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SOME TOPOLOGICAL PROPERTIES OF NORMAL BENZENOIDS AND CORONOIDS

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ABSTRACT

In the present paper, some interesting topological properties of normal benzenoids and coronoids are given and a simple method, which is used for determing that a benzenoid or a coronoid system is normal or not, is proposed.

KEY WORDS

Normal benzenoid - Normal coronoid - Kekulé structure - Conjugated circuit - P-V path

Kekuléan benzenoids and coronoids are divided into essentially disconnected (which have fixed double and/or single bonds) and normal (which have no fixed bonds)[1,2]. In the present paper, coronoids includes single and multiple ones.

Consider a benzenoid (or a coronoid) drawn such that some of its edges are vertical. A peak P is defined as a vertex lying above all its first neighbours, and a valley V is a vertex lying below all its first neighbours[3-6].

In the classical work of Gordon and Davison[3], the following observation was made: in every Kekulé structure of a benzenoid there is a unique monotonous alternating path, (called a perfect P-V path or a conjugated P-V path[5,6]), connecting a peak with a valley, and starting with a double bond. This is true for all peaks and all valleys. The pertinent monotonous alternating paths are mutually independent and form a perfect P-V path system.

In[4], Sachs established a one-to-one correspondence between Kekulé structures and perfect P-V path systems in benzenoids (or coronoids).

Clearly, for a given position of a Kekuléan system, in order to change a perfect P-V path system into another, we only need to change some segments of P-V paths, but not the starting points (peaks) and the terminating points(valleys).

In a given Kekulé structure of a benzenoid or a coronoid, if a circuit with h edges has h/2 conjugated double bonds, then the circuit is called a conjugated circuit[7-9]. If the extremely right vertical edge of a conjugated circuit is a double bond edge, then this circuit is called a right conjugated circuit, otherwise, it is called a left one. If one exchanges the double bonds and the single bonds of a conjugated circuit,then the right/left conjugated circuit is changed into a left/right one. Such a transformation is called a right-left transformation of the conjugated circuit (simply, a RL transformation).

In the present paper, whenever a Kekuléan system is mentioned, it involves a Kekuléan benzenoid or a Kekuléan coronoid, and the following theorems hold not only for benzenoids but also for coronoids.

Theorem 1. By executing a seriers of RL transformations, any Kekulé structure K of a Kekuléan system G can be obtained from a given Kekulé structure K_0 of G,

Proof:

1) At first, consider two special cases in which K is different from K_0 only in one P-V path.

Case A). The difference between K_0 and K is only in one segment of a P-V path, say that the segment $a_c a_{c+1} \cdots a_{c+e} a_{c+e+1}$ in the P-V path $a_1 a_2 \cdots a_c a_{c+1} \cdots a_{c+e} a_{c+e+1} \cdots a_t$ (a_1 and a_t are coincident with a peak and a valley, respectively) of K_0 is different from the segment $a_c b_{c+1} \cdots b_{c+e} a_{c+e+1}$ in the P-V path $a_1 \cdots a_c b_{c+1} b_{c+2} \cdots b_{c+e} a_{c+e+1} \cdots a_t$ of K, where $1 \leq c \leq t-3$; $2 \leq e \leq t-c-1$. Clearly, in K_0 there exists a conjugated circuit C, $a_c a_{c+1} \ldots a_{c+e} a_{c+e+1} b_{c+e} b_{c+e+1} \ldots b_{c+1} a_c$. By executing the RL transformation of C, K_0 changes into K (See Fig.1).

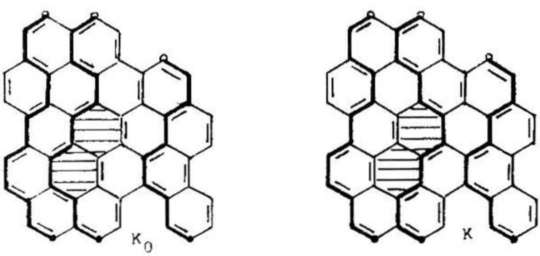


Fig.1 Changing of P-V paths

Case B). The difference between K_0 and K involves several segments of a P-V path of K_0. Similarly to A), by using RL transformations, we can change the segments of the P-V path in K_0 into the same as those in K, one by one.

2) For the general case, by using RL transformations, a unique special Kekulé structure K_s in which all the conjugated circuits are right can be obtained[8,9]. Obviously, in the obtained Kekulé structure K_s, all the P-V paths have been shifted to as left as possible. Starting from the extremely right P-V path in K_s, from right to left, using the method in 1), we can change the P-V paths in K_s into the same as those in K, one by one. Each transformation is only concerned with one P-V path.

Theorem 2. For a Kekulé structure K_0 of a Kekuléan system G, if an edge is on a conjugated circuit, then in any Kekulé structure K, the edge is also on a conjugated circuit.

Proof:

Suppose that an edge ab is on the conjugated circuit C_0 of K_0. According to Theorem 1, by using RL transformations, any Kekulé structure K can be obtained from K_0. Consider a RL transformation of a conjugated circuit C_t of K_0. If ab is a common edge of C_0 and C_t, or if C_0 and C_t have no edges in common, then after transformation, the edge ab is still on C_t. If C_0 and C_t have edges in common other than ab, then after transformation, the edge ab belongs to the new conlugated circuit which is composed of all the edges of C_0 and C_t except their common edges. Q.E.D. (See Fig.2).

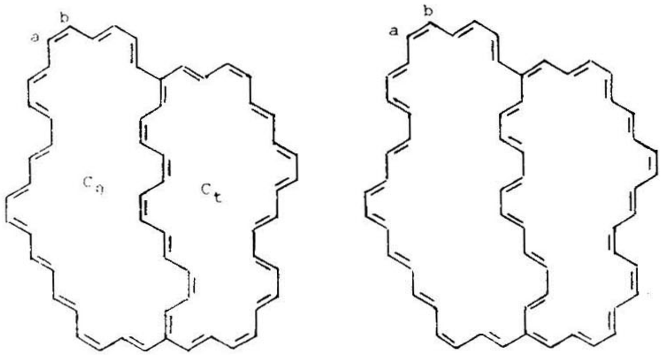


Fig.2 Illustration of Theorem 2

From Theorem 2, we immediately obtain:

Theorem 3. For a Kekuléan system G, an edge is a non-fixed bond, iy and only if the edge is on conjugated circuits in a Kekulé structure of G.

An alternative statement of this theorem is as follows.

Theorem 3a. For a Kekuléan system G, an edge is a fixed bond, if and only if it does not belong to any conjugated circuit in a Kekulé structure of G.

Because a normal Kekuléan system has no fixed bond, we immediately have Theorem 4.

Theorem 4. A Kekuléan system G is normal if and only if all the edges are on conjugated circuits in a Kekulé structure of G.

Now, we give some other theorems about normal systems.

Theorem 5. A Kekuléan system G is normal if and only if for any basic circuit C_0 (hexagon or internal perimeter of a benzenoid or a coronoid) there exists a Kekulé structure K of G where C_0 is conjugated.

Proof:

1) Consider a Kekulé structure K_0 of a normal Kekuléan system G. A basic circuit C_0 is not conjugated in K_0. According to Theorem 2, an edge a_1b_1 on C_0 must belong to a conjugated circuit, say C_1. C_0 and C_1 have edges $a_ta_{t-1}, a_{t-1}a_{t-2}, \cdots, a_2a_1, a_1b_1, b_1b_2, \cdots, b_{s-1}b_s$ ($t\geq 1$ and $s\geq 1$) in common. Obviously, both a_t and b_s are vertices of degree three. Consider vertex b_s. There are three edges, $b_{s-1}b_s$, b_sb_{s+1} and b_sd, terminating on b_s. Among them $b_{s-1}b_s$ is common edge of C_0 and C_1, and b_sb_{s+1} and b_sb_d belong to C_0 and C_1, respectively. (See Fig.3). There exist two cases.

A) If $b_{s-1}b_s$ is a single bond, then b_sd and b_sb_{s+1} are a double bond and a single bond, respectively (See Fig.3b).

B) If $b_{s-1}b_s$ is a double bond, then both b_sd and b_sb_{s+1} are single bonds (See Fig.3a).

For the first case, according to Theorem 2, b_sb_{s+1} is on a conjugated circut, say, C_2. The edge b_sd is also on C_2. Executing RL transformation to C_2, we can obtain another conjugated circuit C_1 which is composed of the unoverlapping edges of C_1 and C_2, including not only edges $a_t a_{t-1}, \cdots, a_2 a_1, a_1 b_1, b_1 b_2, \cdots, b_{s-1} b_s$ but also $b_s b_{s+1}$, (probably, and some other edges of C_0).

For the second case, we cane find another conjugated circuit C_1' in K_0 which contains not only the edges $a_t a_{t-1}, a_{t-1} a_{t-2}, \ldots, a_2 a_1, a_1 b_1, b_1 b_2, \ldots, b_{s-1} b_s$ but also $b_s b_{s+1}$.

To sum up, for any cases, using RL transformations (if necessary), we can make more and more edges of C_0 to be on a conjugated circuit. Finally there exists a Kekulé structure K in which C_0 itself forms a conjugated circuit. (See Fig.3)

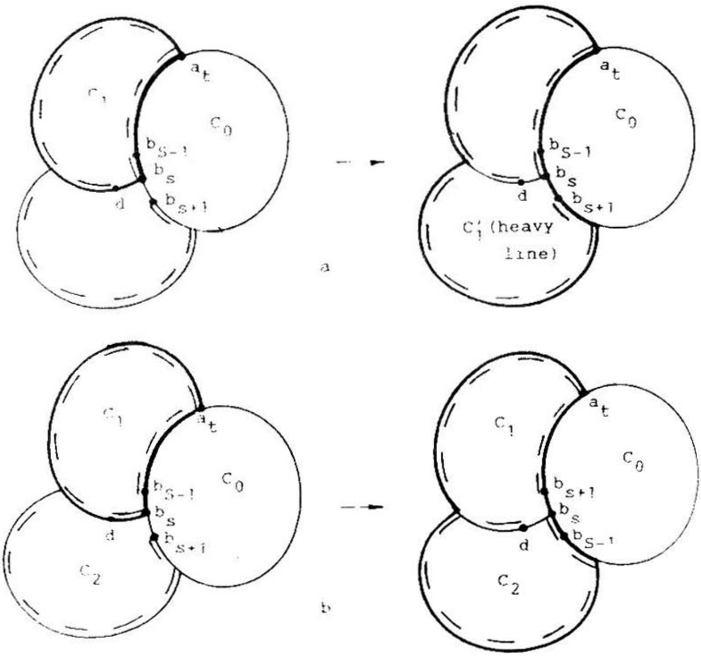


Fig.3 Illustration of the proof procedure of Theorem 5

2) Inversely, if for any basic circuit C_0, there exists a Kekulé structure K of G where C_0 is a conjugated circuit, then, according to Theorem 3a, G has no fixed bond edges. And so G is normal.

By the way, Theorem 5 is useful for investigating the sextet polynomial which is proposed by Hosoya[10]. In fact, from Theorem 5, we immediately obtain the following theorem.

Theorem 6. The coefficient of the term with first power in the sextet polynomial of a normal benzenoid G, which has no supersextet[10] in any Kekulé structure of G, is equal to the number of hexagons in G.

Proof:

Accoding to Theorem 5, for any hexagon C_0 there is a Kekulé structure of G, in which C_0 is conjugated. Using RL transformations, we can change C_0 into a proper sextet (right conjugated six-membered circuit) and the other conjugated hexagons into non-proper sextets (left conjugated six-membered circuits). Similarly to the proof of Theorem 2 in[9], we can prove that such a Kekulé structure is unique. So theorem 6 holds.

Theorem 7. A Kekuléan system G is normal if and only if there exists a Kekulé structure K_e where the external perimeter C_e of G is a conjugated circuit.

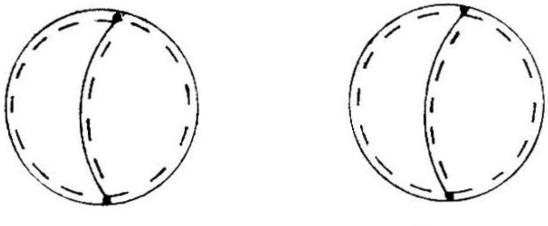
Proof:

1) The proof of necessity is fully analogous to that in

Theorem 5.

2) Now consider a Kekuléan system G having a Kekulé structure in which the external perimeter C_e is conjugated. Suppose that in the interior of C_e, an edge ab is a fixed-bond edge. In the interior of C_e, an alternating path passing through the edge ab can extend to and terminate on C_e. The path divides C_e into two parts. Each part with the path forms a circuit. There seem to be two modes in Fig.4. Mode A is impossible, because both of the two circuits have odd edges. In mode B, one of the two circuits is conjugated. It is in contradiction with the supposition. Hence, in the interior of C_e there are no fixed bond edges, and G is normal.

<u>Corollary</u>. A bezenoid (or a coronoid) system is normal if and only if the remainder G' produced by deleting the external perimeter C_e of G is Kekuléan (one-factorable).



Mode A Mode B

Fig.4 Illustration of sufficiency of Theorem 7

It is convenient to use Theorem 7 and its corollary for determing that a benzenoid or a coronoid system is normal or not. For using the corollary,we need not to know beforehand if the system is Kekuléan or not.

For example, in Fig.5, the system G_1 is not normal, because the remainder obtained by deleting the external perimeter of G_1 is non-Kekuléan; and G_2 is normal,because the remainder obtained by deleting the external perimeter of G_2 is Kekuléan.

G_1 Remainder G_2 Remainder

Fig.5 A normal system G_2 and an essentially disconnected system G_1

Besides, we have the following results.

Theorem 8. In the interior of any conjugated circuit of an arbitrary Kekulé structure, there are no fixed-bond edges.

Theorem 9. If a Kekulé benzenoid (or coronoid) G has some fixed-bond edges, then the remainder system produced by deleting all the fixed-bond edges of G must be a disconnected system and must contain more than one normal component.

Proof:

The proof is analogous to that of sufficiency of Theorem 7. Accoding to Theorem 7, on the external perimeter of G, there must be fixed-bond edges. Suppose that deleting all the fixed-bond edges in G,we obtain only one normal component N. According to Theorem 7, there exists a Kekulé structure of N in which the external perimeter of N is a conjugated circuit. Thus, all the fixed-bond edges of G are outside of N. An alternating path of fixed-bond edges can extend to and terminate on the external perimeter of N. The path divides the perimeter into two parts. Each part with the path forms a circuit. One of the two circuits is conjugated. It is a contradiction. Q.E.D.

According to Theorem 9, an essentially disconnected Kekuléan system must contain two or more normal components $N_1, N_2, \ldots, N_s$, which connect with each other by fixed bond edges.

Denote the numbers of Kekulé structures of $N_1, N_2, \ldots, N_s$ by $K(N_1), K(N_2), \ldots, K(N_s)$, respectively, and the total energies of π-electrons in $N_1, N_2, \ldots, N_s$ by $E_\pi(N_1), E_\pi(N_2), \ldots, E_\pi(N_s)$, respectively. Denote the number of Kekulé structure of G by K(G) and the total energy of π-electrons in G by $E_\pi(G)$.

Then, for any essentially disconnected Kekuléan system, we have

$$K(G) = \prod_{i=1}^{s} K(N_i) \quad ;$$

$$E_\pi(G) = \sum_{i=1}^{s} E_\pi(N_i) .$$

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