5.4 \( LM \)-Conjugated Circuit Polynomials in Some Families of Structurally Related Pericondensed Benzenoid Hydrocarbons

To enumerate \( LM \)-conjugated circuits in some families of structurally related pericondensed benzenoid hydrocarbons, we need to use Theorem 5.8 and procedure 5.1, and often need to deal with several recursive relations of several families of structurally related subgraphs for a family of structurally related peri-\( \text{BH} \) s. We will give some results but omit the operation processes.

We first give the recursive formulae for enumeration of \( LM \)-conjugated circuits of the peri-\( \text{BH} \)s in Fig. (13).

**Corollary 5.10** [107]. Let \( B_j(n) \) be the \( \text{BH} \) shown in Fig. (13g). Then

\[
\begin{align*}
R(B_j(n)) & = 2 \sum_{i=1}^{n-1} [5n + 8 - 5i] R_i + (10n + 6) R_i + 4n + 1 \\
& + 6R_{n+1} + 4R_{n+2} + 2R_{n+3}.
\end{align*}
\]

**Corollary 5.11** [107]. Let \( B_j(n) \) be the \( \text{BH} \) shown in Fig. (13h). Then

\[
\begin{align*}
R(B_j(n)) & = 2 \sum_{i=1}^{n-1} R(B_j(i)) + 2[2 \sum_{i=1}^{n-2} (n - 1 - i) \\
& + 8 \sum_{i=1}^{n-2} K(B_j(i)) R_i + 2[3 \sum_{i=1}^{n-3} (n - 2 - i) \\
& + 8 \sum_{i=1}^{n-3} K(B_j(i)) R_i + 4 \sum_{i=2}^{n-3} (n - 3 - i) K(B_j(i)) R_i],
\end{align*}
\]

where

\[
\begin{align*}
R(B_j(0)) & = 2R_1, \quad R(B_j(-1)) = 2R_1, \\
K(B_j(n)) & = K(B_j(n-1)) + \sum_{j=1}^{n-2} K(B_j(2j+1)) \text{ for } n = 2p, \\
K(B_j(n)) & = K(B_j(n-1)) + \sum_{j=1}^{n-2} K(B_j(2j+1)) \text{ for } n = 2p+1, \\
K(B_j(0)) & = 4, K(B_j(-1)) = 2, K(B_j(-2)) = 1 \text{ and } K(B_j(0)) = 0 \text{ for } j \leq -3.
\end{align*}
\]
Corollary 5.13 [107]. Let $B_j(n)$ be the BH shown in Fig. (13j). Then

\[
R(B_j(n)) = R(B_j(n-1)) + 2R(B_j(n-2)) + \sum_{i=1}^{n-3} R(B_j(i))
+ 2\sum_{i=1}^{n-3} (n-1-i)K(B_j(i)) + 2K(B_j(n-2))R_i
+ 2[2\sum_{i=1}^{n-3} K(B_j(i)) + K(B_j(n-2))]R_1
+ \sum_{i=1}^{n-3} (n-1-i)K(B_j(i)) + 4K(B_j(n-3)) + 4K(B_j(n-4))R_i
+ \sum_{i=1}^{n-3} (n-1-i)K(B_j(i)) + 4K(B_j(n-4))R_1,
\]

where

\[
R(B_j(n)) = 0 \text{ for } n \leq 0,
\]

\[
K(B_j(n)) = K(B_j(n-2)) + \sum_{i=1}^{n-3} K(B_j(i)),
\]

\[
K(B_j(n)) = 1 \text{ for } n = 0, -1, \text{ and } K(B_j(n)) = 0 \text{ for } n \leq -2.
\]

Finally, for the two families of peri-BH s shown in Fig. (16), we give the recursive formulae for enumeration of their LM-conjugated circuit polynomials.

Corollary 5.14 [107]. Let $B_s(n)$ be the BH shown in Fig. (16(1)). Then

\[
R(B_s(n)) = 9R(B_s(n-1)) + 4\sum_{i=1}^{n-2} R(B_s(i))
+ 2\sum_{i=1}^{n-3} (n-1-i)K(B_s(i)) + 5K(B_s(n-1)) + n]R_i
+ 2\sum_{i=1}^{n-3} (8n-7-3i)K(B_s(i)) + 2K(B_s(n-1)) + 2n]R_2
+ 4\sum_{i=1}^{n-3} (n-2-i)K(B_s(i)) + K(B_s(n-1)) + n+2]R_3
+ 2\sum_{i=1}^{n-3} (2n-3-2i)K(B_s(i)) + 3K(B_s(n-2)) + n-1]R_4,
\]

where

\[
R(B_s(0)) = 0, \quad K(B_s(n)) = 5K(B_s(n-1)) + 4\sum_{i=1}^{n-2} K(B_s(i)) + 1,
\]

\[
K(B_s(0)) = 1 \text{ and } K(B_s(i)) = 0 \text{ for } i \leq -1.
\]

Corollary 5.15 [107]. Let $B_s[m,n]$ be the BH shown in Fig. (16(2)). Then

\[
R(B_s[m,n]) = R(B_s[m-1,n]) + R(B_s[m,n-1])
+ 2\sum_{i=1}^{m-1} \sum_{j=1}^{n-1} K(B_s[m-i,n-j])K(B_s[i-1,j-1])R_{s-i,j-1},
\]

where

\[
K(B_s[m,n]) = K(B_s[m-1,n]) + (B_s[m,n-1]),
\]

\[
K(B_s[m,0]) = K(B_s[0,n]).
\]

5.5. Analytical Expressions for the Count of LM-Conjugated Circuits of Benzenoid Hydrocarbons

Although the LMCC-polynomials of several classes of benzenoid hydrocarbons can be directly obtained from the LMCM-polynomials and the Kekulé structure counts of some subgraphs by the above recursive method [105, 108], there are still some classes of benzenoid hydrocarbons whose LMCC-expressions cannot be obtained by the recursive method, e.g., the benzenoid hydrocarbons shown in Fig. (17). So we need to investigate a new method to calculate such LMCC-expressions.

In ref. [108], Guo, Randić, and Klein investigated further properties of LM-conjugated circuits and different contributions of LM-conjugated circuits having different shapes to $R(B)$ and gave a new method for calculating the LMCC-polynomials of polycyclic benzenoid hydrocarbons, which is based on the counts of Kekulé structures of selected subgraphs of benzenoid hydrocarbons. By using the method, the LMCC-polynomials of any benzenoid hydrocarbon can be obtained.

Theorem 5.2 establishes the theoretical basis of the partition of the LMCC-polynomial of B into the LMCC-polynomials of rings of B. The LMCC-polynomial of a ring s of a benzenoid hydrocarbon B, denoted by $R_s(B)$, is the summation of all the minimal conjugated circuits of s, one for each Kekulé structure of B. Note that $R_s(B)$ is just the contribution of s to $R(B)$, and $R(B) = \sum_{s \in S} R_s(B)$ ($R_s(B) = 0$ for $s \not\in S$). And, $R_s(B)$ may also be denoted by a sequence of numbers (ring code) $(r_1(s), r_2(s), \ldots, r_n(s), \ldots)$, where $r_i(s)$ is the coefficient of the term $R_i$ in $R_s(B)$.

Hence, the count of LM-conjugated circuits of a benzenoid hydrocarbon B is reduced to calculations of $R_s(B)$ for every ring s of B. To calculate $R_s(B)$, we need

Fig. (16). Two families of pericondensed benzenoid hydrocarbons.
to investigate further properties of minimal conjugated circuits of benzenoid hydrocarbons.

For a Kekulé structure $K_i$ of a benzenoid hydrocarbon $B$, Theorem 5.1 gives all possible configurations of a minimal $K_i$-conjugated circuit $C$ of a ring $s$ of $B$ (see Fig. 9). We call a configuration of $C$ a minimal configuration ($M$-configuration) with respect to (w.r.t.) the ring $s$. Conversely, for a circuit in $B$ which has an $M$-configuration w.r.t. a ring $s$, we have the following:

**Lemma 5.1** [108]. Let $C$ be a conjugated circuit with an $M$-configuration w.r.t. a ring $s$ in a benzenoid hydrocarbon $B$. Then, for any Kekulé structure $K_i$ in $B - C$, there is exactly one Kekulé structure $K_i$ in $B$ for which $K_i \subset K_i$, and $C$ is a minimal $K_i$-conjugated circuit of $s$ in $B$.

By Lemma 5.1, we can give a new definition of a minimal conjugated circuit of a ring of $B$, which is independent of a Kekulé structure $K_i$ of $B$.

**Definition 5.6** [108]. A conjugated circuit $C$ of a benzenoid hydrocarbon $B$ is said to be minimal if $C$ has an $M$-configuration w.r.t. a ring $s$ in $B$. $C$ is also said to be a minimal conjugated circuit of $s$ in $B$.

**Corollary 5.16** [108]. Let $C$ be a circuit with an $M$-configuration w.r.t. a ring $s$ in a benzenoid hydrocarbon $B$. Then $C$ corresponds to exactly $K(B - C)$ (= $K(B - B[C]))$ Kekulé structures for each of which $C$ is a minimal conjugated circuit of $s$ in $B$.

Note that Corollary 5.16 cannot be used to calculate $R_i(B)$. In general cases, the coefficient $r_i(s)$ of the term $R_i$ in $R_i(B)$ is not equal to $\sum K(B - C_{4n+2})$, here $C_{4n+2}$ is a minimal conjugated circuit of $s$ with size $4n+2$, because for a Kekulé structure $K_i$ and a ring $s$ of $B$, a minimal $K_i$-conjugated circuit $C$ of $s$ may be not unique (see Fig. 18), but calculating $R_i(B)$ requires one to take exactly one minimal conjugated circuit of $s$ for each Kekulé structure. Therefore, we need to investigate the properties of non-unique minimal conjugated circuits of a ring in $B$.

![Fig. (17). Two families of pericondensed benzenoid hydrocarbons.](image)

![Fig. (18). $C_1$ and $C_2$ are two minimal $K_i$-conjugated circuits of a ring $s$.](image)
We call two minimal $K_i$-conjugated circuits of a ring $s$ in $B$ as a pair of minimal $K_i$-conjugated circuits of $s$. By Lemma 5.2, we can classify pairs of minimal conjugated circuits of a ring $s$ in $B$.

**Theorem 5.12** [108]. Let $C_1$ and $C_2$ be a pair of minimal $K_i$-conjugated circuits of a ring $s$ in a benzenoid hydrocarbon $B$ for a Kekulé structure $K_i$ of $B$. Then $C_1 \cup C_2$ belongs to one of the four types of pairs of minimal conjugated circuits as shown in Fig. (19).

Theorem 5.12 gives all possible configurations of a pair of minimal $K_i$-conjugated circuits $C_1$ and $C_2$ of a ring $s$ in $B$. We call these configurations PM-configurations w.r.t. the ring $s$, and $C_1$ and $C_2$ the mutually associated minimal conjugated circuits of $s$. Conversely, for a pair of mutually conjugated circuits $C_1$ and $C_2$ (i.e., $B-C_1 \cup C_2$ has Kekulé structures) with a PM-configuration w.r.t. a ring $s$, $C_1$ and $C_2$ may have different sizes and are called mutually associated conjugated circuits of $S$.

**Lemma 5.3** [108]. Let $C_1$ and $C_2$ be a pair of mutually associated conjugated circuits with the same size and with a PM-configuration w.r.t. a ring $s$ in a benzenoid hydrocarbon $B$. Then, for any Kekulé structure $K_i$ in $B-C_1 \cup C_2$, there is exactly one Kekulé structure $K_i$ in $B$ for which $K_i \subset K_i$ and both $C_1$ and $C_2$ are minimal $K_i$-conjugated circuits of $s$ in $B$.

By Lemma 5.3, we can also give a new definition of a pair of minimal conjugated circuits of a ring in $B$, which is independent of a Kekulé structure $K_i$ of $B$.

**Definition 5.7** [108]. Two mutually conjugated circuits $C_1$ and $C_2$ in a benzenoid hydrocarbon $B$ are said to be a pair of minimal conjugated circuits of a ring $s$ in $B$, if $C_1 \cup C_2$ has a PM-configuration w.r.t. the ring $s$, and $C_1$ and $C_2$ have the same size. We also say that $C_1$ and $C_2$ are mutually associated minimal conjugated circuits w.r.t. $s$.

Recall the construction of a minimal $K_i$-conjugated circuit $C$ of a ring $s$ in $B$ shown in Fig. (9). Let $B'[C]$ be the subgraph of $B[C]$ induced by the hexagons labeled by 0, 1, 2, ..., $a, b, c, ...$, and $C'$, the boundary of $B'[C]$. Clearly, $C'$ also has an $M$-configuration w.r.t. the ring $s$, and $|C'| = |C| = 4(a + b + c + 1) + 2 = 4n + 2$ ($C \rightarrow R_v$). We call $B'[C]$ the underlying configuration of $B[C]$ and say that $C'$ is the underlying circuit of $C$ and that $C'$ has an underlying $M$-configuration w.r.t. $s$. For a minimal $K_i$-conjugated circuit $C$ of a ring $s$ in $B$, there is a unique circuit $C_2 \neq C_1$ with an underlying $M$-configuration w.r.t.
For a circuit $C$ with an $M$-configuration w.r.t. a ring $s$ in $B$ and the underlying circuit $C'$ of $C$, there is a circuit $C^\prime$ with an $M$-configuration w.r.t. $s$ for which the underlying circuit of $C^\prime$ is just $C'$, the interior of $C$ is contained in the interior of $C'$, and $B(C')$ contains as many hexagons as possible. In the case in Fig. (21(1)), $C^\prime$ has the maximum $M$-configuration, called full $M$-configuration. In the case of Fig. (21(2)), $C'$ is said to have a truncated $M$-configuration. We call $C'$ the characteristic circuit of $C'$ and $C$. For a minimal $K_r$-conjugated circuit $C_1$ of a ring $s$ and the associated circuit $C_2$ of $C_1$ according to $K_r$, a characteristic circuit $C'_2$ of $C_2$ such that $C_1 \cup C'_2$ has a $PM$-configuration w.r.t. $s$ is also called the associated characteristic circuit of $C_1$. If a characteristic circuit $C'$ of $C$ has a truncated $M$-configuration, for the edges $f_1, f_2, \cdots, f_t$ on $C'$ which lie on the boundary $b(B)$ of $B$ and whose end vertices have degree three in $B(C')$, let $F_i$ denote the set of the edges in $B(C')$ which contain $f_i$ and are intersected by a same line segment $L_i$ (see Fig. 21(2)). We call $F_i$, $i=1,2,\cdots,t$, the characteristic edge sets of $B(C')$.

**Theorem 5.13** [108]. Let $C_1$ be a minimal $K_r$-conjugated circuit of a ring $s$ of a benzenoid hydrocarbon $B$ for a Kekulé structure $K_r$, the nondegenerated associated circuit of $C_1$ according to $K_r$ with $|C_1| \equiv |C_r|$; and $C'_2$, the associated characteristic circuit of $C_1$. Then, $C_1$ is a unique minimal $K_r$-conjugated circuit of $s$ if and only if either an extreme edge of $C_2$ lies on the boundary of $B$ and is a $K_r$-single bond or $C'_2$ has a truncated $M$-configuration and there is a characteristic edge set $F_j$ of $B(C'_2)$ such that each edge in $F_j$ is a $K_r$-double bond.

By Theorems 5.3 and 5.4, we need only to consider the benzenoid hydrocarbons with no fixed bond. To calculate $R_n(B)$, it is enough to give a method to determine the coefficient $r_n(s)$ of the term $R_n$ in $R_n(B)$ for $n \geq 1$.

From a Kekulé structure $K_r$ and a minimal $K_r$-conjugated circuit $C$ of a ring $s$ in $B$, we have introduced the concepts of the associated circuit and the associated characteristic circuit of $C$, according to $K_r$. Now, we need

![Fig. (20)](image-url)

(1) non-degenerated
(2) degenerated
(3) degenerated

Fig. (20). The associated circuit $C_2$ of a minimal $K_r$-conjugated circuit $C_1$ of a ring $s$ in $B$ according to $K_r$. 

s for which $B[C_2]$ contains as many hexagons as possible so that all interior edges of $B[C_2]$ are $K_r$-single bonds. The circuit $C_2$ is called the associated circuit of $C_1$ according to $K_r$. Particularly, if all edges of $s$ are not on the boundary of $B$, $C_2$ is called the nondegenerated associated circuit of $C_1$ (see Fig. 20). The edges $e_s, e_6$, and $e_e$ indicated in Fig. (20) are called the extreme edges of $C_2$; the sets of the interior edges of $B[C_2]$ parallel to $e_s, e_6$, and $e_e$ are, respectively, denoted by $E_s, E_6$, and $E_e$; and $E_i = E_s \cup \{e_i\}$, $E_6 = E_6 \cup \{e_6\}$, and $E_e = E_e \cup \{e_e\}$. Note that if any one of $e_s, e_6$, or $e_e$ is not on the boundary $b(B)$ of $B$, it must be a $K_r$-double bond. In the other case, it may be a $K_r$-single or $K_r$-double bond. The associated circuit $C_2$ of $C_1$ is different from an associated minimal $K_r$-conjugated circuit of $C_1$, since $C_2$ may be not $K_r$-conjugated and $|C_2|$ may be not equal to $|C_1|$.
to generalize the concepts so that they are independent of a Kekulé structure of $B$.

**Definition 5.8** [108]. For a pair of minimal conjugated circuits $C_1$ and $C_2$ of a ring $s$ in a benzenoid hydrocarbon $B$ and their underlying circuits $C_1^*$ and $C_2^*$, $C_1^* \cup C_2^*$ is said to have an underlying $PM$-configuration w.r.t. $s$. For a minimal conjugated circuit $C_1$ of $s$ and its underlying circuit $C_1^*$, a circuit $C_1^*$ is said to an nondegenerated associated circuit of $C_1$ and $C_1^*$, if $C_1 \cup C_2^*$ has a $PM$-configuration w.r.t. $s$, $C_1^* \cup C_2^*$ has an underlying $PM$-configuration w.r.t. $s$, and any edge of $s$ is not on the boundary of $B$. A characteristic circuit $C_1^*$ of $C_1^*$ is said to be an associated characteristic circuit of $C_1$ and $C_1^*$ if $C_1 \cup C_2^*$ has a $PM$-configuration w.r.t. $s$.

For a minimal conjugated circuit $C_1$ of a ring $s$ in $B$, let

$$A(C_1) = \{C_2 | C_2 \text{ is a nondegenerated associated circuit of } C_1\},$$

$$A_1(C_1) = \{C_2 | C_2 \in A(C_1), \text{ and } C_2 \notin C_1\},$$

$$A_2(C_1) = \{C_2 | C_2 \in A(C_1), \text{ and } C_2 \subseteq C_1\},$$

$$A'(C_1) = \{C_2^* | C_2^* \text{ is an associated characteristic circuit of } C_1\},$$

$$A'_1(C_1) = \{C_2^* | C_2^* \in A'(C_1), \text{ and } C_2^* \subseteq C_1\}, \text{ and } C_2^* \text{ has a truncated } M \text{-configuration},$$

$$A'_2(C_1) = \{C_2^* | C_2^* \in A'(C_1), \text{ and } C_2^* \supseteq C_1\}, \text{ and } C_2^* \text{ has a truncated } M \text{-configuration}.$$  

For calculation of $R_i(B)$, the pairs of circuits with underlying $PM$-configurations play a key role. Fig. (22) shows four types of pairs of circuits with underlying $PM$-configurations w.r.t. a ring $s$.

For a pair of circuits $C_i$ and $C_2$ in $B$ with an underlying $PM$-configuration, we denote by $C'_i$ (respectively, $C'_2$) the characteristic circuit of $C_i$ (respectively, $C_2$) which belongs to $A'(C_i)$ (respectively, $A'(C_2$)), where the circuit $C_i$ (respectively, $C_2$) is said to be of type $i$ ($i \in \{1, 2, 3, 4\}$), if the pair of circuits $C_i \cup C_2$ is of type $i$. A minimal conjugated circuit $C$ of a ring $s$ is said to be of type $i$, if the underlying circuit of $C$ is isomorphic to one of circuits $C_1$ and $C_2$ of type $i$. For convenience, we introduce the following notations:

$$C_n^{(i)}(s) = \{C | C \text{ is a circuit in a pair of circuits } C_1 \text{ and } C_2, \text{ with an underlying } P \text{-configuration w.r.t. a ring } s \text{ in } B \text{ which are of type } i, \text{ and } |C| = 4n \pm 2\}.$$  

$$r_n^{(i)}(s) : \text{the number of all the circuits denoted by } R_n \text{ in } R_i(B) \text{ which are of type } i, i = 1, 2, 3, 4.$$  

$$K(B(C_1, C_1')) : \text{the number of the Kekulé structures of } B \text{ for which all edges in } C_1 \cap C_2 \text{ and all extreme edges } \{e_1, \ldots, e_r, \ldots\} \text{ of } C_1, \text{ and } C_2 \text{ are double bonds, and all interior edges of } B[C_1] \text{ and } B[C_2] \text{ are single bonds}.$$  

$$K(B(C_1, C_1')) : \text{the number of the Kekulé structures of } B \text{ for which all extreme edges of } C_i, \text{ and all edges in } C_i \cap C_2 \text{ and a characteristic edge set of } B[C_1'] \text{ are double bonds, and all interior edges of } B[C_i] \text{ and } B[C_2] \text{ are single bonds}.$$  

$$K(B(C_i, C_i', E_2)) : \text{the number of the Kekulé structures of } B \text{ for which all extreme edges of } C_i, \text{ and the edges in}.$$
Advances of Clar's Aromatic Sextet Theory

The number of the Kekulé structures of $B$ for which all extreme edges of $C$, and the edges in $E(C_1 \cap C_2) \cup E_i$ and a characteristic edge set of $C_2$, are double bonds, and all interior edges of $B[C_1]$ and the edges in $E_2$ are single bonds.

$K(B[C_1, C_2, E_1, E_2])$ : the number of the Kekulé structures of $B$ for which all extreme edges of $C_1$ and $C_2$ are double bonds, and all interior edges of $B[C_1]$ and the edges in $E_2$ are single bonds.

$K(B[C_1, \phi])$ : the number of the Kekulé structures of $B$ for which $A(C_i) = \phi$, and $C_i \cap C_i^*$ is an alternating path (or circuit) in double and single bonds such that the extreme edges of $C_i$ are double bonds.

$E^*_A$ : the edge set $E_A$ for a circuit $C_A \in A(C_i)$ satisfying that, if $C_1 \cup C_2$ is of type 1 (respectively, types 2, 3, 4), $|E^*_A| \leq |E_A| = n-1$, or $|E^*_A| < n-1$ but $e_a$ is on $b(B)$ respectively, $|E^*_A| = |E_A| = n-2$, or $|E^*_A| < n-2$ but $e_a$ is on $b(B)$.

$E^*_{AB}$ : the edge set $E_A$ for a circuit $C_i \in A(C_i)$ satisfying that, if $..$ is of type 1 (respectively, types 2, 3, 4), $|E_{AB}| = n-2$ and $|E^*_{AB}| = n-1 - |E_A|$, or $|E_{AB}| + |E^*_{AB}| < n-1$ but $e_b$ is on $b(B)$ (respectively, $|E_{AB}| \leq n-3$ and $|E_{AB}| + |E^*_{AB}| = n-2$, or $|E_{AB}| + |E^*_{AB}| < n-2$ but $e_b$ is on $b(B)$).

$E^*_{ABC}$ : the edge set $E_c$ for a circuit $C_2 \in A(C_i)$ satisfying that $|E_A| + |E_B| \leq n-2$ and $|E_A| + |E_B| + |E^*_{ABC}| = n-1$, or $|E_A| + |E_B| + |E^*_{ABC}| < n-1$ but $e_c$ is on $b(B)$, where $C_1 \cup C_2$ is of types 2, 3, 4.

Similarly, we can define $K(B[C_1, C_2^*])$, $E_{\phi}$, $E_{\phi_0}$, and $E_{\phi_0}$.

Note that $B[C_1, C_2], B[C_1, C^*_2], B[C_1, E_1, E_2], B[C^*_1, E_1, E_2], \ldots$, denote the graphs obtained from $B$ by labeling some edges as double or single bonds.

**Lemma 5.4** [108]. Let $C_1$ and $C_2$ be a pair of circuits with an underlying PM-configuration w.r.t. a ring $s$ in a benzenoid hydrocarbon $B$, and $C_2^*$ the associated characteristic circuit of $C_1$. Then,
K(B[C_1, C_2^*]) = \sum_{i \leq j \leq \Omega} K(B[C_1, C_2, F_i] - \sum_{i \leq j \leq j} K(B[C_1, C_2, F_i \cup F_j])

+ \sum_{i \leq j \leq \Omega} K(B[C_1, C_2, F_i \cup F_j \cup F_k]) - \sum_{i \leq j \leq j} K(B[C_1, C_2, F_i \cup F_j \cup F_k]),

K(B[C', E_1, E_2]) = \sum_{i \leq j \leq \Omega} K(B[C_2, F_i \cup E_1, E_2]) - \sum_{i \leq j \leq j} K(B[C_2, F_i \cup F_j \cup E_1, E_2])

+ \sum_{i \leq j \leq j} K(B[C_2, F_i \cup E_1, E_2]),

where F_1, F_2, \ldots, F_l are all characteristic edge sets of C_2*.

Now we can give a method for calculating r^i_n(s).

Consequently, r^i_n(s) = \sum_{i=1}^{d} r^i_n(s).

**Theorem 5.15** [108]. Let B be a benzenoid hydrocarbon with no fixed bond, and s, a ring of B. Then,

(i) r^i_n(s) = \sum_{i=1}^{d} \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1^*, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1^*, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1, A])]

where C_1 (\in C_1^*(i)) and C_2 (\in C_2^*(i)) are taken for three possible positions of C_1 \cup C_2 in B.

(ii) r^i_n(s) = \sum_{i=1}^{d} \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1^*, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1, A])]

where C_1 and C_2 are taken for six possible positions of C_1 \cup C_2 in B.

(iii) r^i_n(s) = \sum_{i=1}^{d} \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1^*, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) - K(B[C_1, A])]

where C_1 and C_2 are taken for six possible positions of C_1 \cup C_2 in B.

(iv) r^i_n(s) = \sum_{i=1}^{d} \sum_{j=1}^{d} K(B[C_1, E_1]) + \sum_{i=1}^{d} \sum_{j=1}^{d} K(B[C_1^*, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) + \sum_{j=1}^{d} K(B[C_1^*, A])]

+ \sum_{j=1}^{d} K(B[C_1, E_1]) + \sum_{j=1}^{d} K(B[C_1^*, A])]

where C_1 and C_2 are taken for one possible position of C_1 \cup C_2 in B.

Note that the contribution of R(B) to the resonance energy of B is mostly due to the conjugated circuits denoted by R_1, R_2, R_3. The expressions for r^i_1(s), r^i_2(s) and r^i_3(s) can be obtained from Theorems 5.12 and 5.15.

**Corollary 5.17** [108]. Let B be a benzenoid hydrocarbon with no fixed bond and s a ring of B. Then

(i) r^i_1(s) = 2K(B - s),

(ii) r^i_2(s) = \sum_{j=1}^{d} K(B - s \cup s_j) \text{, where } s_j \text{ is a hexagon adjacent to } s,

(iii) K(B - C_1^* - \nu = e_p) + \sum_{j=1}^{d} K(B - C_1^* - \nu = e_p)

where C_1 and C_2 are taken for three possible positions of C_1 \cup C_2 in B.

0.8cm r^i_3(s) = \sum_{j=1}^{d} K(B - C_1^*),

0.8cm r^i_3(s) = \sum_{j=1}^{d} K(B - C_1^*),

0.8cm r^i_3(s) = 0.

### 6 k-Resonance in Chemical Graphs and k-Cycle Resonant Graphs

Let G be a benzenoid system, open-ended carbon nanotube (tubule), toroidal or Klein-bottle polyhex. We say G is k-resonant if, for 1 \leq t \leq k, any t disjoint hexagons of G are mutually resonant, that is, there is a Kekulé structure (or perfect matching) K of G such that each of the k hexagons is a 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 graphs is closely related to Clar’s aromatic sextet theory, and the concept of $k$-cycle resonant graphs is a natural generalization of $k$-resonant graphs.

Some necessary and sufficient conditions for a benzenoid system or a tubule or a toroidal polyhex (resp. a graph) to be $k$-resonant (resp. $k$-cycle resonant) have been established. A survey on investigations of $k$-resonant benzenoid systems, $k$-resonant tubules, $k$-resonant toroidal polyhexes, and $k$-cycle resonant graphs was given in [109]. For recent works on $k$-resonance, the reader is referred to [69], and [110-115].

CONFLICT OF INTEREST

There is no conflict of interest.

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ABBREVIATIONS

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
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<tbody>
<tr>
<td>VB</td>
<td>Valence-bond</td>
</tr>
<tr>
<td>RE</td>
<td>Resonance energy</td>
</tr>
<tr>
<td>TRE</td>
<td>Topological resonance energy</td>
</tr>
<tr>
<td>DRE</td>
<td>Dewar resonance energy</td>
</tr>
<tr>
<td>LM-conjugated circuit</td>
<td>Linear independent and minimal conjugated circuit</td>
</tr>
<tr>
<td>LM-conjugated circuit polynomial (LMC-expression)</td>
<td>Linear independent and minimal conjugated circuit polynomial</td>
</tr>
<tr>
<td>LMCC-polynomial</td>
<td>LM-conjugated circuit polynomial</td>
</tr>
<tr>
<td>BH</td>
<td>Benzoid hydrocarbon</td>
</tr>
<tr>
<td>BHF</td>
<td>Benzoid hydrocarbon-fragment</td>
</tr>
<tr>
<td>GBH</td>
<td>Generalized benzoid hydrocarbon</td>
</tr>
<tr>
<td>cata-BH</td>
<td>Catacondensed benzoid hydrocarbon</td>
</tr>
<tr>
<td>peri-BH</td>
<td>Pericondensed benzoid hydrocarbon</td>
</tr>
<tr>
<td>M-configuration</td>
<td>Minimal configuration</td>
</tr>
<tr>
<td>PM-configuration</td>
<td>Configurations of a pair of minimal conjugated circuits</td>
</tr>
</tbody>
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REFERENCES

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