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BENZENOID SYSTEMS WHOSE (x,y,z)-INVARIANTS HAVE x = 1 AND x = 2

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Abstract. Let B be a Kekuléan benzenoid system. A new invariant (x,y,z) of B has been introduced in [1]. In this paper the classes of benzenoid systems with x = 1 and x = 2 are determined. The Clar formulas of these benzenoid systems are also examined.

Introduction

A benzenoid system B is a finite connected plane graph (an embedding of a planar graph in the plane) with no cut-vertices, in which every interior region is bounded by a regular hexagon of unit side length. A Kekulé structure K of B is an independent edge set of B in which the edges cover all the vertices of B. In other words, K is a perfect matching or a 1-factor of B. The edges in K are called double bonds of K whereas the other edges are called single bonds of K. Benzenoid systems with Kekulé structures are said to be Kekuléan benzenoid systems.

Many chemists are interested in Kekuléan benzenoid systems because these systems can be regarded as the skeletons of benzenoid hydrocarbon molecules.

Let B be a benzenoid system with a Kekulé structure K. Then K can be partitioned into three subsets $E_1(K)$, $E_2(K)$ and $E_3(K)$, such that all edges in $E_i(K)$, $1 \le i \le 3$, have the same directions. In other words, all the edges belonging to a set $E_i(K)$ are mutually parallel. We adopt the convention that $|E_1(K)| \le |E_2(K)| \le |E_3(K)|$, where $|E_i(K)|$ stands for the cardinality of $E_i(K)$, $i = 1,2,3$. Denote $|E_1(K)| = x$, $|E_2(K)| = y$ and $|E_3(K)| = z$. Then $x \le y \le z$. The following theorem was given in [1].

Theorem 1. For a benzenoid system B with a Kekulé structure K the triple (x,y,z) is independent of K. Therefore (x,y,z) is an invariant of B.

A natural problem in connection with Theorem 1 is to characterize all benzenoid systems having a given invariant (x,y,z). In the present paper we solve this problem for $x = 1$ and $x = 2$.

Within the Clar aromatic sextet theory [2,3] a so-called "Clar formula" is obtained by drawing circles in some of the hexagons of a benzenoid system B. These circles represent the so-called "aromatic sextets". The Clar formulas are constructed according to the following formal rules [2,4]:

(a) It is not permitted to draw circles in adjacent hexagons.

(b) Circles can be drawn in some hexagons if the subgraph obtained from B by deleting these hexagons together with their incident edges has at least one Kekulé structure.

(c) A Clar formula contains the maximum number of circles which can be drawn in accordance with the rules (a) and (b).

An example of a Clar formula is shown in Fig. 1.

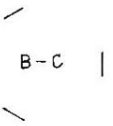


Fig.1 A benzenoid system B with a Clar formula $C=\{S_1,S_2,S_3\}$ and the subgraph B-C.

The importance of Clar formulas in theoretical chemistry is well known and is outlined in due detail in the books [2,3] as well as in a recent review [5]. We note in passing that the Clar formula of a benzenoid system need not be unique [2]. (For instance, the example depicted in Fig. 1 is just one of the two - symmetry equivalent - Clar formulas of coronene.) Furthermore, a benzenoid system possesses a Clar formula if and only if it is Kekuléan [6]. In the general case the problem of characterizing the benzenoid systems having Clar formulas with a fixed number n of aromatic sextets seems to be very difficult. If n = 0, however, then the above problem reduces to the finding of the class of non-Kekuléan benzenoid systems. This latter task has recently been completely settled (see [7-9] and the references quoted therein). In this paper we solve the problem for n = 1.

We also remind that two of the present authors [10] succeeded in finding necessary and sufficient conditions which a triple of integers (x,y,z) must fulfil in order to be the (x,y,z)-invariant of a benzenoid system.

The following theorem describes the relation between the (x,y,z)-invariant and the Clar formulas of a benzenoid system B.

Theorem 2. [1] Let B be a benzenoid system with the invariant (x,y,z). Then the Clar formulas of B contain at most x aromatic sextets.

Preliminary Results

In order to be able to formulate our main results, we first introduce some more notation. Let B be a benzenoid system with a Clar formula C. Then B-C will denote the subgraph obtained from B by deleting all the hexagons with circles in C, together with their incident edges (see Fig. 1).

Lemma 3. Let $\bar{B}$ be a benzenoid system and u its vertex lying on the boundary of $\bar{B}$. By $\bar{B}$-{u} we denote the subgraph obtained by deleting u from $\bar{B}$. If $\bar{B}$-{u} has a Kekulé structure, then an aromatic sextet can be drawn in $\bar{B}$-{u}.

Proof. Assume that $\bar{B}$ has t vertices, h hexagons and m edges. Let the length of the boundary of $\bar{B}$ be p. Recall that the edges lying on the boundary of $\bar{B}$ are called external edges; the other edges of $\bar{B}$ are said to be internal. Then $\bar{B}$ possesses p external and m-p internal edges. Since every internal edge belogs to two hexagons, we have

$$6\,h = 2(m - p) + p$$

i.e.

$$m = 3\,h + p/2 \quad . \tag{1}$$

On the other hand, by Euler's formula,

$$t - m + h = 1 \tag{2}$$

which combined with (1) yields

$$t - 2\,h - p/2 = 1 \quad . \tag{3}$$

Suppose now that a Kekulé structure $\bar{K}$ of $\bar{B}-\{u\}$ contains q external edges and therefore $(t-1)/2-q$ internal edges. If no sextet can be drawn in $\bar{B}-\{u\}$, then at most two edges in each hexagon belong to $\bar{K}$. Therefore,

$$2h \geq q + 2[(t-1)/2 - q] = t - q - 1 \quad . \tag{4}$$

Since the vertex u lies on the boundary of B, it must be

$$q \leq p/2 - 1 \quad . \tag{5}$$

Substituting (5) back into (4) we obtain

$$2h \geq t - p/2$$

i.e.

$$t - 2h - p/2 \leq 0 \quad . \tag{6}$$

Formula (6) is evidently in contradiction with (3) which means that the assumption about the impossibility of drawing a resonant sextet in $\bar{B}-\{u\}$ was false. Lemma 3 follows.

The Main Theorems

We are now in position to formulate our main results.

Theorem 4. Let B be a Kekuléan benzenoid system with the invariant (x,y,z). The following three statements are equivalent:

(*i*) $x = 1$;

(*ii*) B is a linear polyacene L_h (see Fig .2);

(*iii*) each Clar formula of B has exactly n = 1 aromatic sextet.

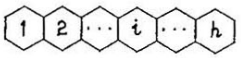


Fig.2 $L_h, h \geq 1$

Proof. $(i) \rightarrow (iii)$

Since B is Kekuléan, at least one aromatic sextet can be drawn in it. On the other hand, since x = 1, by Theorem 2 each Clar formula of B has at most one aromatic sextet. Therefore condition (i) implies condition (iii).

$(iii) \rightarrow (ii)$

For convenience, we use the symbol $B[S_1,\ldots,S_i]$ to denote the subgraph of B induced by the vertices of the hexagons $S_1,\ldots,S_i$ of B. The set of all hexagons of B is denoted by X. Consequently, $B[X] \equiv B$. Let C be the subset of hexagons of B, labeled by circles in the Clar formula under consideration. If condition (iii) holds then $C = \{S\}$ i.e. C consists of a single hexagon S.

Let K^* be a Kekulé structure of B-C. It is not difficult to see that then there exist a subgraph B^* of B, such that B^* is a linear polyacene containing the hexagon S (see Fig. 3). In addition to this, $K^* \cap E(B^*-C)$ is a Kekulé structure of B^*-C (see Fig. 3).

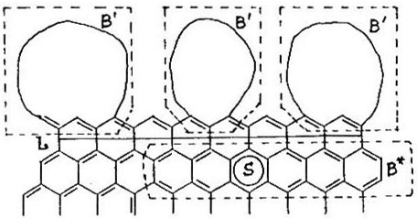


Fig. 3

Suppose that B is not a linear polyacene. We then have to separately examine the following two cases.

Case 1. K^* contains no edge intersected by the horizontal line L (see Fig. 3). Then there exists a benzenoid subsystem B' above L, such that

B′ and B^* have no vertices in common. (The fact that B′ necessarily exists should be evident from Fig. 3: the nonexistence of B′ would imply that the number of vertices above the line L is odd and therefore at least one edge of K^* would have to intersect L.) It is easy to see that B′ either has a Kekulé structure or satisfies the conditions of Lemma 3. As a consequence of Lemma 3, at least one aromatic sextet can be drawn in B′. This contradicts the fact that C pertains to a Clar formula of B. Whence (*iii*) → (*ii*) is true in the case 1.

Case 2. K^* contains at least one edge intersected by the line L. Suppose that the edges $e_1, e_2, \ldots, e_x, e_y$ belong K^* so that $e_1, e_2, \ldots, e_x$ are not, whereas e_y is intersected by the line L (see Fig. 4).

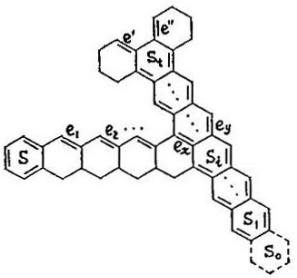


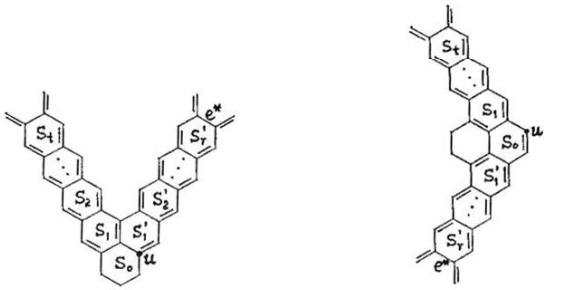
Fig.4

Let t be the maximum number such that there is a series of hexagons $S_1, S_2, \ldots, S_t$ whose vertices are matched by the edges of K^* in a manner indicated in Fig. 4. The edges e′ and e′′ in Fig. 4 are supposed to lie on the boundary of B.

Subcase 2.1. The hexagon S_0 does not belong to B. Then we can find a benzenoid system B′ which is a subgraph of $B[X-\{S_1, \ldots, S_t\}]$ and which

does not contain the hexagon S. We can argue in a similar way as in Case 1 that B′ possesses an aromatic sextet. This also contradicts the fact that C pertains to a Clar formula of B.

Subcase 2.2. The hexagon S_0 belongs to B. Irrespective of whether the vertex u of the hexagon S_0 is matched by a vertical edge of K^* (c.f. diagram (b) in Fig. 5) or not (c.f. diagram (a) in Fig. 5), we are able to find a series of hexagons $S'_1, S'_2, \ldots, S'_r$, such that $B[X-\{S_1, \ldots, S_t, S'_1, \ldots, S'_r\}]$ contains a fragment B′ in which the hexagon S is not present (see Fig. 5), and in which an aromatic sextet can be drawn. This again is a contradiction and, consequently, condition (*iii*) implies condition (*ii*) also in the case 2.



(a) (b)

e* lies on the boundary of B e* lies on the boundary of B

Fig.5

(*ii*) → (*i*)

Immediate from the definition of a linear polyacene (see Fig. 2).

This completes the proof of Theorem 4.

Theorem 5. Let B be a Kekuléan benzenoid system with the invariant (x,y,z). Then x = 2 if and only if B is of Type 1 or of Type 2 as defined below.

Type 1: Let $L_1, L_2, \ldots, L_t$ be horizontal lines intersected by vertical edges of B. We denote the subgraph lying at the upper bank of L_1 by H_1, the subgraph lying at the lower bank of L_t by H_t, the subgraph lying between L_i and L_{i+1} by $H_{i,i+1}$, i = 1,..., t-1. Then H_1 and $H_{1,2}$ are paths of the same even length; the same is true for $H_{t-1,t}$ and H_t. In addition to this, for i = 1,...,t-2, $H_{i,i+1}$ is a path of an odd length (see Fig. 6).

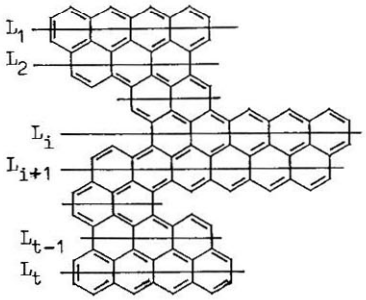
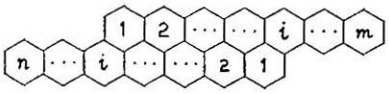


Fig. 6

Type 2: The construction of benzenoid systems of Type 2 is clear from Fig. 7.



$m,n \geq i \geq 1$, and $m+n \geq 3$

Fig.7

Proof. Sufficiency is immediate.

We now assume that $x = 2$. By Theorem 4 the centers of all the hexagons of B cannot lie on the same horizontal line. Thus $t \geq 2$. When $t = 2$ it is easy to see that B is of Type 2. In what follows we therefore suppose that $t \geq 3$.

Let K be a Kekulé structure of B and let the edges in $E_1 = E_1(K)$ be vertical. We want to prove that $|E_1 \cap T_j| = 1$ for $j = 1$ and for $j = t$, where T_j is the set of edges of B intersected by the line L_j. It is not difficult to see that each component of H_1 is a path of an even length. Consequently, in the Kekulé structure K each component of H_1 possesses at least one vertex matched by a vertical double bond of K, i.e. $|E_1 \cap T_1|$ is larger than or equal to the number of the components of H_1. By symmetry, $|E_1 \cap T_t|$ is also larger than or equal to the number of components of H_t. Since $|E_1 \cap T_1| + |E_1 \cap T_t| \leq x = 2$, we have $|E_1 \cap T_1| = |E_1 \cap T_t| = 1$. This imples that both H_1 and H_t have only one component, i.e. H_1 and H_t are paths of an even length. Since $x = 2$ we have $|E_1 \cap T_j| = 0$ for $j = 2,\ldots,t-1$.

Consider $H_{1,2}$. If $H_{1,2}$ would not be connected (see Fig. 8), then $|E_1 \cap T_2|$ would not be less than 1, a contradiction.

Consider $H_{2,3}$. If $H_{2,3}$ would have more than one component, then we would have to distinguish between the three cases which are depicted in Fig. 9.

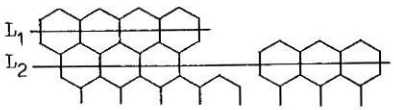
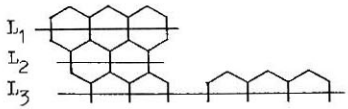
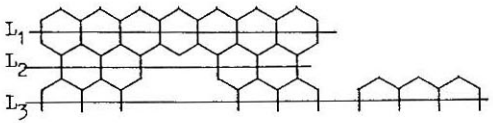


Fig.8





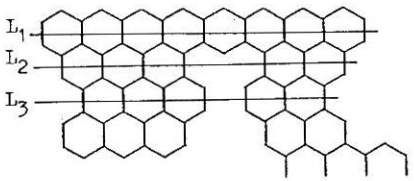


Fig.9

The two first cases are easily seen to be impossible. As to the last case, there will exist a number g, such that $2 \leq g \leq t-1$ and $|E_1 \cap T_g| \geq 1$, still a contradiction.

A similar argument shows that $H_{j,j+1}$ must be a path also for $j = 3,\ldots,t-1$. The parity of the length of $H_{j,j+1}$ is evident since B is supposed to have a Kekulé structure. Finally, by the same way of reasoning we conclude that $H_{1,2}$ and H_1 must have the same lengths. The same applies to $H_{t-1,t}$ and H_t.

This completes the proof of Theorem 5.

From Theorem 5 we might naturally conjecture that the condition of Theorem 5 is equivalent to saying that each Clar formula of B has exactly two aromatic sextets. Unfortunately, however, this conjecture is not true. Fig. 10 shows a benzenoid system having two aromatic sextets, but x = 3.

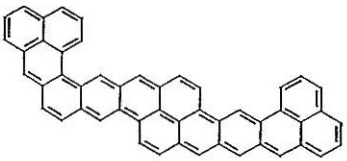


Fig.10

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