Bonds Fixed by Fixing Bonds

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In a normal benzenoid hydrocarbon H no bonds are fixed; i.e., each bond belongs to some perfect matching or Kekulé structure of H. Fixing one of the bonds of H implies the fixation of several other ones. Several results related to such bonds fixed by fixing bonds are obtained: (a) previous algorithms for finding in linear time a Kekulé structure of a benzenoid hydrocarbon H (or showing it has none) and for finding all fixed bonds of H are generalized to obtain all bonds fixed by fixing each of the bonds of H in $O(N^2)$ time where N is the number of carbon atoms of H; (b) the *fixation graph*, which expresses fixation of bonds from bonds fixed, and the *symmetry graph* are introduced and used to find the Pauling bond orders of all edges of H; (c) a characterization is given of *fixable benzenoids*, which possess a bond whose fixing implies the fixation of all other bonds.

1. INTRODUCTION

Benzenoid hydrocarbons are often represented by benzenoid systems.[1-5] A benzenoid system H is a connected subgraph of the infinite hexagonal lattice without cut edges or non-hexagonal interior faces (an edge is a *cut edge* if its deletion results in a disconnected graph). Vertices of H correspond to carbon atoms and edges to single or double bonds between them. Given a benzenoid system H, a first natural question to ask is whether or not it corresponds to a benzenoid hydrocarbon. Empirical results suggest a necessary condition for this to be the case is that H has a perfect matching (or Kekulé structure), i.e., a set of disjoint edges which covers all vertices. Much work has been devoted to the discovery of necessary and/or sufficient conditions for H to be Kekuléan (i.e., to have a Kekulé structure) and to design of efficient algorithms to find a Kekulé structure.[6-13] In ref 13, a linear algorithm is proposed for that purpose. Counting Kekulé structures, when there are some, has also been extensively studied.[2,14] A second question arises when looking more closely at the bonds: are there some bonds which are fixed, i.e., that belong to all or to none of the Kekulé structures of H? This question is related to finding normal components of H, i.e., maximal connected subgraphs of H which contain no fixed bonds. Indeed, as has been long known and recently proved rigorously,[15,16] benzenoid systems with fixed bonds have at least two normal components. Finding all fixed bonds is equivalent to finding normal components; these are of interest in the computation of many topological indices (e.g., the number of Kekulé structures, the Clar number,[2,17,18] etc.) which can be summed or multiplied over all normal components. In ref 19, the linear algorithm for finding a Kekulé structure of a benzenoid system H is extended to find, also in linear time, all fixed bonds of H.

The next question in this line of research is to ask what are the consequences of fixing a bond (as a double or single one) of a normal benzenoid (or of a normal component of a benzenoid). How many other bonds will be fixed single or double bonds due to this fixation, and which ones? This paper studies several problems related to the study of such bonds fixed by fixing bonds.

A first problem is how to find all bonds fixed by fixing each bond of a normal benzenoid system in turn. We show that the linear algorithms of refs 13 and 19 for finding a Kekulé structure and for finding fixed bonds can be extended to determine in $O(N^2)$ time all bonds fixed by fixing bonds. One may then consider possible uses of this information. A first use is the description of the amount of order and short- or long-range order induced by fixation. Two parameters are defined for each edge: its *fixing power* defined as the number of fixed double bonds induced by fixing it as a double bond and its *fixing range* defined as the longest distance from this bond to one fixed as a double bond (the *distance* between two bonds is defined as the number of bonds in a shortest path containing them). Another application leads to our second problem: how to exploit knowledge of bonds fixed by fixing bonds in the efficient computation of the Pauling bond orders[20] of all bonds of a benzenoid H. We define the *fixation directed graph* (or in short, the *fixation graph*) $F(H)$ and the *symmetry graph* $S(H)$ as follows: the vertices of $F(H)$ and $S(H)$ are associated with bonds of H; there is a directed edge from a vertex e to a vertex e' in $F(H)$ if e' is a fixed double bond when e is chosen (or fixed) as a double bond, and two vertices e and e' of $S(H)$ are adjacent if there is an automorphism of H which maps e onto e' (the definition of automorphism will be given later). Using these graphs and linear algebra allows the Pauling bond orders for all bonds to be found from explicit computation for a few bonds only.

A third problem is related to the concept of the *degree of freedom* or *forcing number* of a Kekulé structure. This concept was defined by Klein and Randić[21,22] and Harary et al.[23] as the minimum number of double bonds which simultaneously belong to the given Kekulé structure and to no other one. These last authors called a bond *forcing* if it belongs to a unique Kekulé structure. We call a benzenoid system *fixable* if it has a forcing bond and give a characterization of fixable benzenoid systems.

2. FIXED SETS

Let e be a bond of a graph G. Then $G-e$ denotes the graph obtained from G by deleting e together with its end vertices and incident edges. The set of fixed double bonds of $G-e$ is called the *fixed set* of e. In this section, we present a method to find the fixed set of a given bond of a benzenoid system.

2.1. Previous Results. Let G be a subgraph of the infinite hexagonal lattice in which some edges are vertical. A *peak* (*respectively valley*) of G is a vertex whose neighbors are below (respectively above) it.

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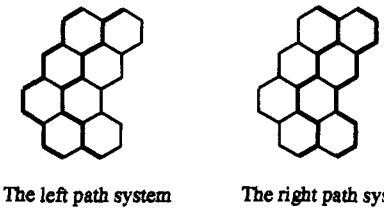

Figure 1. Illustration of left and right path systems.

Let H be a benzenoid system embedded in the plane with some of its bonds vertical.

A *perfect path system* of H is a set of vertex disjoint monotone paths from peaks to valleys which covers all peaks and valleys. Gordon and Davison[6] and Sachs[7] showed that there is a one-to-one correspondence between perfect path systems and perfect matchings of H. The correspondence is as follows: take all nonvertical bonds in and vertical bonds not in the paths of a perfect path system and a perfect matching is obtained; on the other hand, for a given perfect matching deleting all vertical double bonds together with their end vertices from H, a perfect path system is found.

In refs 7 and 12, it was proved that there is a unique matching between peaks and valleys induced by all perfect path systems of H. Let p and v be a peak and a valley, respectively, which match each other in all perfect path systems of H; i.e., p and v are the end vertices of a monotone path in all perfect path systems. Let $R_{p,v}$ (respectively $L_{p,v}$) denote the rightmost (respectively leftmost) monotone path from p to v which is also contained in a perfect path system. It was shown in ref 19 that all $R_{p,v}$ (respectively $L_{p,v}$) together form a perfect path system of H. Let us call the perfect path system consisting of $R_{p,v}$'s (*respectively* $L_{p,v}$'s) the *right* (*respectively the left*) *path system* (see Figure 1 for an illustration of the left and right path systems of a benzenoid system). In ref 13, a linear algorithm (algorithm MHS) to find a perfect matching of H is given. A linear algorithm based on MHS is given in ref 19 to find the left path system as well as the right path system of H. Let $R_{p,v} \oplus L_{p,v}$ be the set of edges which belong to $R_{p,v}$ or $L_{p,v}$ but not to both. Let $G(H)$ be the union of all $R_{p,v} \oplus L_{p,v}$. A *maximal circuit* of $G(H)$ is a circuit which is not contained in the region bounded by another circuit of $G(H)$. In ref 19, it is shown that a bond is fixed in H if and only if it is not contained in the region bounded by a maximal circuit of $G(H)$. On the basis of this result, a linear algorithm, called algorithm FXB, is given in ref 19 to find all fixed bonds of H.

2.2. Fixed Sets. By Algorithm FXB, we can first determine all fixed (single or double) bonds of a benzenoid system H. Thus determining the fixed set of a bond e, i.e., finding all double bonds which are fixed after fixing e as a double bond, can be done for each normal component of H in turn. We assume below all benzenoid systems considered are normal. Let e be a bond of H. Assume that H is embedded in the plane such that e is vertical. Since e is vertical, $H - e$ has the same peaks and valleys as H. We can define the perfect path system for $H - e$ in the same way as for H. Moreover there is a one to one correspondence between perfect matchings and perfect path systems of $H - e$. Note that each perfect path system of $H - e$ is also a perfect path system of H. Since the matching induced by all perfect path systems between peaks and valleys of H is unique, the induced matching between peaks and valleys of $H - e$ is also unique. The left and right path systems for $H - e$ are defined in the same way as those for H. Then we can extend all results of ref 19 from H to $H - e$ in a straightforward way. For example, a bond of $H - e$ is fixed if and only if it is not contained in the region bounded by a maximal circuit of $G(H - e)$ (where $G(H - e)$ is defined in a similar way as $G(H)$). For convenience we next state the main steps of algorithm FXB for finding fixed single and double bonds of $H - e$.

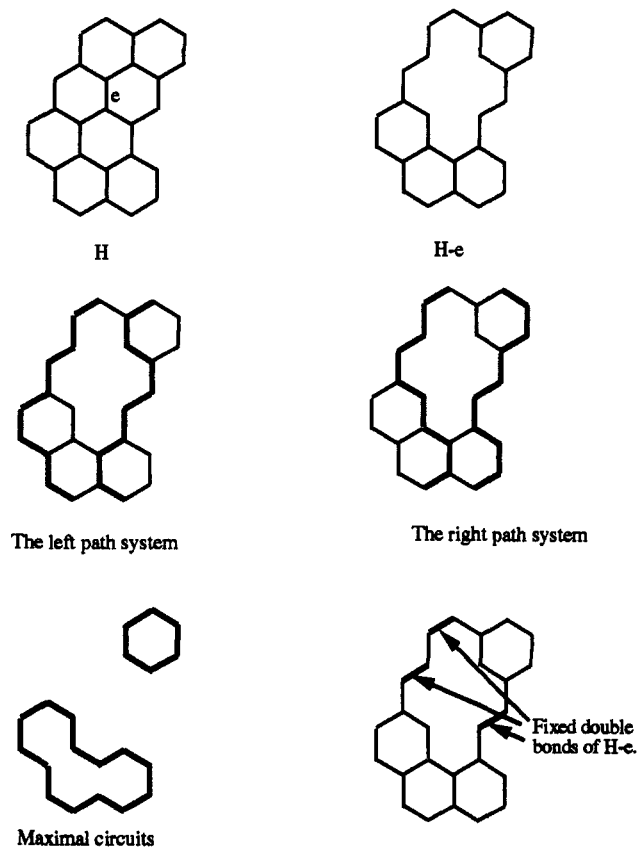

Figure 2. Illustration of algorithm FXB.

Algorithm FXB:

Step 1: Find the left and right path systems of $H - e$. Let M be a perfect matching of $H - e$ which corresponds to the left (or the right) path system.

Step 2: Determine all maximal circuits of $G(H - e)$.

Step 3: All double (single) bonds which belong to (do not belong to) M and are not contained in the regions bounded by a maximal circuit are the fixed double (single) bonds of $H - e$.

Figure 2 shows how the algorithm works.

As in ref 19, the time complexity of the above algorithm is $O(N)$ where N is the number of vertices of the input. Thus the time complexity to find the fixed sets for all bonds is $O(N^2)$.

2.3. Fixed Single Bonds. In this subsection we discuss the following problem: how to find the fixed double and single bonds after fixing a bond as a single bond?

Let e be a bond of a benzenoid system H and $H - \{e\}$ be the graph obtained from H by deleting e but not its end vertices. Then the bonds fixed by fixing e as a single bond are the fixed bonds of $H - \{e\}$. There are two cases:

Case 1. If both end vertices of e are of degree 3, embed H in the plane with e nonvertical. Then $H - \{e\}$ has the same peaks and valleys as H. Thus algorithm FXB can be used to determine all fixed bonds of $H - \{e\}$.

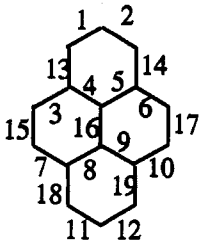

Figure 3. Numbering of edges of a benzenoid.

Table 1. Fixed Set, Fixing Power, and Fixing Range

bonds	fixed double bonds	fixed single bonds	fixing power	fixing range
1	14, 17	2, 5, 6, 10, 13	2	5
2	13, 15	1, 3, 4, 7, 14	2	5
3	1, 7, 11, 14, 16, 17, 19	2, 4, 5, 6, 8, 9, 10, 12, 13, 15, 18	7	5
4	1, 14, 15, 17	2, 3, 5, 6, 7, 10, 13, 16	4	4
5	2, 13, 15, 17	1, 3, 4, 6, 7, 10, 14, 16	4	4
6	2, 10, 12, 13, 15, 16, 18	1, 3, 4, 5, 7, 8, 9, 11, 14, 17, 19	7	5
7	1, 3, 11, 14, 16, 17, 19	2, 4, 5, 6, 8, 9, 10, 12, 13, 15, 18	7	5
8	11, 15, 17, 19	3, 6, 7, 9, 10, 12, 18	4	4
9	12, 15, 17, 18	3, 6, 7, 9, 10, 11, 19	4	4
10	2, 6, 12, 13, 15, 16, 18	1, 3, 4, 5, 7, 8, 9, 11, 14, 17, 19	7	5
11	17, 19	6, 9, 10, 12, 18	2	5
12	15, 18	3, 7, 8, 11, 19	2	5
13	2, 15	1, 3, 4, 7, 14	2	3
14	1, 17	2, 5, 6, 10, 13	2	3
15		3, 7	0	0
16		4, 5, 8, 9	0	0
17		6, 10	0	0
18	12, 15	3, 7, 8, 11, 19	2	3
19	11, 17	6, 9, 10, 12, 18	2	3

Case 2. If e has an end vertex v of degree 2, let e' be the bond of H which is different from e and incident with v. Then e' is a fixed double bond of $H - \{e\}$. The fixed bonds of $H - \{e\}$ are the fixed bonds of $H - e'$ plus e' and the bonds adjacent to e' in $H - e'$. Hence algorithm FXB can be applied.

2.4. Example. Applying algorithm FXB to the benzenoid system of Figure 3 shows that the sets of fixed double and single bonds for each bond (fixed as a double bond) are those given in Table 1. The fixing power and fixing range of each bond are also specified in this table.

3. COMPUTING THE PAULING BOND ORDER

In this section, we show how to use the fixation graph $F(H)$ and the symmetry graph $S(H)$ of a benzenoid system H to reduce the computation effort for Pauling bond order.

The fixation graph $F(H)$ can be built as follows: there is a directed edge from e to e' in $F(H)$ if e' belongs to the fixed set of e in H. A *strong connected component* of $F(H)$ is a maximal subgraph of $F(H)$ such that for any two vertices u and v of this subgraph there is a directed path from u to v and vice versa.

Two graphs G and G' are *isomorphic* if there is a one to one mapping f from the vertex set of G to the vertex set of G' such that v and v' are adjacent in G if and only if $f(v)$ and $f(v')$ are adjacent in G'. We say that f maps an edge e to e' if f maps the vertices of e to the vertices of e'. If G is equal to G', then f is called an automorphism of G. It is easy to see that two isomorphic graphs have the same number of Kekulé structures (or perfect matchings). Two bonds e and e' of H are said to be *symmetric* if they are adjacent in $S(H)$, i.e., if there is an automorphism of H which maps e to e'. Moreover, two

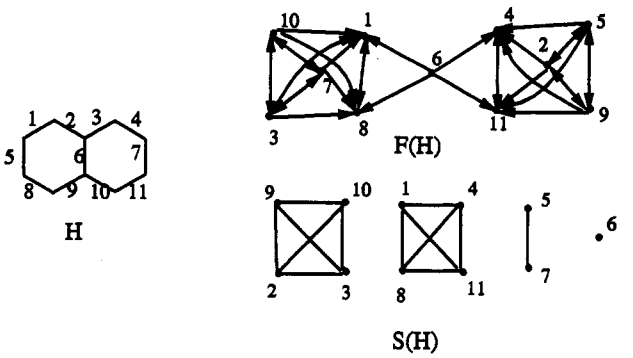

Figure 4. A benzenoid system and its fixation graph and symmetry graph.

symmetric bonds have the same Pauling bond order. This is the basic property which will be used in computing the Pauling bond orders of all edges of H.

We next show how to build $S(H)$. In order to build $S(H)$, we need to know if two bonds are symmetric or not. Let e and e' be two bonds of H and H' a copy of H. Let $N(e)$ (respectively $N(e')$) be the graph consisting of e (respectively e') and all bonds adjacent to it. Then there are at most four isomorphisms from $N(e)$ to $N(e')$. If there is no isomorphism from $N(e)$ to $N(e')$, then there is no automorphism of H mapping e to e'. Thus e and e' are not symmetric. Let g be an isomorphism from $N(e)$ to $N(e')$. According to g, we embed H and H' in the plane such that $N(e)$ and $N(e')$ coincide. Then an embedding of H as well as of H' is obtained. This embedding of H (respectively H') is denoted by $g(H)$ (respectively $g(H')$). If $g(H) = g(H')$, then the embedding induces an automorphism f of H: f maps a vertex v to a vertex v' if v and v' occupy the same position in $g(H)$ and $g(H')$. Moreover, f maps e onto e'. Thus e and e' are symmetric. Using the same notion as above, we obtain the following theorem which leads to the determination of whether or not two bonds are symmetric:

Theorem 1. *Let e and e' be two bonds of a benzenoid system H. Then e and e' are symmetric if and only if there is an isomorphism g from $N(e)$ to $N(e')$ such that $g(H) = g(H')$.*

Proof. Let H' be a copy of H. If e and e' are symmetric, then there is an isomorphism f from H to H' which maps e to e'. Also if we restrict f to $N(e)$, an isomorphism g of $N(e)$ to $N(e')$ is obtained. We embed H and H' in the plane such that v coincides with $f(v)$ for each vertex v of H. This embedding is also uniquely determined by g. Thus $g(H) = g(H')$. On the other hand, let there be an isomorphism g from $N(e)$ to $N(e')$ and $g(H) = g(H')$. Then define f as follows: $f(v)$ is the vertex of H' which occupies the same position as v in the embeddings $g(H)$ and $g(H')$. One can check easily that f is an isomorphism from H to H'. Since H' is a copy of H, f is also an automorphism which maps e onto e'.

By the above theorem, $S(H)$ can be built easily. Figure 4 gives a benzenoid system, the fixation graph, and the symmetry graph.

A *connected component* of a graph is a maximal connected subgraph of it. Let $p(e)$ denote the Pauling bond order of e (where $p(e)$ is equal to the proportion of Kekulé structures containing e). Then we have the following theorem:

Theorem 2. *Let H be a benzenoid system and e and e' be two bonds of H.*

(i) If there is a directed path from e to e' in $F(H)$, then $p(e') \geq p(e)$; if e and e' belong to the same strong connected component of $F(H)$, then $p(e) = p(e')$.

(ii) If e and e' belong to the same connected component of S(H), then p(e) = p(e').

Proof. Let e and e' be two bonds of H. If there is a directed edge from e to e' in $F(H)$, then any perfect matching containing e must contain e'. Thus $p(e') \geq p(e)$. If e and e' belong to the same strong connected component of $F(H)$, then there is a directed path from e to e' and vice versa. By the previous result, we have that $p(e) = p(e')$. If e and e' are adjacent in $S(H)$, then e and e' are symmetric. Thus $p(e) = p(e')$. Similarly, if e and e' belong to the same connected component of $S(H)$, then $p(e) = p(e')$.

We below show how to simplify the computation of the Pauling bond order. Let A be the incidence matrix of H which is defined as follows: rows of A are indexed by vertices, and columns are indexed by bonds of H; the entry in position (v,e) is 1 if v is an end vertex of e. Let $\mathbf{1}$ be the column vector with n entries and each entry equal to 1 (where n is the number of vertices of H). Then the vector $(p(e_1),p(e_2),...,p(e_m))$ (where m is the number of edges of H) of Pauling bond orders of all bonds of H is a solution of the following linear equations:

$$AX = \mathbf{1}$$

Now we give the rules for computing the Pauling bond order through the above linear equations:

(1) Substitute a variable by another variable if they belong to the same strong connected component of $F(H)$.

(2) Substitute a variable by an another variable if they belong to the same connected component of $S(H)$.

(3) Delete repeated linear equations.

Let $BY = \mathbf{1}$ be the remaining linear equations after the above steps. Solve these linear equations by Gaussian elimination thus obtaining a general solution to $BY = \mathbf{1}$ containing some variables (as parameters). Determine the Pauling bond order for each parameter by counting the Kekulé structures which contain the bond related to that parameter and dividing by the total number of Kekulé structures. Then Pauling bond orders for all bonds are obtained by substitution.

These rules are now illustrated by an example. Let H be the benzenoid system shown in Figure 4. Then $AX = \mathbf{1}$ becomes as follows:

$$\begin{aligned} x_1 + x_2 &= 1 \\ x_1 + x_5 &= 1 \\ x_5 + x_8 &= 1 \\ x_8 + x_9 &= 1 \\ x_{10} + x_{11} &= 1 \\ x_3 + x_4 &= 1 \\ x_4 + x_7 &= 1 \\ x_7 + x_{11} &= 1 \\ x_2 + x_3 + x_6 &= 1 \\ x_6 + x_9 + x_{10} &= 1 \end{aligned} \tag{1}$$

By rule 1, we have

$$\begin{aligned} x_5 = x_2 = x_9 \\ x_1 = x_8 \\ x_7 = x_3 = x_{10} \\ x_4 = x_{11} \end{aligned} \tag{2}$$

By rule 2, we have

$$\begin{aligned} x_1 = x_4 = x_8 = x_{11} \\ x_2 = x_3 = x_9 = x_{10} \\ x_5 = x_7 \end{aligned} \tag{3}$$

Finally, by substituting variables in (1) using (2) and (3) and deleting repeated equations, we get the following simplified linear equations:

$$\begin{aligned} x_1 + x_2 &= 1 \\ 2x_2 + x_6 &= 1 \end{aligned}$$

or

$$\begin{aligned} x_1 &= {}^1/_2 + {}^1/_2 x_6 \\ x_2 &= {}^1/_2 - {}^1/_2 x_6 \end{aligned}$$

where x_6 is a parameter.

Since $x_6 = {}^1/_3$, we have

$$\begin{aligned} x_2 &= {}^1/_3 \\ x_1 &= {}^2/_3 \end{aligned}$$

Substituting these values in equations in (2) and (3), the Pauling bond orders for all other bonds of H are determined.

Observe that in the above process, after x_6 is determined, all other variables are determined. So we introduce the following definition: a bond e of a benzenoid system H is *dominating* if the Pauling bond order of any other bond is a function of $p(e)$. Thus bond 6 of the benzenoid system in Figure 4 is dominating. It is easy to show that any bond of benzene (or the hexagon) is dominating. We then ask the following open question:

Which benzenoid systems have a dominating bond?

4. FIXABLE BENZENOID SYSTEMS

In this section, we characterize fixable benzenoid systems. As a corollary, we can show that a benzenoid system with each bond forcing is a hexagon. This is a theorem due to Harary et al.[23]

In refs 15 and 16, it was shown that a benzenoid system H with fixed bonds has at least two normal components. Moreover, each normal component is also a normal benzenoid. Thus if H has fixed bonds, then it is not fixable. We assume below that the benzenoid systems considered are normal.

First we describe a family $\mathcal{F}$ of benzenoid systems. Suppose that all benzenoid systems considered are drawn in the plane such that some bonds are vertical. Let $H(n_1, n_2,..., n_k; m_1, m_2, ..., m_r)$ with integers $n_1 \geq n_2 \geq ... \geq n_k \geq 1$, $m_1 \geq m_2 \geq ... \geq m_r \geq 0$, and $k \geq r$ be a benzenoid system with k horizontal rows of $n_1 \geq n_2 \geq ... \geq n_k$ hexagons and the last hexagon of each row being immediately below and to the right of the last one in the previous row and r diagonal rows of $m_1 \geq m_2 \geq ...$

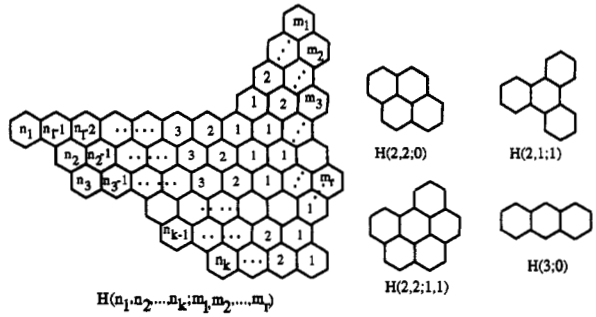

Figure 5. Family $\mathcal{F}$ of benzenoid systems.

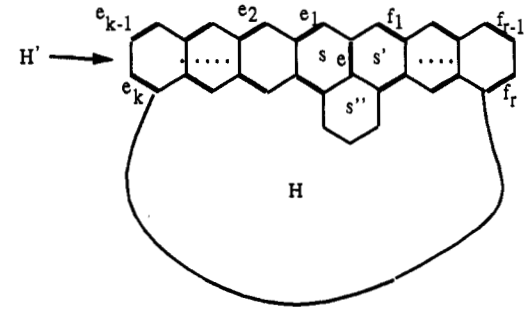

Figure 6. H and H' in the proof of lemma 4.

$\geq m_r$ hexagons and the last hexagon of each row being immediately below and to the left of the last one of the previous row. Such a benzenoid system is shown in Figure 5. Let $\mathcal{F}$ be the set of all benzenoid systems $H(n_1, n_2, ..., n_k; m_1, m_2, ..., m_r)$. A *chain benzenoid* is defined to be a benzenoid system of $\mathcal{F}$ with the form $H(n;0)$. We state the main results below and then give their proofs.

Theorem 3. *A benzenoid system is fixable if and only if it belongs to* $\mathcal{F}$.

Theorem 4. *Let e be a forcing bond of a benzenoid system H. Then the end vertices of e belong to the boundary of H.*

Corollary 1.[23] *A benzenoid system H with each bond forcing is a hexagon.*

Theorem 5. *A benzenoid system which is not a chain benzenoid has at most four forcing bonds.*

In order to prove theorems 3 and 4, we need some further notation and several lemmas.

A bond of a benzenoid system which belongs to the boundary is called an *i-type* bond if the number of its end vertices of degree 2 is i. Thus the end vertices of a 0-type bond are of degree 3. A connected graph G is 2-connected if there is no vertex whose deletion disconnects G.

A *pendant bond* of a graph is a bond which has an end vertex of degree 1.

Lemma 1.[24] *Let G be a 2-connected graph. If G has a perfect matching, then it has at least two perfect matchings.*

Lemma 2.[16] *Let H be a subgraph of the infinite hexagonal lattice without nonhexagonal interior faces and with at most one pendant bond and at least one hexagon. Let M be a perfect matching of H. Then H has a hexagon which contains three double bonds of M. (Moreover, H has at least two perfect matchings.)*

Lemma 3. *Let H be a benzenoid system with a perfect matching. Let $e_1, e_2, ..., e_r$ be r parallel bonds of H such that e_i and e_{i+1} belong to the same hexagon, and their removal (without their end vertices) from H results in a disconnected graph. If there is a perfect matching of H which does not contain any of them, then they are fixed single bonds.*

Proof. Note that we can color vertices of H in two colors, black and white, such that no bonds have both end vertices with the same color. Since the graph H' obtained by removing all e_i's (but not their end vertices) from H has a perfect matching and the end vertices of the e_i's which belong to the same connected component have the same color, no one of the e_i's belongs to a perfect matching of H. Thus they are fixed single bonds.

Proof of Theorem 4. Let e be a forcing bond of H. If the end vertices of e do not belong to the boundary of H, then $H - e$ is 2-connected. By lemma 1, $H - e$ has at least two perfect matchings. Thus e is not a forcing bond. Let M be a perfect matching of H containing e. Suppose that only one of the end vertices of e belongs to the boundary of H. We claim that $H - e$ has two pendant bonds; otherwise by lemma 2, $H - e$ has two perfect matchings, a contradiction. Let s and s' be the two hexagons containing e, and let H' be the chain benzenoid with as many hexagons as possible which is a subgraph of H and contains s and s' (see Figure 6). Also let s'' be the hexagon of H which contains only one end vertex of e. Let $e_1, e_2, ..., e_k$ and $f_1, f_2, ..., f_r$ be the bonds of H' as indicated in Figure 6. Since $H - e$ has two pendant bonds, e_1 and f_1 are the two pendant bonds. Thus e_1 and f_1 belong to M and the boundary of H. Similarly, $H - e - e_1 - f_1$ must have two pendant bonds. Thus e_2 and f_2 belong to the boundary as well as to M. Finally, we can show that all e_i and f_i are in the boundary as well as in M. Since e_k and f_r belong to M, all the vertices of H' match themselves in M. It follows that all the bonds incident with H' and not in it satisfy the condition of lemma 3. Thus they are single fixed bonds of H. But H has no fixed bonds. This is a contradiction.

Lemma 4. *Let H be a benzenoid system. If it has a forcing bond e of 2-type, then H is a chain benzenoid.*

Proof. By induction on the number of hexagons of H. If H is a hexagon, nothing needs to be proved. Suppose that H has more than one hexagon. Let s be the hexagon containing e and e' be the bond of s parallel to e. Let H' be the graph consisting of all hexagons of H except s. Since e is forcing, $H - e$ has a unique perfect matching. By lemma 2, $H - e$ has two pendant bonds. Thus H' is a benzenoid system, and e' is of 2-type in H'. Moreover, e' is a forcing bond of H'. By the induction hypothesis, H' is a chain benzenoid. One can check that $H = s \cup H'$ is a chain benzenoid; otherwise, e is not a forcing bond.

Proof of Corollary 1. Since the number of vertices of degree 2 in the boundary of H is equal to the number of vertices of degree 3 in the boundary of H plus 6,[1] there is a 2-type bond e of H. By the assumption, e is forcing. By lemma 4, H is a chain benzenoid. If H has more than one hexagon, one can check easily that not every bond of H is forcing.

A bond of e of a benzenoid system H is a *separating bond* (or separating edge) if $H - e$ is disconnected.

Lemma 5. *Let H be a benzenoid system. If H has a forcing bond e, then it belongs to* $\mathcal{F}$.

Proof. Let e be a forcing bond and M be a perfect matching containing e. By theorem 4, the end vertices of e belong to the boundary of H. There are three cases:

Case 1. Let e not belong to the boundary of H. Then it is a separating bond. Let H_1 and H_2 be the two benzenoid systems such that their intersection is e and their union is H. Then e is a forcing bond in both of H_1 and H_2. Note that e is a 2-type bond in H_1 and H_2. By lemma 4, H_1 and

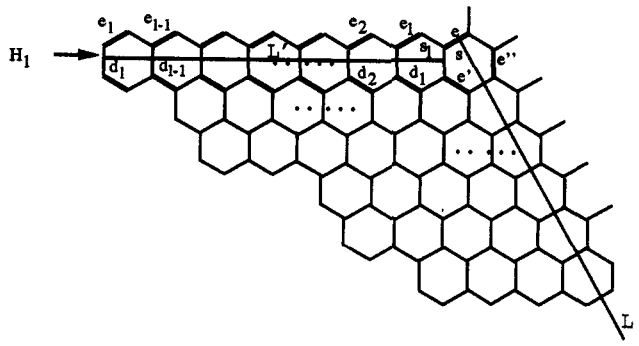

Figure 7. Bonds of H_1 not parallel to e and below L'.

Figure 8. Bond g.

H_2 are chain benzenoids. Thus H is a chain benzenoid, and it belongs to $\mathcal{F}$.

Case 2. Let e be of 2-type. Then by lemma 4, H is a chain benzenoid system which belongs to $\mathcal{F}$.

Case 3. The remaining case is that e is of 0-type or of 1-type. Let s be the hexagon containing e.

Since e is of 0-type or of 1-type, one end vertex of e is of degree 3. Thus there is a hexagon s_1 of H which contains only one end vertex of e. Let H_1 be the chain benzenoid contained in H with s as an end hexagon which contains s and s_1 and has as many hexagons as possible. Without loss of generality, let H_1 be a horizontal chain benzenoid and s be the right end hexagon of H_1. Let L' be the bisector line of the vertical bonds of H_1. Assume also that e is above L'. Let L be the ray perpendicular to e and having the midpoint of e as its end. Let $e_1, ..., e_l$ be the bonds of H_1 which are parallel to e and above L'. Let $d_1, ..., d_l$ be the bonds of H_1 which are not parallel to e and below L' (see Figure 7). Let e' and e'' be the two bonds of s such that e, e', and e'' are disjoint, as shown in Figure 7.

If $H - e$ has only one pendant bond, by lemma 2 $H - e$ has at least two perfect matchings. This is a contradiction. Thus $H - e$ has two pendant bonds and e_1 is one of them. Hence e_1 is of 1-type and belongs to M. Similarly to the above, we have that $H - e - e_1$ has two pendant bonds. Thus e_2 is one of the pendant bonds, and it is of 1-type and belongs to M. By the same reasoning, we can show that $e_3, ..., e_l$ are of 1-type and belong to M and d_l may be of 1-type or of 2-type. Also $d_{l-1}, ..., d_1$ and e' belong to M (but they may not be of 1-type, see Figure 7).

Let H_2 be the graph consisting of the hexagons adjacent to H_1 and below it. Then H_2 has at most one hexagon intersecting L. Since d_l is on the boundary of H, the number of hexagons of H_2 is equal to or less than that of H_1. Note that all vertical bonds of H_2 do not belong to M. If H_2 is not a chain benzenoid or does not contain the hexagon intersecting L, then the removal of its vertical bonds (but not of their end vertices) from H results in a disconnected graph. By lemma 3, H has fixed single bonds. This is a contradiction. Thus H_2 is a chain benzenoid and on the left of L with its right end hexagon intersecting L.

Similarly, by lemma 2 $H' = H - e_1 - ... - e_l - d_l - d_{l-1} - ... - d_1 - e - e'$ has two pendant bonds. Let g be the bond of the left end hexagon of H_2 which is nonvertical and parallel to d_l and does not belong to H_1 (see Figure 8). Then g is one of the pendant bonds of H'. Thus g belongs to M and all bonds of H_2 parallel to g are also in M.

Let H_3 be the graph consisting of the hexagons adjacent to H_2 and below it. If H_3 is not empty, we can similarly show that H_3 has the same property as H_2, i.e., the number of hexagons of H_3 is equal to or less than that of H_2, the nonvertical bonds of H_3 belong to M, etc.

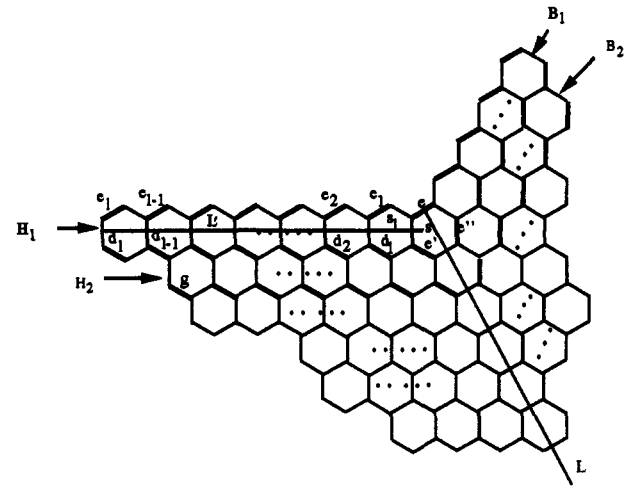

Figure 9. Diagonal chain benzenoids $B_1, B_2, ..., B_r$.

Repeating the foregoing reasoning, we will finally obtain a sequence of chain benzenoids $H_1, H_2, ..., H_k$ with the following properties: (1) the number of hexagons of H_i is equal to or less than that of H_{i-1} and H_i is below H_{i-1} ($i = 2, 3, ..., k$); (2) H_i has its right end hexagon intersecting with L and on the left of L ($i = 1, 2, ..., k$); (3) there are no hexagons below H_k and on the left of all H_i's.

If e is of 0-type, then both of the end vertices of e are of degree 3. Thus there is another hexagon h_1 different from s_1 which contains the other end vertex of e. By symmetry, we can show that there is a sequence of diagonal chain benzenoids $B_1, B_2, ..., B_r$ such that (1) the number of hexagons of B_i is equal to or less than that of B_{i-1} and B_i is below B_{i-1} ($i = 2, 3, ..., r$); (2) B_i has its left end hexagon intersecting with L and on the right of L ($i = 1, 2, ..., r$); and (3) there are no hexagons below B_r and on the right of all B_i's (see Figure 9).

Without loss of generality, let $k \geq r$. Let H_i have n_i hexagons and B_j have $m_j + 1$ hexagons. Then $H = H(n_1, n_2, ..., n_k; m_1, m_2, ..., m_r)$.

If e is of 1-type, then the right vertical bond of s is of 1-type too (this is because $H - e$ has two pendant bonds). Let f_i be the leftmost vertical bond of H_i ($i = 1, 2, ..., k$). Then f_1 is of 1-type and thus belongs to M. Since e is forcing, f_1 is forcing too. Note that $H - e - f_1$ has two pendant bonds (for $H - e - f_1$ has a unique perfect matching). Thus f_2 is of 1-type and belongs to M. Repeating the same argument, we can finally show that all f_i's are of 1-type and belong to M. Thus $H = H(n_1, n_2, ..., n_k; 0)$. The proof is completed.

Corollary 2. *Let H be a benzenoid system and e be a forcing bond. If e is of 0-type, then $H = H(n_1, n_2, ..., n_k; m_1, m_2, ..., m_r)$ with $m_1 \geq 1$. If e is of 1-type or 2-type, then $H = H(n_1, n_2, ..., n_k; 0)$.*

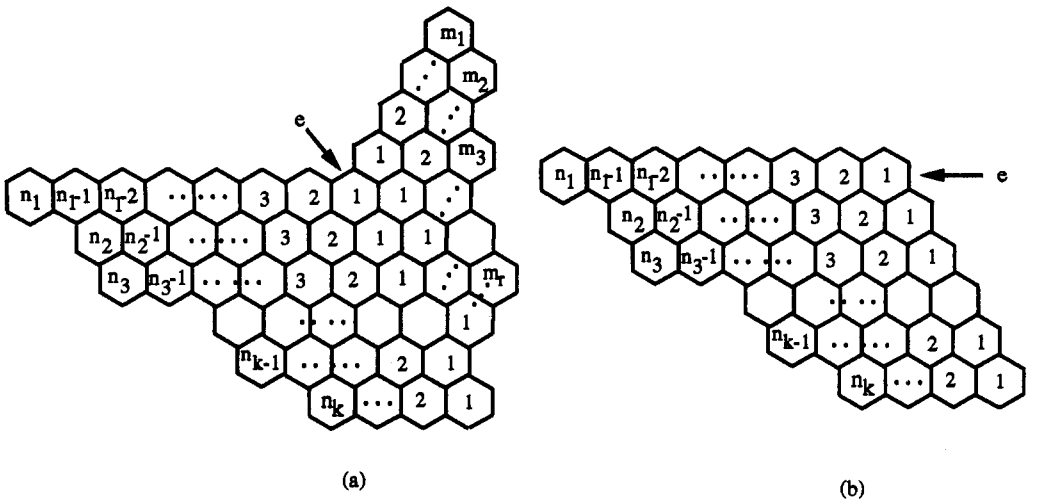

Figure 10. Forcing bonds.

Lemma 6. *If $H \in \mathcal{F}$, then H is fixable.*

Proof. Let $H = H(n_1, n_2, ..., n_k; m_1, m_2, ..., m_r)$. First let m_1 be positive. Let H_1 be the top horizontal chain benzenoid system of H with n_1 hexagons as in its definition (see Figure 10a). Let e be the bond of H which is of 0-type and in the boundary of H and belongs to the right end hexagon of H_1. If $m_1 = 0$, let e be the rightmost vertical bond of H_1 (see Figure 10b). Then as in the proof of lemma 5 we can check that $H - e$ has a unique perfect matching, i.e., e is forcing. Thus H is fixable.

Proof of Theorem 1, by lemmas 5 and 6.

Proof of Theorem 5, by induction on the number of vertices of H. Note that by lemma 4 and the assumption of the theorem, H has no 2-type forcing bonds. Without loss of generality, let H have at least four forcing bonds. Thus H is normal. If H has a separating bond e, then let H_1 and H_2 be the benzenoid systems whose interaction is e and union is H. Since H is normal, e belongs to some perfect matching of H. Thus both of H_1 and H_2 are Kekuléan. If e is a forcing bond of H, then it is a forcing bond of both H_1 and H_2 and of 2-type. By lemma 4, H_1 and H_2 are chain benzenoids. Thus H is a chain benzenoid. This contradicts the assumption of the theorem. Let e' be a forcing bond of H (which is not e) and M be the unique perfect matching of H containing e'. Without loss of generality, let e' belong to H_1. Note that the double bond(s) of M which covers the end vertices of e does not belong to H_2; otherwise $M \cap H_2$ is a perfect matching of H_2; by lemma 2, there is a hexagon of H_2 which contains three double bonds of M; thus e' is not a forcing bond, a contradiction. Therefore $H_2 - e$ has a unique perfect matching; i.e., e is a forcing bond of H_2 and of 2-type. By lemma 4, H_2 is a chain benzenoid. We assert that H_2 contains no forcing bonds of H; otherwise similarly to the above we can show that H_1 is a chain benzenoid. Thus H is a chain benzenoid. This is a contradiction again. Moreover, H_1 is not a chain benzenoid. Since each forcing bond of H is also a forcing bond of H_1, the number of forcing bonds of H_1 is equal to or larger than that of H. Now H_1 is smaller than H. By the induction hypothesis, H_1 has at most four forcing bonds. The conclusion of the theorem is obtained.

If H has no separating bonds then all forcing bonds of H belong to the boundary. There are two cases:

Case 1. Let $H = H(n_1, n_2, ..., n_k; 0)$. Since H is not a chain benzenoid, $k \geq 2$. Since H has no separating bonds, $n_i \geq 2$ (for $i = 1, 2, ..., k$) and $n_1 = n_2$. As in the definition of H (see Figure 5), let H_i be the horizontal chain benzenoids contained in H with n_i hexagons. Thus H_{i-1} is higher than H_i. Let s be the rightmost hexagon of H_1 and s' be the leftmost hexagon of H_k. We assert that all possible forcing bonds of H belong to s or s'. Since H has no 2-type forcing bonds, by this assertion H has at most four forcing bonds.

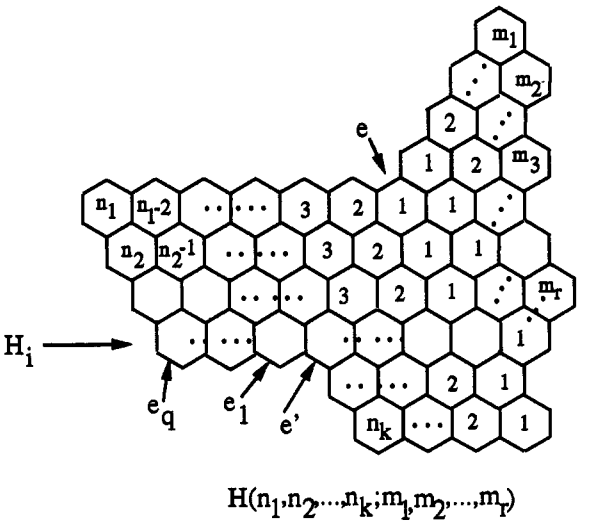

Figure 11. Bonds e', e_1, e_2, ..., e_q in the proof theorem 5.

Now we prove the assertion. Note that H has no 2-type forcing bonds for H is not a chain benzenoid. We need only to check that a 0-type or 1-type bond of H is not forcing if it is not in s or s'. We only check that the 0-type or 1-type bonds of H which belong to H_1 but not to s are not forcing. The other cases can be checked similarly. Let e be a 1-type bond of H belonging to H_1 but not to s. If e does not belong to the leftmost hexagon h of H_1, then $H - e$ has only one pendant bond. By lemma 2, $H - e$ has at least two perfect matchings. Thus e is not forcing. If e belongs to h, let e' be the 2-type bond of H contained in h and disjoint with e. Then e' is a pendant bond of $H - e$. If e is forcing, then e' is forcing. Thus H has a 2-type forcing bond. This is a contradiction again.

Case 2. Let $H = H(n_1, n_2, ..., n_k; m_1, m_2, ..., m_r)$ with $m_r \geq 1$. Since H has no separating bonds, $k \geq 2$ and $r \geq 2$. Moreover $n_1 = n_2$ and $m_1 = m_2$. Let $H_1, H_2, ..., H_k$ be the horizontal chain benzenoid systems and $B_1, B_2, ..., B_r$ be the diagonal chain benzenoid systems as in the definition of H. Let s be the rightmost hexagon of H_1 and e be the 0-type bond of H contained in s. By corollary 2, H has

no 1-type or 2-type forcing bonds. Let e' be a 0-type bond not equal to e. Without loss of generality, let e' belong to H_i (here $i \geq 2$). Let $e_1, e_2, ..., e_q$ be the bonds of H_i which belong to the boundary of H and are parallel to e' (see Figure 11). Then $H - e' - e_1 - ... - e_q$ has only one pendant bond. Note that $H - e$ has a perfect matching. Thus $H - e' - e_1 - ... - e_q$ has a perfect matching. By lemma 3, $H - e' - e_1 - ... - e_q$ has at least two perfect matchings; i.e., e' is not forcing. Thus the only possible forcing bond is e. The proof is completed.

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REFERENCES AND NOTES

(1) Gutman, I.; Cyvin, S. J. *Introduction to the Theory of Benzenoid Hydrocarbons*; Springer: Berlin, 1989.
(2) Gutman, I.; Cyvin, S. J. *Kekulé Structures in Benzenoid Hydrocarbons*; Springer: Berlin, 1988.
(3) Dias, J. R. *Handbook of Polycyclic Hydrocarbons, Part A: Benzenoid Hydrocarbons*; Elsevier: Amsterdam, 1987.
(4) Dias, J. R. *Handbook of Polycyclic Hydrocarbons, Part B: Benzenoid Hydrocarbons*; Elsevier: Amsterdam, 1988.
(5) Trinajstić, N. *Chemical Graph Theory*, 2nd ed.; CRC Press: Boca Raton, FL, 1992.
(6) Gordon, M.; Davison, W. H. T. Theory of Resonance Topology of Fully Aromatic Hydrocarbons I. *J. Chem. Phys.* **1952**, *20*, 428–453.
(7) Sachs, H. Perfect Matchings in Benzenoid Systems. *Combinatorica* **1984**, *4*, 89–99.
(8) John, P.; Sachs, H. Wegesysteme und Linearfaktoren in Hexagonalen und Quadratischen Systemen. In *Graphen in Forschung and Unterricht*; Bodendiek, R., et al., Eds.; Franzbecken: Kiel, Germany, 1985; pp 85–101.
(9) Zhang, F. J.; Chen, R. S.; Guo, X. F. Perfect Matchings in Hexagonal Systems. *Graphs Combinatorics*. **1985**, *1*, 363–368.
(10) Sheng, R. Rapid Ways to Recognize Kekuléan Benzenoid Systems. *Top. Curr. Chem.* **1990**, *153*, 211–226.
(11) He, W.; He, W. On Kekulé Structure and P-V Path Method. In *Studies in Physical and Theoretical Chemistry*; King, R. B., Rouvray, D. H., Eds.; **1987**, *51*, 476–483.
(12) Hansen, P.; Zheng, M. A Revised Peeling Algorithm for Determining If a Benzenoid System is Kekuléan. *J. Mol. Struct. (THEOCHEM)* **1991**, *235*, 293–309.
(13) Hansen, P.; Zheng, M. A Linear Algorithm for Perfect Matching in Hexagonal Systems. *Discrete Math.* **1993**, *122*, 179–196.
(14) John, P.; Sachs, H. Calculating the Number of Perfect Matchings and of Spanning Trees, Pauling's Orders, the Characteristic Polynomial, and the Eigenvectors of a Benzenoid System. *Top. Curr. Chem.* **1990**, *153*, 145–179.
(15) Sheng, R.; Gutman, I.; Cyvin, S. J. "Essentially Disconnected Benzenoids" are Essentially Disconnected. *Match* **1991**, *26*, 191–203.
(16) Hansen, P.; Zheng, M. Normal Components of Benzenoid Systems. *Theor. Chim. Acta* **1993**, *85*, 335–344.
(17) Hansen, P.; Zheng, M. Upper Bounds for the Clar Number of Benzenoid Hydrocarbons. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 1621–1625.
(18) Hansen, P.; Zheng, M. The Clar Number of a Benzenoid System and Linear Programming. *J. Math. Chem.*, to be published.
(19) Hansen, P.; Zheng, M. A Linear Algorithm for Fixed Bonds in Hexagonal Systems. *J. Mol. Struct. (THEOCHEM)* **1992**, *257*, 75–83.
(20) Pauling, L.; Brockway, L. O.; Beach, J. Y. The Dependence of Interatomic Distance on Single Bonds-Double Bonds Resonance. *J. Am. Chem. Soc.* **1935**, *57*, 2705.
(21) Randić, M.; Klein, D. J. In *Mathematical and Computational Concepts in Chemistry*; Trinajstić, N., Ed.; John Wiley & Sons: New York, 1985; pp 274–282.
(22) Klein, D. J.; Randić, M. Innate Degree of Freedom of a Graph. *J. Comput. Chem.* **1987**, *8*, 516–521.
(23) Harary, F.; Klein, D. J.; Živković, T. P. Graphical Properties of Polyhexes: Perfect Mathing Vector and Forcing. *J. Math. Chem.* **1991**, *6*, 295–306.
(24) Kotzig, A. On the Theory of Finite Graphs and Linear Factor, 1 (in Slovak). *Mat.-Fyz. Caspis.* **1959**, *9*, 73–91.