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A NOTE ON THE NUMBER OF KEKULÉ STRUCTURES OF POLYHEX GRAPHS[1]

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Abstract

A polyhex graph is either a benzenoid system or a coronoid system.The enumeration of Kekulé structures in polyhex graphs by means of determinants is discussed. The application of John-Sachs formula is extended to a class of coronoid systems.

A benzenoid system[1], also called "honeycomb system"[2], is a finite connected plane graph with no cut-vertices in which every interior region is bounded by a regular hexagon of side length 1. A coronoid system G [3] is a subgraph graph of a benzenoid system H which is obtained by deleting at least one interior edge (i.e. edge not lying on the perimeter of H) or/and at least one interior vertex (i.e. vertex not lying on the perimeter of H) together with its incident edges such that a unique "hole" (i.e. an interior region bounded by a polygon with more than six edges) emerges and each edge of G belongs to at least one hexagon of G. A coronoid system G and the benzenoid system H from which G is obtained are depicted in Fig.1.

A polyhex graph is either a benzenoid system or a coronoid system. The study concerning polyhex graphs is of chemical relevance since poly-

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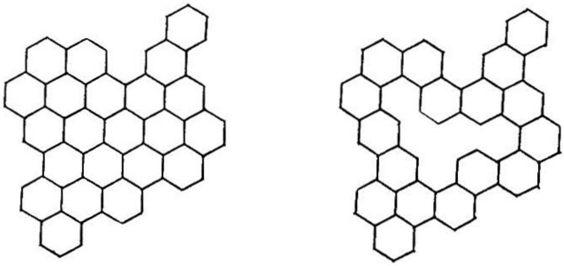
hex graphs are natural graph representations of benzenoid hydrocarbons and coronoid hydrocarbons [4].



H *G*

Fig.1

A coronoid system G and the benzenoid system H from which G is obtained.

A perfect matching of a graph G is a set of disjoint edges covering all vertices of G. Perfect matchings in polyhex graphs which are called Kekulé structures by chemists play significant role in numerous chemical theories [5]. Dozens of papers dealing with the enumeration of Kekulé structures in polyhex graphs have appeared.

For convenience, in the following we assume that a polyhex graph G in question is drawn in the plane so that two edges of each hexagon are vertical. Then a peak is a vertex lying above all its first neighbours. A valley is a vertex lying below all its first neighbours. A monotonous path in G is a path starting from a peak and going downwards.

Let $x_1, x_2, ..., x_s$ be peaks of a polyhex graph G, and let $y_1, y_2, ..., y_t$ be valleys of G. Denote by W the matrix whose element $(W)_{ij}$ is the number of distinct monotonous paths joining the $i-th$ valley with the $j-th$ peak. Evidently, a polyhex graph with Kekulé structures must have $s = t$ (cf.

[1]). It was found[6] that for a benzenoid system G, the number of Kekulé structures $K(G)$ is equal to $\mid detW \mid$, i.e., $K(G) = \mid detW \mid$. This is the so called John-Sachs formula.

A fast algorithm has been developed to determine the elements $(W)_{ij}$ [7]. John-Sachs formula is particularly useful for the enumeration of $K(G)$ by means of computer, and suitable computer programs have been designed [8].

Unfortunately, John-Sachs formula fails for a lot of coronoid systems. This feature may be reviewed as a challenge for mathematical study ([4],chapter 8).

In this note we prove that John-Sachs formula holds for a class of coronoid system. Thus extend the application of this elegant formula.

Let G be a polyhex graph with Kekulé structures. An edge e of G is said to be a fixed single bond if e does not belong to any Kekulé structure of G; e is said to be a fixed double bond if e belongs to all Kekulé structures of G. A fixed bond is either a fixed single bond or a fixed double bond. A polyhex graph with fixed bonds is said to be an essentially disconnected polyhex graph[5].

For a coronoid system G, it has two perimeters: the outer perimeter (i.e. the perimeter of the benzenoid system from which it is obtained) and the inner perimeter (i.e. the perimeter of the "hole").

Definition 1[9] A straight line segment P_1P_2 is called an elementary cut segment of a coronoid system G if

1. each of P_1 and P_2 is the center of an edge on the outer or inner perimeter of G;
2. P_1P_2 is orthogonal to one of the three edge directions;
3. any point of P_1P_2 is either an interior or a boundary point of some hexagon of G.

The set of all the edges intersected by an elementary cut segment is called an elementary cut.

Definition 2[9] A broken line segment $P_1P_2P_3$ is called a generalized cut segment of a coronoid system G if

1. each of P_1 and P_3 is the center of an edge lying on the outer or inner perimeter of G, and P_2 is the center of a hexagon of G;
2. P_1P_2 is orthogonal to one of the three edge directions of G, P_2P_3 and P_1P_2 form an angle of $\pi/3$ or $2\pi/3$;
3. any point of $P_1P_2P_3$ is either an interior or a boundary point of some hexagon of G.

The set of all the edges intersected by a generalized cut segment is called a generalized cut.

A special edge cut is either an elementary cut or a generalized cut. It is evident that each special edge cut E has exactly two edges on the inner or the outer perimeter of G. If these two edges are simultaneously on the outer or the inner perimeter of G, E is said to be of type I. If one of them is on the outer perimeter and the other is on the inner perimeter, then E is said to be of type II.

Theorem 3[9] An essentially disconnected coronoid system possesses an special edge cut consisting of fixed single bonds.

In the following we confine ourselves to those polyhex graphs with Kekulé structures. Since a polyhex graph is bipartite, in the following we assume that the vertices of a polyhex graph G in question are coloured black and white such that any two adjacent vertices are differently coloured. Assume that G has n white vertices $x_1, x_2, ..., x_n$. Then G has n black vertices $y_1, y_2, ..., y_n$. Let B^* denote the square matrix of order n such that $(B^*)_{ij} = 1$ if vertex x_i is adjacent to vertex y_j, and $(B^*)_{ij} = 0$ if vertex x_i is not adjacent to vertex y_j.

Lemma 4 For an essentially disconnected coronoid system G with a special edge cut of type II, we have $K(G) = |detB^*|$.

Proof. By algebraic knowledge the absolute value of the determinant of B^* is independent of the labelling of the vertices of G. Without loss of generality we may label the vertices of G such that white vertex x_i is adjacent to black vertex y_i for $i = 1, 2, ..., n$ since G has Kekulé structures. Let M be a Kekulé structure of G. Recall that an M-conjugated circuit is a circuit whose edges are alternately in M and in $E(G) - M$, where $E(G)$ is the edge set of G. We claim that the length of any M-conjugated circuit L is $4b + 2$ $(b = 1, 2, ..)$. Denote by G' the subgraph of G induced by the vertices on L and in the interior of L. Evidently, $G' \bigcap M$ is a Kekulé structure of G'. Since G has a special edge cut of type II consisting of fixed single bonds, G' cannot contain the inner perimeter of G. Otherwise, a fixed single bond lies on L (an M-conjugated circuit), which is contrary to the fact that any edge on an M-conjugated circuit is not a fixed bond. Assume that G' has z vertices, h hexagons, m edges, and the length of L is d. Then we have $2m = d + 6h$. Thus $d/2 = m - 3h$, which together with Euler's formula $z = m - h + 1$ yields $d/2 = z - 1 - 2h$. Bear in mind that G' has a Kekulé structure. Then z is even. Therefore, $d/2$ is odd, i.e. $d/2 = 2b + 1$, and hence $d = 4b + 2$

$(b = 1, 2, ...)$.

Now consider the determinant of B^*. By the usual definition of a determinant, $detB^* = \sum sgn(\pi) b_{1,\pi_1} b_{2,\pi_2} \cdots b_{n,\pi_n}$, where the summation is over all permutations

$$\pi = \begin{pmatrix} 1 & 2 & \cdots & n \\ \pi_1 & \pi_2 & \cdots & \pi_n \end{pmatrix}$$

Each permutation π can be expressed as the composition of disjoint cycles

$$\begin{pmatrix} i_1 & i_2 & \cdots & i_{s-1} & i_s \\ i_2 & i_3 & \cdots & i_s & i_1 \end{pmatrix}$$

Then $sgn(\pi) = (-1)^{Ne}$, where Ne is the number of even cycles in π. It is not difficult to see that the term corresponding to permutation π is non-zero, i.e. $b_{1,\pi_1} b_{2,\pi_2} \cdots b_{n,\pi_n} = 1$ if and only if the set $\{x_1 y_{\pi_1}, x_2 y_{\pi_2}, \cdots, x_n y_{\pi_n}\}$ is a Kekulé structure M of G. Furthermore, if the term corresponding to π is non-zero , then each cycle

$$\begin{pmatrix} i_1 & i_2 & \cdots & i_{s-1} & i_s \\ i_2 & i_3 & \cdots & i_s & i_1 \end{pmatrix}$$

in π corresponds to an M-conjugated circuit of length $2s$: $x_{i_1} y_{i_2} x_{i_2} y_{i_3} \cdots x_{i_{s-1}} y_{i_s} x_{i_s} y_{i_1} x_{i_1}$.

As mentioned above, the length of any M-conjugated circuit must be $4b + 2$ $(b = 1, 2, ...)$. This implies that s must be odd. Hence, if the term corresponding to π is non-zero, then

$$sgn(\pi) = (-1)^{Ne} = (-1)^0$$

Therefore,

$$|detB^*| = \sum b_{1,\pi_1} b_{2,\pi_2} \cdots b_{n,\pi_n} = K(G)$$

In the following, without loss of generality, we may further assume that the peaks of G are white, and hence the valleys of G are black. Since G has Kekulé structures, G has an equal number of peaks and valleys, as well as an equal number of white vertices and black vertices. Let t and n be the numbers of peaks (valleys) and white (black) vertices of G, respectively. We label the vertices of G in a special way as follows. From the top to the bottom we assign consecutively a number to each horizontal line which passses through white vertices of G such that the highest one (i.e. the one passing through the highest peak) has number 1, the second highest one has number 2, and so on. The n white vertices are arranged such that $x_1, x_2, ..., x_t$ are peaks, $x_{t+1}, ..., x_n$ are non-peaks; and if $j > i$, then the horizontal line passing through x_j is below the horizontal line passing through x_i, or x_j and x_i are on the same horizontal line with x_j on the right of x_i (see Fig.2). The n black vertices of G are arranged such that $y_1, y_2, ...y_t$ are valleys, $y_{t+1}, ..., y_n$ are non-valleys; y_j and x_j are connected by a vertical edge for $j = t+1, t+2, ..., n$.

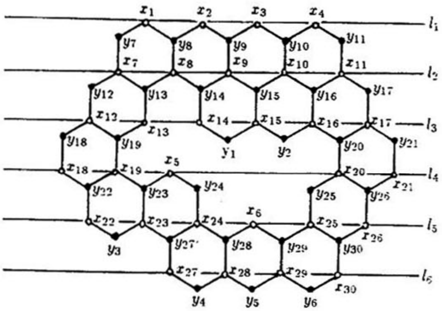


Fig.2 An illustration of the labelling of vertices of coronoid system G

Let the vertex set of G be $V(G) = \{v_1 = x_1, v_2 = x_2, ..., v_n = x_n; v_{n+1} = y_1, v_{n+2} = y_2, ..., v_{2n} = y_n\}$. With the above assumption, it is not difficult to see that the adjacency matrix $A(G)$ of G has the form as shown in Fig.3, where B^T is the transpose of B. Moreover , B^T has the form as shpwn in Fig.4, where Q is a square matrix of order $n - t$ such that $(Q)_{ii} = 1$ for $i = 1, 2, ..., n - t$ and $(Q)_{ij} = 0$ if $j > i$.

$$
A(G) = \begin{array}{c} \\ x_1 \\ x_2 \\ \cdot \\ \cdot \\ x_n \\ y_1 \\ y_2 \\ \cdot \\ \cdot \\ y_n \end{array}
\begin{array}{c} x_1\, x_2 \cdots x_n \quad y_1\, y_2 \cdots\cdots y_n \\
\left[\begin{array}{c:c} O & B \\ \hdashline B^T & O \end{array}\right] \end{array}
$$

Fig.3 The adjacency matrix $A(G)$ of coronoid system G

$$
B^T = \begin{array}{c} \\ y_1 \\ y_2 \\ \cdot \\ y_t \\ y_{t+1} \\ \cdot \\ \cdot \\ y_{n-1} \\ y_n \end{array}
\begin{array}{c} x_1 x_2 \ldots x_t x_{t+1} \cdots x_{n+1} x_n \\
\left[\begin{array}{c|c} O & C \\ \hdashline D & Q \end{array}\right] \end{array}
$$

Fig.4 The matrix B^T

With the above notation, we have the following.

Lemma 5 For a polyhex graph G with Kekulé structures, the following equality holds: $|det B^T| = |det W|$

Proof: Denote by R the $(n-t) \times t$ matrix whose element $(R)_{ij}$ is the number of monotonous paths from peak x_j $(j = 1, 2, ..., t)$ to white vertex x_{t+i} $(i = 1, 2, ..., n-t)$. Then CR is a $t \times t$ matrix whose element $(CR)_{ij}$ equals the number of monotonous paths form peak x_j to valley y_i $(i = 1, 2, ..., t; j = 1, 2, ..., t)$. Hence

$$CR = W \tag{1}$$

Denote by R' the $(n-t)\times t$ matrix whose element $(R')_{ij}$ is defined by $(R')_{ij} = (-1)^{h(x_{t+i})}(R)_{ij}$, where $h(x_{t+i})$ is the label of the horizontal line passing through vertex x_{t+i}. Denote by I' the $t\times t$ matrix whose element $(I')_{ij}$ is defined by

$$(I')_{ij} = \begin{cases} 0 & \text{if} \quad i \neq j \\ (-1)^{h(x_i)} & \text{if} \quad i = j \end{cases}$$

where $h(x_i)$ is the label of the horizontal line passing through peak x_i ($i = 1, 2, ..., t$). Put

$$J = \begin{pmatrix} I' & 0 \\ R' & I \end{pmatrix}$$

where I is the identity matrix of order $n-t$. Evidently, $detJ = detI'detI = 1$ or -1. In the following we prove that

$$DI' + QR' = 0 \tag{2}$$

We first assume that $y_{i+t}(1 \leq i \leq n-t)$ is not adjacent to any peak. Then $(D)_{ip} = 0$ for $p = 1, 2, ..., t$. Hence $(DI')_{ij} = 0$. Since y_{i+t} is not a valley, it is adjacent to two white vertices x_{s+t} and x_{i+t} which are on two neighbouring horizontal lines l' and l'', respectively; or it is adjacent to three white vertices x_{s-1+t}, x_{s+t} and x_{i+t}, where x_{s-1+t} and x_{s+t} are on l', while x_{i+t} is on l''. Note that in the former we have $(R)_{sj} = (R)_{ij}$, and in the latter we have $(R)_{ij} = (R)_{s-1,j} + (R)_{sj}$. Thus

$$\begin{aligned} (QR')_{ij} &= (-1)^{h(x_{s+t})}(R)_{sj} + (-1)^{h(x_{i+t})}(R)_{ij} \\ &= (-1)^{h(x_{s+t})}(R)_{sj} + (-1)^{h(x_{s+t})+1}(R)_{sj} \\ &= 0 \end{aligned}$$

or

$$\begin{aligned} (QR')_{ij} &= (-1)^{h(x_{s-1+t})}(R)_{s-1,j} + (-1)^{h(x_{s+t})}(R)_{sj} + (-1)^{h(x_{i+t})}(R)_{ij} \\ &= (-1)^{h(x_{s-1+t})}(R)_{s-1,j} + (-1)^{h(x_{s-1+t})}(R)_{sj} \\ &\quad +(-1)^{h(x_{s-1+t})+1}[(R)_{s-1,j} + (R)_{sj}] \\ &= 0. \end{aligned}$$

Therefore, $(DI')_{ij} + (QR')_{ij} = 0$.

Now suppose that y_{i+t} is adjacent to exactly one peak $x_a (1 \le a \le t)$. Then we have

$$(DI')_{ij} = \begin{cases} (-1)^{h(x_a)} & \text{if } j = a \\ 0 & \text{if } j \neq a \end{cases}$$

$$(QR')_{ij} = (-1)^{h(x_{i+t})}(R)_{ij} = \begin{cases} (-1)^{h(x_a)+1} & \text{if } j = a \\ 0 & \text{if } j \neq a \end{cases}$$

or

$$\begin{aligned} (QR')_{ij} &= (-1)^{h(x_{s+t})}(R)_{sj} + (-1)^{h(x_{i+t})}(R)_{ij} \\ &= \begin{cases} (-1)^{h(x_{i+t})} = (-1)^{h(x_a)+1} & \text{if } j = a \\ (-1)^{h(x_{s+t})}(R)_{sj} + (-1)^{h(x_{s+t})+1}(R)_{sj} = 0 & \text{if } j \neq a \end{cases} \end{aligned}$$

Hence $(DI')_{ij} + (QR')_{ij} = 0$.

Lastly we consider the case that y_{i+t} is adjacent to two different peaks x_a and x_b $(1 \le a, b \le t)$. Then we have

$$(DI')_{ij} = \begin{cases} (-1)^{h(x_a)} & \text{if } j = a \\ (-1)^{h(x_b)} & \text{if } j = b \\ 0 & \text{if } j \neq a, \neq b \end{cases}$$

$$(QR')_{ij} = (-1)^{h(x_{i+t})}(R)_{ij} = \begin{cases} (-1)^{h(x_{t+i})} & \text{if } j = a, \text{or } j = b \\ 0 & \text{if } j \neq a, \neq b \end{cases}$$

Note that $h(x_a) = h(x_b)$, and $h(x_{t+i}) = h(x_a) + 1 = h(x_b) + 1$, we also have $(DI')_{ij} + (QR')_{ij} = 0$. Therefore, we have established equality (2). Consequently,

$$|detB^T| = |detB^T||detJ| = |detB^T detJ| = |detB^T J|$$

$$= |det \begin{pmatrix} O & C \\ D & Q \end{pmatrix} \begin{pmatrix} I' & O \\ R' & I \end{pmatrix}| = |det \begin{pmatrix} CR' & C \\ O & Q \end{pmatrix}| (\text{Equality } (2))$$

$$= |detCR'detQ| = |detCR'| = |detCR| = |detW| (\text{Equality } (1))$$

Theorem 6 For an essentially disconnected coronoid system G with a special edge cut of type II, John-Sachs formula holds: $K(G) = | detW |$.

Proof: Note that $|detB^T| = |detB^*|$, we have $K(G) = |detB^*|$ (Lemma 4) $= |detB^T| = |detW|$ (Lemma 5).

General remark: Theorem 6 can also be obtained from [6,7]. In doing that, one need to find out all fixed single bonds. The authors of [7] pointed out that John-Sachs formula, i.e. the formula given in Theorem 6, also applies to generalized benzenoid systems. A generalized benzenoid system [7] is defined to be a connected subgraph of a benzenoid system in which the length of the boundary of any region is 4s+2 (s=1,2,...). Compare the definition of a generalized benzenoid system with the definition of an essentially disconnected coronoid system, we find that an essentially disconnected coronoid system need not to satisfy the condition that the length of the boundary of any region is 4s+2 (s=1,2,...). Thus an essentially disconnected coronoid system need not be a generalized benzenoid system. Therefore, Theorem 6 in this paper is not an immediate consequence of the theorem from John-Sachs for benzenoid system [6,7,10].

In [11] John represented elegant algorithms for calculating the determinant W of both benzenoid system and defect benzenoid system. Those algorithms are simple and simply handleable. The so called "defect benzenoid systems" include not only coronoid systems. The algorithm for defect benzenoid systems in which the length of the boundary of any region is 4s+2 (s=1,2,...) differs from the algorithm for defect benzenoid systems in which the length of the boundary of at least one region is 4s (s=1,2,...). For essentially disconnected coronoid systems, it is clear that the length of the boundary of the "hole" may be 4s+2 (see Fig.5) or 4s (see Fig.6). Therefore, in order to apply the algorithms described in [11] to essentially disconnected coronoid systems, we need to find the length of the boundary of the "hole" .

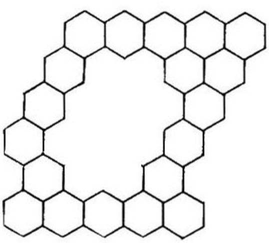


Fig.5

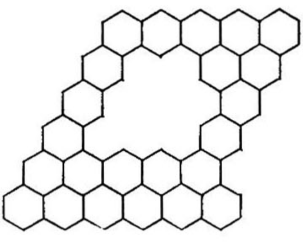


Fig.6

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