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Covering Polyhexes with Hexagons

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Dedicated to Prof. Fuji Zhang on the occasion of his 70th birthday

Abstract

A special type of covering of polyhexes introduced by Gutman [1] is investigated. It is proved that for a primitive coronoid system the number of covers is equal to the number of Kekulé structures minus three.

1. Introduction

A benzenoid system can be defined as follows. Let C be a cycle on the hexagonal lattice. Then the vertices and edges lying on C and in the interior of C form a benzenoid system [2]. A coronoid system can be regarded as a sort of benzenoid system with holes. The precise definition is given below. Let C_0 be a cycle on the hexagonal lattice, $C_1, C_2, \cdots, C_t (t \geq 1)$ be pairwise disjoint cycles within C_0. Then the vertices and edges lying on $C_0, C_1, \cdots, C_t$ and in the interior of C_0 but not in the interior of any $C_i (i = 1, 2, \cdots, t)$ form a coronoid system[3].

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The term polyhexes[3] is here used for benzenoid systems and coronoid systems taken together. Polyhexes correspond in a nature way to benzenoid hydrocarbons and coronoid hydrocarbons. A Kekulé structure of a polyhex with n vertices is a selection of $n/2$ edges such that no two of them are incident.

Let G be a polyhex. The concept "cover" was introduced by Gutman [1]. Let $K = \{s_1, \cdots, s_p\}(p \geq 1)$ be a collection of pairwise disjoint hexagons of G. $G - K$ denotes the subgraph obtained by deleting from G all the vertices of hexagons in K and all the incident edges. If $G - K$ has a Kekulé structure, or $G - K$ is an empty graph, K is said to be a cover of G. Note that the above terminology "cover" is a graph-theoretical reformation of a concept occurring in chemistry, within Clar aromatic sextet theory.

2. A property of covers of polyhexes

It was observed by Hosoya and Yamaguchi [4] that for a cata-condensed benzenoid system, the number of covers equals the number of Kekulé structures minus one. This result was proved by Gutman et al. [5]. But this property does not hold for peri-condensed benzenoid systems in general. Zhang and Chen [6] characterized the peri-condensed benzenoid systems that possess the above property. In the following we give the relation between the number of covers and the number of Kekulé structures for polyhexes.

Let G be a polyhex. For convenience, we assume that G has been placed on a plane so that two edges of each hexagon are parallel to the vertical line. Let P be a Kekulé structure of G. An edge e is said be a P-double bond if $e \in P$. The six vertices of a hexagon of G can be matched by three P-double bonds in two ways. They are called P-proper and P-improper hexagons, respectively (see Fig.1, where P-double bonds are bold). If P is a Kekulé structure of G and there is no P-proper hexagon, then P is said to be a root Kekulé structure.

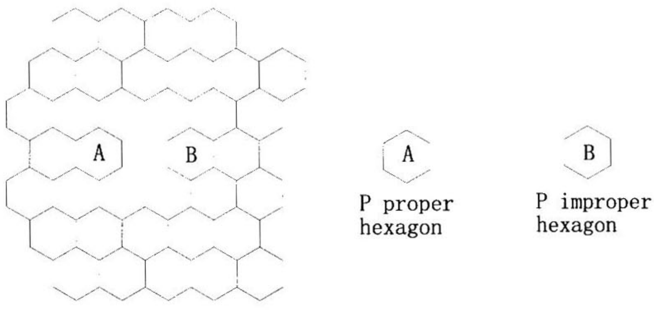


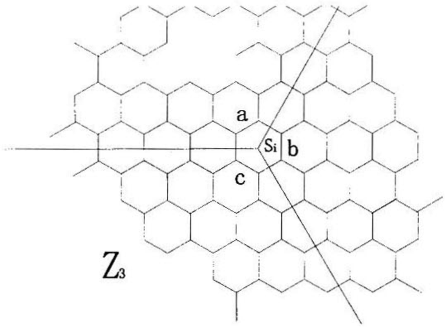
Fig.1 A polyhex G with a Kekulé structure P (the edges in P are bold), a P-proper hexagon A and a P-improper hexagon B.

By M and N we denote the set of Kekulé structures and the set of covers of G, respectively. Now we define a mapping f from M to $N \cup \{\phi\}$. For any Kekulé structure $P \in M$, denote by $K(P) = \{s_1, \cdots, s_p\}$ the set of P-proper hexagons. We define the image of P under mapping f to be $K(P)$ i.e. , $f(P) = K(P)$.

Lemma 2.1 Let P be a Kekulé structure of G, $K(P)$ be the set of P-proper hexagons. Then for any $s^* \in K(P)$, there exists a Kekulé structure P^* of G such that the set of P^*-proper hexagons is $K(P) - \{s^*\}$.

Proof. Starting from the center of s^* we divide the plane into three areas Z_1, Z_2 and Z_3 (cf. Fig.2). Let G_1 be the subgraph of G with maximum number of hexagons satisfying:

1. G_1 is a benzenoid system containing s^* ;
2. the vertices of G_1 lying in areas Z_1, Z_2 and Z_3 are matched by edges of P parallel to the P-double bonds a, b and c of s^*, respectively;
3. $P \cap G_1$ is a Kekulé structure of G_1, the boundary C_1 of G_1 is a $(P \cap G_1)$-alternating cycle (i.e., a cycle whose edges are alternately in $P \cap G_1$ and not in $P \cap G_1$)(cf. Fig.2(1), where G_1 is shaded).



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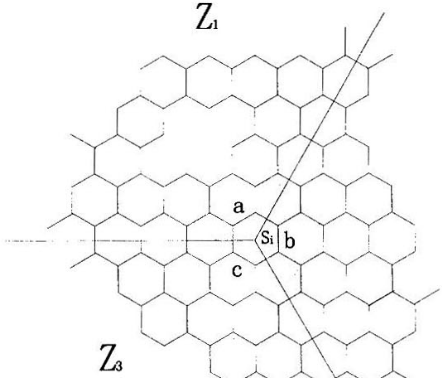


(2)

Fig.2 Illustrations for the proof of lemma 2.1.

The symmetric difference $P_1 = P\Delta C_1$ is another Kekulé structure of G. We claim that the set $K(P_1)$ of P_1-proper hexagons satisfies $K(P_1) \subseteq K(P)$. Otherwise, there is a P_1-proper hexagon $s' \notin K$. Then s' must have an edge lying on C_1 (cf. Fig 2(1)). This contradicts the maximality of G_1. If $C_1 \cap s^* \neq \phi$, then s^* is not a P_1-proper hexagon, and $K(P_1) = K(P) - \{s^*\}$. Let $P^* = P_1$, the lemma is proved. Otherwise $C_1 \cap s^* = \phi$, let $G_2 = G_1 - C_1$. One can check that the boundary C_2 of G_2 is a P_1-alternating cycle. By the same argument as above, if $C_2 \cap s^* \neq \phi$, then s^* is not a P_2-proper hexagon, where $P_2 = C_2\Delta P_1$, and the set $K(P_2)$ of P_2-proper hexagon is just $K(P) - \{s^*\}$ (cf. Fig 2(2)). If $C_2 \cap s^* = \phi$, we can continue the discussion as above. Since G is finite, we eventually reach a subgraph G_t of G such that the boundary C_t of G_t and s^* have some edges in common, and the set $K(P_t)$ of P_t-proper hexagons is $K(P) - \{s^*\}$, where $P_t = C_t\Delta P_{t-1}$. Lemma 2.1 follows.

lemma 2.2 With the above notation, for any member K in $N \cup \{\phi\}$, there exists a Kekulé structure P in M such that $f(P) = K$.

Proof By using lemma 2.1 repeatedly, we have a Kekulé structure P such that the set of P-proper hexagons is an empty set ϕ, i.e., $f(P) = \phi$.

Let $K = \{s_1, s_2, \cdots, s_k\}(k \geq 1)$ be a cover in N. By the definition of a cover, there is a Kekulé structure P of G such that the set of P-proper hexagons is $\{s_1, \cdots, s_k\} \cup \{s_{k+1}, \cdots, s_{k+q}\}(q \geq 0)$, where $s_{k+t}(t = 1, 2, \cdots, q)$ is a P-proper hexagon in $G - K$. Also by using lemma 2.1 repeatedly, we obtain a Kekulé structure P^* of G such that the set of P^*-proper hexagons is just $K = \{s_1, s_2, \cdots, s_k\}$, i.e., $f(P^*) = K$. The lemma is thus proved.

By lemma 2.2 we have the following theorem immediately:

Theorem 2.3 For a polyhex the number of covers is less than or equal to the number of Kekulé structures minus one.

3. Primitive Coronoid Systems

We now concentrate ourselves to a special class of polyhexes—primitive coronoid systems[7]. A primitive coronoid system consists of an even number of segments in a circular arrangement. In other words, the dualist[10] of a primitive coronoid system is a single cycle (cf. Fig.3).

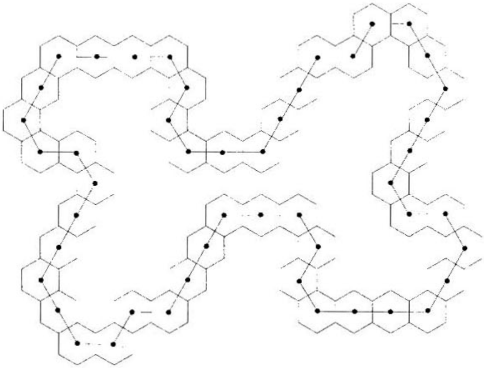


Fig.3 A primitive coronoid system and its dualist.

Property 3.1 Let P be a root Kekulé structure of a primitive coronoid system G. Then both the outer perimeter C_0 and the inner perimeter C_1 of G are P-alternating cycles.

Proof Note that each vertex of a primitive coronoid system G lies either on the outer perimeter C_0 or on the inner perimeter C_1. For a Kekulé structure P of G, if one of C_0 or C_1 is a P-alternating cycle, then the other is also a P-alternating cycle. Now suppose that none of C_0 and C_1 is a P-alternating cycle. Then there is a P-double bond ab with one end vertex a on C_0 and the other end vertex b on C_1. Without loss of generality, we may assume that ab is vertical (cf. Fig.4(1)). If edge h is a P-double bond, then no matter s_1 or s_2 belongs to G, there is a P-proper hexagon, contradicting that P is a root Kekulé structure (cf. Fig.4(1)). Hence h is a P-single bond and both p and q are P-double bonds. We also find a P-proper hexagon (cf. Fig.4(2)), again a contradiction . Therefore, both C_0 and C_1 are P-alternating cycles.

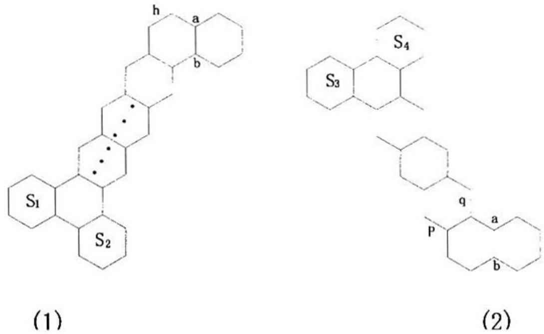


Fig.4 Illustrations for the proof of lemma 3.1

Remark 3.2 Let P be a Kekulé structure of a primitive coronoid system G such that both C_0 and C_1 are P-alternating cycles. There are only three possible positions for a hexagon to be a P-proper hexagon (cf. Fig.5). We call the hexagons in these positions as special hexagons. Let $s_1, s_2, \cdots, s_t$ be all the special hexagons of G in circular arrangement. One can check that if s_i (no matter s_i is of position I, II or III) is a P-proper hexagon, then s_{i+1} (no matter s_{i+1} is of position I, II or III) is also a P-proper hexagon, where $1 \leq i \leq t$, $i+1$ is taken modulo t (cf. Fig.6).

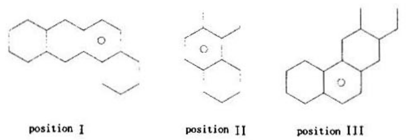


Fig.5 Special hexagons (cycled) in three positions.

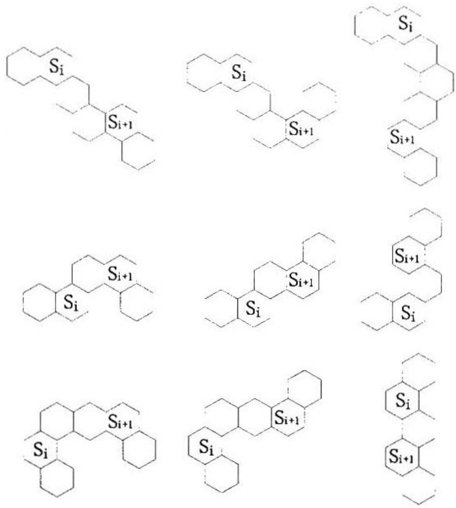


Fig.6 Nine possible combinations of s_i and s_{i+1}.

Property 3.3. For a primitive coronoid system G, there are exactly three root Kekulé structures

Proof. Let P be a root Kekulé structure of G. By Property 3.1 both C_0 and C_1 are P-alternating cycles. By Remark 3.2, among the four Kekulé structures for each of which both C_0 and C_1 are alternating cycles, only one Kekulé structure P^* is not a root Kekulé structure. Therefore, there are exactly three root Kekulé structures.

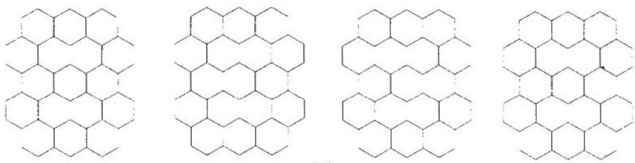
Lemma 3.4 Let P_1, P_2, P_3 and P_4 be the four Kekulé structures of a primitive coronoid system G such that both C_0 and C_1 are P_i-alternating cycles for $i = 1, 2, 3, 4$. Then three of them are root Kekulé structures.

Proof. This is a direct corollary of Remark 3.2 and Property 3.3.

Theorem 3.5 Let G be a primitive coronoid system. Then the number of covers of G is equal to the number of Kekulé structures minus three.

Proof. Let P_1 and P_2 be two Kekulé structures such that $f(P_1) = f(P_2)$. The symmetric difference $P_1 \Delta P_2$ constitutes some $P_1(P_2)$-alternating cycles. Let D be such a $P_1(P_2)$-alternating cycle. If $D \neq C_0, D \neq C_1$, then D must contain an edge $e = ab$ with a on C_0 and b on C_1. Without loss of generality, we may assume that e is a P_1-double bond and is not a P_2-double bond. Then there is a P_1-proper hexagon corresponding to e (cf. Fig.4 and the proof of Property 3.1) which is not a P_2-proper hexagon, contradicting that $f(P_1) = f(P_2)$. Therefore D must be C_0 or C_1. This means that both C_0 and C_1 are $P_1(P_2)-$ alternating cycles. Since $f(P_1) = f(P_2)$, now by lemma 3.4, both P_1 and P_2 are root Kekulé structures. The theorem follows from Property 3.3..

Remark 3.6 For non-primitive coronoid systems it remains a open problem to find the relation between the number of covers and the number of Kekulé structures. Even for cata-condensed multiple coronoid systems (i.e. coronoid systems in which each vertex lies on some perimeter, cf. Fig.7) the lower bond of the difference $|M| - |N|$ is still unknown.



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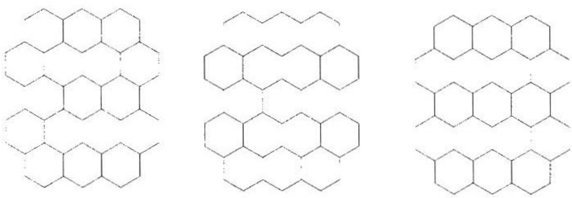

(2)

Fig.7 Illustrations for Remark 3.6.

The main difficulty lies in the fact that the number of root Kekulé structures are uncertain (the cata-condensed coronoid system depicted in Fig.7(1) has four root Kekulé structures), and that $f(P_1) = f(P_2)$ does not mean P_1 and P_2 are root Kekulé structures (cf. Fig.7(2)).

Remark 3.7 In [8] XF Guo and FJ Zhang introduced for the first time a series of explicit definitions such as g-sextet, g-root Kekulé structure, super sextet, and established a one-to-one correspondence between the set of Kekulé structures and the set of covers (sextet patterns). Our paper deals with the difference between the number of Kekulé structures and the number of covers. This difference is actually the number of super rings.

References

[1] Gutman I., Covering hexagonal systems with hexagons, In: Proceedings of the Fourth Yugoslav Seminar on Graph Theory, pp.51-60, Novi Sad: Institute of Mathematics, University of Novi Sad (1983).

[2] Gutman I., Cyvin S. J., Introduction to the Theory of Benzenoid Hydrocarbons, Springer Berlin Heidelberg New York (1989).

[3] Cyvin S. J., Brunroll J., Rong Si Chen, Cyvin B.N., Fuju Zhang, Theory of Coronoid Hydrocarbons II, Lecture Notes in Chemistry 62, Springer, Berlin, 1994.

[4] Hosoya H., Yamaguchi T., Sextet polynomial, Tetrahedron Letters (1975),4659-4662.

[5] Gutman I., Yamaguchi T., Motoyama A., Kuboi N., Topological propertils of benzenoid systems III, Recursion relation for the sextet polynomial, Bull. Soc. Chim. Beograd 42 (1977), 503-510.

[6] Zhang Fuji, Chen Rongsi, A Theorem concerning polyhex graphs, MATCH Communications in Mathematical and in Computer Chemistry 19 (1986) 179-188.

[7] Cyvin S.J., Cyvin B.N., Brunroll J., Hosoya H., Zhang Fuji, Chen Rongsi, Polansky O.E., Chemical Monthy 122(1991),435-444.

[8] Guo Xiaofeng and Zhang Fuji, Mathematical properties and structures of sets of sextet patterns of generalized polyhexes, J.Mathematical Chemistry 9(1992)122,279-290.

[9] Zhang Fuji and Chen Rongsi, A complete solution of Hosoya's mystery, ACTA MATHEMATICAE APPLICATAE SINICA, 12(1996),59-63.

[10] Nikolić S., Trinajstić N., Knop J.V., Muller W.R. and Szymanski K., On the concept of the weighted spanning trees of dualist, J.Math.Chem 4(1990),357.