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

Shan Zhou, Heping Zhang,*, Ivan Gutman

School of Mathematics and Statistics, Lanzhou University, Lanzhou, Gansu 730000, PR China
Faculty of Science, P.O. Box 60, 34000 Kragujevac, Serbia

Received 14 March 2006; received in revised form 16 August 2007; accepted 26 August 2007
Available online 25 October 2007

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.

© 2007 Elsevier B.V. All rights reserved.

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...
sextet-rotation-tree and is denoted by $R(H)$; details of its construction are given below. Analogously, counter-sixtet 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

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

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 the sense 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 $H$.\footnote{1 Another non-equivalent definition, much used in the chemical literature [6], requires that the number of hexagons be maximal.} Hence $cs(H) \leq cc(H) = nl(H)$, where $cs(H)$ is the number of Clar structures of $H$. The Clar polynomial [3] of a hexagonal system $H$ can be defined as

$$\rho(x, H) = \sum_{i \geq 0} \rho(i, H)x^i$$

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 $H$, $r(H) \leq K(H)$, 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 $M$-alterating if its edges belong alternately in $M$ and $E(H) \setminus M$. A path $P$ is $M$-alterating 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 $M$-alterating cycle $C$ of $H$ is said to be proper if each edge of $C$ belonging to

\[ \text{DRE}(H) = 1.2475 \ln K(H) - 0.1106 \ln nl(H) \]

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 the 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 $H$.\footnote{1 Another non-equivalent definition, much used in the chemical literature [6], requires that the number of hexagons be maximal.} Hence $cs(H) \leq cc(H) = nl(H)$, where $cs(H)$ is the number of Clar structures of $H$. The Clar polynomial [3] of a hexagonal system $H$ can be defined as

$$\rho(x, H) = \sum_{i \geq 0} \rho(i, H)x^i$$

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 $H$, $r(H) \leq K(H)$, 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 $M$-alterating if its edges belong alternately in $M$ and $E(H) \setminus M$. A path $P$ is $M$-alterating 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 $M$-alterating cycle $C$ of $H$ is said to be proper if each edge of $C$ belonging to
$M$ goes from a white vertex to a black vertex, and \textit{improper} otherwise. So a proper (resp. improper) sextet of $M$ means a proper (resp. improper) $M$-alternating hexagon.

The \textit{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 \textit{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 \textit{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 \textit{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 \textit{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].

\textbf{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.

\textbf{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 $R(H)$. \hfill $\square$

A spanning subgraph of $H$ is called a \textit{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 $\mathcal{C}$ be the set of Clar covers without alternating hexagons in $H$. Let $\mathcal{M}$ be the set of perfect matchings corresponding to the non-leaves of $R(H)$. Recall that $nl(H) := |\mathcal{M}|$ and $cc(H) := |\mathcal{C}|$.

\textbf{Theorem 2.2.} Let $H$ be a hexagonal system with a perfect matching. Then

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

\textbf{Proof.} Define a mapping $\phi : \mathcal{M} \rightarrow \mathcal{C}$ as follows: For each $M \in \mathcal{M}$, 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 $C_M \in \mathcal{C}$ and $\varphi$ is a mapping. Next we show that $\varphi$ is surjective. For any $C \in \mathcal{C}$, 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 $\mathcal{M}$ and $\varphi(M) = C$. Finally, for any perfect matchings $M_1$ and $M_2$ of $\mathcal{M}$, 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 $\varphi$ is injective. Hence $\varphi$ is a one-to-one correspondence from $\mathcal{M}$ to $\mathcal{C}$ 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, $r(H) \leq k(H)$, 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 $C_0$. 
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 \( H \) \cite{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 \( h_t \) 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 \( h'_{j} \) 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, \( P_1 P_2 \) 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 \( P_1 P_2 P_3 \) is a required g-cut line and statement (2) holds. \( \square \)

Lemma 3.4 (Zhang \cite{24, Theorem 3.2.1}). Let \( G \) be a 2-connected plane bipartite graph with perfect matchings. Then \( r(G) \leq K(G) \), and equality holds if and only if there do not exist disjoint cycles \( R \) and \( C \) such that (a) \( R \) is a facial boundary lying in the interior of \( C \) and (b) \( C \cup R \) is a nice subgraph of \( G \).
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 \( L = P_1 P_2 P_3 \) 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 \( \angle P_1 P_2 P_3 = \pi/3 \), and the two end-points of \( L \) lie on \( C^* \). Since \( C^* \) is the boundary of coronene and \( \angle P_1 P_2 P_3 = \pi/3 \), 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 \( cs(H) \leq cc(H) = nl(H) \). 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 \( C \) without alternating hexagons in \( H \), which is not a Clar structure of \( H \). Let \( M \) be a perfect matching of \( H \) corresponding to \( C \), such that all hexagons in \( C \) are proper \( M \)-alternating. Since \( C \) is not a Clar structure, there exists another perfect matching \( M' \) in \( H \), different from \( M \), such that all hexagons in \( C \) 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 \( C \). Otherwise, by Lemma 4.1 \( I[C] \) would contain an \( M \)-alternating hexagon \( h' \) which would be disjoint from any hexagon in \( C \). This contradicts to \( C \) 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 \( cs = cc \).
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 $\mathcal{I}$ denote the set of edges of $L_{m,n}$ intersecting $L$. $L_{m,n} - \mathcal{I}$ (the removal of all edges in $\mathcal{I}$ 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 $\mathcal{I}$. 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 $\mathcal{I}^*$. Since the difference between the numbers of white and black vertices in each component of $C_0 - \mathcal{I}^*$ is two, every perfect matching $M$ of $C_0$ contains exactly two edges of $\mathcal{I}^*$. 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 $\rho(x, H) = 3x^4 + 6x^3 + 3x^2$. 

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 $\mathcal{C}$ without alternating hexagons in $H$, $H - \mathcal{C}_s$ 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 $H - \mathcal{C}_s$, where $\mathcal{C}_s$ denotes the set of hexagons in $\mathcal{C}$.

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

**Sufficiency:** For a Clar cover $\mathcal{C}$ of $H$ without alternating hexagons in $H$, $H - \mathcal{C}_s$ has a cycle $C$ intersecting a hexagon $h$ along a path of odd length, such that $C \cup h$ is a nice subgraph of $H - \mathcal{C}_s$. 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 $H - \mathcal{C}_s$, the perfect matching of $C \cup h$ can be extended to a perfect matching $M$ of $H - \mathcal{C}_s$. As $h$ is an $M$-alternating hexagon in $H - \mathcal{C}_s$, $H - (\mathcal{C}_s \cup h)$ has a perfect matching. Thus the hexagons in $\mathcal{C}_s \cup h$ and a perfect matching of $H - (\mathcal{C}_s \cup h)$ compose a Clar cover $\mathcal{C}'$ of $H$. As $\mathcal{C}_s \subset \mathcal{C}'$, we conclude that $\mathcal{C}$ is not a Clar structure of $H$. Hence $cs < cc$.

**Necessity:** Suppose $cs < cc$. Then there must exist a Clar cover $\mathcal{C}$ without alternating hexagons in $H$, but $\mathcal{C}$ is not a Clar structure of $H$. So there is another perfect matching $M'$ in $H$ such that all hexagons in $\mathcal{C}$ are proper $M'$-alternating,
and there exists at least one $M'$-alternating hexagon $h$ in $H - \mathcal{C}_s$. Let $M$ be a perfect matching of $H$ corresponding to $\mathcal{C}$, such that all hexagons in $\mathcal{C}$ 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 $C \subset H - \mathcal{C}_s$ 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. \Box

**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 $\mathcal{C}$ without alternating hexagons in $H_1$, there is exactly one hexagon $h$ which intersects $L$ belonging to $\mathcal{C}$. 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 $\mathcal{C}_s$, then the resulting graph is isomorphic to graph $H^1$ shown in Fig. 14. If one of the hexagons 2, \ldots, $\ell$ belongs to $\mathcal{C}_s$, 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 $\mathcal{C}$ of $H_1$ without alternating hexagons, $H_1 - \mathcal{C}$ 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. □

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 $\mathcal{C}$ of $H_1$ without alternating hexagons, and assume that the hexagon $i$ belongs to $\mathcal{C}_s$. If $i \geq 2$, then $\rho_1(x, H_1) = (\ell - 1) \cdot x \cdot \rho(x, C_0)$. If the hexagon 1 belongs to $\mathcal{C}_s$, 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:

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

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

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

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.](image-url)
For the hexagonal system \( C_{2m-1,n} \) \((m > 1)\) (see Fig. 17), if \( n - m + 1 \geq 2 \), then \( cs < cc \).
Proof. Let \( n - m + 1 = k \). Then both the top and the bottom of \( C_{2m-1,n} \) have \( k (k \geq 2) \) 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: \( k \geq 3 \) 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 \( c_s < cc \).

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 \(\partial H_0\) 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 \(cs < cc\).

Acknowledgement

The authors are grateful to the referees for their careful reading and many valuable suggestions.

References