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Article

Kekulé Structure of Angularly Connected Even Ring Systems

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Abstract: An even ring system G is a simple 2-connected plane graph with all interior vertices of degree 3, all exterior vertices of either degree 2 or 3, and all finite faces of an even length. G is angularly connected if all of the peripheral segments of G have odd lengths. In this paper, we show that every angularly connected even ring system G, which does not contain any triple of altogether-adjacent peripheral faces, has a perfect matching. This was achieved by finding an appropriate edge coloring of G, derived from the proof of the existence of a proper face 3-coloring of the graph. Additionally, an infinite family of graphs that are face 3-colorable has been identified. When interpreted in the context of the inner dual of G, this leads to the introduction of 3-colorable graphs containing cycles of lengths 4 and 6, which is a supplementation of some already known results. Finally, we have investigated the concept of the Clar structure and Clar set within the aforementioned family of graphs. We found that a Clar set of an angularly connected even ring system cannot in general be obtained by minimizing the cardinality of the set A. This result is in contrast to the previously known case for the subfamily of benzenoid systems, which admit a face 3-coloring. Our results open up avenues for further research into the properties of Clar and Fries sets of angularly connected even ring systems.

Keywords: Kekulé structure; Clar structure; perfect matching; benzenoid system; even ring system; face coloring; edge coloring; Clar set

MSC: 05C15; 05C90; 92E10

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1. Introduction

Perfect matchings in chemical graphs have been a significant focus of research for decades due to their essential role in modeling molecular structures. Chemical compounds are frequently represented as graphs, where perfect matchings correspond to Kekuléan structures—resonance forms that illustrate the arrangement of double bonds within the molecule. These Kekuléan structures offer valuable insights into the stability and reactivity of various compounds. Aromatic compounds, in particular, are of special interest, with benzenoid systems standing out as especially important due to their unique carbon ring structures, which render them suitable for mathematical study [1].

Perfect matchings of benzenoid systems have been studied for some time in the context of Clar structures and Clar numbers [2–6], resonance graphs (Z-transformation graphs) [7–10], and matching polynomials [11,12]. In [8], the author focuses on determining and enumerating perfect matchings for planar graphs, with applications in chemistry. Recently, Chen et al. obtained reduction formulas to compute the matching polynomial and independence polynomial of any benzenoid chain [12].

In the past, researchers have investigated whether a given benzenoid system obtains a perfect matching. For example, in [13,14], the authors employed algorithms to explain the existence of a perfect matching by searching for appropriate paths within the graph. Moreover, the authors in [15] presented a linear time algorithm to determine whether a benzenoid system is Kekuléan.

Even ring systems, a class of bipartite graphs consisting of even-length cycles, are used to model various aromatic chemical structures, including benzenoid systems. Within this broader class, catacondensed even ring systems (CERSs), introduced in [16], represent a specific subclass of outerplane graphs that model many known structures, such as catacondensed benzenoid graphs [1], phenylenes, catafusenes [17], cyclooctatetraenes [18], catacondensed C_4C_8 systems [19], etc.

The Clar number was firstly observed on the family of Kekuléan benzenoid systems [4], where some particular bounds and heuristic method of determining Clar numbers were given. In [5], the authors presented a simple method to determine the Clar number of catacondensed benzenoid hydrocarbons. They found that this number equals the minimum number of lines required to intersect all hexagons in the structure. Bašić et al. proved an upper bound for the Clar number of catacondensed benzenoid graphs and characterized the graphs that attain this bound [2]. In [6], it was shown that the number of Clar formulas of a Kekuléan benzenoid system equals the number of subgraphs of its resonance graph isomorphic to a hypercube of dimension that is equal to the Clar number. In [2], the authors explored upper bounds for the Clar number of catacondensed benzenoid graphs and characterized graphs that achieve this bound. They found that for a catacondensed benzenoid graph with n hexagons, the Clar number is less than or equal to $\left\lfloor \frac{2n+1}{3} \right\rfloor$. In [20], the authors developed the method of constructing Kekuléan structures for benzenoids that generally give good estimates for the Clar numbers. In [21], the Clar number of fullerenes was investigated. The authors showed that the Clar number of fullerenes is upper bounded by $\frac{|V|}{6} - 2$. Furthermore, in [22], the same authors characterized extremal fullerene graphs whose Clar numbers corresponded to this upper bound. In [23], a different characterization of these extremal graphs was achieved using the leapfrog construction.

The concept of a face coloring of a planar graph G was motivated from the classic map-coloring problem, where countries on a map are colored to ensure that neighboring countries have different colors. It involves assigning colors to the faces of a planar graph such that no two adjacent faces share the same color. By planar duality, the face coloring of a planar graph corresponds to the vertex coloring of its dual graph. In 1976, the famous Four-Color Problem was solved, which states that for every map drawn on a sheet of paper, it can be colored with only four colors in such a way that countries sharing a common border receive different colors [24]. The concept of a face 3-coloring will provide a framework for identifying a perfect matching of an angularly connected even ring system.

Research into the perfect matchings (Kekuléan structures), of chemical graphs began primarily with the investigation of catacondensed benzenoid systems [1]. These findings were later generalized to some other catacondensed graphs (e.g., catacondensed polygonal systems containing hexagons and tetragons [17] and catacondensed even ring systems [16]). In this paper, we extend the research by finding the perfect matching of Kekuléan chemical graphs that are not necessarily catacondensed. While previous studies often formulate results with statements in terms of, "Let G be a Kekuléan benzenoid system/even ring system", our work identifies an infinite family of graphs for which these results hold. This contribution enhances and expands the scope of existing research by uncovering an infinite set of graphs to which the established results can be applied.

The article is structured as follows. In the next section, the fundamental definitions and notation are presented. Next, results related to the existence of a proper face 3-coloring are stated for any angularly connected even ring system G that does not contain a triple of altogether-adjacent peripheral faces. Subsequently, we demonstrate that such face coloring can always be used to obtain a proper edge 3-coloring of G. This result serves as the main tool to prove that angularly connected even ring systems, which do not contain any triple of altogether-adjacent peripheral faces, are Kekuléan. In the last section, we explore the concepts of Clar structures and Clar sets within the family of angularly connected even ring systems. We show that a Clar set of an angularly connected even ring system cannot be determined simply by minimizing the cardinality of the set $|A|$. Finally, we present some open problems related to the determination of Clar structures and the Clar and Fries numbers within the mentioned family of graphs.

2. Preliminaries

Let G be a plane graph. The regions bounded by the edges of G are called *faces* of G. A face F of G is called a *finite face* if F represents a finite region and the *infinite face* otherwise. Two finite faces of G are *adjacent* if they share a common edge. In addition, we denote the set of edges that surround a face F of G by $E(F)$. The *neighborhood* of a finite face F, namely $N(F)$, represents all of the finite faces that are adjacent to F. The subgraph induced by the edges in $E(F)$ is the *periphery of F.*

The periphery of the infinite face is also called the *periphery of G.*

The vertices on the periphery of G are called *exterior vertices* and the remaining vertices are *interior vertices.* We call a cycle C of G to be *interior* if every vertex that belongs to C is interior. In addition, the edges on the periphery of G are called *exterior edges* and the remaining edges are *interior edges.* The *distance between two edges e* and f of G is equal to the distance between the corresponding vertices in the line graph of G, and denoted by $d_G(e, f)$, or, in short, $d(e, f)$. A face adjacent to the infinite face is called a *peripheral face*. Let F be a finite face, and F_0 the infinite face. A connected component of the graph induced by the edges in $E(F_0) \setminus E(F)$ is called a *peripheral segment* of F.

In [16], an *even ring system* is defined as a simple bipartite 2-connected plane graph with all interior vertices of degree 3 and all exterior vertices of degree 2 or 3. In [25], the so-called “Two-Color Theorem” was stated as follows.

Theorem 1 ([25])**.** *The chromatic number of a graph G does not exceed 2 if and only if G contains no odd cycles.*

Since every even ring system G is bipartite, its chromatic number is 2, which means that G consists only of cycles of even length. This implies that all faces of G are even. Therefore, an even ring system could also be defined as a simple 2-connected plane graph with all interior vertices of degree 3 and all exterior vertices of degree 2 or 3, and all finite faces of an even length. If G is an even ring system, then any exterior edge that has both endpoints of degree 2 is called an *exposed edge* of G and all other exterior edges are called *non-exposed edges.* Suppose that F_1, F_2, and F_3 are three finite faces of an even ring system G. If face F_1 is adjacent to face F_2, F_2 is adjacent to F_3, and F_3 is adjacent to F_1, we say that these faces are *altogether adjacent.* The *inner dual* of an even ring system G is a graph that consists of vertices corresponding to the finite faces of G. Moreover, two vertices of the inner dual are adjacent if and only if the corresponding faces in G have a common edge.

The smallest example of an even ring system, which consists of three altogether-adjacent peripheral faces, is called phenalene and is depicted in Figure 1.

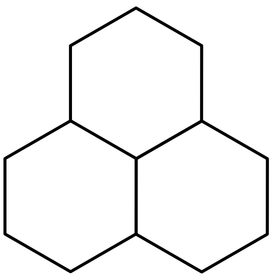

Figure 1. The phenalene.

Let G be an even ring system and T be its inner dual. If T is a tree, then G is called the *catacondensed even ring system* (or, in short, *CERS*). In [26], a definition of regular triple of faces of CERSs was given, and in [27], a definition of regular CERSs was given. Since the terminology “regular” is different from that which is usually used to define those graphs whose vertices all have the same degree, we have renamed the concept using "angularly connected faces" and "linearly connected faces". Let F_1, F_2, and F_3 be three finite faces of a CERS G such that F_1 and F_2 have the common edge e, and F_1 and F_3 have the common edge f. Then, the triple (F_1, F_2, F_3) is called an *adjacent triple of finite faces.*

The adjacent triple of finite faces (F_1, F_2, F_3) of G is *angularly connected* if $d(e, f)$ is even, and *linearly connected* otherwise. Moreover, the CERS G is called *angularly connected* if G does not have any adjacent triple of finite faces that is linearly connected.

In the following, we generalize this concept to the family of all even ring systems.

Definition 1. *Let G be an even ring system. Then, G is angularly connected if all peripheral segments of G have odd lengths.*

Note that if G is an angularly connected CERS, then G has all the peripheral segments of odd length, and each peripheral segment is a path that starts with a vertex that lies on a common edge between two adjacent faces and also ends with a vertex that lies on a common edge between two adjacent faces. It follows that every triple of finite faces of G is angularly connected, which concludes that the definition of an angularly connected even ring system is really a generalization of Definition 4.1 from [27].

In the following, we will consider a special subfamily of angularly connected even ring systems that do not contain any triple of altogether-adjacent peripheral faces. An example of such an angularly connected benzenoid is depicted in Figure 2.

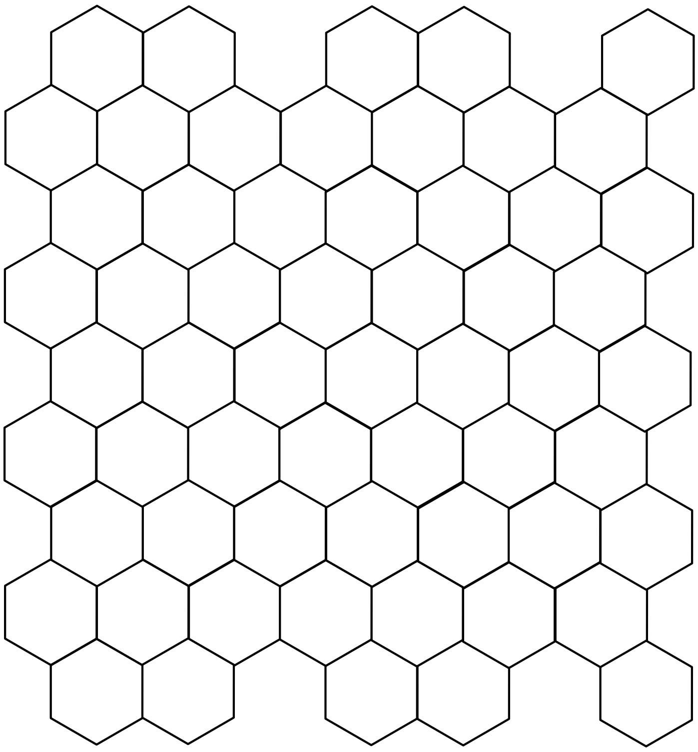

Figure 2. An example of an angularly connected even ring system that does not contain any triple of altogether-adjacent peripheral faces.

In the context of an even ring system G, its Kekulé configuration (if such a structure exists) can be mathematically interpreted as a set of edges K in G, with the condition that each vertex in G is adjacent to precisely one edge in K. In the graphical representation, these Kekuléan structures are mainly denoted by the presence of double bonds corresponding to the edges in K. Not every even ring system possesses a perfect matching, but when it does, it is referred to as being *Kekuléan.*

3. Kekuléan Structure of Angularly Connected Even Ring Systems

In this section, we prove the main result of the paper, which states that every angularly connected even ring system that does not contain any triple of altogether-adjacent peripheral faces is Kekuléan. This is in some way a generalization of the result from [16], where it was shown that every CERS has a perfect matching. Let us begin by proving the next lemma.

Lemma 1. *Let G be an even ring system. Then, any two adjacent faces of G share exactly one edge.*

Proof. First, assume that there exist adjacent finite faces F and F' of an even ring system G that have at least two edges in common, and that there is a pair of these edges that have a common endpoint, namely u. Suppose that u is an exterior vertex. Then, there exists an interior vertex of degree 2 (the red vertex in Figure 3), which is a contradiction to the definition of an even ring system. Therefore, u must be an interior vertex and (since every interior vertex must have degree 3) have another neighbor, u', such that $u' \notin \{V(F), V(F')\}$. Note that u' is surrounded by one of the faces F or F' (wlog. F) and has no neighbor in $V(F) \cap V(F')$ other than u. Again, by the definition of an even ring system, there must exist another vertex u'' such that $u'u'' \in E(G)$, and u'' has no neighbor in $V(F) \cup V(F')$. With a similar line of reasoning, we conclude that it is not possible to complete the path $(u, u', u'', \ldots)$ such that it forms a finite face, which leads to a contradiction.

Suppose now that F and F' have at least two edges in common and that these edges are pairwise disjointed. From a short consideration, one can observe that there should exist such nonadjacent vertices x and y from $V(F) \cap V(F')$ that are on the same path, and this path is not in $F \cap F'$ (see Figure 4, where the bold edges represent common edges of F and F'; the gray curve represents the path between x and y of a length of at least 2; and u is a vertex lying on that path). Since each interior vertex has exactly three neighbors and x and y are endpoints of common edges of F and F', there exists another face F'' (see Figure 4). Moreover, since every interior vertex must be of degree 3, there exists the neighbor u' of u other than those neighbors on the gray path, and it is surrounded by F' or F''. Using the same reasoning as in the first part of the proof, it is not possible to complete the path $(u, u', \ldots)$ to obtain a finite graph, which leads to a contradiction. □

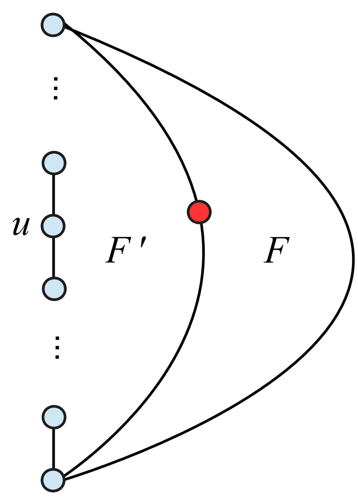

Figure 3. Graph G from the proof of Lemma 1 that could not be an even ring system, since the red vertex is the interior and of degree 2.

In the following, we will prove that every Kekuléan structure of an angularly connected even ring system G that does not contain any triple of altogether-adjacent peripheral faces can be found by finding the corresponding proper face coloring of G. A *face k-coloring* of a planar graph is a coloring in which each face is colored with one of the k colors. A face k-coloring is called *proper* if no two adjacent faces are colored with the same color. Next, we deal with the case where $k = 3$. Note that due to the definition of the face 3-coloring, an infinite face should also be colored. It turns out that a sufficient condition for the existence of a proper face three-coloring is that there exists a proper coloring of the peripheral faces and the infinite face of G with three colors. The next lemma will therefore be a tool to provide this result.

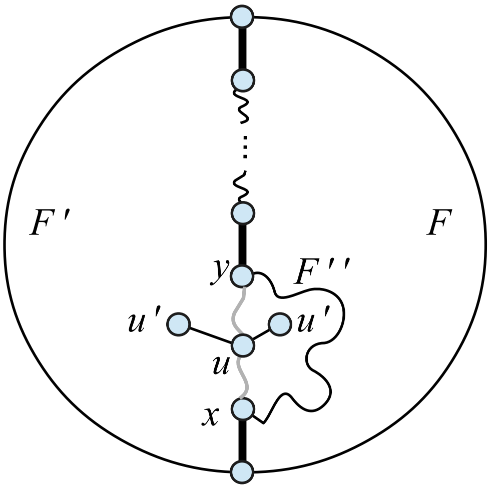

Figure 4. Second subgraph from the proof of Lemma 1.

Lemma 2. *Let G be an angularly connected even ring system that does not contain any triple of altogether-adjacent peripheral faces. Then, the subgraph of the corresponding dual graph of G, induced only on the vertices that represent the peripheral faces of G, is bipartite.*

Proof. If G has only one finite face, then its dual graph is the one-vertex graph, which is bipartite by definition. Therefore, let G have at least two finite faces and let G^* be its dual graph. Moreover, let $[B(G^*)]$ denote the subgraph of G^* induced only on the vertices that represent the peripheral faces of G. According to the fact that G does not contain any triple of altogether-adjacent peripheral faces, there are no triangles in $[B(G^*)]$. Let us therefore assume that there is an induced cycle C of odd length in $[B(G^*)]$, other than 3. Then, consider the subgraph of G that is induced on the peripheral faces, which forms the cycle C, namely $[B(C)]$. Since there are no three altogether-adjacent peripheral faces in G, and by Lemma 1, the peripheral faces that correspond to the vertices of $[B(C)]$ produce an odd number of common edges between all the adjacent faces. Then, one of the following holds: (a) the vertices and edges of G that correspond to $[B(C)]$ and are on the periphery of $[B(C)]$ form a cycle of odd length; or (b) the vertices and edges of G that correspond to $[B(C)]$ and are not on the periphery of $[B(C)]$ form a cycle of odd length. In both cases, there exists a cycle of G with an odd length, and therefore, G is not bipartite, a contradiction to the definition of an even ring system. □

By Lemma 2, we can properly color the peripheral faces of some angularly connected even ring system in such a way that we assign to them colors from the two of the color classes (the infinite face then obtains the third color). The next theorem assures the existence of a face 3-coloring for any angularly connected even ring system.

Theorem 2. *Every angularly connected even ring system that does not contain any triple of altogether-adjacent peripheral faces is face 3-colorable.*

Proof. Let G be an angularly connected even ring system that does not contain any triple of altogether-adjacent peripheral faces. By Lemma 2, there always exists a proper face 3-coloring of the peripheral faces of G, where the finite faces are colored with two of the color classes and the infinite face with the third one. Therefore, suppose that G has at least one non-peripheral face. Let G' be the graph, obtained from G by deleting all the edges that are not part of any non-peripheral face. Note that G' consists of k pairwise disjointed connected components $G'_i, i \in \{1, 2, \ldots, k\}$. Therefore, we start coloring the faces of G by choosing the faces from one of such components, wlog. G'_1, via the following steps:

1. First, we color a finite face of G'_1 that is adjacent in G to some peripheral face, namely F_1, with color 1, and all the adjacent faces of F_1 in G alternately with colors 2 and 3. Note that by Lemma 1, two adjacent faces of G share exactly one edge; therefore, for every edge of F_1, there exists another finite face and, since F_1 is of even length, such a coloring is proper so far. Note also that by doing so, we fix the colors on the periphery of G (with colors 2 and 3).
2. Next, we color a finite face F_2 of G'_1 that is adjacent to two of the already colored faces of G (of course, colored by 2 and 3) with color 1 (note that if such a face does not exist, then all of the faces of G'_1 have already been colored). Further, we color the still non-colored adjacent faces of F_2 alternately with colors 2 and 3 (again, by Lemma 1 and by the fact that G is an even ring system, we have to color an even number of adjacent faces of F_2; therefore, such a coloring is proper).
3. We continue this procedure by choosing a new non-colored face F_3 of G'_1, adjacent to at least two colored faces from $N(F_1)$, and color it with color 1 (again, if such a face does not exist, it means that we already colored all of G'_1). Again, by alternately coloring the non-colored neighborhood of F_3 with colors 2 and 3, the coloring remains proper.
4. We perform step 3, until all the faces of G'_1 that are adjacent to some face from $N(F_1)$ has been colored, and we denote the sequence of the successively chosen faces of color 1 by $F_4, F_5, \ldots, F_r$.
5. For every $i = 2, \ldots, r$, we now consider a finite face F_i of G'_1 that has already been colored with color 1. We choose a non-colored face (if exists) of G'_1 that is adjacent to at least two of the already colored faces of $N(F_i)$ and color it with color 1. Again, by the same reasoning as in step 3, we alternately color all its adjacent faces, and obtain the proper coloring of faces. We perform this step until all the faces that are adjacent to some face from $N(F_i)$ have been colored.
6. We repeat step 5 for the $N(N(F_i)), i = 1, 2, \ldots, r$ and further, until we color all the faces of G'_1.

In the next step, we choose F as a finite face of the component G'_i that has already two colored neighbors or, for some of its adjacent faces, there already exists a colored face. Now, we again perform steps 1–6 (with the only difference that the colors of faces around F has already been fixed by previous steps) until all the faces from G'_i have been properly colored. Repeating this procedure throughout the rest of the graph, coloring the still non-colored peripheral faces, and coloring the infinite face with color 1 provide the proper face 3-coloring of G. □

Note that by the above construction of the proper face 3-coloring, there is no possibility to obtain the "whole" of non-colored faces during the procedure. This means that in each step, only the starting and ending faces, alternately shifting around the face with color 1, will meet a face that has already been colored in the previous steps. From now on, we will call such a face the 3-coloring of G, defined in the proof of Theorem 2 as *Face coloring 1.*

In 2016, Kang et al. [28] proved the next result:

Theorem 3 ([28])**.** *Every planar graph without cycles of length 4, 6, 9 is 3-colorable.*

By Theorem 2, we have found an infinite family of graphs which are face 3-colorable. If we consider this result in the language of the inner dual of an even ring system, we have found an infinite family of graphs that are 3-colorable and contain cycles of lengths 4 and 6, which in some way supplements the upper result.

In the following, we will construct a proper edge 3-coloring of an angularly connected even ring system from Face coloring 1, which will help us in proving the existence of a perfect matching. Note that since every even ring system is bipartite, then by Theorem 17.2

from [29], we need exactly three colors to color the edges. Therefore, the graph family of angularly connected even ring systems is of the so-called *class 1 graphs* regarding proper edge coloring.

Let G be an angularly connected even ring system that does not contain any triple of altogether-adjacent peripheral faces, and let us color the faces of G with Face coloring 1. Then, color every edge that does not lie on the periphery of G with the color different from the color of the corresponding adjacent faces. Next, color the remaining exterior edges of G with a color different from the colors of edges that share an endpoint of degree 3 with that edge, and color the rest of the non-colored non-exposed exterior edges with the same color. Lastly, color the remaining exposed exterior edges with the color of the peripheral face to which these edges belong. Of course, the obtained edge coloring is proper (since G is angularly connected), and we have used the colors from the three color classes.

We denote such a proper edge 3-coloring as *Edge coloring 1*. In Figure 5, Face coloring 1 and Edge coloring 1 of the angularly connected even ring system without three adjacent peripheral faces is shown.

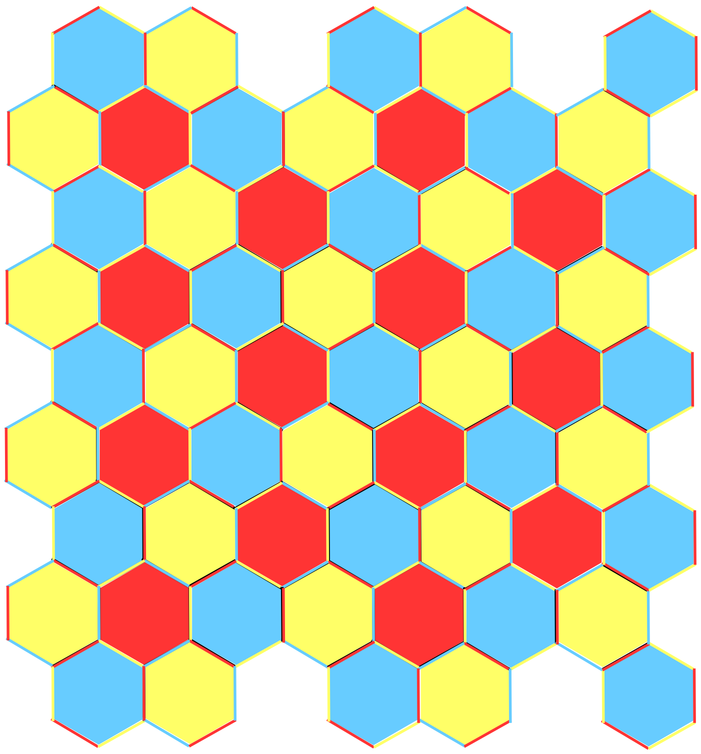

Figure 5. Face coloring 1 together with Edge coloring 1 of an angularly connected even ring system.

The next result confirms the existence of perfect matchings for any angularly connected even ring system.

Corollary 1. *Every angularly connected even ring system that does not contain any triple of altogether-adjacent peripheral faces has a perfect matching.*

Proof. Let G be an angularly connected even ring system without triples of altogether-adjacent peripheral faces. Note that Edge coloring 1 prescribes to every exposed edge of G the color of the same color class. Since G is angularly connected, the exposed edges cover all the vertices of degree 2. On the other hand, every vertex of degree 3 has adjacent edges of all three of the edge color classes; therefore, the color class with exposed edges represents a perfect matching. □

A perfect matching of an angularly connected benzenoid system that has no triples of altogether-adjacent peripheral faces is shown in Figure 6, where the double edges represent the edges that are part of the perfect matching and coincide with the red edges from Figure 5. In addition, Figure 7 shows an example of an angularly connected even ring system G that is not a benzenoid system. The finite faces in the figure are colored with *Face coloring 1*. In addition, the red edges belong to the color class of *Edge coloring 1*, which represents a perfect matching of the graph G.

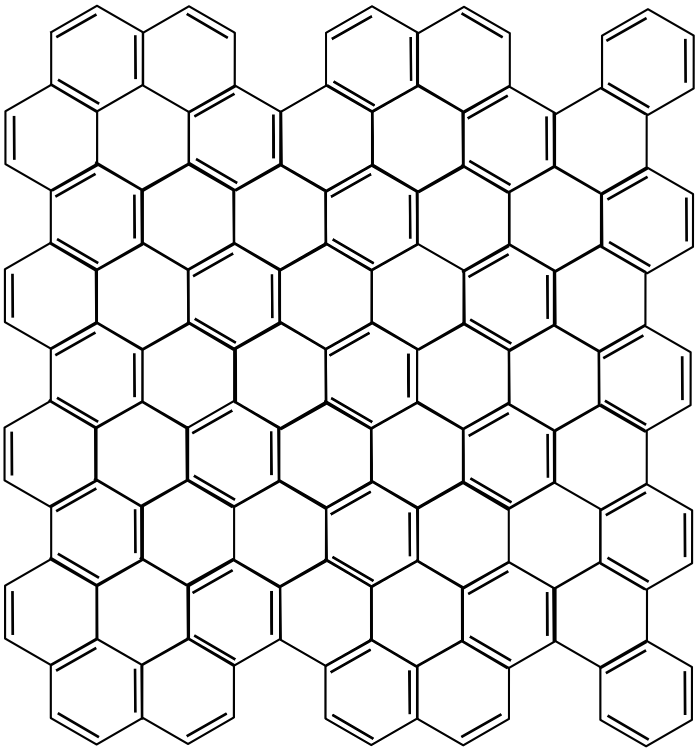

Figure 6. A perfect matching of an angularly connected even ring system.

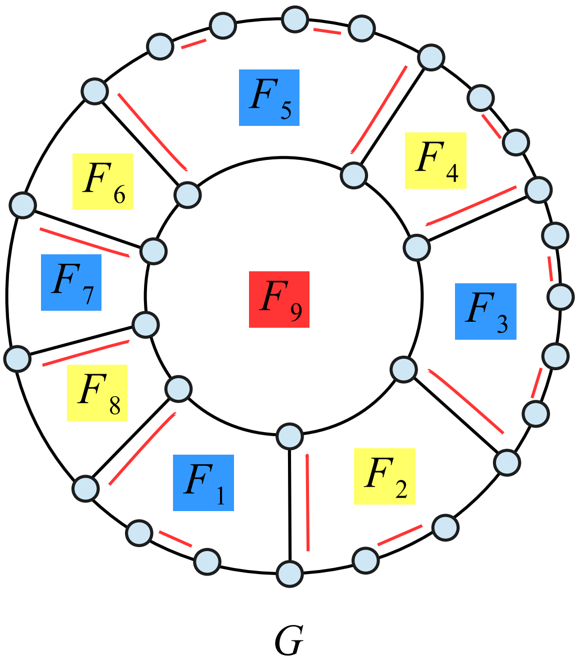

Figure 7. A perfect matching (red edges) of an angularly connected even ring system G that is not a benzenoid system.

4. Clar Set of an Angularly Connected Even Ring System

We begin this section with the definition of the Clar and Fries numbers of an even ring system. We also define the Fries set and the Clar set, whereby the latter appears under this name for the first time in [30], but was also previously known as the maximum cardinality resonant set, or Clar formula [5]. First, we need to define what the alternating face of a Kekuléan even ring system is.

Let G be a Kekuléan even ring system, and let K be a corresponding Kekuléan structure. For each finite face of G with n vertices, $0, 1, 2, \ldots, n-2$ or $n-1$ of its edges are contained in K. Let F be a finite face of G that has exactly $n-1$ edges in K. Then, we call such a face *an alternating face* of G.

Definition 2. *Let G be a Kekuléan even ring system. The Fries number of G is the maximum number of alternating faces over all possible Kekuléan structures of G. The set of these faces is called the Fries set. The Clar number of G is the maximum number of independent alternating faces over all possible Kekuléan structures of G. An independent set of these faces is called the textitClar set.*

Let F be a finite face of an angularly connected even ring system G. Then, we say that an edge $e \in E(G)$ *exits* at face F if e shares exactly one vertex with F.

The next lemma is the generalization of Lemma 2.2 from [30].

Lemma 3. *Let G be a Kekuléan even ring system and K a Kekuléan structure on G. Then, an even number of edges of K exit each finite face of G.*

Proof. Let F be a finite face of G and $e_1, e_2, \ldots, e_k \in K$ with all edges lying on F. Since each pair of these edges is pairwise disjointed and each such edge coincides with exactly two vertices of F, and since F is of even length, an even number of vertices of F must still be covered by the edges from K. We can only cover them with the edges of K that exit F, so there is an even number of such edges. □

Let G be a Kekuléan even ring system. Then, a *chain* is an alternating sequence $F_0, e1, F_1, e_2, \ldots e_k, F_k$ of faces F_i of G and edges e_i in K, such that e_i and e_{i+1} are the edges exiting F_i for $1 \leq i \leq k-1$, e_1 exits F_0, and e_k exits F_k. If $F_0 = F_k$, we call the chain *closed*, otherwise it is *open*.

Let G be a planar graph. A *vertex covering* of G, (C, A), is a pair of finite faces C and edges A of G such that each vertex of G coincides with exactly one covering element (face of C or an edge of A).

The next definition was given analogously in [3] for benzenoid systems and fullerenes, and is now generalized to our family of graphs.

Definition 3. *Let G be a Kekuléan even ring system. Let $F_1, F_2, \ldots, F_k$ be the finite faces of G, and n_i the cardinality of F_i. A vertex covering (C, A) is called a Clar structure if each finite face F_i contains at most $n_i - 1$ edges of A.*

Let K be a Kekuléan structure of G. Then, according to the above definition, C is the maximal independent set of alternating faces with respect to K, and A is a set of edges of K that are not incident with the faces of C.

In [30], the next result was proven.

Lemma 4 ([30])**.** *Let G be a plane graph with a vertex covering (C, A). On every face of G of an even degree, there is an even number (possibly zero) of edges in A that exit the face.*

Let A^* denote the set of edges of A that are not exposed edges of G. From Lemmas 3 and 4, we can directly formulate the next result.

Proposition 1. *Let G be a Kekuléan even ring system. Let (C, A) be a Clar structure of G and let F be a finite face of G. If $F \in C$, then no edge of A exits F. If $F \notin C$, then $2, 4, \ldots, |F|$ edges of A^* exit F.*

Let G be a Kekuléan even ring system and (C, A) a Clar structure on G. Then, a *Clar chain* is a sequence of finite faces and edges $F_0, e_1, F_1, e_2, \ldots e_k, F_k$ of G, in which each edge e_i lies in A^*, and e_i and e_{i+1} are edges that exit F_i for $1 \leq i \leq k-1$; e_1 exits F_0 and e_k exits F_k. Proposition 1 ensures that every Clar chain of an angularly connected even ring system is either an open or closed chain. Note that each closed Clar chain divides G into three parts—the chain $F_0, e_1, F_1, e_2, \ldots e_k, F_k$ and two regions. We will refer to the region outside the chain as the *exterior* of the chain, and the region inside the chain as the *interior* of the chain.

The next lemma describes the important characteristic of any open or closed Clar chain of any angularly connected even ring system.

Lemma 5. *Let G be a Kekuléan even ring system and let (C, A) be a Clar structure for G. Moreover, let $F_0, e_1, F_1, e_2, \ldots, e_k, F_k, e_{k+1}$ be a corresponding Clar chain. If we color the faces and edges of G with Face coloring 1 and Edge coloring 1, then the faces $F_i, i \in \{0, 1, \ldots, k\}$ and the edges $e_i, i \in \{1, 2, \ldots, k+1\}$ of the chain are in the same color class.*

Proof. Consider a corresponding Clar chain $F_0, e_1, F_1, e_2, \ldots, e_k, F_k, e_{k+1}$. First, suppose that only the finite faces of G are contained in this Clar chain. By the definition of Face coloring 1, all faces $F_i, i \in \{1, 2, \ldots, k\}$ must be in the same color class, and from the definition of Edge coloring 1, every edge that exits some face belongs to the same color class as the corresponding face. Secondly, let us consider the case where the infinite face is contained in the chain, wlog. Let F_i be the infinite face (that is, F_{i-1} and F_{i+1} are the peripheral faces). Again, from Face coloring 1, the peripheral faces of G are from the two of the color classes. Therefore, F_{i-1} and F_{i+1} are from the same color class, and since e_i and e_{i+1} exit those two faces, they also have the same color (note that by the definition of the Clar chain, exposed edges cannot be included in any of them; therefore, F_{i-1} and F_{i+1} always exist). From this, we can conclude that the edges of the Clar chain are in the same color class. □

The example in Figure 7 illustrates that each Clar chain of G runs through the red face F_9 and is continued with two red edges that exit face F_9.

We continue the investigation with the next lemma, which shows that if we have a Clar set and a corresponding Clar structure, there are only open Clar chains (no closed ones). A similar result was proven in [3] for benzenoid systems, and now, we generalize the result for all Kekuléan even ring systems.

Lemma 6. *Let G be a Kekuléan even ring system, let C be a Clar set of G, and let (C, A) be the corresponding Clar structure of G. Then, there are no closed chains in the chain decomposition given by (C, A).*

Proof. On the contrary, suppose that there exists a closed Clar chain of a Clar structure (C, A) for a Kekuléan even ring system G, and denote it by the sequence $\mathcal{C} = F_0, e_1, F_1, e_2, \ldots, e_k, F_k, e_{k+1}$. Moreover, denote by $I_1, I_2, \ldots, I_k$ the faces in the interior of $\mathcal{C}$ that are incident with the edges $e_1, e_2, \ldots, e_k$. Also, denote with $\widehat{C}$ all faces of C that lie in the interior of $\mathcal{C}$, and with $\widehat{A}$ all edges of A that lie in the interior of $\mathcal{C}$, including all edges, e_i. Now, form a new Clar structure $(C' \cup \mathcal{F}, A')$, where $A' = A \setminus \widehat{A}$, $C' = C \setminus \widehat{C}$, and $\mathcal{F}$ is a set containing all faces of $\mathcal{C}$ together with all faces from the interior of $\mathcal{C}$ that are in the same color class as $F_i, i \in \{1, 2, \ldots, k\}$ (note that according to Lemma 5, all faces of the chain are in the same color class). $(C' \cup \mathcal{F}, A')$ is then a vertex covering, and since $|A'| < |A|$, $|C| < C' \cup \mathcal{F}$, we come to a contradiction to the fact that C is a Clar set. □

The following theorem can be proved directly from the above lemmas.

Theorem 4. *Let G be an angularly connected even ring system, let C be a Clar set of G, and let (C, A) be the corresponding Clar structure. If we color the edges of G with the Edge coloring 1, then all edges of A^* are in the same color class.*

Proof. From Lemma 6, only open Clar chains can be included in a Clar structure that has a Clar set of faces in C. Since every open Clar chain starts and ends with an edge that exits the infinite face, it should be colored with the color of the infinite face. By Lemma 5, all edges of A^* are then colored with the same color. □

Finally, we can state the next theorem, which prevents non-exposed edges from being contained in any set A of a Clar structure (C, A), where C is a Clar set.

Theorem 5. *If G is an angularly connected even ring system, C is the Clar set for G, and (C, A) is the corresponding Clar structure of G, then there are no non-exposed edges included in A.*

Proof. Let us color the faces and edges of G with Face coloring 1 and Edge coloring 1. Since Lemma 6 holds, there exist only open Clar chains in the chain decomposition given by (C, A). Moreover, by Theorem 4, all edges of each open Clar chain are in the same color class. Since every non-exposed edge exits some face of the periphery of G (which comes from one of the two color classes other than the color of the infinite face), it cannot be from the same color class as the edges of A^*. Therefore, it cannot be contained in any of the open Clar chains. □

In [3], the authors proved that if G is a benzenoid system with a vertex covering (C, A), then C is a Clar set if $|A|$ is minimized. The above result does not apply to the family of angularly connected even ring systems. Figure 8 shows an example of angularly connected even ring systems with a face of degree 16 and two quadrilateral faces. If the degree-16 face is a face in C of a vertex covering (C, A) of G, then $|A| = 4$ and $|C| = 1$. However, if the two quadrilateral faces are in C, then $|A| = 6$ and $|C| = 2$. Therefore, the Clar set is not obtained by minimizing the cardinality of the set A. This implies that the proof of the assumption that every Clar set of G is a subset of a Fries set does not follow directly from the above facts, and therefore, this problem remains open for future work.

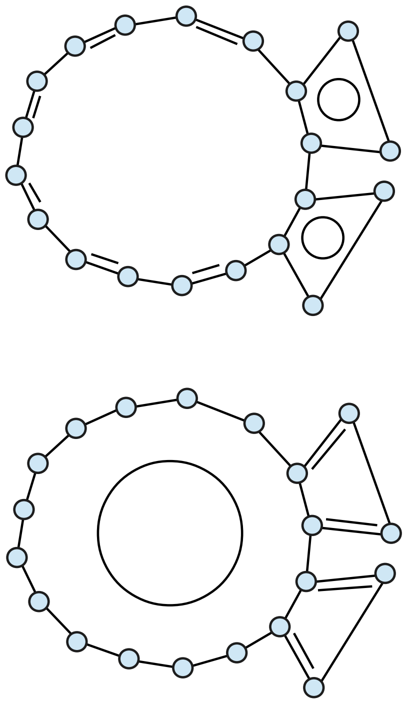

Figure 8. Example of the two Clar structures of an angularly connected even ring system where minimizing $|A|$ does not maximize $|C|$.

5. Conclusions

In this paper, it has been shown that every angularly connected even ring system G, which does not contain any triple of altogether-adjacent peripheral faces, has a perfect matching. This was achieved by finding an appropriate edge coloring of the graph G, derived from a selected proper face 3-coloring of G.

In the main results, the restriction for the graph G is that it must not contain any triple of altogether-adjacent peripheral faces. As future work, it is believed that the result could be extended to a more general setting, although the proof becomes technically more challenging when such triples are allowed. Therefore, the following conjecture is proposed as motivation for further research in this area:

Conjecture 1. *Every angularly connected even ring system has a perfect matching.*

In [3], it was shown that if G is a benzenoid system in which the faces on the periphery belong to two color classes, then the Clar set is always a subset of the Fries set. It is also shown in [30] that this assumption is incorrect for a large class of fullerenes.

In our research, we have identified a specific family of graphs for which this theorem holds. Due to the fact that a Clar set of an angularly connected even ring system cannot be obtained by minimizing the cardinality of the set A, the generalization of this theorem remains an open problem. With respect to the above, we can state the following conjecture:

Conjecture 2. *Let G be an angularly connected even ring system. Then, every Clar set of G is a subset of the Fries set of G.*

Using our results, we can always find a Clar structure (C, A) of an angularly connected even ring system such that $|C|$ is equal to the larger of the two color classes from Face coloring 1 that correspond to the peripheral faces of G. Intuitively, it seems that the maximum independent subset of the faces corresponding to the color classes from the periphery of G forms a Clar set of G. However, the answer to this question remains open.

It is obvious that the Fries number of any angularly connected CERS G is equal to the number of all finite faces of G. It would be interesting to solve the next problem:

Problem 1. *Find the Fries number of an angularly connected even ring system.*

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References

1. Gutman, I.; Cyvin, S.J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer: Berlin, Germany, 1989.
2. Bašić, N.; Estélyi, I.; Škrekovski, R.; Tratnik, N. On the Clar Number of Benzenoid Graphs. *MATCH Commun. Math. Comput. Chem.* **2018**, *80*, 173–188.
3. Graver, J.E.; Hartung, E.J.; Souid, A.Y. Clar and Fries numbers for benzenoids. *J. Math. Chem.* **2013**, *51*, 1981–1989. [CrossRef]
4. Hansen, P.; Zheng, M. Upper bounds for the Clar number of a benzenoid hydrocarbon. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 1621–1625. [CrossRef]
5. Klavžar, S.; Žigert, P.; Gutman, I. Clar number of catacondensed benzenoid hydrocarbons. *J. Mol. Struct. THEOCHEM* **2002**, *586*, 235–240. [CrossRef]

6. Salem, K.; Klavžar, S.; Vesel, A.; Žigert, P. The Clar formulas of a benzenoid system and the resonance graph. *Discrete Appl. Math.* **2009**, *157*, 2565–2569. [CrossRef]
7. Tratnik, N.; Ye, D. Resonance Graphs on Perfect Matchings of Graphs on Surfaces. *Graphs Combin.* **2023**, *39*, 68. [CrossRef]
8. Vukičević, D. Applications of Perfect Matchings in Chemistry. In *Structural Analysis of Complex Networks*; Dehmer, M., Ed.; Birkhäuser: Boston, MA, USA, 2011.
9. Zhang, F.; Guo, X.; Chen, R. Z-transformation graphs of perfect matchings of hexagonal systems. *Discrete Math.* **1988**, *72*, 405–415.
10. Pleteršek, P.Ž. Resonance Graphs of Kinky Benzenoid Systems Are Daisy Cubes. *MATCH Commun. Math. Comput. Chem.* **2018**, *80*, 207–214.
11. Gutman, I. Characteristic and matching polynomials of benzenoid hydrocarbons. *J. Chem. Soc.* **1983**, *79*, 337–345. [CrossRef]
12. Chen, H.; Liu, X.; Shen, J. Matching Polynomials and Independence Polynomials of Benzenoid Chains. *MATCH Commun. Math. Comput. Chem.* **2024**, *92*, 779–809. [CrossRef]
13. Guo, X.; Zhang, F. Recognizing Kekuléan benzenoid system by C-P-V path elimination. *J. Math. Chem.* **1990**, *5*, 157–170.
14. Sachs, H. Perfect matchings in hexagonal systems. *Combinatorica* **1984**, *4*, 89–99. [CrossRef]
15. Hansen, P.; Zheng, M. A linear algorithm for perfect matching in hexagonal systems. *Discrete Math.* **1993**, *122*, 179–196. [CrossRef]
16. Klavžar, S.; Brinkmann, G.; Žigert, P. Resonance graphs of catacondensed even ring systems are median. *Discrete Math.* **2002**, *253*, 35–43. [CrossRef]
17. Cyvin, S.J.; Cyvin, B.N.; Brunvoll, J. Unbranched catacondensed polygonal systems containing hexagons and tetragons. *Croat. Chem. Acta* **1996**, *69*, 757–774.
18. Randić, M. π-electron currents in polycyclic conjugated hydrocarbons of decreasing aromatic character and a novel structural definition of aromaticity. *Open Org. Chem. J.* **2011**, *5*, 11–26. [CrossRef]
19. Črepnjak, M.; Tratnik, N. The Szeged index and the Wiener index of partial cubes with applications to chemical graphs. *Appl. Math. Comput.* **2017**, *309*, 324–333. [CrossRef]
20. Graver, J.E.; Hartung, E.J. Kekuléan benzenoids. *J. Math. Chem.* **2014**, *52*, 77–989. [CrossRef]
21. Zhang, H.; Ye, D. An upper bound for the Clar number of fullerene graphs. *J. Math. Chem.* **2007**, *41*, 123–133. [CrossRef]
22. Ye, D.; Zhang, H. Extremal fullerene graphs with the maximum Clar number. *Discrete Appl. Math.* **2009**, *157*, 3152–3173. [CrossRef]
23. Hartung, E. Fullerenes with complete Clar structure. *Discrete Appl. Math.* **2013**, *161*, 2952–2957. [CrossRef]
24. Appel, K.; Haken, W. The Four-Color Problem. In *Mathematics Today Twelve Informal Essays*; Steen, L.A., Ed.; Springer: New York, NY, USA, 1978.
25. Kempe, A.B. On the geographical problem of the four colours. *Amer. J. Math.* **1879**, *2*, 193–200. [CrossRef]
26. Brezovnik, S.; Tratnik, N.; Žigert Pleteršek, P. Resonantly equivalent catacondensed even ring systems. *MATCH Commun. Math. Comput. Chem.* **2019**, *82*, 625–638.
27. Brezovnik, S.; Tratnik, N.; Žigert Pleteršek, P. Resonance graphs of catacondensed even ring systems. *Appl. Math. Comput.* **2020**, *374*, 125064. [CrossRef]
28. Kang, Y.; Jin, L.; Wang, Y. The 3-colorability of planar graphs without cycles of length 4, 6 and 9. *Discrete Math.* **2016**, *339*, 299–307. [CrossRef]
29. Bondy, J.A. *U.S.R. Murty, Graph Theory*; Springer: Berlin, Germany, 2008.
30. Hartung, E.J. The Clar Structure of Fullerenes. Ph.D. Dissertation, Syracuse University, Syracuse, NY, USA, 2012.