MATCH
Communications in Mathematical and in Computer Chemistry

MATCH Commun. Math. Comput. Chem. **60** (2008) 157-178

ISSN 0340 - 6253

Concealed non-Kekuléan single coronoid systems with $|H| \leq 15$ benzenoid rings [*]

Cui Yu and Rong Si Chen [†]

Center for Discrete Mathematics and Theoretical Computer Science,

Software College, Fuzhou University, Fuzhou, 350002, P.R.China

(Received: July 30, 2007)

Abstract

In this paper we prove that there is no concealed non-Kekuléan coronoid systems with $|H| \leq 14$ benzenoid rings. Moreover, we construct all the concealed non-Kekuléan coronoid systems with $|H| = 15$ benzenoid rings.

[*]Supported by Fujian Natural Science Foundation (2006J0206) and National Natural Science Foundation of China (10431020)

[†]Corresponding author, email address: chenrongsi@fzu.edu.cn

1. Introduction

A systematic search for concealed non-Kekuléan polyhexes [15] appears to have started in 1974 with Gutman [1], who stated that no concealed non-Kekuléan benzenoid systems with less than eleven hexagons can be constructed. Later, Hosoya [2], Cyvin and Gutman [3] depicted a set of eight concealed non-Kekuléan benzenoid systems, each of which has eleven hexagons (cf. Fig.5). In fact, the eight constructed concealed non-Kekuléan benzenoid systems are the only smallest concealed non-Kekuléan benzenoid systems. This was done by computer-generations and classifications of polyhexes conducted independently in the P.R.China and Norway, using entirely different principles in the programming [4]. Later, the same conclusion was reached by Zhang and Guo [5], who employed a graph-theoretical analysis. With the aid of computer programming W.C.He et al. [7] found that there are exactly 98 concealed non-Kekuléan benzenoid systems with 12 hexagons. The construction methods for concealed non-Kekuléan benzenoid systems with $|H| = 12$ and 13, respectively, were given by Guo and Zhang [8].

In this paper we confine ourselves to coronoid systems. we claim explicitly that there is no concealed non-Kekuléan coronoid systems with $|H| \leq 14$ benzenoid rings. Moreover, we construct all the concealed non-Kekuléan coronoid systems with $|H| = 15$ benzenoid rings.

2. Some definitions

A benzenoid system is a finite 2-connected plane graph with no cut vertices in which every interior face is a regular hexagon. A benzenoid system whose vertices are all on the perimeter is called a catacondensed benzenoid system; otherwise, pericondensed benzenoid system. let G be a benzenoid system and let P be a nonempty set of pairwise disjoint cycles in G which satisfies (i) each cycle in P contains no vertex on the boundary of G, (ii) no cycle in P contains another cycle in P in its interior, and (iii) the length of each cycle in P is greater than six. By deleting all the vertices and the edges of G in the interior of each cycle in P, a coronoid system is obtained. Let $P = C_1 \cup C_2 \cup \cdots \cup C_m$

($m \geq 1$). These cycles are called the inner boundaries of H. If H has exactly one inner boundary, H is called a single coronoid system; otherwise, a multiple coronoid system.

A polyhex is either a benzenoid system or a coronoid system. A polyhex H is a bipartite graph, so it has a bipartition (V_1, V_2) of its vertex set, where each of V_1 and V_2 is an independent vertex set. We usually color the vertices of V_1 and V_2 white and black, respectively. At this time, the bipartition is denoted by $(W(H), B(H))$.

A perfect matching of a graph H is a set of disjoint edges covering all vertices of H. Perfect matchings in polyhex graphs which are called Kekulé structures by chemists play a significant role in numerous chemical theories and the graphs with Kekulé structures are said to be Kekuléan.

It is known that each Kekuléan polyhex H has the same number of black and white vertices, i.e., $|W(H)| = |B(H)|$. However, this is not a sufficient condition for a polyhex to be Kekuléan. A polyhex H is called a concealed non-Kekuléan polyhex if it satisfies $|B(H)| = |W(H)|$ but has no perfect matching. In the following we use $|H|$ to designate the number of hexagons of H.

Let H be a polyhex. Denote by C_0 the outer boundary of H and by $C_1, C_2, \ldots, C_m$ the inner boundaries of H (if any).

Definition 1[9] A straight line segment P_1P_2 is called an elementary cut segment from C_i to C_j if

1. P_1 is the center of an edge e_1 on C_i and P_2 is the center of an edge e_2 on C_j;
2. P_1P_2 is orthogonal to both e_1 and e_2;
3. any point of P_1P_2 is either an interior or a boundary point of some hexagon of H.

Definition 2[9] A broken line segment P_1QP_2 is called a generalized cut segment from C_i to C_j if

1. P_1 is the center of an edge e_1 on C_i and P_2 is the center of an edge e_2 on C_j;
2. P_1Q and P_2Q are orthogonal to e_1 and e_2, respectively;
3. Q is the center of a hexagon of H, P_1Q and P_2Q form an angle of $\frac{\pi}{3}$ or $\frac{5\pi}{3}$;
4. any point of P_1QP_2 is either an interior or a boundary point of some hexagon of H.

A special cut segment is either an elementary cut segment or a generalized cut segment. A special edge-cut E_{ij} from C_i to C_j is the set of edges of H intersected by a special cut segment from C_i to C_j. E_{ij} is said to be of type I if $i = j$, otherwise it is said to be of type II. Two special edge-cuts are said to be disjoint if their corresponding special cut segments are disjoint.

Definition 3[10] Let $E = E_{i_1i_2} \cup E_{i_2i_3} \cup \cdots \cup E_{i_ri_1}$, where $E_{i_1i_2}$, $E_{i_2i_3}$, $\cdots$, $E_{i_ri_1}$ are r disjoint special edge-cuts of type II, $E_{i_ji_k}$corresponds to a special cut segment from C_{i_j} to C_{i_k} and $i_s \neq i_t$ if $s \neq t$. E is said to be a standard combination if the end vertices of the edges of E have the same color when they lie in the same component of $H - E$.

Suppose that S is a subset of the vertex set of H. The neighbor set $N(S)$ of S is the set of vertices which are not in S but adjacent to at least one vertex in S. By $< S \cup N(S) >$ we denote the induced subgraph of H, i.e., the subgraph of H whose vertex set is $S \cup N(S)$ and whose edge set is the set of those edges of H that have both end vertices in $S \cup N(S)$. Let H be a polyhex with $|W(H)| = |B(H)|$. Assume that E is a special edge-cut or a standard combination of H. Then the two components of $H - E$, say H_1 and H_2, satisfy: $H_1 =< B(H_1) \cup W(H_1) >, H_2 =< B(H_2) \cup W(H_2) >$, where $B(H) = B(H_1) \cup B(H_2)$, $W(H) = W(H_1) \cup W(H_2)$. Without loss of generality, we may assume that $B(H_1) = N(W(H_1))$, $W(H_2) = N(B(H_2))$. We set $d(E) = |B(H_1)| - |W(H_1)| = |W(H_2)| - |B(H_2)|$.

A coronoid system is primitive if its dualist graph is a cycle. Then the coronoid system is called a primitive coronoid system. If a primitive coronoid system can be obtained from H by deleting all the hexagons except those which have at least one vertex lying on the inner boundary of H, then we denote the primitive coronoid system by H^*. Denote by K the subgraph of H induced by the hexagons adjacent to the hexagons in H^*.

Definition 4 A single coronoid system H (see Fig.1) is said to be of type I if it satisfies:

1. a primitive coronoid system H^* can be obtained from H by deleting all the hexagons except those which have at least one vertex lying on the inner boundary of H;
2. K is a catacondensed benzenoid system whose dual graph is a straight line segment;
3. the hexagons in K incident with neither e_1 nor e_n.

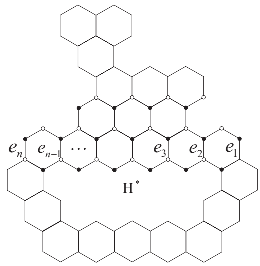


Fig.1 A single coronoid system of type I

Definition 5 A single coronoid system H (see Fig.2) is said to be of type II if it satisfies:

1. a primitive coronoid system H^* can be obtained from H by deleting all the hexagons except those which have at least one vertex lying on the inner boundary of H;
2. K is a catacondensed benzenoid system whose dual graph is a straight line segment;
3. e_1 is incident with some hexagon in K, but e_n is incident with no hexagon in K.

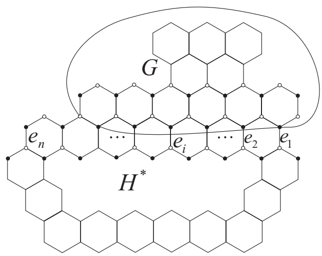


Fig.2 A single coronoid system of type II

Definition 6 A single coronoid system H (see Fig.3) is said to be of type III if it satisfies:

1. a primitive coronoid system H^* can be obtained from H by deleting all the hexagons except those which have at least one vertex lying on the inner boundary of H;
2. K is a catacondensed benzenoid system whose dual graph is a straight line segment;

3. there exist two hexagons in K incident with e_1 and e_n, respectively.

Definition 7 A single coronoid system H which is not of type I, type II or type III is said to be of type IV if a primitive coronoid system could be obtained from H by deleting all the hexagons except those which have at least one vertex lying on the inner boundary of H. A non-primitive single coronoid system which is not of type I, II, III or IV is said to be of type V.

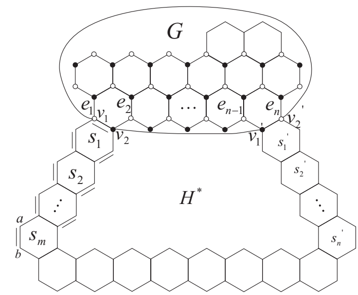


Fig.3 A single coronoid system of type III

If H is of type IV and on the outer perimeter of H^* there are some hexagons adjacent to some hexagons in H^*, then the dual graph of K isn't a straight line segment. If H is of type V, denote by H^{**} the coronoid system obtained by deleting all hexagons except those which have at least one vertex lying on the inner boundary of H, then H^{**} isn't a primitive coronoid system. The smallest single coronoid system of type V has 12 hexagons (see Fig.4).

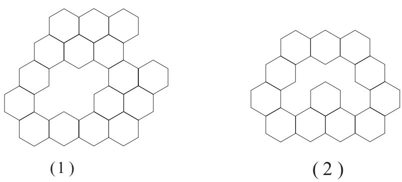


Fig.4 (1) A single coronoid system of type IV (2) A single coronoid system of type V

3. Some lemmas

Lemma 1[10] Let H be a single coronoid system. Then H is Kekuléan if and only if:

1. $|W(H)| = |B(H)|$;
2. $d(E) \geq 0$ for every special edge-cut E of type I and for every standard combination E of type II.

Lemma 2[5] For a concealed non-Kekuléan benzenoid system, it has at least 11 hexagons. There are exactly eight concealed non-Kekuléan benzenoid systems each of which has 11 hexagons (see Fig.5).

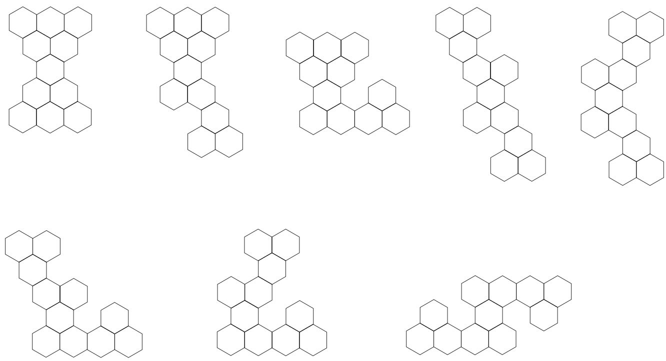


Fig.5 Eight smallest concealed non-Kekuléan benzenoids

Lemma 3[11] Let H be a bipartite graph with bipartition (X, Y). Then H contains a matching that saturates every vertex in X if and only if $|N(S)| \geq |S|$ for all $S \subseteq X$.

Lemma 4 Let H be a single coronoid system of type I. Then H is Kekuléan if and only if G is Kekuléan, where G is the subgraph of H induced by the hexagons which belong to neither H^* nor K (cf. Fig.1).

This lemma is obvious. In fact, if H is Kekuléan, it must be an essentially disconnected polyhex [10].

Lemma 5 Let H be a single coronoid system of type II. Then H is Kekuléan if and only if G is Kekuléan, where G is the subgraph of H induced by the hexagons of H which are not in H^* (cf. Fig.2).

Proof. Sufficiency is obvious.

Necessity: Assume that G is a non-Kekuléan benzenoid system. It is not difficult to see that $|W(G)| = |B(G)|$ (cf. Fig2). Then G is a concealed non-Kekuléan benzenoid system. By lemma 1 there exists a special edge-cut E of G such that $d(E) < 0$. By G_1 and G_2 denote the two components of $G - E$, where $G_1 =< B(G_1) \cup W(G_1) >$, $G_2 =< B(G_2) \cup W(G_2) >$. Without loss of generality, we may assume that $B(G_1) = N(W(G_1))$, $W(G_2) = N(B(G_2))$. Then $d(E) = |B(G_1)| - |W(G_1)| = |W(G_2)| - |B(G_2)|$. E can not be a special edge-cut of H since H is Kekuléan. Then there exists i such that $e_i^{'}$ or $e_i^{''}$ belongs to E (cf. Fig.6). Suppose that $e_i^{'}$ belongs to E. Let $E^{'} = E \cup e_1 \cup e_2 \cup \cdots \cup e_i$. Note that $E^{'}$ is an edge-cut of H which is not necessarily a special edge-cut of H. But $H - E^{'}$ consists of two components and one of them is just G_1. By lemma 3 we have $|N(W(G_1))| - |W(G_1)| = |B(G_1)| - |W(G_1)| \geq 0$ since H is Kekuléan . Then $d(E) \geq 0$, a contradiction. Now we suppose that $e_i^{''}$ belongs to E. Let $E^{'} = (E - e_i^{''}) \cup e_{i+2}^* \cup e_{i+3}^* \cup \cdots e_{k+1}^*$. Similarly, $E^{'}$ is an edge-cut of H which is not necessarily a special edge-cut of H. But $H - E^{'}$ consists of two components and one of them is just a subgraph of G_1, denoted by $H^{'}$ which satisfies $B(H^{'}) = N(W(H^{'}))$ and $|W(G_1) - W(H^{'})| = |B(G_1) - B(H^{'})|$. Then $|B(H^{'})| - |W(H^{'})| = (|B(G_1)| - |B(G_1) - B(H^{'})|) - (|W(G_1)| - |W(G_1) - W(H^{'})|) = |B(G_1)| - |W(G_1)| = d(E)$. Since H is a Kekuléan coronoid system, by lemma 3, we have $|B(H^{'})| - |W(H^{'})| \geq 0$. Then $d(E) \geq 0$, again a contradiction. Therefore, G is a Kekuléan benzenoid system. The necessity is thus proved.

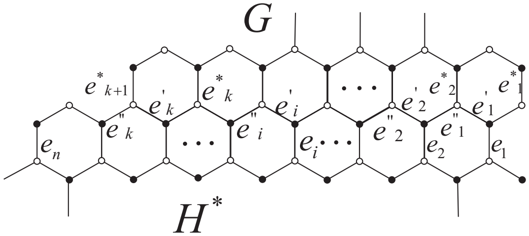


Fig.6 An illustration for the proof of lemma 5

Lemma 6 Let H be a single coronoid system of type III. Then H is Kekuléan if and only if G is Kekuléan, where G is the subgraph induced by the hexagons of $H\backslash H^*$ together with the hexagons incident with $H\backslash H^*$ (cf. Fig.3).

Proof. Sufficiency: Let M_1 be a Kekulé structure of G. Then v_1, v_2, v_1', v_2' are matched by the vertices in G. Since the subgraph induced by the hexagons s_1, $s_2, \cdots$, s_{m-1} is a linear catacondensed benzenoid system, denoted by P, it has a Kekulé structure M_2 (see Fig.3) such that $(v_1, v_2) \in M_2$. As $H\backslash(G \cup P \cup s_m)$ is a catacondensed benzenoid system, it has a Kekulé structure M_3 such that $(v_1', v_2') \in M_3$. Then $H\backslash G$ has a Kekulé structure $M_4 = M_2 \cup M_3 \cup (a, b)$ satisfying: $(v_1, v_2) \in M_4$ and $(v_1', v_2') \in M_4$. If either (v_1, v_2) or (v_1', v_2') belongs to M_1, without loss of generality, we may assume that $(v_1, v_2) \in M_1$, then $M = M_1 \cup M_4 - (v_1', v_2')$ is a Kekulé structure of H. If not, then $M = M_1 \cup M_4$ is a Kekulé structure of H.

The sufficiency is thus proved.

The proof of necessity is similar to that of necessity of lemma 5. We omit the details.

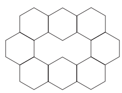


Fig.7 The smallest primitive coronoid system

By lemma 4, 5, 6, we know that if concealed non-Kekuléan single coronoid system H is of type I or type II or type III, then the corresponding subgraph G is a concealed non-Kekuléan benzenoid system. Since the smallest primitive coronoid system has 8 hexagons (Fig.7), by lemma 2, we can deduce that $|H| \geq 20$ or $|H| \geq 19$ or $|H| \geq 16$, respectively.

From the above, we find that if a single coronoid system H with $|H| \leq 15$ and $|W(H)| = |B(H)|$ is of type I or type II or type III, it is Kekuléan.

Immediately, we have:

Lemma 7 Let H be a single coronoid system of type I or type II or type III. Then H is Kekuléan if $|H| \leq 15$ and $|B(H)| = |W(H)|$.

By Lemma 1 any non-Kekuléan coronoid system H possesses a special edge-cut of type I or a standard combination E such that $d(E) < 0$. But it need not possess a special edge-cut of type I E such that $d(E) < 0$. Suppose that E is a special edge-cut of type I. By H_1 and H_2 denote the two components of $H - E$. It is evident that one of H_1 and H_2 contains no hexagon which has at least one vertex lying in the inner perimeter of H.

Lemma 8 Let H be a non-Kekuléan coronoid system of type IV with $|H| \leq 15$. If there exists a special edge-cut $E^{'}$ of type I satisfying $d(E^{'}) < 0$, then there must exist a special edge-cut E of type I satisfying:

1. $d(E) < 0$;
2. let H_1 be the component of $H - E$ that contains no hexagon which has at least one vertex lying in the inner perimeter of H; X be the set of the hexagons in H_1 . Then the subgraph $H[X]$ induced by the hexagons in X is connected.

Proof. For the special edge-cut $E^{'}$ of type I, if it also satisfies condition 2 in the lemma, then there is nothing to prove. Now suppose that condition 2 is not satisfied. Denote by $H_1^{'}$ and $H_2^{'}$ the two components of $H - E^{'}$, where $B(H_1^{'}) = N(W(H_1^{'}))$, $W(H_2^{'}) = N(B(H_2^{'}))$. Denote by Z, $X^{'}$ and $Y^{'}$ the sets of the hexagons of H, $H_1^{'}$ and $H_2^{'}$, respectively; by $T^{'}$ the set of the hexagons each of which has two edges belong to $E^{'}$. Suppose that $H[X^{'}]$ is disconnected. Let the number of the components of $H[X^{'}]$ be m. Denote by R_1, R_2, $\cdots$, R_m the sets of the hexagons of the components. Then $(|W(H[R_1])| - |B(H[R_1])|) + (|W(H[R_2])| - |B(H[R_2])|) + \ldots + (|W(H[R_m])| - |B(H[R_m])|) \geq |W(H_1^{'})| - |B(H_1^{'})| + m - 1 \geq m$ (cf. Fig.8). Let S be the set of the vertices belonging to the hexagons in $T^{'}$ but not belonging to $H_2^{'}$. Then $|B(S)| - |W(S)| = 1$. Since $d(E^{'}) = |W(H_2^{'})| - |B(H_2^{'})| < 0$, $|B(H[Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)])| - |W(H[Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)])| = (|B(H_2^{'})| + |B(S)|) - (|W(H_2^{'})| + |W(S)|) = |B(H_2^{'})| - |W(H_2^{'})| + 1 \geq 2$. Note that $H[Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)]$ is a coronoid system. Then if $H[Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)]$ could be obtained by adding one hexagon to a primitive coronoid system, then $||W(H[Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)])| - |B(H[Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)])|| \leq 1$, a contradiction. Therefore, in order to obtain the coronoid system $H[Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)]$, at least two hexagons must be added, i.e., $|Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)| \geq 10$. We claim that $m \leq 2$. Otherwise, if there exists a natural number i $(1 \leq i \leq m)$ such that $|W(H[R_i])| - |B(H[R_i])| > 1$, then $|R_i| \geq 6$ (cf. the proof of Theorem 3 in [5]). Together with $|R_j| \geq 1$ $(j \neq i)$, we have

$|H| = |Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)| + |R_1 \cup R_2 \cup \cdots \cup R_{i-1} \cup R_{i+1} \cup \cdots \cup R_m| + |R_i| \geq 10+2+6 = 18$, a contradiction. Then all the m benzenoid systems satisfy $|W(H[R_i])| - |B(H[R_i])| = 1$. Hence $|R_i| \geq 3$. Therefore, $|H| = |Z\backslash(R_1 \cup R_2 \cup \cdots \cup R_m)| + 3 \times m \geq 10 + 3 \times 3 = 19$, again a contradiction.

Since $H[X^{'}]$ is disconnected, there exists v_0, v_1, v_2, $\cdots$, v_k belonging to the hexagons in T (cf. Fig.8). Let $H_1 =< B(H_1) \cup W(H_1) >$, $H_2 =< B(H_2) \cup W(H_2) >$, where $B(H_1) = N(W(H_1))$, $W(H_2) = N(B(H_2))$.

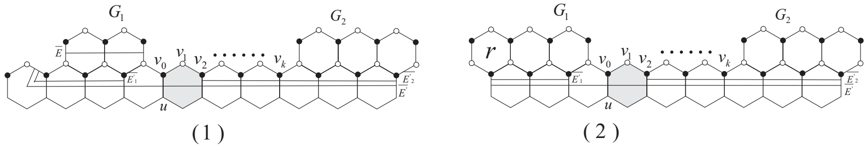


Fig.8 $H[X]$ consists of two components and E is a special edge-cut.

Suppose that $k > 0$. Delete v_0, v_1 together with their incident edges from $H_1^{'}$. Let $\bar{E}'$ be the special cut segment corresponding to $E^{'}$. Then $\bar{E}'$ is divided into two segments $\bar{E}_1'$ and $\bar{E}_2'$. Let $E_1^{'}$ and $E_2^{'}$ be the edge-cuts corresponding to $\bar{E}_1'$ and $\bar{E}_2'$, respectively. Note that $d(E^{'}) = |B(H_1^{'})| - |W(H_1^{'})| < 0$. Then $|W(H_1^{'})| - |B(H_1^{'})| = (|W(G_1)| - |B(G_1)|) + (|W(G_2)| - |B(G_2)|) > 0$, where G_1, G_2 are the two components of $H_1^{'} - v_0 - v_1$. It is easy to see that there exists at least one component satisfying $|W(G_i)| - |B(G_i)| > 0$ $(i = 1, 2)$ $\cdots\cdots$ (*).

Suppose that $|W(G_2)| - |B(G_2)| > 0$. No matter $\bar{E}'$ is an elementary cut segment or a generalized cut segment, $E = E_2^{'} \cup (v_1, v_2)$ is a special edge-cut such that $d(E) < 0$ and $H[X]$ is connected.

Now suppose that $|W(G_1)| - |B(G_1)| > 0$. We distinguish two cases:

Case 1. $\bar{E}'$ is a generalized cut segment (cf. Fig.8(1)). Then an elementary cut segment $\bar{E}$ will be obtained (cf. Fig.8(1)). Denoted by T the set of the hexagons each of which has two edges belong to E, where E is the elementary edge-cut corresponding to $\bar{E}$. It is obvious that $H[Y]$ is a coronoid system but not a primitive coronoid system. Then $H[Y]$ is connected and $|Y| \geq 9$. It is evident that $d(E) = |B(H_1)| - |W(H_1)| = |B(G_1)| - |W(G_1)| < 0$. We claim that $H[X]$ is connected. Otherwise, there exists at least one edge in E incident with no hexagon in X and $|T'| \geq 2$. Then $|W(H[X])| - |B(H[X])| \geq |W(H_1)| - |B(H_1)| + 1 \geq 2$. Thus $|X| \geq 6$. On the other hand, $|X| = |H| - |Y| - |T'| \leq 15 - 9 - 2 = 4$, a contradiction.

Case 2. $\bar{E}'$ is an elementary cut segment (cf. Fig.8(2)). If hexagon r doesn't exist, the proof is quite similar to the case when $\bar{E}'$ is a generalized cut segment. In the following, we assume that hexagon r belongs to H_1'. Then all the edges in E_1' are incident with some hexagons in G_1. i.e., $G_1 = H[R_1]$. Since S is the set of the vertices belonging to the hexagons in T but not belonging to H_2', $|W(S)| - |B(S)| = -1$. Note that $|B(H_2')| - |W(H_2')| = |W(H_1')| - |B(H_1')| > 0$. Then $|B(H[Z \backslash (R_1 \cup R_2)])| - |W(H[Z \backslash (R_1 \cup R_2)])| = (|B(S)| + |B(H_2')|) - (|W(S)| + |W(H_2')|) = (|B(H_2')| - |W(H_2')|) + 1 \geq 2$. Note that $H[Z \backslash (R_1 \cup R_2)]$ is a coronoid system. If $H[Z \backslash (R_1 \cup R_2)]$ is a coronoid system obtained by adding one hexagon to a primitive coronoid system, then $||W(H[Z \backslash (R_1 \cup R_2)])| - |B(H[Z \backslash (R_1 \cup R_2)])|| \leq 1$, a contradiction. Therefore, in order to obtain the coronoid system $H[Z \backslash (R_1 \cup R_2)]$, at least two hexagons must be added, i.e., $|Z \backslash (R_1 \cup R_2)| \geq 10$. If $|W(G_1)| - |B(G_1)| = 1$, then $|R_1| \geq 3$ and $|W(H_1')| - |B(H_1')| = (|W(G_1)| - |B(G_1)|) + (|W(G_2)| - |B(G_2)|) = 1 + (|W(G_2)| - |B(G_2)|) > 0$. Bear in mind that $|W(G_2)| - |B(G_2)| \leq 0$. Then $|W(G_2)| - |B(G_2)| = 0$. Thus $|R_2| \geq 3$. Therefore, $|H| = |Z \backslash (R_1 \cup R_2)| + |R_1| + |R_2| \geq 10 + 3 + 3 = 16$, a contradiction. If $|W(G_1)| - |B(G_1)| \geq 2$, then $|R_1| \geq 6$. Together with $|R_2| \geq 1$, we have $|H| \geq 10 + 6 + 1 = 17$, again a contradiction. In other words, if G_1 satisfies $|W(G_1)| - |B(G_1)| > 0$, then $|H| \geq 16$, a contradiction.

Now suppose that $k = 0$. Delete v_0 together with their incident edges from H_1'. Then $\bar{E}'$ is divided into two segments $\bar{E}_1'$ and $\bar{E}_2'$. $|W(H_1')| - |B(H_1')| = (|W(G_1)| - |B(G_1)|) + (|W(G_2)| - |B(G_2)|) - 1 > 0$, where G_1 and G_2 are the two components of $H_1' - v_0$. We have $(|W(G_1)| - |B(G_1)|) + (|W(G_2)| - |B(G_2)|) > 1$. It is easy to see that there exists at least one component satisfying $|W(G_i)| - |B(G_i)| > 1$ ($i = 1, 2$). Otherwise both of the two components have: $|W(G_i)| - |B(G_i)| = 1$. Then $|R_1| \geq 3$, $|R_2| \geq 3$. $|B(H_2')| - |W(H_2')| = |W(H_1')| - |B(H_1')| = (|W(G_1)| - |B(G_1)|) + (|W(G_2)| - |B(G_2)|) - 1 = 1$. By a similar reasoning as above, we have $|W(H[Z\backslash(R_1 \bigcup R_2)])| - |B(H[Z\backslash(R_1 \bigcup R_2)])| = |B(H_2^{'})| - |W(H_2^{'})| + 1 = 2$. Then $|Z\backslash(R_1 \bigcup R_2)| \geq 10$. Thus $|H| = |Z\backslash(R_1 \bigcup R_2)| + |R_1| + |R_2| \geq 10 + 3 + 3 = 16$, a contradiction. Suppose that $|W(G_2)| - |B(G_2)| > 1$. The proof is quite similar to that for the case $k > 0$ and $|W(G_2)| - |B(G_2)| > 0$. Now suppose that $|W(G_1)| - |B(G_1)| > 1$. If $E^{'}$ is a generalized edge-cut, then by a similar reasoning as in the proof for $k > 0$ and $|W(G_1)| - |B(G_1)| > 0$, an elementary edge-cut E is obtained which satisfies conditions 1 and 2. If $E^{'}$ is an elementary edge-cut, then let $E = E_1^{'} \cup (v_0, u) \cup (v_0, v_1)$. It is obvious that E is a generalized edge-cut satisfying conditions 1 and 2.

This Lemma is thus proved.

4. Main results

Theorem 1 Let H be a coronoid system with $|H| \leq 14$. Then H is a Kekuléan coronoid system if and only if $|B(H)| = |W(H)|$.

Proof. Necessity is obvious.

Sufficiency: Since the smallest concealed non-Kekuléan multiple coronoid system has 17 hexagons [13], concealed non-Kekuléan coronoid systems with $|H| \leq 14$ must be single coronoid systems. If H is a coronoid system of type I or type II or type III satisfying $|W(H)| = |B(H)|$ and $|H| \leq 14$, then H is Kekuléan (Lemma 7). So in the following we need only to consider single coronoid systems of type IV and type V.

Assume that H is a concealed non-Kekuléan coronoid system. By Lemma 1 there exists a special edge-cut of type I or a standard combination E such that $d(E) < 0$. Denote the two components of $H - E$ by H_1 and H_2, respectively; where $H_1 =< W(H_1) \cup B(H_1) >$, $H_2 =< W(H_2) \cup B(H_2) >$. Without loss of generality, we may assume that $B(H_1) = N(W(H_1))$, $W(H_2) = N(B(H_2))$. Then $d(E) = |B(H_1)| - |W(H_1)| < 0$. Let X, Y, Z be the sets of the hexagons in H_1, H_2 and H, respectively. Then $T = Z\backslash(X \cup Y)$ is the set of the hexagons each of which has two edges belong to E.

Now we distinguish two cases.

Case 1: E is a standard combination. Let $E = E^1 \cup E^2$, where both of E^1 and E^2 are special edge-cuts of type II. Then $|T| \geq 2$. Thus $|X| + |Y| = |H| - |T| \leq 14 - 2 = 12$.

Without loss of generality, we may assume that $|X| \leq |Y|$. Then $|X| \leq 6$. Bear in mind that $|W(H_1)| - |B(H_1)| > 0$. If all the edges in E are incident with some hexagons in H_1, then $H_1 = H[X]$ and $|W(H_1)| - |B(H_1)| = |W(H[X])| - |B(H[X])| \geq 1$. If at least one edge in E is not incident with any hexagon in H_1, then $|W(H[X])| - |B(H[X])| \geq |W(H_1)| - |B(H_1)| + 1 \geq 2$. Thus we conclude that $|W(H[X])| - |B(H[X])| \geq 1$.

Suppose that all the edges in E are not parallel. Firstly, we consider the case: all the edges in E are incident with some hexagons in X. We claim that $|E^1| = 2$ and $|E^2| = 2$. Otherwise, without loss of generality, we may assume that $|E^1| > 2$. Note that $|W(H[X])| - |B(H[X])| \geq 1$ and $|X| \leq 6$. We deduce that $|E^1| = 3$ and $|E^2| = 2$ (cf. Fig.9). Then there exists one edge in E^2 incident with no hexagon in X , contradicting our assumption. Therefore, $|E^1| = 2$. Similarly, $|E^2| = 2$. It is evident that there are 4 white vertices and 2 black vertices of the hexagons in T which are not in H_1. Then $|W(H[X \cup T])| - |B(H[X \cup T])| = (|W(H_1)| + 4) - (|B(H_1)| + 2) \geq 3$. By our assumption, all the edges in E are incident with some hexagons in X. Then the smallest $H[X \cup T]$ must be one of the graphs as shown in Fig.10. It is easy to see that $|X \cup T| \geq 9$. Note that $|E^1| = |E^2| = 2$ and $|T| = 2$. Thus $|X| \geq 9 - 2 = 7$, contradicting that $|X| \leq 6$. Now we consider the case: there exists at least one edge in E incident with no hexagon in X. Then $|W(H[X])| - |B(H[X])| \geq |W(H_1)| - |B(H_1)| + 1 \geq 2$. Thus $|X| \geq 6$. Combining with $|X| \leq 6$, we have $|X| = 6$. Then $|E^1| = |E^2| = 2$. $H[X]$ must be one of the graphs as shown in Fig.11. Thus $|W(H_1)| - |B(H_1)| = 0$, again a contradiction.

Now suppose that all the edges in E are parallel each other. Note that $|E| \geq 4$. Firstly, we consider the case $|E| = 4$, which implies that $|E^1| = |E^2| = 2$. If all the edges in E are incident with some hexagons in X, then $H[X] = H_1$. Thus $|W(H[X])| - |B(H[X])| \geq 1$. We have $|X| \geq 5$. Bear in mind that $|X| \leq 6$. Then $5 \leq |X| \leq 6$. We deduce that $H[X]$ must be one of the graphs as shown in Fig.12. It is obvious that there exists no special edge-cut E^2 of H such that all the edges in E^2 are parallel to all the edges in E^1 and all the edges in E^2 are incident with some hexagons in X, a contradiction. If there exists at least one edge in E incident with no hexagon in X, then $|W(H[X])| - |B(H[X])| \geq 2$. $H[Z \backslash Y]$ must be one of the graphs as shown in Fig.13, which implies that $|W(H_1)| - |B(H_1)| = 0$, contradicting that $|W(H_1)| - |B(H_1)| > 0$. Now we consider the case $|E| \geq 5$. Then

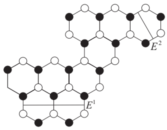


Fig.9 $H[X]$ satisfies: $|W(H[X])| - |B(H[X])| \geq 1$, $|X| \leq 6$ and $|E^1| = 3$.

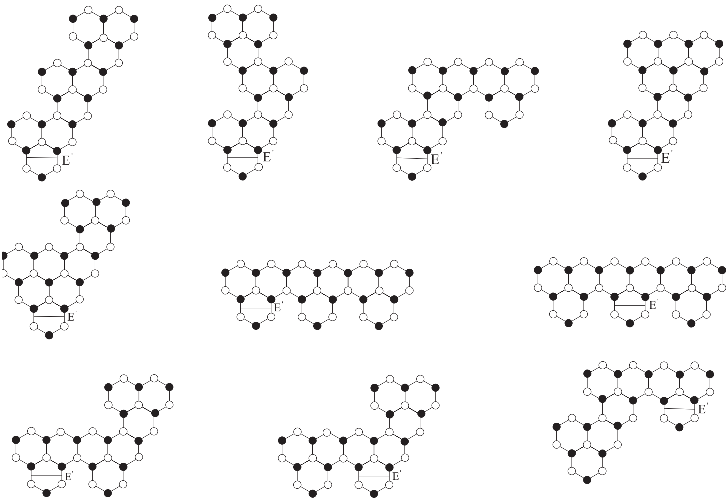


Fig.10 The smallest $H[X \cup T]$ satisfying: all the edges in E are incident with some hexagons in X and $|W(H[X \cup T])| - |B(H[X \cup T])| \geq 3$, where E is a standard combination and $|T| = 2$.

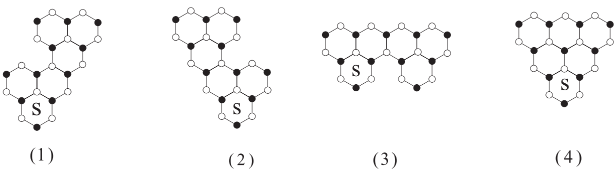


Fig.11 $H[X]$ satisfies: $|W(H[X])| - |B(H[X])| \geq 2$ and $|X| = 6$.

$|T| \geq 3$. Thus $|X| + |Y| = |H| - |T| \leq 14 - 3 = 11$. Bear in mind that $|X| \leq |Y|$, we have $|X| \leq 5$. All the edges in E must be incident with some hexagons in X. Otherwise,

$|W(H[X])| - |B(H[X])| \geq |W(H_1)| - |B(H_1)| + 1 \geq 2$. Then $|X| \geq 6$, a contradiction. Thus $|X| = 5$, $|E| = 5$. Therefore, $|W(H_1)| - |B(H_1)| = 0$, again a contradiction.

Therefore, E can not be a standard combination.

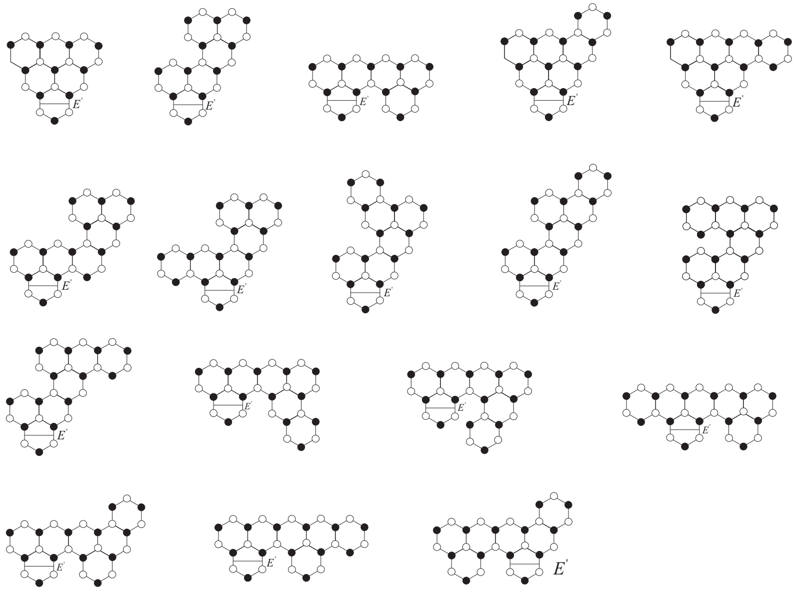


Fig.12 $H[X]$ satisfies: $|W(H[X])| - |B(H[X])| \geq 1$, $5 \leq |X| \leq 6$ and all the edges in E^1 are incident with some hexagons in X, where $|E^1| = 2$.

Fig.13 There exists at least one edge in E incident with no hexagon in X and $|X| = 6$.

Case 2: E is a special edge-cut.

Subcase 2.1: H is of type IV. By lemma 8, we may suppose that $H[X]$ is connected.

Subcase 2.1.1: There are some hexagons in T belonging to H^*, where H^* is obtained by deleting all the hexagons except those which has at least one vertex lying on the inner boundary of H. Since $H[Z \backslash X]$ is a coronoid system, $|Z \backslash X| \geq 8$. If $|Z \backslash X| = 8$, then $H[Z\backslash X]$ is the smallest primitive coronoid system and H must be of type I or II or III, contradicting that H is of type IV. Thus $|Z\backslash X| \geq 9$. As $|H| \leq 14$, then $|X| = |H| - |Z\backslash X| \leq 14 - 9 = 5$. Similarly, E must be an elementary edge-cut and there must exist $|E|$ hexagons in X incident with the edges in E. It is not difficult to see that $|E| \geq 3$. Then $|X| - |E| \leq 5 - 3 = 2$. Thus $|W(H_1)| - |B(H_1)| \leq 0$, again a contradiction.

Subcase 2.1.2: There is no hexagon in T belonging to H^*. Then $|Y| \geq 9$. Otherwise H must be of type I or type II or type III, a contradiction. $|X| = |H| - |Y| - |T| \leq 14 - 9 - 1 = 4$. Similarly, all the edges in E must be incident with some hexagons in X. It is easy to see that $|E| \geq 2$. Then $|X| - |E| \leq 4 - 2 = 2$. Thus $|W(H_1)| - |B(H_1)| \leq 0$, again a contradiction. Consequently, H can not be of type IV.

Subcase 2.2: H is of type V. Since the smallest coronoid system of type V has 12 hexagons, i.e., $|Z\backslash X| \geq 12$, $|X| \leq |H| - |Z\backslash X| = 14 - 12 = 2$. If $|E| > 2$, there exists at least one edge in E which is incident with no hexagon in X. Then $|W(H[X])| - |B(H[X])| \geq 2$, $|X| \geq 6$, a contradiction. Thus $|E| = 2$. Combining with $|X| \leq 2$, we have $|W(H_1)| - |B(H_1)| \leq 0$, which contradicts that $|W(H_1)| - |B(H_1)| > 0$.

The theorem is thus proved.

Theorem 2 There are exactly 23 concealed non-Kekuléan coronoid systems each of which has 15 hexagons.

Proof. Suppose that H is a concealed non-Kekuléan coronoid system with $|H| = 15$. Then H must be a single coronoid system. By lemma 7 H can not be of type I or type II or type III. So in the following we need only to consider the coronoid systems of type IV and type V. By lemma 1 there exists a special edge-cut or a standard combination E such that $d(E) < 0$. Let the two components of $H - E$ be H_1 and H_2, where $H_1 =< W(H_1) \cup B(H_1) >$, $H_2 =< W(H_2) \cup B(H_2) >$. Without loss of generality, we may assume that $B(H_1) = N(W(H_1))$, $W(H_2) = N(B(H_2))$. Then $d(E) = |B(H_1)| - |W(H_1)| < 0$. Let X, Y, Z be the sets of the hexagons in H_1, H_2 and H, respectively. Then $T = Z\backslash(X \cup Y)$ is the set of the hexagons each of which has two edges in E.

We distinguish two cases.

Case 1. E is a standard combination. Let $E = E^1 \bigcup E^2$, where both of E^1 and E^2

are special edge-cuts of type II. By a similar reasoning as in the proof of theorem 1, we have $|W(H[X])| - |B(H[X])| \geq 1$, $|X| + |Y| \leq 15 - 2 = 13$. Without loss of generality, we may assume that $|X| \leq |Y|$. Then $|X| \leq 6$.

Suppose that all the edges in E are not parallel. If all the edges in E are incident with some hexagons in X, by a similar reasoning as in the proof of theorem 1, we deduce that H does not exist. If there exists at least one edge in E incident with no hexagon in X, by a similar reasoning as in the proof of theorem 1, we come to the conclusion that $|X| = 6$ and $H[X]$ must be one of the graphs as shown in Fig.12. Then $4 \leq |E| \leq 5$. Thus $|W(H_1)| - |B(H_1)| \leq 0$, a contradiction.

Now we suppose that all the edges in E are parallel each other. Note that $|E| \geq 4$. Firstly, we consider the case $|E| = 4$, which implies that $|E^1| = |E^2| = 2$. By a similar reasoning as in the proof of theorem 1, H doesn't exist. Now we consider the case $|E| \geq 5$. If all the edges in E are incident with some hexagons in X, then $|X| \geq 5$. Note that $|X| \leq 6$. Therefore, $|X| = 5$ or $|X| = 6$. We have $|W(H_1)| - |B(H_1)| \leq 0$, a contradiction. Hence, there exists at least one edge in E incident with no hexagon in X. Then $|W(H[X])| - |B(H[X])| \geq 2$ and $|X| \geq 6$. Together with $|X| \leq 6$, we have $|X| = 6$. $H[Z \backslash Y]$ must be as shown in Fig.14, which implies that $|W(H_1)| - |B(H_1)| < 0$, again a contradiction.

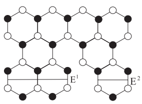


Fig.14 An illustration for case 1 of the proof of Theorem 2

Therefore, E can not be a standard combination.

Case 2: E is a special edge-cut.

Subcase 2.1: H is of type IV. By lemma 8, we may suppose that $H[X]$ is connected.

Subcase 2.1.1: There are some hexagons in T belonging to H^*. Since $H[Z \backslash X]$ is a coronoid system, by a similar reasoning as in the proof of theorem 1, we have $|Z \backslash X| \geq 9$. Then $|X| = |H| - |Z \backslash X| \leq 15 - 9 = 6$.

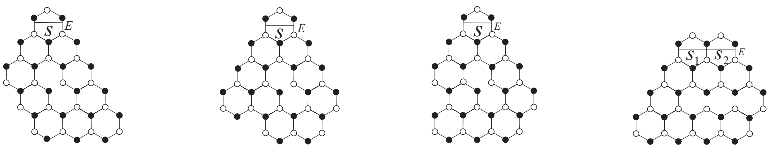
Suppose that there exists at least one edge in E incident with no hexagon in X. Then $|W(H[X])| - |B(H[X])| \geq |W(H_1)| - |B(H_1)| + 1 \geq 2$. Thus $|X| \geq 6$. Combining with $|X| \leq 6$, we have $|X| = 6$. Therefore $|Z\backslash X| = |H| - |X| = 9$ and $H[X]$ must be one of the graphs as shown in Fig.12. Thus $|W(H[X])| - |B(H[X])| = 2$. $H[Z\backslash X]$ is not a primitive coronoid system. Otherwise H is of type I or II or III, a contradiction. Together with $|Z\backslash X| = 9$, H^* must be the smallest primitive coronoid system (as shown in Fig.7). Then $H[Z\backslash X]$ must be obtained by adding one hexagon to H^*. Thus $||W(H[Z\backslash X])| - |B(H[Z\backslash X])|| \leq 1$. From Fig.12, we conclude that there are at most two hexagons in T adjacent to some hexagon in X. If there is only one hexagon in T adjacent to some hexagon in X, then $|W(H)| - |B(H)| = (|W(H[X])| + |W(H[Z\backslash X])| - 1) - (|B(H[X])| + |B(H[Z\backslash X])| - 1) = (|W(H[X])| - |B(H[X])|) + (|W(H[Z\backslash X])| - |B(H[Z\backslash X])) = 2 + (W(H[Z\backslash X]) - B(H[Z\backslash X])|) \neq 0$, a contradiction. If there are two hexagons in T adjacent to some hexagon in X, then there are at least two edges in E incident with no hexagon in X such that $|W(H_1)| - |B(H_1)| = 0$, again a contradiction.

Now suppose that all the edges in E are incident with some hexagons in X. Since there are some hexagons in T belonging to H^*, $|E| \geq 3$. Note that $|X| \leq 6$. If $|E| > 3$, then $|W(H_1)| - |B(H_1)| \leq 0$, a contradiction. Then $|E| = 3$ and $H[X]$ must be as shown in Fig.10. Thus $|X| = 6$, $|W(H[X])| - |B(H[X])| = 1$. $|Z\backslash X| = |H| - |X| = 9$. By a similar reasoning as above, we have $||W(H[Z\backslash X])| - |B(H[Z\backslash X])|| \leq 1$. Then $|W(H)| - |B(H)| = (|W(H[X])| + |W(H[Z\backslash X])| - 2) - (|B(H[X])| + |B(H[Z\backslash X])| - 3) = 2 + |W(H[Z\backslash X])| - |B(H[Z\backslash X])| \neq 0$, again a contradiction.

Subcase 2.1.2: There is no hexagon in T belonging to H^*. Then $|E| \geq 2$ and $|T| \geq 1$. Similarly, $H[Y]$ isn't a primitive coronoid system. $|Y| \geq 9$. $|X| = |H| - |Y| - |T| \leq 15 - 9 - 1 = 5$. Thus E must be an elementary edge-cut and there are $|E|$ hexagons in X incident with the edges in E. We claim that $|E| = 2$. Otherwise $|W(H_1)| - |B(H_1)| \leq 0$, a contradiction. Bear in mind $|W(H_1)| - |B(H_1)| > 0$. Then $|W(H[Z\backslash Y])| - |B(H[Z\backslash Y])| = (|W(H_1)| + 2) - (|B(H_1)| + 1) \geq 2$. Thus $|Z\backslash Y| \geq 6$. On the other hand, $|Z\backslash Y| = |H| - |Y| \leq 15 - 9 = 6$. Then $|Z\backslash Y| = 6$. $H[Z\backslash Y]$ is one of the graphs as shown in Fig.12. It is easy to see that all the edges in E are incident with some hexagon in H_1 and $|W(H[X])| - |B(H[X])| = 1$. $|Y| = |H| - |Z\backslash Y| = 9$. Since $H[Y]$ is not a primitive coronoid system, $H[Y]$ must be obtained by adding one hexagon to the smallest coronoid system. Then $||W(H[Y])|-|B(H[Y])|| \leq 1$. We claim that all the edges in E are incident with some hexagons in Y. Otherwise $|W(H)| - |B(H)| = (|W(H[X])| - |B(H[X])|) + (|W(H[Y])| - |B(H[Y])|) + 1 = 2 + |W(H[Y])| - |B(H[Y])| \neq 0$, contradicting that $|W(H)| = |B(H)|$. Then $|W(H)| - |B(H)| = (|W(H[X])| - |B(H[X])|) + (|W(H[Y])| - |B(H[Y])|) = 1 + (|W(H[Y])| - |B(H[Y])|) = 0$, Thus $|W(H[Y])| - |B(H[Y])| = -1$. $H[Z\backslash X]$ must be one of the graphs as shown in Fig.15. Since $H[Z\backslash Y]$ is one of the graphs as shown in Fig.11, it is easy to see that if $H[Z\backslash X]$ is as shown in Fig.15(1), (2), (3), there are 5 concealed non-Kekuléan coronoid systems, respectively, if $H[Z\backslash X]$ is as shown in Fig.16(4) no matter exists s_1 or s_2, there are 4 concealed non-Kekuléan coronoid systems, respectively. Then the number of concealed non-Kekuléan coronoid systems with $|H| = 15$ is just $3 \times 5 + 4 \times 2 = 23$. All the concealed non-Kekuléan coronoid systems with $|H| = 15$ are shown in Fig.16.

Subcase 2.2: H is of type V. $|E| \geq 2$. Since $H[Z\backslash X]$ is a non-primitive coronoid system , $|Z\backslash X| \geq 12$ (cf. Fig.4(2)). $|X| = |H| - |Z\backslash X| \leq 15 - 12 = 3$. If there exists at least one edge in E incident with no hexagon in X, then $|X| \geq 6$, a contradiction.
If not, then $|E| = 2$ or $|E| = 3$. Thus $|W(H_1)| - |B(H_1)| \leq 0$, again a contradiction.

The theorem is thus proved.



(1) (2) (3) (4)

Fig.15 4 coronoid systems satisfying $|W(H[Y])| - |B(H[Y])| = -1$

Remark: Under the assumption that the smallest concealed non-Kekuléan coronoid systems must be a single coronoid system each of which contains a naphthalenic hole (consisting of two hexagons), the authors in [13] depicted 23 concealed non-Kekuléan coronoid systems by computer-generations (cf. Fig.16). They thought all the concealed non-Kekuléan coronoid systems with a naphthalenic hole and $|H| = 15$ are generated by (1) adding one hexagon at a time to the 22154 systems with a naphthalenic hole satisfying $|H| = 14$ and $|W(H)| = |B(H)|$, using the one-, three- and five-contact additions, and (2) adding one hexagon at a time to the 26919 systems with a naphthalenic hole satisfying $|H| = 14$ and $||W(H)| - |B(H)|| = 1$, using the two- and four-contact additions. After sifting they obtained 23 concealed non-Kekuléan coronoid systems. But no one claimed explicitly that the constructed 23 systems with a naphthalenic hole are the only smallest concealed non-Kekuléan coronoid systems.

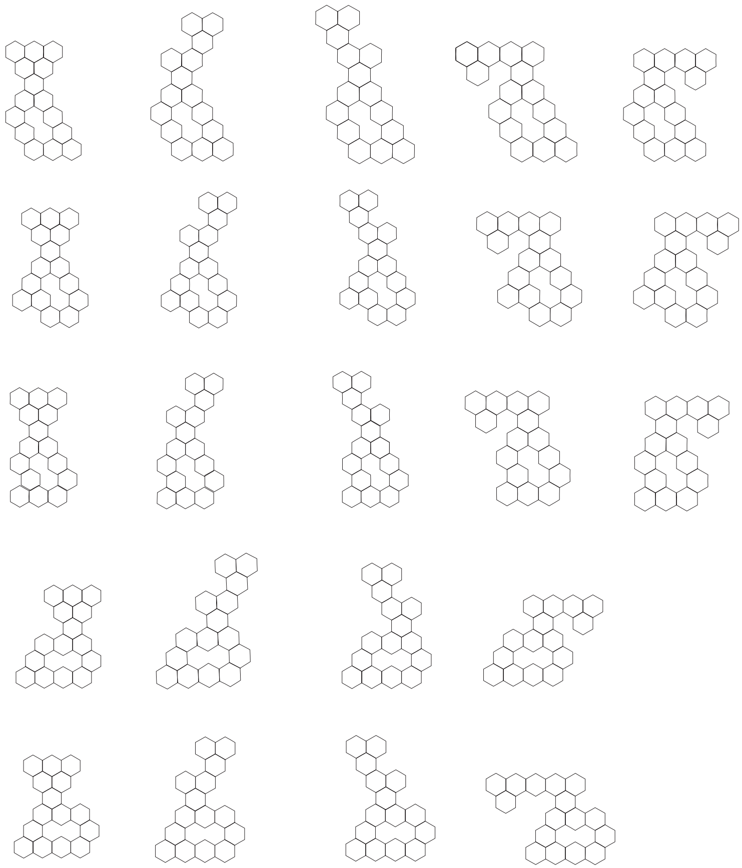


Fig.16 23 concealed Non-Kekuléan coronoid systems (each has 15 hexagons).

References

[1] I. Gutman, *Croat. Chem. Acta* 46 (1974) 209-215.

[2] H.Hosoya, *Croat. Chem. Acta* 59 (1986) 583-590.

[3] S.J.Cyvin and I.Gutman, *J. Mol. Struc. (THEOCHEM)* 150 (1987) 157-169.

[4] W.C.He, W.J.He, B.N.Cyvin, S.J.Cyvin and J.Brunvoll, *MATCH Commun. Math. Comput. Chem.* 22 (1987) 105-109.

[5] FJ Zhang, XF Guo, *MATCH Commun. Math. Comput. Chem.* 23 (1988) 229-238.

[6] XF Guo, FJ Zhang, J.Brunvoll, B.N.Cyvin, S.J.Cyvin, *J.Chem. Inf. Comput. Sci.* 35 (1995) 226-232.

[7] W.C.He, W.J.He, B.N.Cyvin, S.J.Cyvin, J.Brunvoll, *MATCH Commun. Math. Comput. Chem.* 23 (1988) 201-207.

[8] XF Guo and FJ Zhang, *MATCH Commun. Math. Comput. Chem.* 24 (1989) 85-104.

[9] RS Chen, S.J.Cyvin, B.N.Cyvin, *MATCH Commun. Math. Comput. Chem.* 25 (1990) 71-81.

[10] RS Chen, LZ Zhang, *MATCH Commun. Math. Comput. Chem.* 49 (2003) 117-126.

[11] FJ Zhang, RS Chen, *Acta Math. Appl. Sin.* 5 (1989) 1-5 .

[12] S.J.Cyvin, J.Brunvoll, B.N.Cyvin, *J. Math. Chem.* 4 (1990) 47-54.

[13] S.J.Cyvin, J.Brunvoll and B.N.Cyvin, *J.Chem. Inf. Comput. Sci.* 29 (1989) 236-244.

[14] RS Chen, *MATCH Commun. Math. Comput. Chem.* 43 (2001) 99-109.

[15] S.J. Cyvin, A.T. Balaban, *Struct. Chem.* 2 (1991) 485-488.