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Normal components of benzenoid systems

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Summary. Consider a benzenoid system with fixed bonds and the subgraph obtained by deleting fixed double bonds together with their end vertices and fixed single bonds without their end vertices. It has often been observed for particular benzenoid systems, and conjectured (or stated) that, in general, such a subgraph has at least two components, and that each component is also a benzenoid system and is normal. But there are no rigorous proofs for that. The aim of this paper is to present mathematical proofs of those two facts. It is also shown that if a benzenoid system has a single hexagon as one of its normal components then it has at least three normal components.

Key words: Benzenoid system – Normal component – Fixed bond – Kekulé structure

1 Introduction

A benzenoid system H [1] is a finite connected subgraph of the infinite hexagonal lattice without cut vertices or nonhexagonal interior faces (see Fig. 1). Benzenoid systems are extensively used in the study of benzenoid hydrocarbons [1–4], as they aptly represent the skeleton of such molecules. A Kekulé structure of H is a perfect matching of the vertices of H (or, in other words, a covering of all vertices of H by disjoint edges). All benzenoid systems mentioned later have Kekulé structures unless otherwise specified. A linear algorithm to find a Kekulé structure of a benzenoid system H or show that there are none is given in [5]. A bond of benzenoid system H is a *fixed single* (*fixed double*) bond if it belongs to none (all) of the Kekulé structures of H. A bond is *fixed* if it is either a fixed single bond or a fixed double bond. A linear algorithm to find all fixed bonds of a benzenoid system is presented in [6]. A non-polynomial algorithm for the same purpose is outlined in [7]. A benzenoid system with a Kekulé structure and without fixed bonds is called *normal*. If a benzenoid system H has fixed bonds

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Fig. 1.

then the subgraph induced by all nonfixed bonds of H is (possibly) the union of disjoint connected components (see Fig. 2). We denote this induced subgraph by $N(H)$, and call it the *unfixed subgraph* of H. An equivalent definition of $N(H)$ is that it is equal to the subgraph of H obtained by deletion of all fixed double bonds together with their end vertices and of all fixed single bonds without their end vertices. These two operations are illustrated in Fig. 2. That a benzenoid system H having fixed bonds implies that its unfixed subgraph $N(H)$ has at least two connected components and that each of them is a normal benzenoid system are considered to be well-known facts [1], [2, p 51]. However, to the best of our knowledge, there are no rigorous proofs of these facts. The aim of this paper is to give mathematical proofs for both of them. It follows that a benzenoid system H with fixed bonds has at least two normal components, i.e. two disjoint maximal connected subgraphs which are normal benzenoid systems. We also prove that if a benzenoid system has a single hexagon as one of its normal components then it has at least three normal components.

These results imply that the usual well-known classification of Kekulean benzenoid systems as normal or essentially disconnected [1, 2] is indeed justified in that any benzenoid system which is not normal has several disconnected normal components. As mentioned above, fixed bonds of H and hence normal components can be found in linear time. In addition to the insight into the structure of the corresponding benzenoid hydrocarbon so obtained, finding normal components is useful in the computation of many invariants of benzenoid systems. To illustrate, note that the number of Kekulé structures of H is the product of the numbers of Kekulé structures of each of its normal components. It follows from this observation that the Pauling bond order [8, 9] of a bond, which is equal to the proportion of Kekulé structures which contain it, can be computed considering only the normal component to which it belongs. Also a Clar formula of H [10, 11] for a benzenoid hydrocarbon, i.e., a representation of a maximum set of mutually resonant hexagons (which are disjoint and for which there is a Kekulé structure in which each of them contains three double bonds) can be obtained by considering each normal component of H in turn,

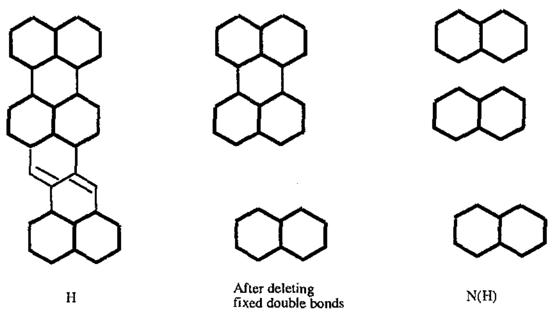

Fig. 2.

finding a Clar formula for it and assembling them into a Clar formula for H [12]. It also follows from Lemma 1 below that each of the conjugated circuits of H is contained in a normal component of H. This property can be exploited in enumerating them, for instance in the conjugated circuit model [13, 14, 15]. Note that enumeration of all normal and essentially disconnected benzenoid systems as well as of other classes and subclasses of benzenoids has been the object of much recent study (e.g. [16, 17, 18]).

2 Definitions

A generalized benzenoid system [19, 20] is a finite connected subgraph of the infinite hexagonal lattice. It may therefore contain cut vertices or nonhexagonal interior faces, as indicated by the graphs of Kekulene and biphenyl in Fig. 3. The concepts of Kekulé structure and of fixed bond extend to generalized benzenoid systems in a straightforward way. A benzenoid system is a generalized benzenoid system but the converse is not true (see Fig. 3, where only the third graph is a benzenoid system). A circuit C (or closed simple path) of a generalized benzenoid system H is a *conjugated circuit* if there is a Kekulé structure of H in which the vertices of C match themselves, or in other words, if after deleting C from H together with all its vertices and adjacent edges the remaining graph has a Kekulé structure. None of the bonds belonging to a conjugated circuit are fixed. A *cut bond* of a generalized benzenoid system H is a bond whose removal (without its end vertices) disconnects H. Clearly, if a generalized benzenoid system has no fixed bonds then it has no cut bonds.

A bond of a benzenoid system H is a separating bond if the removal of its end vertices disconnects H. If e is a separating bond, then let $H(e)$ and $H(e)'$ denote the benzenoid systems obtained by splitting H at e such that $H(e)$ and $H(e)'$ share e only (see Fig. 4). The degree of a vertex is defined to be the number of vertices adjacent to it.

A generalized benzenoid system H partitions the plane into a number of connected regions; these regions are called the *faces* of H. The one with infinite

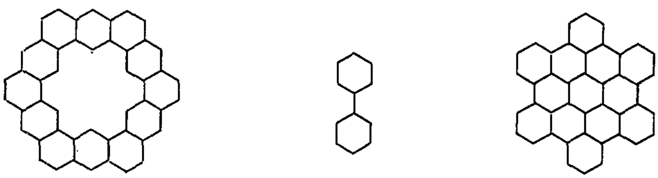

Fig. 3.

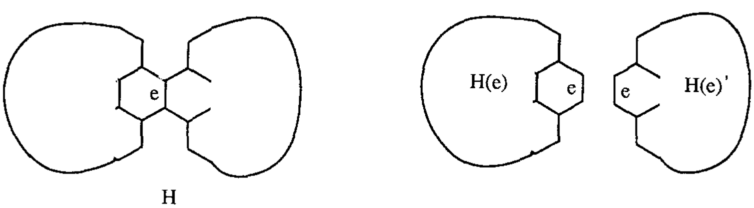

Fig. 4.

size is called the *exterior face* of H. If H has no cut bond, then the boundary of the exterior face is defined to be the boundary of H.

3 Normal components

The following theorem was proved in [19]:

Theorem 1. Let H be a generalized benzenoid system without cut bonds. Then H has no fixed bonds if and only if the boundary of each nonhexagonal face of H is a conjugated circuit.

Theorem 1 is illustrated in Fig. 5.

The second fact mentioned in the introduction will first be proved. To that effect we need the following:

Lemma 1. A bond of a generalized benzenoid system H is not fixed if and only if it belongs to a conjugated circuit of H.

Proof. Let e be a nonfixed bond. Let M and M' be two Kekulé structures of H such that e belongs to M but not to M'. Then e belongs to a circuit of the symmetric difference of M and M', i.e., $M \cup M' - M \cap M'$ (see Fig. 6). This circuit is a conjugated circuit of H. Conversely, let C be a conjugated circuit of H containing e. Let K be a Kekulé structure of H in which the vertices of C match themselves. Let K' be the Kekulé structure obtained by rotating K along C. Then e belongs to exactly one of K and K'. So it is not fixed. □

It was shown in [21] that if a graph different from K_2 (i.e., the graph with two vertices and one edge) and with no cut vertices (a cut vertex is a vertex whose removal disconnects the graph) has a perfect matching then it has at least two perfect matchings. So a benzenoid system with a Kekulé structure has at least two Kekulé structures, and therefore it has some nonfixed bonds and $N(H)$ is not empty.

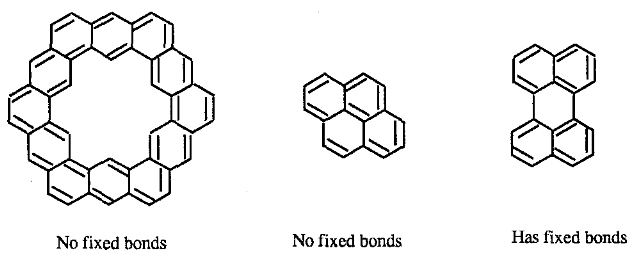

Fig. 5.

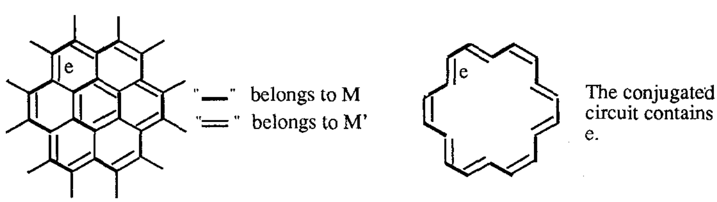

Fig. 6.

We now prove:

Theorem 2. Each connected component of the unfixed subgraph $N(H)$ of a benzenoid system H is a normal benzenoid system.

Proof. Let N be a connected component of $N(H)$. We must show that N has a Kekulé structure and no fixed bonds nor nonhexagonal interior faces. First note that all edges joining a vertex of N to a vertex out of N are fixed single bonds. Hence any Kekulé structure of H induces a Kekulé structure of N and any Kekulé structure of N can be extended to a Kekulé structure of H. So any conjugated circuit of H contained in N is also a conjugated circuit of N and any conjugated circuit of N is a conjugated circuit of H. Since no bonds of N are fixed in H, by Lemma 1, all belong to some conjugated circuits of H. As these conjugated circuits are connected and contain no fixed bonds of H, they are contained in N. So they are conjugated circuits of N. Thus N itself has no fixed bonds. Hence N has no cut bonds. By Theorem 1, the boundary C of the exterior face of N is a conjugated circuit of N and also of H. To show that N has no nonhexagonal inferior faces, we prove that no bonds of H contained in the inside of C are fixed in H and thus N is equal to the subgraph N' of H induced by the vertices of C and its inside. Let K be a Kekulé structure of H in which the vertices of C match themselves (K exists as C is a conjugated circuit of H). Then $N' \cap K$ is a Kekulé structure of N' in which the vertices of C match themselves. C is a conjugated circuit of N'. By Theorem 1, N' has no fixed bonds. So each bond of N' is contained in a conjugated circuit of N'. It can be checked easily that any conjugated circuit of N' is also a conjugated circuit of H. Therefore each bond of N' is contained in a conjugated circuit of H. By Lemma 1, none of the bonds of H contained in the inside of C are fixed in H. Thus $N' = N$. This completes the proof. □

From now on, we call a connected component of $N(H)$ a *normal component* of H. To prove the first fact mentioned in the introduction we need several lemmas. The first one comes from [1], page 22:

Lemma 2. The number of vertices of degree 2 of a benzenoid system H is equal to the number of vertices of degree 3 which belong to the boundary of H plus 6.

Since $N(H)$ is not empty for a benzenoid system H, by Theorems 1 and 2, H has at least one conjugated circuit. The following lemma generalizes slightly this result.

Lemma 3. Let H be a generalized benzenoid system without nonhexagonal interior faces which has at most one pending bond. Let K be a Kekulé structure of H. Then H has a hexagon which contains three double bonds in K (this hexagon is a conjugated circuit).

Proof. Delete the cut bonds (but not their end vertices) if any from H. The remaining graph G may have several connected components (some of which may contain only one vertex). We assert that there is a connected component H' of G which is a benzenoid system and has at most one vertex incident to a cut bond of H. If H has no cut bonds, then H is a benzenoid system. Let $H' = H$. The assertion is true. If H has cut bonds, then start at the pending vertex of H if it exists, otherwise at any connected component of G and repeat the following: follow unvisited cut bonds from the current visited connected component to the next unvisited connected component of G, until there is nowhere to go. Then the last visited connected component of G has the described property.

There are two cases:

Case 1. There is a vertex of H' which matches in K a vertex not in H'. Let f be the number of faces of H' including its exterior face. Clearly, all faces of H', possibly except one, are hexagons. Let us call the double bonds of K contained in H' but not in its boundary *inner* double bonds and the double bonds of K in the boundary of H' *outer* double bonds. Let e be the number of bonds and v be the number of vertices of H'. Let k_1 be the number of outer double bonds and k_2 be the number of inner double bonds. Suppose that the lemma is not true. Then each hexagon of H' contains at most two double bonds. Each inner double bond belongs to exactly two hexagons and each outer double bond belongs to exactly one hexagon. So $2(f-1) \geqslant 2k_2 + k_1$ (where $f-1$ is the number of hexagons of H'). By Euler's formula for planar graphs, $f + v = e + 2$. Thus $2e + 2 - 2v \geqslant 2k_2 + k_1$. Note that $v = 2(k_1 + k_2) + 1$. So $2e \geqslant 6k_2 + 5k_1$. Let $d(x)$ denote the degree of vertex x of H' and $V(H')$ be the set of vertices of H', then

$$2e = \sum_{x \in V(H')} d(x) \geqslant 6k_2 + 5k_1$$

(the first equality comes from the fact that each bond of H' is counted twice in $\sum_{x \in V(H')} d(x)$). The following facts are true:

(1) The double bonds in K contained in H' cover all vertices of H' except the one which matches in K a vertex not in H'.

(2) The sum of degrees of the end vertices of an inner double bond is 6.

(3) Since the boundary of H' has an even number of vertices (for H' is a bipartite graph) one of which matches in K a vertex not in H', there is at least one inner double bond which has an end vertex belonging to the boundary of H'.

(4) By Lemma 2 and (3), the number of vertices of degree 3 covered by the outer double bonds plus 6 is less than or equal to the number of vertices of degree 2 covered by the outer double bonds.

By (4), the sum of degrees of vertices in the boundary of H' which are covered by outer double bonds is less than or equal to $5k_1 - 3$. So the sum of degrees of the vertices of H' not covered by the inner double bonds (including the vertex adjacent to a cut bond) is less than or equal to $5k_1 - 1$. The sum of degrees of vertices covered by inner double bonds is $6k_2$. So

$$2e = \sum_{x \in V(H')} d(x) \leqslant 6k_2 + 5k_1 - 1.$$

This is a contradiction.

Case 2. $K \cap H'$ is a Kekulé structure of H'. Similarly to Case 1, we can prove the lemma. □

Before proving the next theorem, the following notations are needed. Let H be a benzenoid system, e be a bond of H, and s be a hexagon of the infinite hexagonal lattice which contains e (note that s may or may not be a hexagon of H). Let $L_{s,e}$ denote the segment of the perpendicular bisector of e which starts from the midpoint of e and ends at the central point of s if s does not belong to H, and otherwise passes through s, ends at the boundary of H and is totally contained in the interior region of H (see Fig. 7).

By Lemma 2 of [19], the following is true:

Lemma 4. Let H be a benzenoid system, K be a Kekulé structure of H and e be a fixed single bond of H. If the bonds e_1 and e_2 of K which cover the end vertices of e belong to a hexagon s of the infinite hexagonal lattice, then the bonds of H intersecting $L_{s,e}$ are all fixed single bonds.

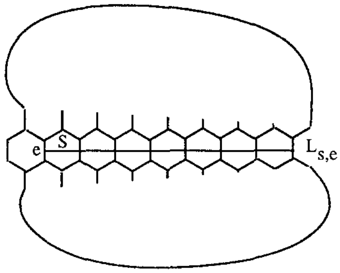

Fig. 7.

Theorem 3. Let H be a benzenoid system. If H has fixed bonds then it has at least two normal components.

Proof. By contradiction. Let H be the smallest counterexample to the conclusion. So H has only one normal component and $N(H)$ is connected. There are two cases:
Case 1. Suppose that there is a nonfixed bond which belongs to the boundary of H. Since H is the smallest counterexample and $N(H)$ contains some bonds which belong to the boundary of H, the graph of H_1 obtained by deleting all vertices of $N(H)$ together with their incident bonds from H is connected, and all of its bonds are fixed in H as well as in itself. Let C be the boundary of $N(H)$. By Theorem 1 it is a conjugated circuit of $N(H)$. It is also a conjugated circuit of H. By Theorem 1 and the assumption, some but not all of C's bonds belong to the boundary of H (otherwise, H has no fixed bonds). Let P_1 be a segment of the boundary of H such that only its end vertices belong to C. Let P_2 be a segment of C which has the same end vertices as P_1 but is not contained in the boundary of H (see Fig. 8). Let H' be the subgraph whose boundary is $P_1 \cup P_2$ (see Fig. 8). Let K be a Kekulé structure of H in which the vertices of C match themselves. If P_2 has an even number of vertices, by the choice of K we can assume that the vertices of P_2 match themselves in K. So $K \cap H'$ is a Kekulé structure of H'. By Lemma 3, H' has a hexagon which contains three double bonds in K. Hence H has a nonfixed bond which is not in $N(H)$, a contradiction. If P_2 has an odd number of vertices, without loss of generality, let v_1 be the end vertex of P_2 which matches a vertex v_2 out of P_2 in K. Let (v_1, v_2) be the double bond in K. Then the generalized benzenoid system which is the union of H' and (v_1, v_2) satisfies the condition of Lemma 3. So H' has a hexagon which contains three double bonds in K. But this hexagon contains a bond which is not fixed in H and does not belong to $N(H)$. This is a contradiction.
Case 2. Let all bonds in the boundary of H be fixed bonds. Suppose H is drawn on the plane such that some of it's bonds are vertical. Let K be a Kekulé structure

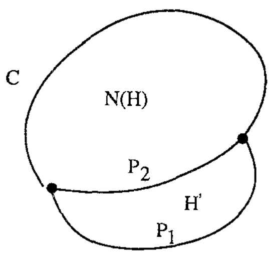

Fig. 8.

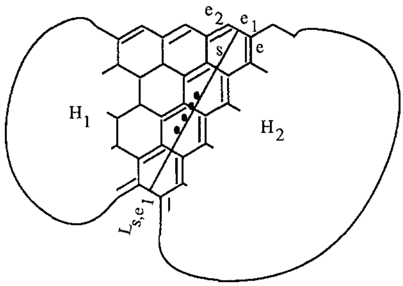

Fig. 9.

of H. One can check easily that there is a vertical bond e in the top level which belongs to K. Let s be the hexagon which contains e. Without loss of generality, let e be the right vertical bond of s. Let e_1 and e_2 be the two bonds of s as shown in Fig. 9. Then e_2 belongs to K. Since e_1 is a fixed single bond, all bonds intersecting L_{s,e_1}, by Lemma 4, are fixed single bonds. Let H_1 and H_2 be the two connected subgraphs obtained by deleting all the bonds intersecting L_{s,e_1} (but not their end vertices) from H. Then both of them have at most one pending vertex (possibly e_2 or e) and no nonhexagonal interior faces. By Lemma 3 and considering K, H_i ($i = 1, 2$) has a hexagon which contains three double bonds in K. So H has at least two normal components. A contradiction again. This completes the proof. □

4 Small normal components

The size of the normal components may influence their number as we next show.

Theorem 4. If a benzenoid system H with more than one hexagon has a normal component which is a single hexagon, then H has at least three normal components.

Proof. Let s be the hexagon which is a normal component. Then all bonds which are adjacent to s but not in s are fixed single bonds. Let K_1 be a Kekulé structure of H in which the vertices of s match themselves. Let K_2 be the Kekulé structure obtained by rotating K_1 along s. There are two cases:
Case 1. There is a bond, e, of s which is a separating bond of H. Without loss of generality let $H(e)$ contain s and e belong to K_1. Clearly $K_1 \cap H(e)'$ is a Kekulé structure of $H(e)'$. Moreover, the two bonds of $H(e)'$ adjacent to e are fixed single bonds of $H(e)'$. Otherwise, they are not fixed single bonds in H, a contradiction. By Theorem 3, $H(e)'$ has at least two normal components. It can be verified easily that each of the normal components of $H(e)'$ is also a normal component of H. So H has at least three normal components.
Case 2. No bonds of s are separating bonds of H. So there are two adjacent hexagons of H (two hexagons are adjacent if they share a common bond), s_1 and s_2 which are adjacent to s. Let e_1, e_2, e_3, e_4, e_5, e_6, a, b and c be the bonds shown in Fig. 10. Also let s_3 and s_4 denote the hexagons shown in Fig. 10 which may or may not belong to H. Without loss of generality, let e_1 and e_2 belong to K_1 (see Fig. 10). There are two subcases:
Subcase 1. Suppose that e_3 belongs to K_1 (see Fig. 11). It is in K_2 as well. By Lemma 4 and considering K_2, all bonds intersecting $L_{s_1,a}$ and $L_{s_4,c}$ are fixed

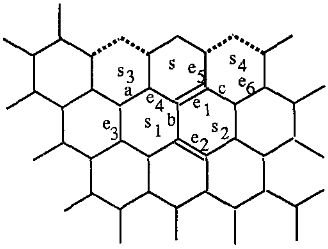

Fig. 10.

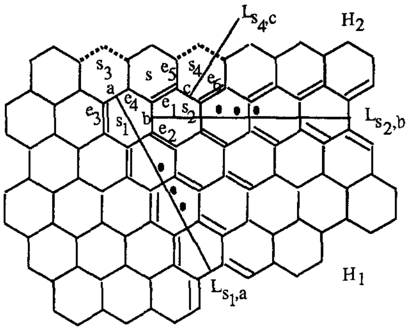

Fig. 11.

single bonds. Similarly, by Lemma 4 and considering K_1, the bonds intersecting $L_{s_2,b}$ are fixed single bonds. Let H' be the subgraph obtained by deleting the fixed single bonds but not their end vertices which intersect $L_{s_2,b}$, $L_{s_1,a}$ and $L_{s_4,c}$ from H. Let H_1 and H_2 be the two connected components of H' which contain e_2 and e_6 respectively (see Fig. 11). Both have no nonhexagonal interior faces. Each of H_1 and H_2 has only one pending vertex and no nonhexagonal interior faces. Considering K_1, by Lemma 3, H_1, as well as H_2, contains a normal component of H. Thus H has at least three normal components.

Subcase 2. Suppose e_3 does not belong to K_1. Then considering K_1, a, and s_3, by applying Lemma 4, the bonds intersecting $L_{s_3,a}$ are fixed single bonds (see Fig. 12). Let H_3 be the generalized benzenoid system of H which is the connected component containing e_2 of the subgraph obtained by deleting all fixed single bonds (but not their end vertices) intersecting $L_{s_3,a}$ and $L_{s_2,b}$ from H (see Fig. 12). Then H_3 has no pending vertex and nonhexagonal interior faces. By Lemma 3 and considering K_1, H_3 contains a normal component of H. Also as in Subcase 1, H_2 contains another normal component of H. So H has at least three normal components. □

The following example (Fig. 13) shows that there are some benzenoid systems which have a single hexagon as one of their normal components.

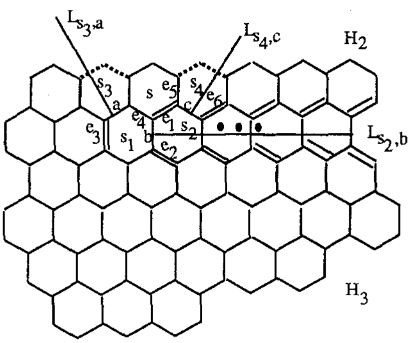

Fig. 12.

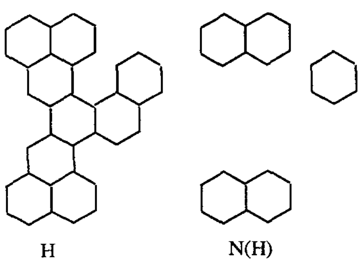

Fig. 13.

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