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A Method to Recognize Fixed Bond Regions in an Essentially Disconnected Benzenoid

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Abstract: A Simple method is developed which allows all fixed bonds and all normal components of an essentially disconnected benzenoid to be recognized.

In this paper all the terms are applied in consistence with those given in[1–7].

The set B_K of Kekuléan benzenoids decomposed into the class B_N of normal benzenoids (which have no fixed bonds) and the class B_{ED} of essentially disconnected benzenoids (which have some fixed bonds).

Let $B \in B_K$ be drawn in the usual way in the plane (see Fig.1) and let h denote a hexagon (i.e., a closed hexagonal region) of B. If none of the edges of h represent a fixed bond, then h is called free. Clearly, $B \in B_N$ if and only if all hexagons of B are free.

The region covered by all free (non-free) hexagons of B decomposes into maximal connected parts; each such part is called a normal component (fixed bond component) of B. By definition, no edge in the interior and on the boundary of a normal component represents a fixed bond. As shown in Fig.1, the smallest normal component contains only one hexagon.

In[1], we proved the following result.

Theorem 1 Every fixed bond component of a $B \in B_{ED}$ is adjacent to at least two normal components. No normal component surrounds another component.

Note that a fixed bond component may surround other components (see, e.g., Fig.1).

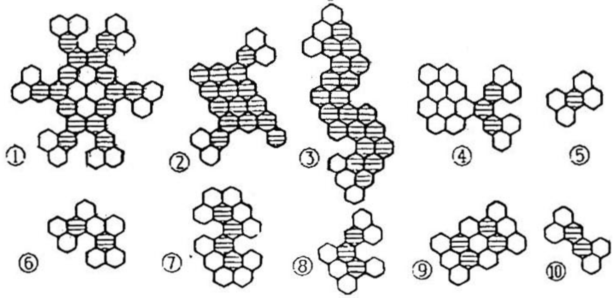


Fig.1 Normal components and fixed bond components in essentially disconnected benzenoids

It has been shown[5] that every normal component represents a normal benzenoid.

There are two problems which are interesting for chemists: How does one determine whether an edge is or is not of a fixed bond type? How does one find all the fixed bond components?

For the two problems, in 1935, L. Pauling et al. proposed the following formula[9]:

$$p_{rs} = k_{rs}/k, \qquad (1)$$

where k is the number of Kekulé structures of a benzenoid B, r and s are two adjacent carbon atoms in B, and k_{rs} is the number of Kekulé structures of a benzenoid in which there is a double bond between r and s. If $p_{rs} = 1$, then rs is a fixed double bond edge; if $p_{rs} = 0$, then rs is a fixed single bond edge.

In[10], Sachs proposed the "horizontal cut method" to find the fixed bond edges. In[11], F.J.Zhang et al. indicated that there exist Benzenoid systems in which the fixed bond edges cannot be found by the method, and proposed the "horizontal g-cut method". However, all the above methods are cumbersome and time-consuming.

In this paper , we propose a new method to find the normal and fixed components in a $B \in B_{ED}$.

Consider a Kekuléan benzenoid B having no holes with size larger than one hexagon. It is drawn in the manner that some of its edges are vertical. According to Sachs' 1-to-1 correspondence theorem[11], a Kekulé structure K of B corresponds to a P-V (peak to valley) path system of B. In any Kekulé structure of B, all the oblique edges in the corresponding P-V path system, and all the vertical edges not in the P-V path system are of a double-bond type; the others are of a single-bond type[11]. Obviously, in all possible Kekulé structures of B, if an edge is in no P-V path system, or if an edge is in every P-V path system, then the edge must be of a fixed bond type. If there are no such edges in B, then B is normal, otherwise, it is essentially disconnected.

Consider $B \in B_{ED}$. It has three possible orientations. Let e be a fixed single (double) bond edge. Then, for precisely one of the three orientations, e is in every (no) P-V path system, but for the remaining orientations, e is in no (every) P-V path system.

Let $\omega, \omega', \omega''$ be the three orientations of B, and consider one of them, say ω. The number p of the peaks is equal to the number v of the valleys[12]. Denote by P_{ij} the i-th P-V path of the j-th P-V path system, which goes from peak p_i to valley v_i, where $i = 1, 2, \cdots, p$; $j = 1, 2, \cdots, k(B)$, where $k(B)$ is the number of possible Kekulé structures of B. The correspondence (p_i, v_i) between peaks and valleys is independent of the choice of P-V systems[13,14].

Let T_{ij} be the set of the edges belonging to P_{ij}, and let

$$T_i = \bigcup_{j=1}^{K(B)} T_{ij}, \quad T = \bigcup_{i=1}^{p} T_i . \qquad (2)$$

Denote by $\overline{T}$ the set of all edges in B which do not belong to T. Obviously, all the edges in $\overline{T}$ are of fixed bond type. Similarly, for the other two orientations, ω', ω'' of B, we can find sets $\overline{T'}$ and $\overline{T''}$.

Thus, $T_F = \overline{T} \cup \overline{T'} \cup \overline{T''}$, (3)

where T_F is the set of all fixed bond edges of B.

To find T_F by the method stated above is not easy. In this paper we propose a new method.

Consider the P-V paths which are the monotone downwards parths starting from p_i and ending at $v_i (i = 1, 2, \cdots, p)$ where the correspondence between p_i and v_i is coincident with that in any P-V path system of B. Possibly, some of these paths do not belong to any P-V path system. An example is shown in Fig.2 by heavy line.

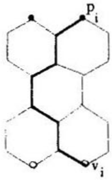


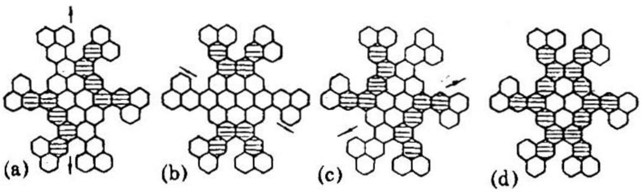
Fig.2 A P-V path not belonging to any P-V path system

Among these paths the extreme left one and the extreme right one are S^{il} and S^{ir}, respectively. Let $E_i (i = 1, 2, \cdots, p)$ be the set of the edges on S^{il} and S^{ir} and between them.

Put $E = \bigcup_{i=1}^{p} E_i$ (4)

Obviously, $T_i \subseteq E_i$, and $T \subseteq E$. We denote by $\overline{E}$ the set of all edges in B which do not belong to E. All the edges in $\overline{E}$ are of fixed bond type. Similarly, for the other two orientations ω', ω'' of B, we can find sets $\overline{E'}$ and $\overline{E''}$.

Let $E_F = \overline{E} \cup \overline{E'} \cup \overline{E''}$. (5)



The arrows represent the vertical direction

Fig.3 $E_F = \overline{E} \cup \overline{E'} \cup \overline{E''}$

An example is shown in Fig.3. The sets of the edges in the unshaded regions of Fig.3a,b,c are E, E', E'', respectively.

We can prove $E_F = T_F$. To prove this, we need only to prove the following two theorems.

For a given orientation of a hexagonal network, the set of vertical edges in an edge set W is denoted by $VD(W)$.

Theorem 2. $VD(T)=VD(E)$ (6)

Proof:

From $T \subseteq E$, we immediately have

$$VD(T) \subseteq VD(E). \tag{7}$$

On the other hand, we will prove also that

$$VD(E) \subseteq VD(T). \tag{8}$$

Assume that there exists a vertical edge ab belonging to $VD(E)$, but not to $VD(T)$ i.e.,

$$ab \in VD(E)\backslash VD(T). \tag{9}$$

Without loss of generality, assume that $ab \in VD(E_{i_0})$. Denote by $M_{ab}^{i_0}$ the set of all the P-V paths starting from p_{i_0}, ending at v_{i_0}, and having the edge ab in common. $S_{ab}^{i_0 l}(S_{ab}^{i_0 r}) \in M_{ab}^{i_0}$ is the extreme left (right) P-V path belonging to $M_{ab}^{i_0}$ which is shown in Fig.4 by heavy line.

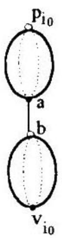


Fig.4 $S_{ab}^{i_0 l}$, $S_{ab}^{i_0 r} \in M_{ab}^{i_0}$

Benzenoids have no holes larger than one hexagon. Any P-V path S divides B into two parts. One lies at the left bank of S, and is denoted by $L(S)$. The other is $R(S)$. Both $L(S)$ and $R(S)$ contain the path S.

$L(S) \cap R(S) = S$ and $L(S) \cup R(S) = B$.

Firstly, we show that for a given $j_0(1 \le j_0 \le k(B))$ and for a P-V path $p_{ij_0}(1 \le i \le p;\ i \ne i_0)$ satisfying that $p_{ij_0} \cap S_{ab}^{i_0 l} \ne \phi$ and $p_{ij_0} \cap S_{ab}^{i_0 r} \ne \phi$, the following two cases are impossible.

In case 1, suppose that one of the two vertices p_{i_0} and v_{i_0} belongs to $L(p_{ij_0})$, the other to $R(p_{ij_0})$. (see Fig.5)

If so, the P-V path $p_{i_0j_0}$ would pass above p_i (or below v_i) and B would become a coronoid system[13]. ($p_{i_0j_0}$ is shown in Fig.5 by heavy line. p_i is enclosed in a circuit formed by $p_{i_0j_0}$ and $S_{ab}^{i_0r}$.)

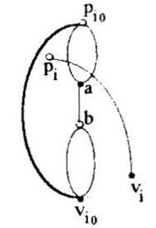


Fig.5 Case 1

In Case 2, suppose that $p_{i_0}, v_{i_0}, ab \in R(p_{ij_0})$ $(L(p_{ij_0}))$, where $p_{ij_0} = p_i edfv_i$ (see Fig.6a,b).

Put $L = p_{ij_0} \cap S_{ab}^{i_0r}$. For the case of Fig.6a, $L \neq p_{ij_0} \cap R(S_{ab}^{i_0r})$, and for the case of Fig.6b, $L = p_{ij_0} \cap R(S_{ab}^{i_0r})$.

In Fig.6a, we can find a monotone downwards path $S(= p_{i_0}edfabv_{i_0}) \in M_{ab}^{i_0}$ shown by heavy line. $S \in R(S_{ab}^{i_0r})$, and $S \neq S_{ab}^{i_0r}$. It is a contradiction in the definition of $S_{ab}^{i_0r}$.

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With regard to Fig.6b, obviously, $L \cap C_e = \phi$, where C_e is the contour of B (otherwise, $p_{i_0j_0}$ wouldn't exist). Consider a path segment $edf \subseteq L$, Vertices e, f are adjacent to $e', f' \in (S_{ab}^{i_0r} \backslash L)$, respectively. Obviously, both ee', ff' are not external edges of B. Thus, we immediately find a monotone downwards path $S'(= p_{i_0}e'd'f'abv_{i_0}) \in M_{ab}^{i_0}$ shown in the figure by heavy line. $S' \in R(S_{ab}^{i_0r})$ and $S' \neq S_{ab}^{i_0r}$. It is also a contradiction in the definition of $S_{ab}^{i_0r}$.

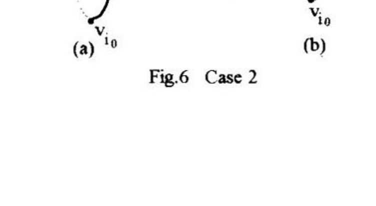


Fig.6 Case 2

Secondly, we prove that for the other cases, $ab \in VD(T)$. We only need to consider the following two cases: A and B.

Case A For a given $j_0(1 \le j_0 \le k(B))$, some P-V paths $p_{ij_0}(i = i_1, i_2 \cdots;\ i \ne i_0)$ satisfy that 1) $p_{ij_0} \cap S_{ab}^{i_0 l} \ne \phi$, and $p_{ij_0} \cap S_{ab}^{i_0 r} \ne \phi$;

2) $p_{i_0}, v_{i_0} \in R(p_{ij_0})\ (L(p_{ij_0}))$, while $ab \in L(p_{ij_0})\ (R(p_{ij_0}))$.

Among the P-V paths p_{ij_0} satisfying the conditions stated above, the one nearest to a and b is $p_{i_1j_0}$ (see Fig.7). Denote the highest and the lowest common points of $p_{i_1j_0}$ and $S_{ab}^{i_0 r}$ by e and f, respectively. Then the P-V path $S_1(=p_{i_1}eabfv_{i_1})$ containing ab satisfies the following formula:

$$S_1 \cap \bigcup_{i=1,\, i\ne i_1}^{p} p_{ij_0} = \phi$$

Thus, S_1 and $\bigcup_{i=1,\, i\ne i_1}^{p} p_{ij_0}$ form a new P-V path system of B. Hence, $S_1 \in \bigcup_{j=1}^{k(B)} p_{i_1 j}$ and $ab \in VD(T)$ contradicting (9).

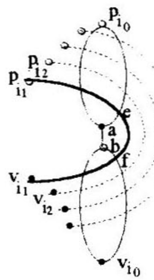


Fig.7 Case A

Case B As shown in Fig.8, for a given $j_0(1 \le j_0 \le k(B))$, two P-V paths $p_{i_1j_0}$, $p_{i_2j_0}$ satisfy that

1) $p_{i_1j_0} \cap S_{ab}^{i_0 r} = \phi$, $p_{i_2j_0} \cap S_{ab}^{i_0 l} = \phi$ $(0 \le i_1, i_2 \le p;\ \ i_1, i_2 \ne 0)$;

2) $p_{i_0}, v_{i_0}, ab \in H$, where $H = R(p_{i_1j_0}) \cap L(p_{i_2j_0})$, and the choice of i_1 and i_2 make the region H become minimum.

For the case of i_1 or (and) $i_2 = 0$, although p_{0j_0} does not exist, we define that $R(p_{0j_0}) = L(p_{0j_0}) = B$. In this case, let $S_{ab}^{i_0 l}$(or $S_{ab}^{i_0 r}$)$=p_{i_0j_0}$, which contains ab.

For the case of $i_1, i_2 \ne 0$, it is impossible that one of the vertical edges in $p_{i_1j_0}$ and one of those in $p_{i_2j_0}$ belong to the same hexagon (i.e., the bottle-neck of H must be wider than a hexagon). If there were such a narrow bottle-neck (shown in Fig.8a), then the P-V path $p_{i_0j_0}$ would pass above one of p_{i_1} and p_{i_2} and pass below one of v_{i_1} and v_{i_2}, and B would become a coronoid system; or

p_{i_0} and v_{i_0} themselves would be on the boundary of the holes of a coronoid system. Therefore, for a benzenoid B, such a narrow bottle-neck in H can not exist.

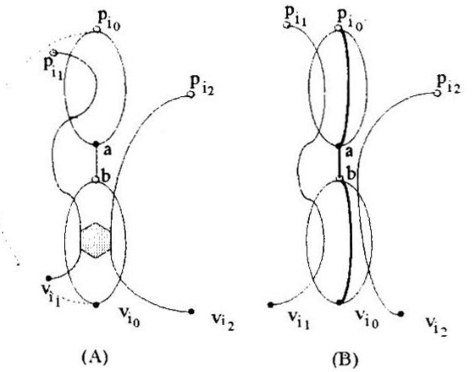


Fig.8 Case B

Thus, we can surely find a P-V path $S_0 \in M_{ab}^{i_0}$ shown in Fig.8b by heavy line. $S_0 \cap \bigcup_{i=1, i\neq i_0}^{p} p_{ij_0} = \phi$. S_0 and $(\bigcup_{i=1, i\neq i_0}^{p} p_{ij_0})$ form a new P-V path system of B. $S_0 \in \bigcup_{j=1}^{k(B)} p_{i_0j}$, and $ab \in VD(T)$ contradicting (9).

We obtain that for all actual cases, $ab \in VD(T)$ cotradicting (9).

Hence, $VD(E) \subseteq VD(T)$.

Finally, considering (7) and (8), we have

$$VD(E) = VD(T). \qquad \text{Q.E.D.}$$

Furthermore, $VD(E_F) = VD(T_F)$.

Theorem 3. If ab is a fixed single bond edge, then

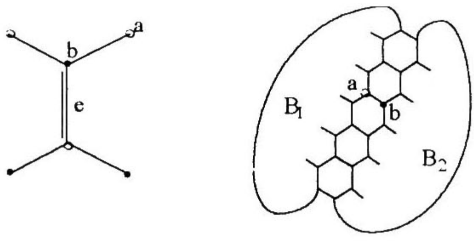
$$ab \notin \{E \cap E' \cap E''\} \text{ (or } ab \in \{\overline{E} \cup \overline{E'} \cup \overline{E''}\}.$$

Proof:

If ab is adjacent to a fixed double bond edge e, then for one of the three possible orientations of B, say ω, e is vertical. According to Theorem 2, for this orientation, there is no P-V path passing through e. And so there is no P-V path passing through ab. Thus, $ab \notin E$. (see Fig.9a)

If ab is not adjacent to any fixed double bond edges, then according to Theorem 4 in[15], ab can be only adjacent to two disjoint Kekuléan subhexagonal systems B_1 and B_2. For two of the three possible orientations of B, ab is oblique. Consider one of the two orientations (see Fig.9b). Then all the peaks and valleys in B_1 are 1-1 correspondent in any P-V path system of B_1. So are those in B_2. Thus, there is no P-V path containing ab. If there were such a P-V path, then it would become non-monotone downwards. So

$ab \notin E$. Q.E.D.



(a) (b)

Fig.9 Fixed single bond edge

According to Theorems 2 and 3, we have $E_F = T_F$.

In a benzenoid B, the region covered by all the hexagons having edges belonging to E_F is the fixed bond region (which need not be connected), and the remaining part is the normal region.

References

[1] He Wenchen and He Wenjie, Match, 25, 225(1990).
[2] He Wenchen and He Wenjie, Match, 25, 237(1990).
[3] S.J.Cyvin and I.Gutman. Z.Naturforsch, 41a, 1079(1986)
[4] A.T.Balaban, J.Brunvoll, J.Cioslowski, B.N.Cyvin, S.J.Cyvin, I.Gutman, He Wenchen, He Wenjie, J.V.Knop, M.Kovačević, W.R.Müller, K.Szymanski, R.Tošić and N.Trinajstić, Z.Naturforsch, 42a, 863(1987).
[5] I.Gutman, Bull.Soc.Chim.Beograd, 47, 453(1982)
[6] I.Gutman and O.E.Polansky, Mathematical Concepts in Organic Chemistry, Springer-Verlag, Berlin 1986.
[7] He Wenjie and He Wenchen, Theor.Chim.Acta, 75, (389)1989.
[8] S.J.Cyvin and I.Gutman, Comp & Math with Appls 12B, (859)1986.
[9] L.Pauling, L.O.Brockway, J.Y.Beach, J.Am .Chem.Soc. 57, 2705(1935).
[10] H.Sachs, Combinatorica, 4, 89(1984)
[11] Zhang Fuji, Guo Xiaofeng and Chen Rongsi, Topics in Current Chemistry, Vol.153, Springer-Verlag, Berlin-Heidlberg, p.181, 1990.
[12] He Wenjie and He Wenchen. In R.B.King, D.H.Rouvray (eds), Graph Theory and Topology in Chemistry, Elservier, Amsterdam, p.476, 1987.
[13] He Wenjie, He Wenchen and He Ying, On the Correspondence between Peaks and Valleys in P-V Path System of Benzenoids, Match, in press.
[14] P.Hansen and Maolin Zheng, J.Mol.Struct.(Theochem), 235, 293(1991).
[15] Zhang Fuji and Li Xueliang, Match, 25, 251, 1990.