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Relations between Clar structures, Clar covers, and the sextet-rotation tree of a hexagonal system☆

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Abstract

Sextet rotations of the perfect matchings of a hexagonal system H are represented by the sextet-rotation-tree $R(H)$, a directed tree with one root. In this article we find a one-to-one correspondence between the non-leaves of $R(H)$ and the Clar covers of H, without alternating hexagons. Accordingly, the number (*nl*) of non-leaves of $R(H)$ is not less than the number (*cs*) of Clar structures of H. We obtain some simple necessary and sufficient conditions, and a criterion for $cs = nl$, that are useful for the calculation of Clar polynomials. A procedure for constructing hexagonal systems with $cs < nl$ is provided in terms of normal additions of hexagons.

Keywords: Hexagonal system; Perfect matching; Clar cover; Clar structure; Sextet-rotation-tree

1. Introduction

A *hexagonal system* is a connected plane graph without cut vertices, in which each interior face is a regular hexagon of side of length one [16]. In this paper we are interested in hexagonal systems that possess perfect matchings. A *perfect matching* of a graph H is a set of pairwise disjoint edges that cover all vertices of H.

One should note that the carbon-atom skeleton of a benzenoid hydrocarbon is a hexagonal system [6]. Therefore hexagonal systems and their mathematical properties were much studied in chemistry. In chemistry instead of perfect matchings one speaks of “Kekulé structures” and the edges contained in a perfect matching are referred to as the “double bonds” of the respective Kekulé structure.

Kekulé structures have numerous applications in chemistry [6]. For instance, various Kekulé-structure-related models for approximating the Dewar resonance energy (DRE) [17] of benzenoid hydrocarbons have been proposed, such as the Swinborne-Sheldrake [20], the Herndon–Hosoya [11], etc.

In the Swinborne-Sheldrake model, DRE is expressed in terms of the number of Kekulé structures. Eventually an improved formula for DRE was put forward [9], based in the sextet-rotation-tree.

The sextet rotation, transforming all proper sextets of a Kekulé structure into improper sextets, results in a directed tree with one root [13,1]; in what follows this tree, pertaining to a hexagonal system H, is referred to as the

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sextet-rotation-tree and is denoted by $R(H)$; details of its construction are given below. Analogously, counter-sextet rotation also produces a directed tree $R^c(H)$, which, in the general case, needs not be isomorphic with $R(H)$. On the other hand, $R(H)$ and $R^c(H)$ have the same height and width (the number of leaves, vertices of in-degree 0). This remarkable property was first observed by Gutman et al. in [8] and later verified by Zhang et al. [25] in a more extensive sense. Hence $nl(H)$, the number of non-leaves in $R(H)$, is an invariant. In [9] the formula

$$DRE(H) = 1.2475 \ln K(H) - 0.1106 \ln nl(H) \tag{1}$$

was deduced, where $K(H)$ denotes the number of Kekulé structures of H.

In view of these chemical applications, it is purposeful to classify the Kekulé structures into "leaves" and "non-leaves", according to the structure of the sextet-rotation-tree.

A spanning subgraph of H is called a *Clar cover* [26] if each of its components is either a hexagon or K_2. An *alternating hexagon* of a Clar cover of H is a hexagon of H whose edges belong alternately to the edge set of the Clar cover and its component (with respect to the edge set of H). In this article we first establish a one-to-one correspondence between the non-leaves of $R(H)$ and the Clar covers of H, without alternating hexagons. Hence $nl(H) = cc(H)$, where $cc(H)$ denotes the number of Clar covers without alternating hexagons.

In the Herndon–Hosoya's model, the concept of (generalized) Clar structure was introduced, see below. In connection with this, El-Basil and Randić [15,14,3] conceived the Clar polynomial, the counting polynomial of Clar structures (in terms of the number of hexagons they contain), and described various approaches for its computation.

Based on the concept of Clar cover, a more precise graph-theoretical definition of Clar structure could be given [18]: A Clar cover of H is called a *Clar structure* if the set of hexagons is maximal (in the sense of set-inclusion) within all Clar covers of H.[1] Hence $cs(H) \leqslant cc(H) = nl(H)$, where $cs(H)$ is the number of Clar structures of H. The Clar polynomial [3] of a hexagonal system H can be defined as

$$\rho(x, H) = \sum_{i \geqslant 0} \rho(i, H) x^i \tag{2}$$

with $\rho(i, H)$ denoting the number of Clar structures of H with i circles (or hexagons). Actually, Gutman [5] stated that every perfect matching of a hexagonal system contains three edges of a hexagon. Then the index i may start from 1 as there are no Clar structures with zero hexagons.

Clearly, if $cs(H) = cc(H)$, then the problem of computing Clar polynomial is somewhat less difficult, since it can be solved by constructing all Clar covers without alternating hexagons.

In order to characterize the hexagonal systems with $cs(H) = nl(H)$, in Section 3 we recall a classical result of Zhang and Chen [21]: For a hexagonal system H, $r(H) \leqslant K(H)$, and equality holds if and only if H contains no coronene (see Fig. 3) as its nice subgraph. Here $r(H)$ denotes the number of sextet patterns in H, a set of hexagons in a Clar cover.

Below we provide a simpler proof of this result, using the concepts of cut lines and g-cut lines. In Section 4 this approach is used to find a simple sufficient condition for $cs(H) = cc(H)$: If a hexagonal system H has no coronene as its nice subgraph, then $cs(H) = nl(H)$. The converse of this statement does not hold, and in the sequel we deduce a general necessary and sufficient criterion. Various examples of hexagonal systems with $cs(H) = nl(H)$ are constructed and their Clar polynomials are computed. Finally a construction procedure for hexagonal systems with $cs < nl$ is provided in terms of normal additions of hexagons.

2. Identity $cc(H) = nl(H)$

For convenience, any hexagonal system H considered, is assumed to be placed in the plane so that one of its edge-directions is vertical. The peaks and valleys of H (see [6]) are colored black and white, respectively. In what follows, all cycles considered are assumed to be oriented clockwise. This convention will play an important role in the following considerations.

Let H be a hexagonal system with a perfect matching M. A cycle C of H is said to be M-alternating if its edges belong alternately in M and $E(H) \backslash M$. A path P is M-alternating if every inner vertex of P is incident with an edge in $P \cap M$, but the end edges of P are not in M. An M-alternating cycle C of H is said to be *proper* if each edge of C belonging to

[1] Another non-equivalent definition, much used in the chemical literature [6], requires that the *number* of hexagons be maximal.

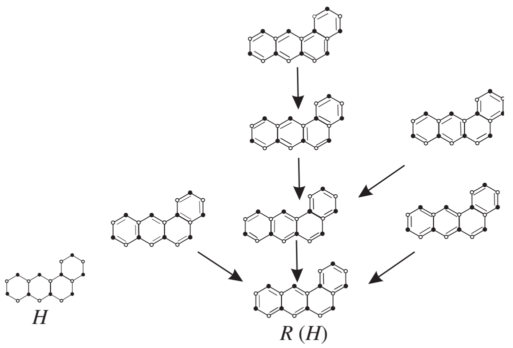

Fig. 1. A sextet-rotation graph $R(H)$.

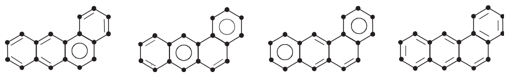

Fig. 2. Four Clar covers, one containing two alternating hexagons.

M goes from a white vertex to a black vertex, and *improper* otherwise. So a proper (resp. improper) sextet of M means a proper (resp. improper) M-alternating hexagon.

The *root perfect matching* of H is the unique perfect matching without proper sextets [13]. Given a perfect matching M_i of H, other than the root, the *sextet rotation* is a transform that changes all proper sextets of M_i into improper sextets, and leaves the other edges unchanged. By this, from M_i another perfect matching M_j is obtained; we write this as $R(M_i) = M_j$.

The sextet-rotation digraph $R(H)$ of H is constructed in the following manner: Its vertex set is the set of all perfect matchings of H, and there is an arc from M_i to M_j if and only if $R(M_i) = M_j$. An example (taken from the paper [13]) is presented in Fig. 1. *A directed tree* is an orientation of tree with only one vertex of out-degree 0. Chen [1] showed that $R(H)$ is a directed tree with one root. A *leaf* of a directed tree is a vertex whose in-degree is 0. The following is a well-known result, which can be obtained by Theorem 3.6 in Ref. [4].

Lemma 2.1. *A perfect matching M of a hexagonal system H corresponds to a non-leaf of $R(H)$ if and only if each proper M-alternating hexagon* (*if such exists*) *intersects some improper M-alternating hexagon.*

Proof. Let M be a perfect matching of H corresponding to a non-leaf of $R(H)$. Then H has another perfect matching M' such that $R(M') = M$. Let S be the set of proper M'-alternating hexagons. So each hexagon in S is improper M-alternating. Further, each proper M-alternating hexagon does not belong to S and intersects some hexagon in S.

Conversely, suppose that each proper M-alternating hexagon (if such exists) intersects some improper M-alternating hexagon. Let S' be the union of all improper M-alternating hexagons. We have that $S' \neq \emptyset$ by the above-mentioned result due to Gutman [5]. Taking the symmetric difference of M and the edge set of S', we get a perfect matching M' of H. Hence $M' \neq M$ and $R(M') = M$; that is, M is a non-leaf of $R(H)$. □

A spanning subgraph of H is called a *Clar cover* if each of its components is either a hexagon or K_2. A hexagon belonging to a Clar cover is often indicated by drawing a circle inside this hexagon; for example, see Fig. 2. Let $\mathscr{C}$ be the set of Clar covers without alternating hexagons in H. Let $\mathscr{M}$ be the set of perfect matchings corresponding to the non-leaves of $R(H)$. Recall that $nl(H) := |\mathscr{M}|$ and $cc(H) := |\mathscr{C}|$.

Theorem 2.2. *Let H be a hexagonal system with a perfect matching. Then*

$$cc(H) = nl(H). \tag{3}$$

Proof. Define a mapping $\varphi : \mathscr{M} \longrightarrow \mathscr{C}$ as follows: For each $M \in \mathscr{M}$, let C_M be the union of all improper M-alternating hexagons of H and the other edges of M. Then C_M is a Clar cover of H. By Lemma 2.1, each proper M-alternating hexagon must intersect some improper M-alternating hexagon. Therefore $C_M \in \mathscr{C}$ and φ is a mapping. Next we show that φ is surjective. For any $C \in \mathscr{C}$, place three edges into each hexagon in C so that they form improper sextets, whereas the other edges remain unchanged. By this a perfect matching M of H is obtained. Because C is a Clar cover without alternating hexagons, each proper M-alternating hexagon must intersect some hexagon in C, which is improper M-alternating. By Lemma 2.1, M belongs to $\mathscr{M}$ and $\varphi(M) = C$. Finally, for any perfect matchings M_1 and M_2 of $\mathscr{M}$, such that $\varphi(M_1) = \varphi(M_2) = C$, H has the same improper M_1- and M_2-alternating hexagons, and other edges of M_1 and M_2 (not in alternating hexagons) coincide. So $M_1 = M_2$ and φ is injective. Hence φ is a one-to-one correspondence from $\mathscr{M}$ to $\mathscr{C}$ and $nl(H) = cc(H)$. □

3. Sextet patterns

Let G be a plane bipartite graph. From now on, for a subgraph H of G, $G - H$ always means $G - V(H)$, i.e. a subgraph obtained from G by deleting all vertices of H together with their incident edges. A subgraph H of G is said to be *nice* if $G - H$ has a perfect matching. Obviously, a perfect matching (if such does exist) of a nice subgraph H can be extended to a perfect matching of the entire graph. A face f of G is said to be *resonant* if its boundary is a nice cycle. A set S of disjoint interior faces of G is called a *resonant pattern* if G has a perfect matching M such that all face-boundaries in S are simultaneously M-alternating cycles. Let $K(G)$ and $r(G)$ be the numbers of perfect matchings and resonant patterns of G, respectively.

An edge of G is called *allowed* if it belongs to some perfect matching of G; *forbidden* otherwise (see [12]). A connected bipartite graph with a perfect matching is said to be *normal* if it has no forbidden edges [19].

A *generalized* hexagonal system (GHS) is a connected subgraph of a hexagonal system. The *boundary* of a GHS is the union of the boundaries of its infinite face and the non-hexagonal finite faces (holes).

For a hexagonal system with perfect matchings, a resonant pattern of H is called always a *sextet pattern* since it consists of hexagons. Equivalently, a sextet pattern of H means a set of hexagons of a Clar cover.

Theorem 3.1 (*Gutman et al. [7], Zhang and Chen [21]*). *For a hexagonal system H with perfect matchings, $r(H) \leqslant K(H)$, and equality holds if and only if H contains no coronene (see Fig. 3) as its nice subgraph.*

By applying the concept of a g-cut line, we are able to give a simpler proof of Theorem 3.1.

Definition 3.1 (*Zhang and Chen [22]*). Let H be a GHS. A broken line $L = P_1P_2P_3$ is called a *g-cut line* of H (see Fig. 4) if:

(1) P_1 and P_3 lie in the centers of two boundary edges of H;
(2) if $P_2 \neq P_1, P_3$, then P_2 is the center of some hexagonal face and $\angle P_1P_2P_3 = \pi/3$;
(3) the segments P_1P_2 and P_2P_3 are orthogonal to edge-directions; and
(4) all the points in L lie in hexagonal faces of H except for the degenerated case of $P_1 = P_2 = P_3$.

In particular, if $P_2 = P_1$ or P_3, L is a *cut line*. Note when some edge in H is not in any hexagon the g-cut line passing through it can degenerate to a point.

Lemma 3.2 (*Zhang and Zhang [27]*). *Let G be a connected plane bipartite graph with perfect matchings. Assume that the cycle C of G lies in the boundary of some face of G. If $\frac{1}{2}|V(C)|$ independent edges of C are allowed, then C is a nice cycle.*

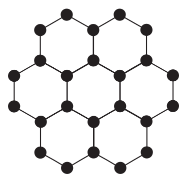

Fig. 3. Coronene C_0.

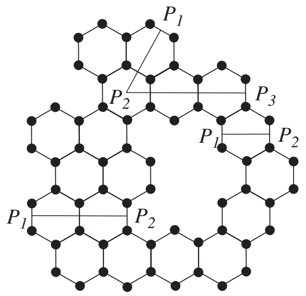

Fig. 4. Cut lines P_1P_2 and a g-cut line $P_1P_2P_3$.

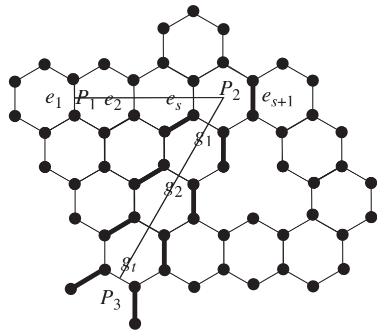

Fig. 5. Illustration of the proof of Lemma 3.3 (thick lines represent edges in M).

Lemma 3.3. *Let H be a GHS with a perfect matching. The following statements hold*:

(1) *If H has a forbidden edge, then there exists a forbidden edge in the boundary of H* [23].
(2) *If a boundary edge of H is a forbidden edge, then there is a g-cut line L intersecting it, and all edges intersecting L are forbidden edges.*

Proof. Let e_1 be a forbidden edge of H. If e_1 is a boundary edge of H, Statement (1) is trivial. Otherwise, let a hexagon h_1 of H contain e_1, and let e_2 be the edge of h_1 opposite to e_1. If a hexagon h_2 of H (other than h_1) contains e_2, let e_3 be the edge of h_2 opposite to e_2. In this way, we produce a series of parallel edges $e_1, e_2, e_3, \ldots$ (cf. Fig. 5). Let e_s be the last forbidden edge in this sequence; that is, $e_1, e_2, \ldots, e_s$ are forbidden and either this sequence ends at e_s or e_{s+1} is an allowed edge. If e_s is a boundary edge, Statement (1) holds. Otherwise, suppose that H has a hexagon $h_s(\neq h_{s-1})$ containing e_s. Then e_{s+1} is an edge of h_s opposite to e_s. Hence e_{s+1} is in some perfect matching M of H. By Lemma 3.2, one (say g) of two edges adjacent to e_s in h_s is forbidden.

Let L be a straight segment from the center P_2 of the hexagon h_s to the center P_3 of a boundary edge of H through the center of edge g such that all the points of L lie in hexagons of H. Let $g_1(=g), g_2, g_3, \ldots, g_t$ be the all edges intersecting L such that any consecutive g_i and g_{i+1} are contained in a hexagon h'_i of H. Then g_t is a boundary edge and its center is P_3. If $t > 1$, both edges adjacent to g_1 in h'_1 belong to M. Since g_1 is a forbidden edge, g_2 is also forbidden by Lemma 3.2. If $t > 2$, both edges adjacent to g_2 in h'_2 belong to M and g_3 is a forbidden edge. Continuing this process we arrive in that all the g_i's are forbidden. Hence statement (1) holds.

Now we choose a forbidden edge e_1 in the boundary of H in the above proof. Let P_1 be the center of e_1. If e_s is a boundary edge, P_1P_2 is a required cut line. Otherwise, points P_2 and P_3 are the centers of a hexagon h_s and an edge g_t, respectively. Then $P_1P_2P_3$ is a required g-cut line and statement (2) holds. $\square$

Lemma 3.4 (Zhang *[24, Theorem 3.2.1]*). *Let G be a* 2*-connected plane bipartite graph with perfect matchings. Then $r(G) \leqslant K(G)$, 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.*

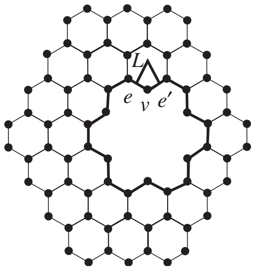

Fig. 6. A GHS $I[C]-h$.

A New Proof of Theorem 3.1. We only show that $r(H)=K(H)$ if and only if H contains no coronene as its nice subgraph. The necessity follows by Lemma 3.4.

For sufficiency, suppose, to the contrary, that $r(H)<K(H)$. By Lemma 3.4, there exist a hexagon h and a cycle C such that h lies in the interior of C and $H-C-h$ has a perfect matching. Let $I[C]$ be the subgraph of H consisting of C together with its interior. Then $I[C]-h$ is a GHS with precisely one non-hexagonal interior face, that is "hole" (see Fig. 6), and its boundary C is a nice cycle. Denote by C^* the boundary of this hole. We now show that $I[C]-h$ is normal.

Suppose that $I[C]-h$ has a forbidden edge. By Lemma 3.3, there exists a g-cut line $L=P_1P_2P_3$ such that all edges intersecting L are forbidden. As C is a nice cycle of $I[C]-h$, L can only be a broken line with $\angle P_1P_2P_3=\pi/3$, and the two end-points of L lie on C^*. Since C^* is the boundary of coronene and $\angle P_1P_2P_3=\pi/3$, the end-points of L can only lie on the adjacent edges e and e' of the same hexagon. Let v be the vertex shared by e and e'. Since both e and e' are forbidden in $I[C]-h$, and v is of degree 2 and v cannot be matched to other vertices of $I[C]-h$. This contradicts to the assumption that $I[C]-h$ has a perfect matching. So $I[C]-h$ is normal. Consequently, each face of $I[C]-h$ is resonant [23] and C^* is a nice cycle of $I[C]-h$, which implies that the coronene spanned by h and C^* is a nice subgraph of H, contradicting the condition of Theorem 3.1. □

4. Characterization of $cs(H)=cc(H)$

A Clar cover without alternating hexagons is not necessarily a Clar structure. For example, the left-hand side diagram in Fig. 7 is not a Clar structure of tribenzo[*a,g,m*]coronene, whereas the right-hand side one is. On the other hand, both diagrams are Clar covers without alternating hexagons.

For any hexagonal systems H, we have $cs(H)\leqslant cc(H)=nl(H)$. For the hexagonal system depicted in Fig. 1, all Clar covers without alternating hexagons of H are also Clar structures, as shown in Fig. 2; hence, in this case, $cs=cc$. It is natural to pose the question when both quantities are equal. We first give a sufficient condition for this.

Lemma 4.1 (*Zhang and Zhang [27]*). *Let G be a plane elementary bipartite graph with a perfect matching M and let C be an M-alternating cycle. Then there exists an M-resonant face in $I[C]$, where $I[C]$ denotes the subgraph of H consisting of C together with its interior.*

Theorem 4.2. *If a hexagonal system H has a perfect matching and contains no coronene as its nice subgraph, then $cs=cc$.*

Proof. Suppose that $cs<cc$. Then there exists a Clar cover $\mathscr{C}$ without alternating hexagons in H, which is not a Clar structure of H. Let M be a perfect matching of H corresponding to $\mathscr{C}$, such that all hexagons in $\mathscr{C}$ are proper M-alternating. Since $\mathscr{C}$ is not a Clar structure, there exists another perfect matching M' in H, different from M, such that all hexagons in $\mathscr{C}$ are proper M'-alternating. Then there is an M' and M-alternating cycle C in $M\oplus M'\neq\emptyset$ (symmetric difference).

We claim that the interior of C contains at least one hexagon h of $\mathscr{C}$. Otherwise, by Lemma 4.1 $I[C]$ would contain an M-alternating hexagon h' which would be disjoint from any hexagon in $\mathscr{C}$. This contradicts to $\mathscr{C}$ being a Clar cover of H without alternating hexagons. As C and h are disjoint M-alternating cycles, and h lies in the interior of C, by Theorem 3.1 and Lemma 3.4, H has a coronene as its nice subgraph, a contradiction. Thus $cs=cc$. □

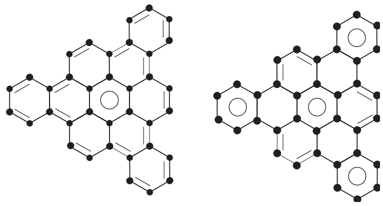

Fig. 7. Two Clar covers of tribenzo[*a,g,m*]coronene.

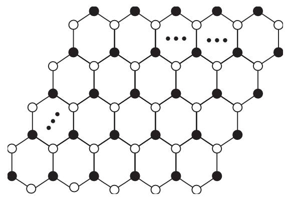

Fig. 8. The parallelogram $L_{m,n}$.

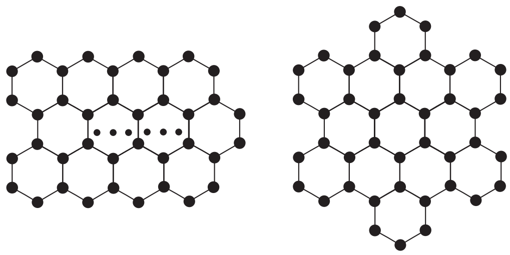

Fig. 9. Two hexagonal systems with $cs = cc$.

Corollary 4.3. *For the parallelogram* $L_{m,n}$ (*see* Fig. 8), $cs = cc$.

Proof. Draw a cut line L in each row of $L_{m,n}$ such that L intersects only vertical edges. Let $\mathfrak{I}$ denote the set of edges of $L_{m,n}$ intersecting L. $L_{m,n} - \mathfrak{I}$ (the removal of all edges in $\mathfrak{I}$ from $L(m, n)$) possesses exactly two components and the difference between the numbers of white and black vertices in each component is one. Then each perfect matching M of $L_{m,n}$ contains exactly one edge in $\mathfrak{I}$. Similarly, draw a cut line L in the middle row of coronene (C_0) and denote the set of edges intersecting L in coronene by $\mathfrak{I}^*$. Since the difference between the numbers of white and black vertices in each component of $C_0 - \mathfrak{I}^*$ is two, every perfect matching M of C_0 contains exactly two edges of $\mathfrak{I}^*$. Thus coronene is not a nice subgraph of the parallelogram $L_{m,n}$. By Theorem 4.2, $cs = cc$. □

Corollary 4.4. *For the hexagonal systems shown in* Fig. 9, $cs = cc$.

Proof. By a similar argument as used in Corollary 4.3, we can show that the hexagonal systems in Fig. 9 contain no coronene as their nice subgraph. By Theorem 4.2, we then have $cs = cc$. □

The converse of Theorem 4.2 does not hold. For example, as Fig. 10 shows, all Clar covers without alternating hexagons in coronene are identical to their Clar structures. Hence $cs(C_0) = cc(C_0)$. So we can obtain the Clar polynomial of coronene by enumerating Clar covers without alternating hexagons as follows:

$$\rho(x, C_0) = 2x^3 + 3x^2 + 2x$$

which, of course, agrees with the earlier result of [14]. For another hexagonal system H with $cs = cc$ in Fig. 11, in a similar manner we get $\rho(x, H) = 3x^4 + 6x^3 + 3x^2$.

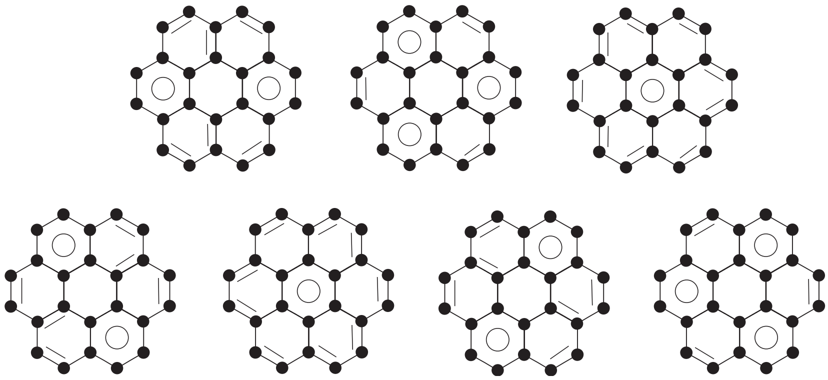

Fig. 10. All Clar structures of coronene.

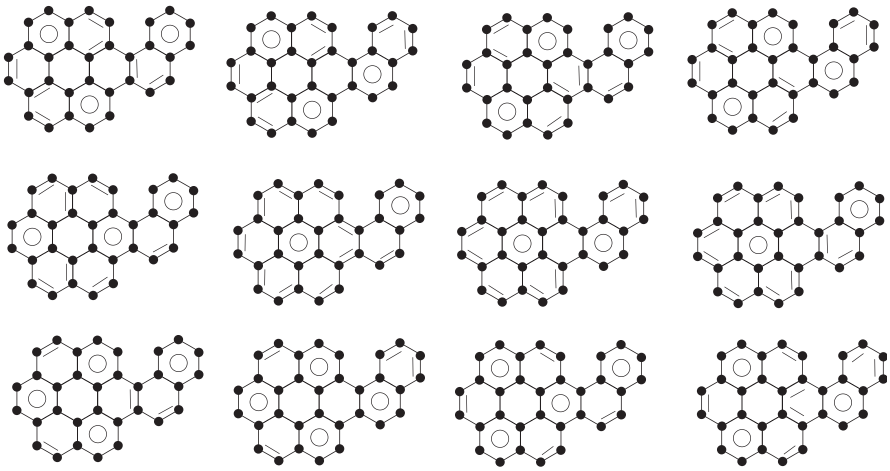

Fig. 11. All Clar structures of a hexagonal system.

We now give a necessary and sufficient criterion for hexagonal systems with $cs = cc$.

Theorem 4.5. *Let H be a hexagonal system with perfect matchings. Then $cs = cc$ if and only if for each Clar cover $\mathscr{C}$ without alternating hexagons in H, $H - \mathscr{C}_s$ does not have a cycle C intersecting a hexagon h along a path of odd length such that $C \cup h$ is a nice subgraph of $H - \mathscr{C}_s$, where $\mathscr{C}_s$ denotes the set of hexagons in $\mathscr{C}$.*

Proof. We prove the contrapositive statement of the theorem. That is, $cs < cc$ if and only if for some Clar cover $\mathscr{C}$ without alternating hexagons in H, $H - \mathscr{C}_s$ has a cycle C intersecting a hexagon h along a path of odd length, such that $C \cup h$ is a nice subgraph of $H - \mathscr{C}_s$.

Sufficiency: For a Clar cover $\mathscr{C}$ of H without alternating hexagons, suppose that the intersection of a hexagon h and cycle C in $H - \mathscr{C}_s$ is a path of odd length and $C \cup h$ is a nice subgraph of $H - \mathscr{C}_s$. Then h and C are in one of the modes L_1, L_3, L_5 (cf. Fig. 15). Let $P := C \cap h$. Since P is a path of odd length, $C - P$ is a path of odd length and $h - P$ is a path of odd length or empty. Taking the perfect matchings of these three paths, we have that their union forms a perfect matching of $C \cup h$. Since $C \cup h$ is a nice subgraph of $H - \mathscr{C}_s$, the perfect matching of $C \cup h$ can be extended to a perfect matching M of $H - \mathscr{C}_s$. As h is an M-alternating hexagon in $H - \mathscr{C}_s$, $H - (\mathscr{C}_s \cup h)$ has a perfect matching. Thus the hexagons in $\mathscr{C}_s \cup h$ and a perfect matching of $H - (\mathscr{C}_s \cup h)$ compose a Clar cover $\mathscr{C}'$ of H. As $\mathscr{C}_s \subset \mathscr{C}'_s$, we conclude that $\mathscr{C}$ is not a Clar structure of H. Hence $cs < cc$.

Necessity: Suppose $cs < cc$. Then there must exist a Clar cover $\mathscr{C}$ without alternating hexagons in H, but $\mathscr{C}$ is not a Clar structure of H. So there is another perfect matching M' in H such that all hexagons in $\mathscr{C}$ are proper M'-alternating,

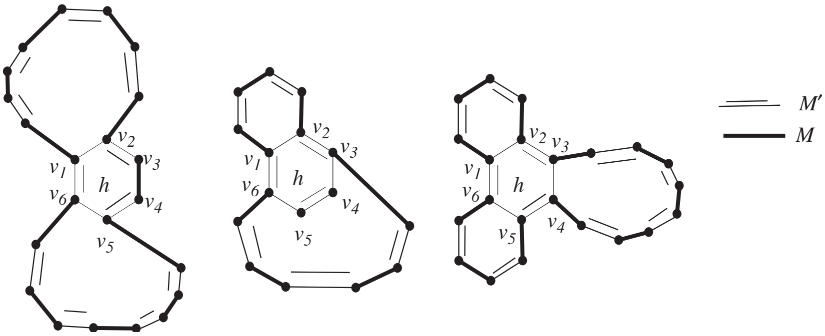

Fig. 12. Illustration to the proof of Theorem 4.5.

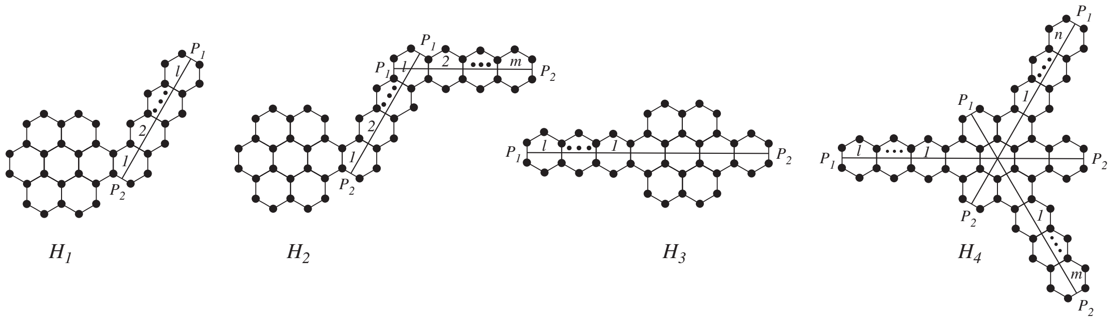

Fig. 13. Examples of hexagonal systems ($\ell, m, n \geqslant 2$) with $cs = cc$.

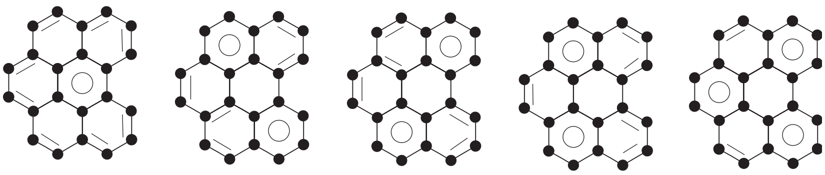

Fig. 14. All Clar structures of the hexagonal system H^1.

and there exists at least one M'-alternating hexagon h in $H - \mathscr{C}_s$. Let M be a perfect matching of H corresponding to $\mathscr{C}$, such that all hexagons in $\mathscr{C}$ are proper M-alternating. Since h is M'-alternating but not M-alternating, there is an M and M'-alternating cycle C in $M \oplus M'$ intersecting h. Then $C \subset H - \mathscr{C}_s$ and $C \neq h$. There exists a path P in C which is internally disjoint from hexagon h, and the two end-vertices (say, v_1 and v_2) of P lie on h (see Fig. 12). Because both C and h are M'-alternating cycles, P is an M'-alternating path, both end-edges of which are not in M'. Hence the restriction of M' on $P \cup h$ is its perfect matching and $P \cup h$ is a nice subgraph of H. Since P is a path of odd length, its end vertices v_1 and v_2 are of distinct colors. Hence h is divided into two paths of odd length by the pair of vertices v_1 and v_2, and $P \cup h$ can be expressed as the union of a cycle C' and h, such that $C' \cap h$ is a path of odd length. $\square$

Corollary 4.6. *For the hexagonal systems shown in* Fig. 13, $cs = cc$.

Proof. Draw a cut line L of H_1 as shown in Fig. 13. For each perfect matching M of H_1, there is exactly one edge in M, intersecting L. That is, for each Clar cover $\mathscr{C}$ without alternating hexagons in H_1, there is exactly one hexagon h which intersects L belonging to $\mathscr{C}$. Delete the hexagon h and both end-vertices of all edges which lie in all perfect matchings of $H_1 - h$ from H_1. If hexagon 1 belongs to $\mathscr{C}_s$, then the resulting graph is isomorphic to graph H^1 shown in Fig. 14. If one of the hexagons $2, \ldots, \ell$ belongs to $\mathscr{C}_s$, the resulting graph is isomorphic to coronene. Each Clar cover without alternating hexagons in H^1 (or in coronene) (see Figs. 10 and 14) together with the hexagon 1 (or one of the hexagons $2, \ldots, \ell$) and other K_2 components induce a Clar cover of H_1 without alternating hexagons. Clearly these are all the Clar covers without alternating hexagons in H_1. Hence for each Clar cover $\mathscr{C}$ of H_1 without alternating hexagons, $H_1 - \mathscr{C}_s$ has no cycles C intersecting a hexagon h at a path of odd length. By Theorem 4.5, $cs(H_1) = cc(H_1)$. By the same arguments, we can deduce that equation $cs = cc$ holds for the other three hexagonal systems in Fig. 13. $\square$

By Corollary 4.6, we can obtain the Clar polynomials of these hexagonal systems by constructing Clar covers without alternating hexagons. Such a computing is exemplified for H_1.

Consider the Clar covers $\mathscr{C}$ of H_1 without alternating hexagons, and assume that the hexagon i belongs to $\mathscr{C}_s$. If $i \geqslant 2$, then $\rho_1(x, H_1) := (\ell - 1) \cdot x \cdot \rho(x, C_o)$. If the hexagon 1 belongs to $\mathscr{C}_s$, then $\rho_2(x, H_1) = x \cdot \rho(x, H^1) = x(x^3 + 3x^2 + x)$, where H^1 is the hexagonal system shown in Fig. 14. Adding the two above polynomials we obtain the Clar polynomial of H_1:

$$\rho(x, H_1) = \rho_1(x, H_1) + \rho_2(x, H_1) = (2\ell - 1)x^4 + 3\ell x^3 + (2\ell - 1)x^2.$$

In a similar manner, we obtain also the following Clar polynomials:

$$\rho(x, H_2) = (2m\ell - 3m - 2\ell + 3)x^5 + (3m\ell - 3m - 3\ell + 5)x^4 + (2m\ell - 3m - 2\ell + 6)x^3 + 2x^2,$$

$$\rho(x, H_3) = (5\ell + 1)x^4 + (\ell + 2)x^2,$$

$$\rho(x, H_4) = 2mn\ell x^6 + \ell(m + n)x^5 + [(2 + \ell)mn + m + n + \ell + 1]x^4 + x^2.$$

5. Construction of hexagonal systems with $cs < cc$

There are many hexagonal systems with $cs < cc$. We now give a construction approach, based on a series of normal additions of hexagons, starting from coronene such that in each step the coronene is a nice subgraph of the hexagonal system.

We recall the concept of normal additions. Under a *normal addition* [6] is understood an addition of a new hexagon to a hexagonal system, such that the added hexagon acquires the modes L_1, L_3, or L_5 (see Fig. 15). In fact a normal addition of a hexagon is to add a path of length 1, 3 or 5 to a hexagonal system H such that both end vertices identify vertices of distinct colors in H, it is internally disjoint H and the resultant is a larger hexagonal system. Such paths of odd length are called *ears*.

For a normal hexagonal system the following construction was originally conjectured by Cyvin and Gutman [2], and eventually rigorously proved by He and He [10].

Theorem 5.1 (*He and He [10]*). *Any normal hexagonal system with $h + 1$ hexagons can be generated from a normal hexagonal system with h hexagons by a normal addition of one hexagon.*

We call a construction specified in Theorem 5.1 a *normal construction*. All hexagonal systems in Figs. 11 and 13 have $cs = cc$, and can be obtained by normal constructions starting from their nice subgraph coronene. In order to obtain a hexagonal system with $cs < cc$ by normal construction, some further conditions must be needed.

By $C_0 \cup h$ (see Fig. 16) we denote the hexagonal system obtained by attaching to coronene C_0 a new hexagon h in mode L_1. In this section we also assume that all cycles considered are oriented clockwise, and, without loss of

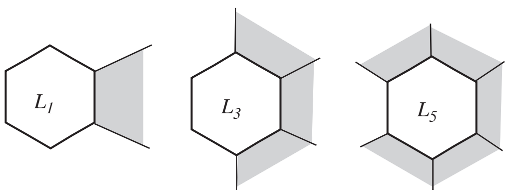

Fig. 15. Three modes of normal additions.

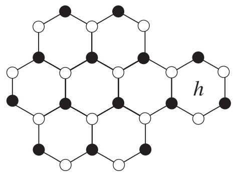

Fig. 16. $H_0 = C_0 \cup h$.

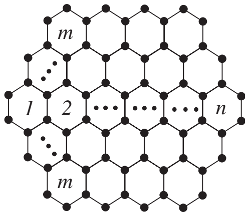

Fig. 17. Hexagonal system $C_{2m-1,n}$.

generality, the vertices of $C_0 \cup h$ are colored so that h starts at a white vertex of C_0 along the boundary $\partial(C_0 \cup h)$ of $C_0 \cup h$.

Suppose that H has a normal construction $(H_0, H_1, \ldots, H_r = H)$, associated with the ear sequence $(P_0, P_1, \ldots, P_{r-1})$ and hexagon sequence $(S_0, S_1, \ldots, S_{r-1})$. Each ear P_i is added to H_i to get H_{i+1} so that only two end-vertices of P_i lie on the boundary ∂H_i of H_i, adding ear P_i to H_i is equivalent to a normal addition of hexagons S_i, and P_i starts and ends at vertices of H_i in the sense of the clockwise orientation of ∂H_{i+1}, $i = 0, 1, \ldots, r-1$.

Theorem 5.2. *Let H be a hexagonal system with a perfect matching. If H has a normal construction $(H_0 = C_0 \cup h, H_1, \ldots, H_r = H)$, associated with the ear sequence $(P_0, P_1, \ldots, P_{r-1})$ and hexagon sequence $(S_0, S_1, \ldots, S_{r-1})$, such that if the two end-vertices of ear P_i lie on ∂H_0, and P_i and h start at vertices of different colors, the two end-vertices of the ear P_{i+1} must lie on ∂S_i, and P_{i+1} and h start at vertices of the same color, then $cs < cc$.*

Proof. Construct a perfect matching M of H such that ∂H_0 is an improper M-alternating cycle, the central hexagon of coronene C_0 is improper M-alternating, and each ear P_i is an M-alternating path, $i = 1, 2, \ldots, r-1$. The union of all improper M-alternating hexagons and the other edges from M form a Clar cover $\mathscr{C}'$ of H. If there is no other M-alternating hexagon in $H - \mathscr{C}'_s$ left, $\mathscr{C}'$ is a Clar cover without alternating hexagons in H. Otherwise, there exist other M-alternating hexagons in $H - \mathscr{C}'_s$. These hexagons must be proper M-alternating. Hence these are mutually disjoint and also disjoint from the hexagons in $\mathscr{C}'_s$. Then the proper M-alternating hexagons together with the other edges of M in $H - \mathscr{C}'_s$ form a Clar cover $\mathscr{C}''$. Hence $\mathscr{C} := \mathscr{C}'_s \cup \mathscr{C}''$ is a Clar cover without M-alternating hexagons in H. If an ear whose end-vertices lie on ∂H_0 starts at a vertex of the same color as h, then the added hexagon intersects ∂H_0 and cannot be M-alternating. If it has at most one end-vertex lying on ∂H_0 and the added hexagon intersects ∂H_0, then that the hexagon is not M-alternating. Thus it does not belong to $\mathscr{C}$. So assume that there exists at least one ear, say P_i, whose end-vertices lie on ∂H_0, and P_i starts at a vertex of color different than h. Although the hexagon S_i is proper M-alternating, S_{i+1} is improper M-alternating since the end-vertices of the ear P_{i+1} lie on ∂S_i, and P_{i+1} starts with the same color as h. By the choice of $\mathscr{C}$, S_{i+1} belongs to $\mathscr{C}$. Since S_i and S_{i+1} have an edge in common, S_i cannot belong to $\mathscr{C}$. In each case, $\mathscr{C}_s \cap \partial H_0 = \emptyset$. The hexagon h is thus an $M \oplus C$-alternating hexagon in $H - \mathscr{C}_s$. That is, the set of hexagons in $\mathscr{C}$ is not maximal. Hence $\mathscr{C}$ is not a Clar structure of H and $cs < cc$ (cf. Theorem 4.5). $\square$

In Fig. 7, the two hexagons added to H_0 start with the same color as h. By using Theorem 5.2, we have that $cs < cc$ holds for tribenzo[*a*,*g*,*m*]coronene. Trivially, for $H_0 = C_0 \cup h$, $cs < cc$.

Corollary 5.3. *For the hexagonal system $C_{2m-1,n}$ $(m > 1)$ (see Fig. 17), if $n - m + 1 \geqslant 2$, then $cs < cc$.*

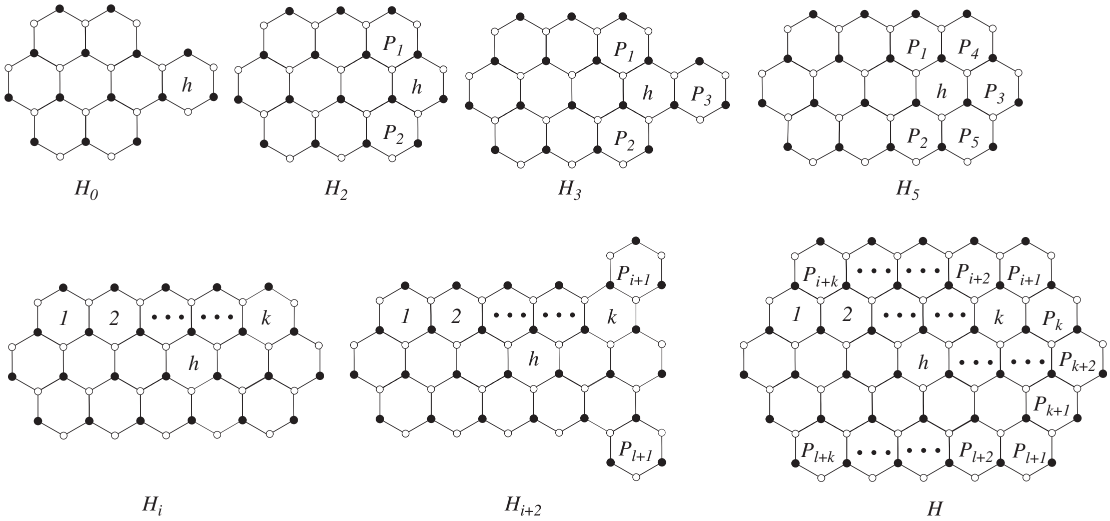

Fig. 18. The main steps of normal construction of $C_{2m-1,n}$ for $k \geqslant 3$.

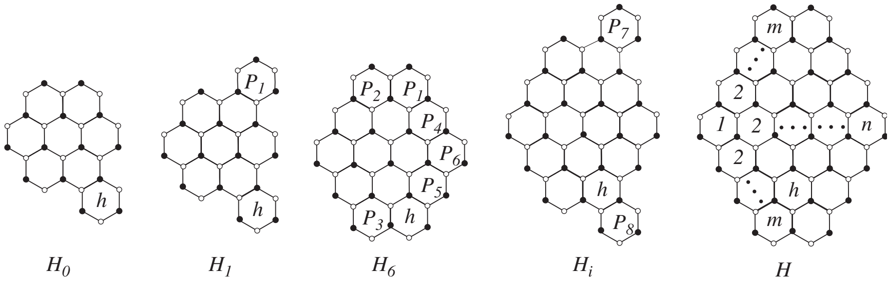

Fig. 19. The main steps of normal construction of $C_{2m-1,n}$ for $k = 2$.

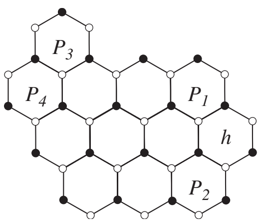

Fig. 20. Hexagonal system H'.

Proof. Let $n - m + 1 = k$. Then both the top and the bottom of $C_{2m-1,n}$ have k ($k \geqslant 2$) hexagons. We can give a normal construction of $C_{2m-1,n}$ from H_0 which satisfies the conditions of Theorem 5.2. Figs. 18 and 19 sketch such a construction, pertaining to the two cases: $k \geqslant 3$ and $k = 2$. The details are omitted. □

Corollary 5.4. *Let H be a normal hexagonal system with a perfect matching. If H contains H' (see Fig. 20) as its nice subgraph, then cs < cc.*

Proof. Since H' is a nice subgraph of H, H has a normal construction starting from H' (cf. [27]). As for H', it has a normal construction starting from $H_0 = C_0 \cup h$ as follows. First add ears P_1 and P_2 of mode L_3 to H_0, so that P_1 starts at a white vertex of C_0 and P_2 at a white vertex of h. Then add the ear P_3 of mode L_1 so that P_3 starts at a white vertex of C_0. Finally, add the ear P_4 of mode L_3 so that P_4 starts at a white vertex of C_0. Hence H has a normal construction starting from $H_0 = C_0 \cup h$. Since the ears with two end-vertices lying on ∂H_0 can only start with the same color as h, by Theorem 5.2, $cs < cc$. □

Though we have given some examples constructing hexagonal systems with $cs < cc$ by using Theorem 5.2, we are not sure whether this method can be used to construct all hexagonal systems with $cs < cc$.

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