Recursive Method for Enumeration of Linearly Independent and Minimal Conjugated Circuits of Benzenoid Hydrocarbons

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The linearly independent and minimal conjugated (LM-conjugated) circuits of benzenoid hydrocarbons (BHs) play the central role in the conjugated circuit model. For a general case, the enumeration of LM-conjugated circuits of BHs may be tedious as it requires construction of all Kekule structures. In the present paper, we investigate the properties and the construction of minimal conjugated circuits of BHs, and give the necessary and sufficient condition for a set of conjugated circuits of a BH to be linearly independent and minimal. Furthermore, we establish some recursive relations for enumeration of LM-conjugated circuits for several classes of BHs, one class of which consists of all the BHs containing no crown subunit. By these recursive relations, the summation expressions of LM-conjugated circuits (LMC-expressions) of the several classes of BHs can be directly obtained from the LMC-expressions and the Kekule structure counts of their subgraphs.

1. INTRODUCTION

The concept of conjugated circuits in polycyclic conjugated systems was first introduced by Randić.[1-3] Enumeration of conjugated circuits led to expressions for the resonance energies of polycyclic conjugated hydrocarbons.[4] In recent years, many investigations on the conjugated-circuit model have been made,[4-12] 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.

According to the conjugated-circuit model, the resonance energies of conjugated benzenoid hydrocarbons can be expressed as contributions arising from linearly independent conjugated circuits. More precisely, we prefer to say linearly independent and minimal conjugated (LM-conjugated) circuits rather than say linearly independent conjugated circuits. The sets of linearly independent conjugated circuits of a Kekule structure of a benzenoid hydrocarbon are not necessarily unique, and some sets may have different total circuit lengths. Hence, a rigorous definition of LM-conjugated circuits of benzenoid hydrocarbons is as follows.

Definition 1. A set S of linearly independent and minimal conjugated circuits of a Kekule structure K_i 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_i, and has the minimum length.

We denote a circuit of size $4n + 2$ in S by R_n, and the summation expression of S by $R(K_i) = \sum_{R_j \in S} R_j = \sum_{n=1,2,\ldots} r_n(K_i) R_n$, where $r_n(K_i)$ is the number of the circuits of size $4n + 2$ in S. The summation expression of all sets of LM-conjugated circuits of all Kekule structures of B is denoted by $R(B) = R = \sum_{K_i} R(K_i) = \sum_{n=1,2,\ldots} r_n R_n$, where $r_n = \sum_{K_i} r_n(K_i)$. We also say $R(B)$ is the summation expression of LM-conjugated circuits of B or simply the LMC expression of B. $R(B)$ may also be denoted by a sequence of numbers $(r_1, r_2, r_3, \ldots, r_n, \ldots)$, called the LMC-code of B.

Note that a set S of LM-conjugated circuits of a Kekule structure K_i is also not unique (see Figure 1); however, the summation expression $R(K_i)$ is uniquely determined, and hence $R(B)$ is unique.

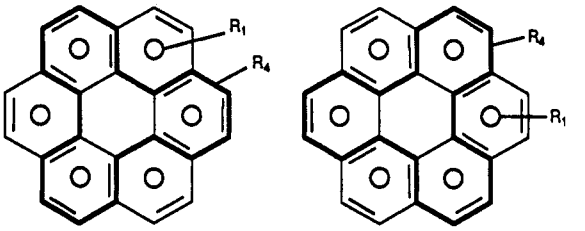

Figure 1. Two sets of LM-conjugated circuits of a Kekule structure K_i with the sumation expression $R(K_i) = 6R_1 + R_4$.

The LM-conjugated circuits of benzenoid hydrocarbons play the 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 Kekule structures of B. In a recent work,[13] the summation expressions of LM-conjugated circuits were applied to calculate generalized bond orders of polycyclic conjugated hydrocarbons. Thus the calculation of the summation expressions of LM-conjugated circuits of benzenoid hydrocarbons becomes a very fundamental problem in the conjugated-circuit model. In a general case, the computational scheme for LM-conjugated-circuit calculations contains (as stated by Trinajstić et al. in refs 6 and 8) two combinatorial problems: (1) the enumeration (and generation) of all Kekule structures of a benzenoid hydrocarbon and (2) the enumeration of LM-conjugated circuits of every Kekule structure. There are a number of methods available for generating and counting all Kekule structures of a benzenoid hydrocarbon B.[14,15] Once all Kekule structures of B have been given, there is a nice method[4] for enumerating LM-conjugated circuits of every Kekule structure, which is restated as follows:

Procedure 1. Let K_i be a Kekule structure of a benzenoid hydrocarbon B, and let $S_h(B) = \{s_1, s_2, \ldots, s_j, s_{j+1}, \ldots, s_h\}$ be the set of hexagons of B.

1. Set $j = 1$.
2. For the ring s_j, find a K_i-conjugated circuit R_{n_j} which has the minimum length and whose interior contains the interior of s_j. Then assign the label n_j to the ring s_j.
3. If $j < h$, set $j+1 \rightarrow j$, go to step 2.
4. If $j = h$, set $R(K_i) = \sum_{s_j \in S_h(B)} R_{n_j}$.

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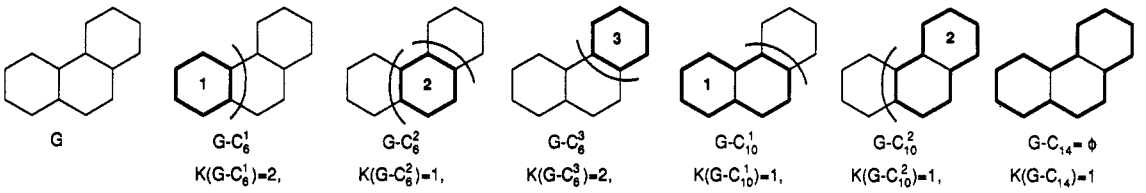


Figure 2. Example of the application of formula 1.

The summation expression $R(B)$ can be obtained by first using procedure 1 for all Kekule structures of B and then taking $\sum_{K_i} R(K_i)$.

The above method is suitable for smaller benzenoid hydrocarbons. However, when sizes of molecules increase the numbers of Kekule structures increase quickly; hence obtaining the summation expressions of LM-conjugated circuits of benzenoid hydrocarbons by the above method becomes tedious.

It was suggested in ref 4 that for some larger molecules rather than considering individually each single molecule it may be better to review a family of related structures of which the molecule in question is a member. By analyzing a sequence of structures and a sequence of expressions for the molecular resonance energy, one tries to find some regularity for the coefficients indicating the contributions of the conjugated circuits of different size. In this way one can obtain the expressions of resonance energies for still larger members of a family of structurally related structures.

A very useful idea in that approach is a partitioning of resonance energy to the expressions for the individual rings of the structures considered. Note that in procedure 1 for a Kekule structure K_i of B, every ring of B is given a label which corresponds to a minimal K_i-conjugated circuit whose interior contains the interior of the ring. When we use procedure 1 for all Kekule structures of B, a ring s_j of B obtains $K(B)$ labels which correspond to $K(B)$ LM-conjugated circuits of B with respect to the ring s_j. The summation expression of these LM-conjugated circuits is said to be the contribution of the ring s_j to the LMC-expression $R(B)$ of B, or simply the LCM-expression of the ring s_j. In ref 4, the contribution of a ring s_j to $R(B)$ is denoted by a sequence of numbers, $(r_1(s_j), r_2(s_j), r_3(s_j), ...)$, where $r_n(s_j)$ is the coefficient of the term R_n in the LMC-expression of the ring s_j, which is also called the ring code of s_j. Clearly, the total sum of LMC-expressions of all rings of B is just equal to $R(B)$, and the total sum of ring codes of all rings is equal to $(r_1, r_2, ..., r_n, ...)$, where r_n is the coefficient of the term R_n in $R(B)$.

For some families of structurally related structures, use of the ring codes has special advantage. It allows one to perceive regularities for the coefficients from the count of conjugated circuits of different size more readily. In this way one can arrive at the expressions for still larger members of the families of structures considered without explicit construction of Kekule structures. In ref 4, ring codes of some families of benzenoid hydrocarbons were given by finding the intercorrelations of the coefficients of various conjugated circuits or finding the regularities of a recursion of ring codes to smaller members of the families.

The method developed in ref 4 is available only for some families of related structures. In general cases, it is usually very difficult to find such regularities among the coefficients of various conjugated circuits and the ring codes between smaller members of a family of related structures.

Another approach for enumeration of conjugated circuits was outlined by Klein et al.[16-19] These authors illustrated a simple and valuable way to enumerate all conjugated circuits

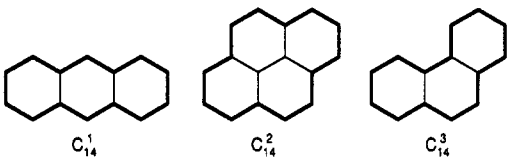


Figure 3. Three different shapes of C_{14}.

of polycyclic systems using Kekule structure counts for their constituting fragments. The approach is based on a relationship between the counts of Kekule structures of selected subgraphs in BHs and the counts of conjugated circuits of BHs. The number of conjugated circuits of size N, $(CC)_N$, is given by[16-20]

$$(CC)_N = 2\sum_{C_N}^{G} K(G-C_N) \qquad (1)$$

here $G - C_n$ denotes the graph obtained from G by deleting a cycle C_N (N = 4, 6, 8, ...) and edges incident on C_N.

The enumeration of all conjugated circuits is thus reduced to Kekule structure counts for different fragments of G. Klein and co-workers[16-19] linked the above formula with the transfer-matrix method and produced a very efficient and elegant procedure for a computer-assisted enumeration of all conjugated circuits.

However, formula 1 is not available for enumeration of LM-conjugated circuits of polycyclic conjugated structures. An example[6,8] of the application of the formula is illustrated in Figure 2 on phenanthrene. It gives the summation expression of all conjugated circuits of phenanthrene as $10R_1 + 4R_2 + 2R_3$. However, the count of LM-conjugated circuits of phenanthrene is $R(G) = 10R_1 + 4R_2 + R_3$.

The difference occurs because larger conjugated circuits may have different shapes, for example, C_{14} has three different shapes: C_{14}^1, C_{14}^2, and C_{14}^3 depicted in Figure 3. For the shape of C_{14}^3, one of two conjugated circuits denoted as R_3 is not minimal, and so is dependent of other LM-conjugated circuits of a Kekule structure. Hence the contribution of C_{14}^3 to $R(G)$ is not equal to $2\sum_{C_{14}^3}^{G} K(G - C_{14}^3)$. In addition, if $N = 4n + 2 > 14$, the number of all different shapes of C_N will be greater than the number of the different shapes of R_n in LM-conjugated circuits, since there are some restrictions for the shapes of LM-conjugated circuits.

It is of interest to obtain modified version of formula 1 that applies to the model based on LM-conjugated circuits. For this, we need to investigate the different contributions of R_n having different shapes to $R(G)$. This work is in progress and will be reported.[22]

In the present paper, we investigate the properties and the construction of minimal conjugated circuits of benzenoid hydrocarbons, and give the necessary and sufficient condition for a set of conjugated circuits of a benzenoid hydrocarbon to be linearly independent and minimal. Furthermore, we establish some recursive relations for enumeration of LM-conjugated circuits of several classes of benzenoid hydrocarbons, so that the LMC-expressions of the several classes of

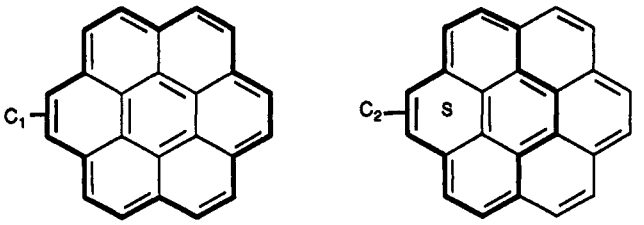


Figure 4. The conjugated circuit C_1 is not minimal; the circuit C_2 is a minimal conjugated circuit of the ring s.

benzenoid hydrocarbons can be directly obtained from the LMC-expressions and the Kekule structure counts of their some subgraphs.

2. PROPERTIES AND CONSTRUCTION OF MINIMAL CONJUGATED CIRCUITS

We first give some necessary definitions and notations.

Definition 2. A benzenoid hydrocarbon (BH) is a two-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 two-connected BHF is said to be a generalized BH (GBH). Let B be a BH or GBH. B is said to be normal if B contains no fixed bond (i.e., bond appearing as a double or a single bond in every Kekule structure), otherwise B is 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^*. The boundary of an interior face of a BH or BH-fragment B is called a ring of B.

Definition 3. Let s be a ring of a benzenoid hydrocarbon B, and K_i a Kekule structure of B. A conjugated circuit C of K_i (simply, a K_i-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_i-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 Figure 4).

As shown in Figure 1, for a Kekule structure K_i, the minimal conjugated circuits of a ring s may not be unique, but they have same length. Some properties and the construction of minimal conjugated circuits of a ring s of a benzenoid hydrocarbon B are given in the following.

Since B is bipartite, we can color the vertices of B black and white so that any two adjacent vertices have different colors. For a circuit C in B, let $B[C]$ denote the maximal subgraph of B bounded by C. A K_i alternating path in B is said to be monotonous if all single bonds on the path have same direction when B is embedded in a plane (that is, they are parallel).

Lemma 1. Let K_i be a Kekule structure of a benzenoid hydrocarbon B, and C a minimal K_i-conjugated circuit of a ring s of B. Then $C \cap s \neq \phi$.

Proof. Suppose that $C \cap s = \phi$. Since s is not a K_i-conjugated circuit, there are $2i$ ($1 \leq i \leq 3$) vertices of s, say $u_1, u_2, \ldots, u_{2i}$, which are incident with double bonds not on s, and so divide s as $2i$ segments each of which is a K_i-alternating path with the end edges being single bonds (see Figure 5). Without loss of generality, we assume the end vertices of double bonds on C are colored in the way shown in Figure 6, and u_1 is a white vertex. Take a monotonous K_i-alternating path $P(u_1-v_1)$ ($P(u_{2i}-v_{2i})$) starting from u_1 (u_{2i}) and the double bond incident with u_1 (u_{2i}), going in the second step to the right (left), and terminating in a vertex v_1 (v_{2i}) on C. Then the two paths together with a v_1–v_{2i} segment on C and a u_{2i}–u_1 segment on s form a K_i-conjugated circuit C' which has smaller length than C. The interior of C' contains the interior of s, contradicting that C is a minimal K_i-conjugated circuit of s.

Now we can characterize the construction of LM-conjugated circuits.

Theorem 1. Let K_i be a Kekule structure of a benzenoid hydrocarbon B, and let C be a minimal K_i-conjugated circuit of a ring s of B. Then $B[C]$ is one of the BHs shown in Figure 7, and the K_i double bonds in $B[C]$ are uniquely determined.

Proof. By lemma 1, s contains at least one edge lying on C. If $C = s$, $B[C]$ is the BH in Figure 7 with $a = b = c = 0$. If $C \neq s$, let u_1 be an end vertex of a path in $C \cap s$. u_1 must be incident with one double bond not on s (see Figure 7). We go along C starting from u_1 and a double bond. At the vertex v_1, we have to go to the right. Otherwise, in $B[C]$ there is a monotonous K_i-alternating path starting from v_1, going in the first step to the right, and terminating in a vertex v_i' on C (see Figure 8). The monotonous K_i-alternating path together with a v_1'–v_1 segment on C would form a smaller K_i-conjugated circuit than C whose interior contains the interior of s, contradicting that C is a minimal K_i-conjugated circuit of s. By the same reason, at the vertex v_2 on C shown in Figure 7, we must go to the right. However, at the vertex v_3, we must go to the left, since $B[C]$ is normal by theorem 6 in ref 21. On the basis of the above regularities, we can certainly arrive at the vertex v_4 on C. The u_1–v_4 segment on C is thus determined in the shape shown in Figure 7. The other v_4–u_1 segment on C can be determined in a similar way. Clearly, the K_i double bonds in $B[C]$ are also determined uniquely.

From theorem 1, one can easily find the following corollary.

Corollary 1. Let C be a minimal K_i-conjugated circuit of a ring s of a benzenoid hydrocarbon B. Then, for any K_i-conjugated circuit C' in $B[C]$, (1) $C \cap C' \neq \phi$, (2) $C \cap C'$ is a connected path, and (3) the interior of C' does not contain the interior of s.

Lemma 2. Let C be a minimal K_i-conjugated circuit of a ring s of B. Then, for a ring s' in $B[C]$ other than s, a minimal K_i-conjugated circuit C' of s' in B is a unique minimal K_i-conjugated circuit of s' and the interior of C' is contained in the interior of C.

Proof. In $B[C]$, there is a minimal K_i-conjugated circuit of s', say C'. We will prove C' is also a unique minimal K_i-conjugated circuit of s' in B.

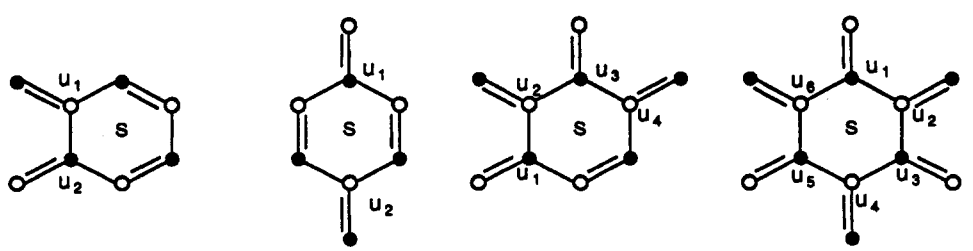


Figure 5. Distribution of double bonds incident with the vertices of the ring s.

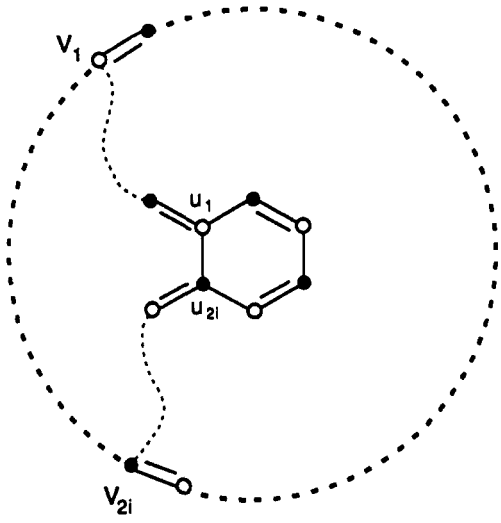


Figure 6.

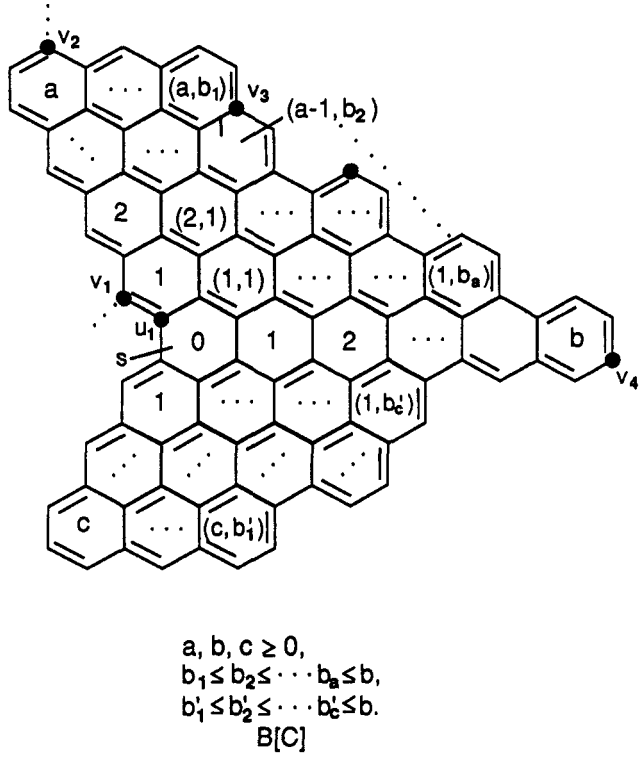


Figure 7. Construction of minimal conjugated circuits of a ring s of a benzenoid hydrocarbon B.

Suppose that there is a minimal K_i-conjugated circuit C'' of s' in B other than C'. It is not difficult to see from theorem 1 and Figure 7 that in $B[C]$ C' is a unique minimal K_i-conjugated circuit. Thus C'' must contain some edges not in $B[C]$. Since C'' is minimal in B, the interior of C'' cannot contain the interior of C'. By lemma 1 and corollary 1, the union $C'' \cup C$ must be in the way shown in Figure 9, and the interior of C'' must contain the interior of s.

Let C^* be a minimal K_i-conjugated circuit of s in $B[C'']$. Then C^* has smaller length than C'', and C' has smaller length than C. On the other hand, the length of C^* is greater than or equal to the length of C, since C is minimal in B. Therefore the length of C'' would be greater than that of C', contradicting that C'' is minimal in B.

By corollary 1 and lemma 2, we have the following.

Corollary 2. Let C be a minimal K_i-conjugated circuit of a ring s of a benzenoid hydrocarbon B. Then C corresponds

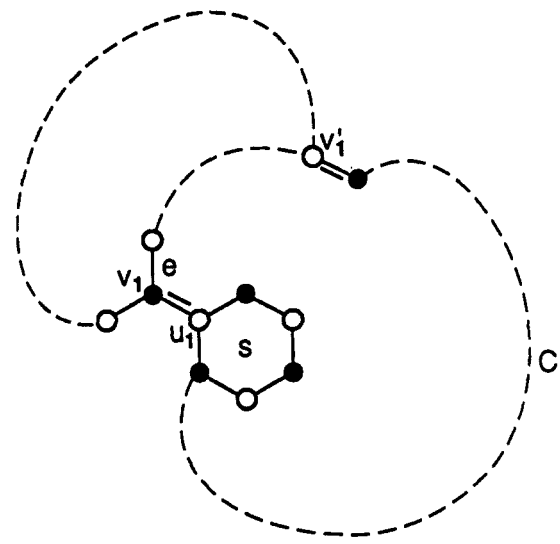


Figure 8.

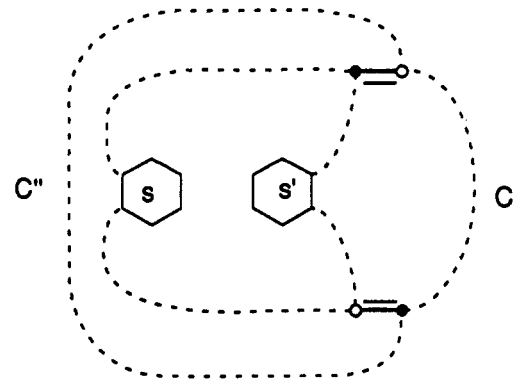


Figure 9. Union of C'' and C.

to a unique ring s such that C is a minimal K_i-conjugated circuit of s in B.

From theorem 1 and lemma 2, we also have the following.

Corollary 3. Let C_1 be a minimal K_i-conjugated circuit of a ring s of a benzenoid hydrocarbon B, and let $C_2, C_3, ..., C_t$ be all minimal K_i-conjugated circuits of all other rings than s in $B[C_1]$. Then $C_1, C_2, C_3, ..., C_t$ are linearly independent and t is just equal to the number of rings of $B[C_1]$.

3. NECESSARY AND SUFFICIENT CONDITION ON LM-CONJUGATED CIRCUITS OF A BENZENOID HYDROCARBON

Now we can give a necessary and sufficient condition for a set of K_i-conjugated circuits of a benzenoid hydrocarbon B to be a set of LM-conjugated circuits.

Theorem 2. Let K_i be a Kekule structure of a benzenoid hydrocarbon B. A set $S = \{C_1, C_2, C_3, ..., C_t\}$ 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_j in S such that C_j is a minimal K_i-conjugated circuit of s_j.

Proof. Necessity. Suppose S is a set of LM-conjugated circuits of K_i. For a circuit C_j in S, there is a ring s_j in $B[C_j]$ which is independent of $C_1, C_2, ..., C_{j-1}, C_{j+1}, ..., C_t$ since S is a circuit basis of K_i-conjugated circuits. C_j must be a minimal K_i-conjugated circuit of s_j. Otherwise, let C' be a minimal K_i-conjugated circuit of s_j, then $C_1, C_2, ..., C_{j-1}, C', C_{j+1}, ..., C_t$ are also linearly independent and have smaller total circuit length than circuits in S, a contradiction. Hence any circuit C_j in S corresponds to a unique ring s_j such that

C_j is a minimal K_r-conjugated circuit of s_i by corollary 2. Now we need to prove the corresponding t rings of t circuits in S are mutually different.

Suppose there are two circuits C_j and C_k in S which correspond to the same ring s. Then C_j and C_k have same length, and by the construction of minimal conjugated circuits characterized in theorem 1, $B[C_j]$ and $B[C_k]$ have only one common ring s. By lemma 2, for any ring s' ($\neq$s) in $B[C_j]$ ($B[C_k]$), there is a unique minimal K_r-conjugated circuit C' of s' in B which is contained in $B[C_j]$ ($B[C_k]$). By corollary 3, all of the minimal K_r-conjugated circuits in $B[C_j]$ ($B[C_k]$) are linearly independent. In other words, C' is independent of all other minimal K_r-conjugated circuits in $B[C_j]$ ($B[C_k]$). In addition, for any minimal K_r-conjugated circuit C_i in S, no matter whether or not the interior of C_i contains the interior of s', C' is independent of all minimal K_r-conjugated circuits in $B[C_i]$ except C' itself. Hence C' is independent of all circuits in S except C' (if $C' \in S$). This implies that C' and all minimal K_r-conjugated circuits in $B[C_j] \cup B[C_k]$ must belong to S. However, the number of all minimal K_r-conjugated circuits in $B[C_j] \cup B[C_k]$ is greater than the number of rings of $B[C_j] \cup B[C_k]$; one of C_j and C_k is dependent of all the other minimal K_r-conjugated circuits in $B[C_j] \cup B[C_k]$. Thus circuits in S would be also linearly dependent, contradicting our assumption.

Sufficiency. Suppose S satisfies the condition of the theorem. We first prove by induction on sizes of circuits in S that the circuits $C_1, C_2, C_3, ..., C_t$ in S are linearly independent.

All the circuits in S denoted as R_1 are obviously linearly independent. Now assume all the circuits in S denoted as R_j, $j = 1, 2, ..., n$, are linearly independent. Let $j = 1, 2, ..., n + 1$. For any circuit C_k in S denoted as R_{n+1}, by corollary 2, C_k corresponds to a unique ring s_k such that C_k is a minimal K_r-conjugated circuit of s_k. By lemma 2, the interior of s_k is not contained in the interior of any circuit in S denoted as R_j, $j \leq n + 1$, other than C_k. Hence C_k is independent of all the circuits in S denoted as R_j, $j = 1, 2, ..., n + 1$, except itself. This means that all the circuits in S denoted as R_j, $j = 1, 2, ..., n + 1$, are linearly independent.

Now we can assert that S is a set of LM-conjugated circuits of B. Otherwise, there is another set S' of K_r-conjugated circuits of B which are linearly independent and minimal and have smaller total length than circuits in S. However, by the proof of necessity, for any ring s_j in all normal components B^* of B, there is exactly one circuit C_j' in S' such that C_j' is a minimal K_r-conjugated circuit of s_j, implying that S' and S have same total circuit length, a contradiction.

Theorem 2 establishes the theoretical basis of procedure 1 and 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 $R_s(B)$, is determined by taking the summation expression of the minimal conjugated circuits of s, one for every Kekule structure of B, and $R(B) = \sum_s^B R_s(B)$. $R_s(B)$ may also be denoted by a sequence of numbers (ring code) $(r_1(s), r_2(s), ..., r_n(s))$, where $r_n(s)$ is the coefficient of the term R_n in $R_s(B)$. Theorem 2 also enables us to establish some recursive relations for enumeration of LM-conjugated circuits of B.

4. SOME RECURSIVE RELATIONS

Definition 4. For an edge $e = uv$ of a benzenoid hydrocarbon B, let B_e ($B_{\bar{e}}$) denote the labeled graph of B for which the edge e is labeled as double (single) bond, and Let B_e^* ($B_{\bar{e}}^*$) denote the normal components of $B-u-v$ ($B-e$) (B_e^* and $B_{\bar{e}}^*$ may be thought as the normal components of B_e ($B_{\bar{e}}$), since e is in fact a fixed double (single) bond in $B_e(B_{\bar{e}})$). The subgraph of B_e ($B_{\bar{e}}$) induced by the hexagons in B_e ($B_{\bar{e}}$) which are not in B_e^* ($B_{\bar{e}}^*$) is denoted by B_e' ($B_{\bar{e}}'$). The contribution of all rings in B_e^* ($B_{\bar{e}}^*$) to $R(B_e)$ ($R(B_e)$) is denoted by $R^*(B_e)$ ($R^*(B_{\bar{e}})$), and the contribution of all rings in B_e' ($B_{\bar{e}}'$) to $R(B_e)$ ($R(B_{\bar{e}})$) is denoted by $R'(B_e)$ ($R'(B_{\bar{e}})$).

Clearly, $R(B_e)$ and $R(B_{\bar{e}})$ are just the LMC-expressions of all the Kekule structures of B containing and not containing the edge e, respectively. Thus we have that

$$R(B) = R(B_e) + R(B_{\bar{e}}) \tag{2}$$

Furthermore

$$R(B_e) = R^*(B_e) + R'(B_e) \tag{3}$$

$$R(B_{\bar{e}}) = R^*(B_{\bar{e}}) + R'(B_{\bar{e}}) \tag{4}$$

Combining expressions 2–4, we have

$$R(B) = R^*(B_e) + R^*(B_{\bar{e}}) + R'(B_e) + R'(B_{\bar{e}}) \tag{5}$$

The above expressions give some partitions of LM-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.

Although a benzenoid hydrocarbon B is 2-connected, a subgraph of B may be disconnected or only 1-connected not 2-connected. B may also be essentially disconnected. So we need to give some recursive relation for disconnected BH-fragments and essentially disconnected BHs.

Theorem 3. Let $B_1, B_2, ..., B_t$ be t mutually disjoint BHs, or BH-fragments, and $B = B_1 \cup B_2 \cup ... \cup B_t$. Then

$$R(B) = R(B_1 \bigcup B_2 \bigcup ... \bigcup B_t) = \sum_{i=1}^{t} \frac{K(B)}{K(B_i)} R(B_i)$$

Proof. For any Kekule structure of $B_1 \cup ... \cup B_{i-1} \cup B_{i+1} \cup ... \cup B_t$, B_i contributes $R(B_i)$ to $R(B)$, and so the total contribution of B_i to $R(B)$ is equal to $K(B_1 \cup ... \cup B_{i-1} \cup B_{i+1} \cup ... \cup B_t)\, R(B_i) = (K(B)/K(B_i))R(B_i)$. It follows that

$$R(B) = \sum_{i=1}^{t} \frac{K(B)}{K(B_i)} R(B_i)$$

Theorem 4. Let $B_1, B_2, ..., B_t$ be the normal components of an essentially disconnected BH or a BH-fragment B. Then

$$R(B) = R(B^*) = \sum_{i=1}^{t} \frac{K(B)}{K(B_i)} R(B_i)$$

Proof. Since a fixed bond of B cannot be contained in any conjugated circuit, all conjugated circuits of B only appear in $B^* = B_1 \cup B_2 \cup ... \cup B_t$, implying that

$$R(B) = R(B^*) = \sum_{i=1}^{t} \frac{K(B)}{K(B_i)} R(B_i)$$

For a normal benzenoid hydrocarbon B, we need to use expression 5 to obtain some recursive relations. However, in general cases, the terms $R^*(B_e)$ and $R^*(B_{\bar{e}})$ in expression 5 may be not equal to $R(B_e^*)$ and $R(B_{\bar{e}}^*)$, respectively. For example, Figure 10 shows a labeled graph B_e of a coronene (a crown) B, in which $R(B_e) = 47R_1 + 33R_2 + 17R_3 + R_4$, $R'(B_e) = 5R_1 + 6R_2 + 2R_3$, $R^*(B_e) = R(B_e) - R'(B_e) = 42R_1$

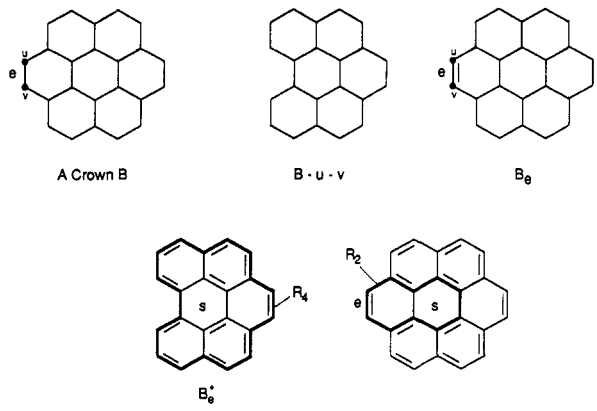


Figure 10. (bottom left) A minimal K_i^*-conjugated circuit R_4 of the ring s in R_e^* which is not minimal in B_e, and (bottom right) a minimal K_i-conjugated circuit R_2 of the ring s in B_e, where $K_i = K_i^* \cup \{e\}$.

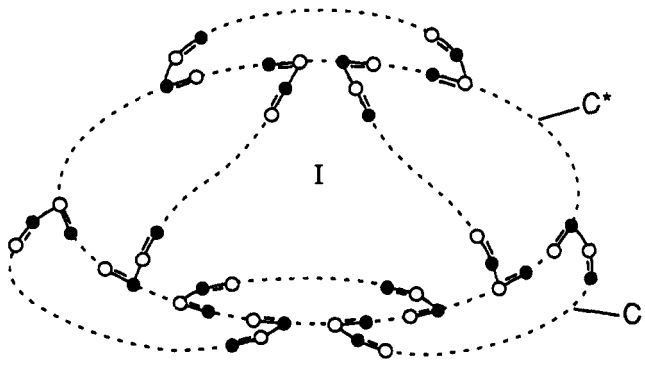


Figure 11. Union of two conjugated circuits C and C^*.

$+ 27R_2 + 15R_3 + R_4$, but $R(B_e^*) = 42R_1 + 26R_2 + 13R_3 + 4R_4 \neq R^*(B_e)$.

The problem occurs because a minimal conjugated circuit of a ring in B_e^* is not certainly a minimal conjugated circuit of the ring in B_e (see Figure 10). The same applies also to $B_{\bar{e}}^*$ and $B_{\bar{e}}$. We have to investigate cases when any minimal conjugated circuit in B_e^* ($B_{\bar{e}}^*$) is still minimal in B_e ($B_{\bar{e}}$).

Theorem 5. Let B be a BH which contains no crown as its subgraph. Then for any edge $e = uv$ of B, each of LM-conjugated circuits of B_e^* ($B_{\bar{e}}^*$) is also a minimal in B_e ($B_{\bar{e}}$).

Proof. Suppose that in B_e^* ($B_{\bar{e}}^*$) there is a minimal K_i^*-conjugated circuit C^* of a ring s which is not minimal in $B_e(B_{\bar{e}})$. Then there is a minimal K_i-conjugated circuit C of s in B_e ($B_{\bar{e}}$), where the Kekule structure K_i of B_e ($B_{\bar{e}}$) consists of K_i^* together with the fixed double bonds in B_e ($B_{\bar{e}}$). Since C contains some edges not in B_e^* ($B_{\bar{e}}^*$) and the length of C is smaller than of C^*, $C \cap C^* \neq \phi$. The intersection $C \cap C^*$ consists of $2t$ ($t \geq 1$) K_i (K_i^*) alternating paths with the end edges being K_i (K_i^*) double bonds. The way to joining $C \setminus C \cap C^*$ with C^* can only be as shown in Figure 11, because C is a minimal conjugated circuit of B_e ($B_{\bar{e}}$) and the interior of the ring s is contained in the intersection I of the interiors of C and C^*. It is not difficult to see that the ring s is an interior hexagon of B, implying that there is a subgraph of B which is a crown.

From Theorem 5, we can give the following recursive relation.

Theorem 6. Let B be a normal BH, which contains no crown as its subgraph. Then, for any edge e of B,

$$R(B_e) = R'(B_e) + R(B_e^*), \quad R(B_{\bar{e}}) = R'(B_e) + R(B_{\bar{e}}^*),$$
$$R(B) = R(B_e^*) + R(B_{\bar{e}}^*) + R'(B_e) + R'(B_{\bar{e}}) \quad (6)$$

For BHs with a crown subgraph, we need to find some special edges of them such that the recursive relation in theorem 6 is also available.

Theorem 7. Let B be a normal BH with a local structure as shown in Figure 12(1). Then, for the marked edge e, (1) each of LM-conjugated circuits of B_e^* ($B_{\bar{e}}^*$) is also a minimal conjugated circuit of B_e ($B_{\bar{e}}$); (2) $R(B) = R(B_e^*) + R(B_{\bar{e}}^*) + R'(B_e) + R'(B_{\bar{e}})$.

Proof. (1) We need only to prove the conclusion for B_e, since B_e and $B_{\bar{e}}$ have a similar structure.

The distribution of double bonds on the common boundary of B_e^* and B_e' has three possibilities as shown in Figure 13. It is easy to see that, for a ring s in B_e^*, any minimal conjugated circuit of s in B_e is certainly contained in B_e^*, implying each of LM-conjugated circuits of B_e^* is also minimal in B_e.

The conclusion of (2) holds immediately from (1).

Theorem 8. Let B be a normal BH with a local structure as shown in Figure 14(1). Then, for the marked edge e, (1) each of LM-conjugated circuits of B_e^* ($B_{\bar{e}}^*$) is also a minimal conjugated circuit of B_e ($B_{\bar{e}}$); (2) $R(B) = R(B_e^*) + R(B_{\bar{e}}^*) + R'(B_e) + R'(B_{\bar{e}})$. (The conclusions of the theorem are also available for the marked edges $e_1, e_2, \ldots, e_{p-1}$ of B. We omit the proofs for them here.)

Proof. (1) The common boundary of $B_{\bar{e}}^*$ and $B_{\bar{e}}'$ is similar to the cases in theorem 7. We need only to prove the conclusions for B_e.

Suppose that, for a ring s in B_e^*, a minimal conjugated circuit C^* of s in B_e^* is not minimal in B_e, then there is a minimal conjugated circuit C of s in B_e which is not contained in B_e^*.

Clearly, C must contain the edge e. In addition, C must contain the vertex w in B_e (see Figure 14(2)). Otherwise, C would be a minimal conjugated circuit in $(B-f)_e$ (see Figure 15). However, the common boundary of $(B-f)_e^*$ and $(B-f)_e'$ is similar to the cases in theorem 7, implying that C is not minimal, a contradiction.

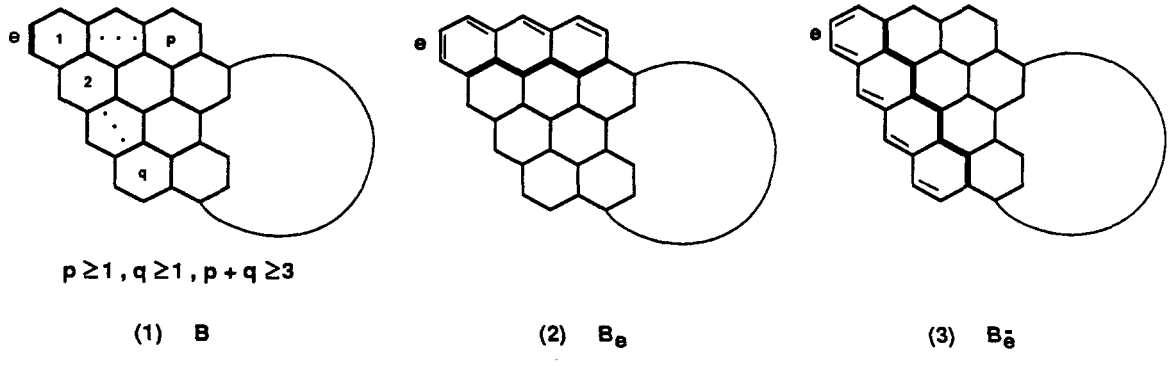


Figure 12. (1) B, where $p \geq 1$, $q \geq 1$, $p + q > 3$. (2) B_e. (3) $B_{\bar{e}}$.

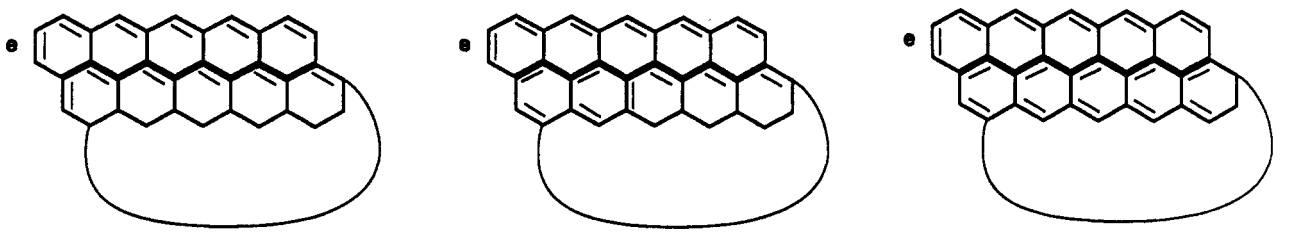


Figure 13. Distribution of double bonds on the common boundary of B_e^* and B_e'.

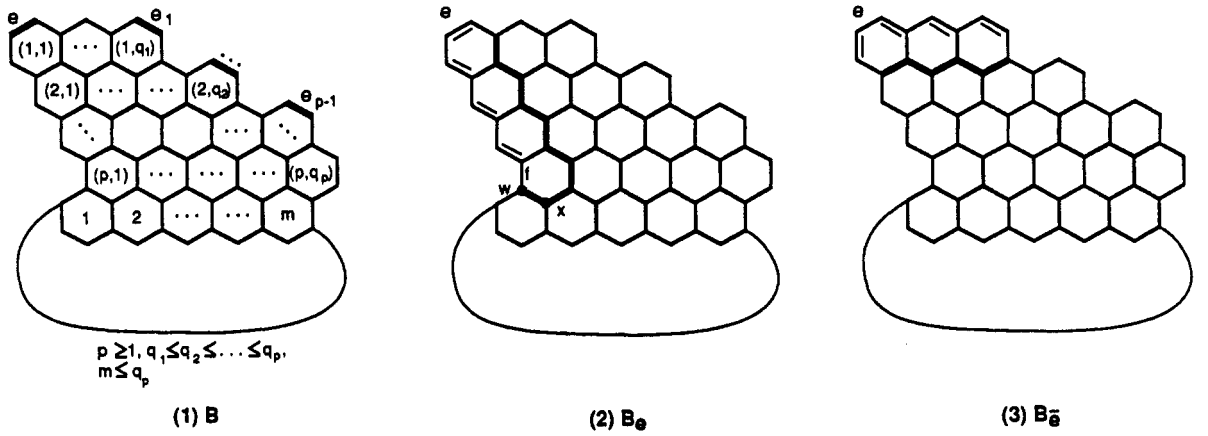


Figure 14. (1) B, where $p \geq 1$, $q_1 \leq q_2 \leq \ldots \leq q_p$, and $m \leq q_p$.

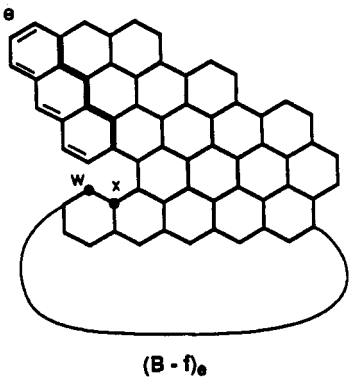


Figure 15. $(B-f)_e$.

Now we consider the following three cases based on the distribution of double bonds on the incident edges of the vertices w and x.

Case 1. The vertices w, x are incident with two parallel double bonds.

Then the distribution of double bonds on the common boundary of B_e^* and B_e' has two possibilities as shown in Figure 16. In Figure 16(1), one can find another minimal conjugated circuit of s in B_e which is contained in B_e^*, contradicting our assumption. In Figure 16(2), one can see that C is not minimal in B_e. This also contradicts our assumption.

Case 2. The vertices w, x are incident with two double bonds not parallel, say wy, xz (see Figure 17(1)).

Then the edges $f_2, f_3, \ldots, f_m$ must be single bonds, since they are fixed single bonds in B–w–x–y–z. Furthermore, each of them cannot be contained on C. Otherwise the segment on C from $wy\ldots$ to an end vertex u_i of some f_i ($i \geq 2$) next to f_i (single bond) would be an alternating path of double and single bonds with the end being double bonds. However, this is impossible, because w and u_i have the same color.

Hence $f_1 = xz$ must be on C, and C is a minimal conjugated circuit of s in $(B–f_2–f_3–\ldots–f_m)_e$ (see Figure 17 (2)). Then $(B–f_2–\ldots–f_m)_e^*$ is disconnected, and s can only belong to the upper component in Figure 17(2), say B_1 (otherwise, C would not be minimal). However, the common boundary of B_1 and $(B–f_2–\ldots f_m)_e'$ is similar to the cases in theorem 7 again, implying that C is not minimal in $(B–f_2–\ldots–f_m)_e$, a contradiction.

Case 3. The edge wx is a double bond (see Figure 18).

Then all of the edges $f_0, f_1, f_2, \ldots, f_m$ must be single bonds, since wx itself is double and $f_2, f_3, \ldots, f_m$ are fixed single bonds

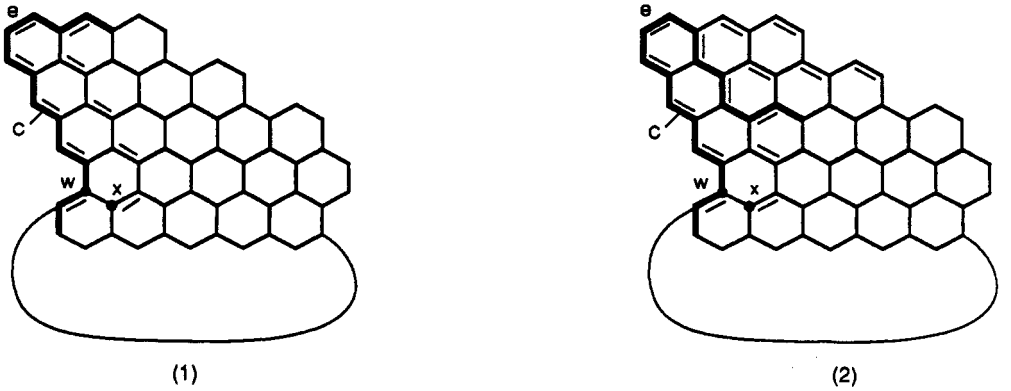
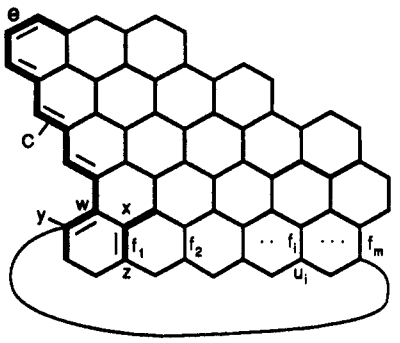
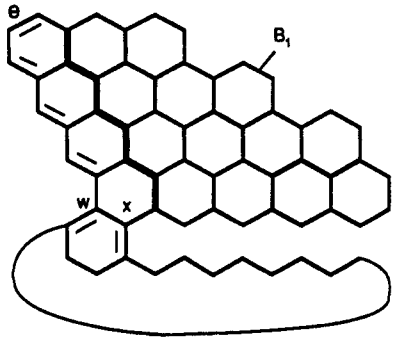


Figure 16. Distribution of double bonds on the incident edges of the vertices w and x.



(1) B_e



(2) $(B-f_2-\cdots-f_m)_e$

Figure 17. (1) B_e. (2) $(B-f_2-f_3 \ldots -f_m)$.

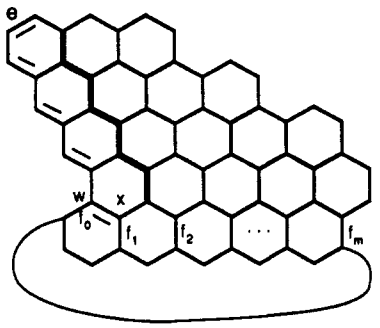
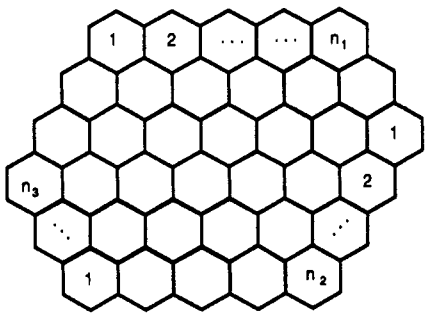


Figure 18.



$n_1, n_2, n_3 \geq 2$

Figure 19. $n_1, n_2, n_3 \geq 2$.

in B–w–x. In addition, each of $f_0, f_1, f_2, \ldots, f_m$ cannot be contained on C, and so C is restricted in the upper component of B–f_0–f_1–...–f_m. By a similar analysis as in the proof of theorem 7, C is not minimal in B_e. This contradiction completes our proof.

The conclusion of (2) follows from (1) immediately.

For BHs with a crown subgraph, we have not exhausted all possibilities of local structures of them so far. Some of them seem to contain no such local structures that satisfy the recursive relations in theorems 6–8. For example, the BHs shown in Figure 19 contain no edge fitting for expression 6. The recursive relations for enumeration of LM-conjugated circuits of the BHs with a crown subgraph but without the local structures shown in Figure 12 and Figure 14 need to be further investigated.

5. COMPUTATIONAL SCHEME FOR $R'(B_e)$ and $R'(B_{\hat{e}})$

In order to apply the recursive relation given in theorems 6–8, one needs to compute $R'(B_e)$ and $R'(B_{\hat{e}})$. By definition, they denote the contributions of all rings in B_e' and $B_{\hat{e}}'$ to $R(B_e)$ and $R(B_{\hat{e}})$, respectively. Procedure 1 may be used to obtain $R'(B_e)$ and $R'(B_{\hat{e}})$, but it still requires construction of all Kekule structures of B_e and $B_{\hat{e}}$. For any ring s in B_e' ($B_{\hat{e}}'$), one needs to find $K(B_e)$ ($K(B_{\hat{e}})$) minimal conjugated circuits of s, one for every Kekule structure of $B_e(B_{\hat{e}})$. This is also tedious. We therefore will investigate some additional properties of the minimal conjugated circuits of the rings in B_e' and $B_{\hat{e}}'$, from which an efficient method for computing $R'(B_e)$ and $R'(B_{\hat{e}})$ follows.

Lemma 3. Let $e = uv$ be an edge on the boundary of a benzenoid hydrocarbon B, and K_i a Kekule structure of B_e ($B_{\hat{e}}$). Let s be a ring in B_e' ($B_{\hat{e}}'$), and C a minimal K_i-conjugated circuit of s in B_e ($B_{\hat{e}}$). Then (1) C must contain the edge e. (2) C is a unique minimal K_i-conjugated circuit of s in B_e ($B_{\hat{e}}$).

Proof. (1) By the definition of B_e and $B_{\hat{e}}$, any ring s in B_e' ($B_{\hat{e}}'$) contains at least one edge which is a fixed bond in B–u–v (B–e). thus in B–u–v (B–e) there is no conjugated circuit whose interior contains the interior of s by theorem 6 in ref 21. This means that C must contain the edge e.

(2) Suppose there is a minimal K_i-conjugated circuit C' of s other than C in B_e ($B_{\hat{e}}$). By (1), e is contained in $C \cap C'$. Then e would be an interior edge in $B[C] \cap B[C']$ (see Figure 11), and so were in the interior of B, contradicting that e is on the boundary of B.

Theorem 9. Let e be an edge on the boundary of a benzenoid hydrocarbon B, and let $S_h(B_e')$ ($S_h(B_{\hat{e}}')$) be the set of rings in B_e' ($B_{\hat{e}}'$). Let $C_s(B_e)$ ($C_s(B_{\hat{e}})$) denote the set of minimal conjugated circuits of a ring s in B_e ($B_{\hat{e}}$). Then (1)

$$\text{for } s \in S_h(B_e'), \qquad R_s(B_e) = \sum_{C \in C_s(B_e)} K(B\text{–}C) R_{(|C|-2)/4}$$

$$\text{for } s \in S_h(B_{\hat{e}}'), \qquad R_s(B_{\hat{e}}) = \sum_{C \in C_s(B_{\hat{e}})} K(B\text{–}C) R_{(|C|-2)/4}$$

where $|C|$ denotes the length of C, $K(B$–$C)$ is the number of Kekule structures of B–C; (2)

$$R'(B_e) = \sum_{s \in S_h(B_e')} R_s(B_e) = \sum_{s \in S_h(B_e')} \sum_{C \in C_s(B_e)} K(B\text{–}C) R_{(|C|-2)/4}$$

$$R'(B_{\hat{e}}) = \sum_{s \in S_h(B_{\hat{e}}')} R_s(B_{\hat{e}}) = \sum_{s \in S_h(B_{\hat{e}}')} \sum_{C \in C_s(B_{\hat{e}})} K(B\text{–}C) R_{(|C|-2)/4}$$

Proof. (1) For $s \in S_h(B_e')$, let C be a minimal conjugated circuit of s in B_e. Then C corresponds to $K(B$–$C)$ Kekule structures of B_e for each of which, say K_i, C is a K_i-conjugated circuit. By lemma 3, C is a unique minimal conjugated circuit of s for the $K(B$–$C)$ Kekule structures of B_e. Thus C

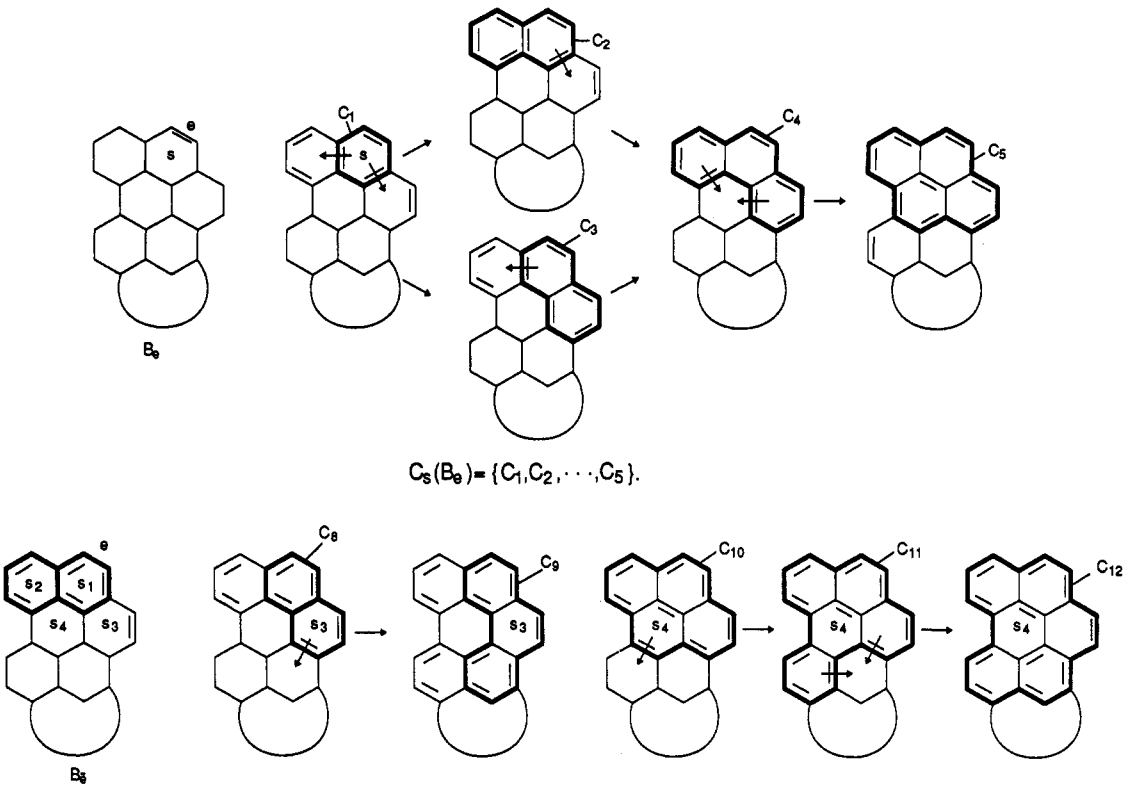


Figure 20. The arrows indicate the extendable hexagons.

contributes $K(B-C)R_{(|C|-2)/4}$ to $R_s(B_e)$, and so

$$R_s(B_e) = \sum_{C \in C_s(B_e)} K(B-C)R_{(|C|-2)/4}$$

For $s \in S_h(B_{\bar{e}}')$, by a similar argument, we have

$$R_s(B_{\bar{e}}) \sum_{C \in C_s(B_{\bar{e}})} K(B-C)R_{(|C|-2)/4}$$

Now (2) follows from (1).

Theorem 9 enables us to compute $R'(B_e)$ and $R'(B_{\bar{e}})$ by the Kekule structure counts for subgraphs of B. This completes our recursive method which is synthesized as follows:

Definition 5. Let e by an edge on the boundary of a benzenoid hydrocarbon B. If B and e satisfy the conditions in theorem 6, 7, or 8, then e is said to be a recursive edge of B.

Theorem 10. Let B be a BH which contains a recursive edge e on the boundary of B. Then

$$R(B) = B(B_e^*) + R(B_{\bar{e}}^*) + \sum_{C \in C_s(B_e)\, s \in S_h(B_e')} K(B-C)R_{(|C|-2)/4} + \sum_{C \in C_s(B_{\bar{e}})\, s \in S_h(B_{\bar{e}}')} K(B-C)R_{(|C|-2)/4} \quad (7)$$

Before concluding our paper, we will give a procedure for enumeration of all minimal conjugated circuits of a ring in $S_h(B_e')$ or $S_h(B_{\bar{e}}')$.

Definition 6. 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 $C \cap s' \neq \phi$ and the interior of s' is contained in the exterior of C. If $C' = C \Delta s'$ (the symmetry difference of edge sets of C and s') is also a minimal conjugated circuit of s, then we say C' is obtained from C by a extension and s' is a extendable hexagon of C.

For a ring s in B_e' ($B_{\bar{e}}'$), a minimal conjugated circuit C of s in B_e ($B_{\bar{e}}$) is said to be minimum if C has the smallest length and $B[C]$ contains a smallest number of hexagons.

Theorem 11. Let e be a recursive edge of a benzenoid hydrocarbon B, and let s be a ring in B_e' ($B_{\bar{e}}'$). Let C be a minimal conjugated circuit of s in B_e ($B_{\bar{e}}$) which is not minimum. Then C can be obtained from another minimal conjugated circuit of s in B_e ($B_{\bar{e}}$) by a extension.

Proof. Let K_i be a Kekule structure of B_e ($B_{\bar{e}}$) such that C is a K_i-conjugated circuit. Since C is not minimum, there is a minimum K_j-conjugated circuit C' of s in B_e ($B_{\bar{e}}$). $C \Delta C'$ consists of K_i (K_j)-conjugated circuits, and does not contain the edge e. For a K_i (K_j)-conjugated circuit C'' in $C \Delta C'$, the interior of C'' must be contained in the exterior of C' (since C' is minimum), and so contained in the interior of C. In $B[C']$ there is a ring s^* which is K_j-conjugated. By corollary 1, $s^* \cap C \neq \phi$. If we interchange single and double bonds of s^* to obtain another Kekule structure $K_1 = K_i \Delta s^*$, then $C^* = C \Delta s^*$ is a K_1-conjugated circuit containing the edge e. If C^* is not minimal, then there is a minimal K_1-conjugated circuit C^{**} of s. By lemma 3, C^{**} must also contain the edge e. However, then e is in $C^* \cap C^{**}$, and so e would be an interior edge of B, a contradiction. Hence C^* is a minimal K_1-conjugated circuit of s in B_e ($B_{\bar{e}}$), implying that C ($=C^* \Delta s^*$) can be obtained from a minimal conjugated circuit of s by a extension.

Procedure 2. Let e be a recursive edge of a benzenoid hydrocarbon B, and s a ring in B_e' ($B_{\bar{e}}'$). Let C^* be a unique minimum conjugated circuit of s in B_e ($B_{\bar{e}}$).

1. Set $S_0 = \{C^*\}$, $S_i = S_0$.
2. For every minimal conjugated circuit C_i in S_i, find all extendable hexagons of C_i, extend C_i to new minimal conjugated circuits, and set them to S_{i+1}.

3. If $S_{i+1} = 0$, then go to 4. Otherwise set $i + 1 \rightarrow i$, go to 2.

4. Set $C_s(B_e) = \cup_{j=1}^{i} S_j$ ($C_s(B_e) = \cup_{j=1}^{i} S_j$).

An example illustrating procedure 2 is given in Figure 20.

Using the above recursive method, we can deduce the recursive formulas for LMC-expressions of all catacondensed BHs and some families of large pericondensed BHs which will be reported in a continued paper of the present paper.

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