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MINIMAL REGULAR CORONOIDS

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Abstract: A coronoid system can be viewed as a benzenoid system with a hole, i.e., a non-hexagonal interior face. A coronoid system is said to be normal if it has no fixed bond. A normal coronoid system is called regular if it can be constructed from a smaller one that has already been recognized as regular by adding one hexagon in some special ways. In this paper the concept "minimal regular coronoids" is introduced, and the structure feature for minimal coronoids is given.

A benzenoid system (or simply a benzenoid) [1] is a planar geometrical object consisting of congruent regular hexagons. A coronoid system (or simply a coronoid) [2] is a benzenoid-like system which has a "hole" (referred to as the corona hole), i.e., a non-hexagonal interior face. A coronoid can be obtained from a benzenoid by deleting some internal vertices and/or internal edges so that one hole with the size of at least two hexagons emerges. A coronoid has two perimeters, the inner perimeter of which determines the corona hole and is completely embraced by the outer perimeter. Benzenoids and coronoids are widely used in the study of benzenoid hydrocarbons and coronoid hydrocarbons [1,2] because they are the natural graph representations of the skeletons of molecules of benzenoid hydrocarbons and coronoid hydrocarbons, respectively.

A Kekulé structure of a benzenoid or a coronoid is a set of disjoint edges covering all the vertices of the system. The term is transferred from organic and physical chemisry. The importance of Kekulé structure is generally recognized in theoretical chemistry [3].

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There has been considerable interest in the enumeration and classification of benzenoids and coronoids in the past few years [4]. According to whether or not benzenoids or coronoids possess Kekulé structures, the systems are divided into Kekuléan or non-Kekuléan systems. It may happen that an edge of a Kekuléan system in a particular position is or is not selected in all Kekulé structures of that system. The fixed bonds are just associated with such edges. The term "essentially disconnected" [5] was used to indicate those Kekuléan systems with fixed bonds. Kekuléan systems without fixed bonds are referred to as "normal".

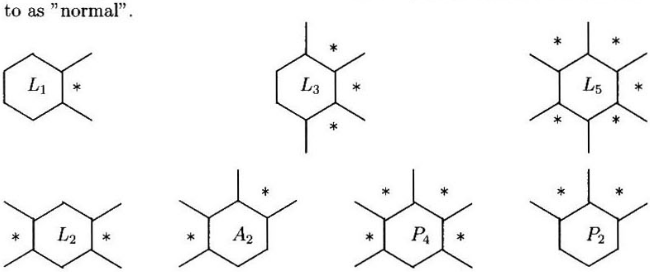


Fig. 1 The seven modes of hexagons in a benzenoid or coronoid.

It was conjectured by Cyvin and Gutman [6] that a normal benzenoid with $h+1$ hexagons can be generated from a normal benzenoid with h hexagons by a normal addition [2], i.e., adding one hexagon to a system such that the added hexagon acquires the mode L_1, L_3 or L_5 (cf. Fig.1, where each of the neighboring hexagons of a hexagon with one of the seven modes are labelled with a star). This conjecture implies that a normal benzenoid can be generated from a single hexagon (benzene) by a series of normal additions, each time only one hexagon being added. Later the above conjecture was proved by He and He [8].

The opposite process of a normal addition is a normal tearing down [2].Thus a normal benzenoid can be subjected to a series of normal tearing down, hexagon by hexagon, right down to one hexagon.

The situation for coronoids is not so simple as that for benzenoids (cf. Ch7 in [7]). When talking about the generation of coronoids, the concept "corona-condensation" is needed. A corona-condensation [2] is an addition of a hexagon into the mode L_2 or A_2 so that a corona hole is created. The opposite process of a corona-condensation is a corona-tearing down. A corona-tearing down turns a coronoid into a benzenoid. It was once thought that a normal coronoid can be subjected to a series of normal tearings down plus a corona-tearing down, each time only one hexagon being removed , right down to one hexagon. Further study showed that the above statement only applies to a subclass of normal coronoids. This subclass of normal coronoids is defined as regular [2].

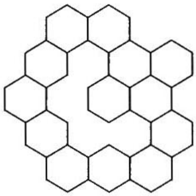


Fig. 2 A regular coronoid which can not be torn down to a primitive coronoid by normal tearings down.

Recall that a primitive coronoid [2] is a coronoid consisting of a single chain of hexagons in a macrocyclic arrangement. Primitive coronoids are all regular and may be torn down in an obvious way. A natural question emerges: when a regular coronoid is torn down by a series of normal tearings down only (i.e., a corona-tearing down is not applied), does it result in a primitive coronoid ? In other words, when no more normal tearing down can be applied to a regular coronoid, is it a primitive coronoid ? A glance at the regular coronoid G^* depicted in Fig.2 will indicate that the answer to the above question is negative. G^* is not primitive. Clearly, when a corona-tearing down is applied to G^*, a normal benzenoid is obtained. Thus one believes that G^* is regular (other simple and equivalent condition for G^* to be regular is given below). But G^* possesses no hexagon of mode L_1, or mode L_3, or mode L_5, no normal tearing down can be applied to G^*. In the following we introduce the concept "minimal regular coronoids" to indicate those regular coronoids which can not be torn down by normal tearings down. Moreover, the structure feature for minimal coronoids is described.

In the following we confine ourselves to Kekuléan systems. Let G be a regular coronoid, K a Kekulé structure of G. The set of edges of G is denoted by $E(G)$. A cycle P of G is said to be a $K-$alternating cycle if the edges of P are alternately in K and $E(G)-K$. The following theorems give simple criteria for a benzenoid or a coronoid to be normal or regular.

Theorem 1[9] A Kekuléan benzenoid B is normal if and only if B possesses a Kekulé structure K such that the perimeter of B is a $K-$alternating cycle.

Theorem 2[10] A Kekuléan coronoid G is normal if and only if each of the outer and inner perimeters of G is a $K-$alternating cycle for some Kekulé structure K of G.

Theorem 3[7] A Kekuléan coronoid G is regular if and only if G possesses a Kekulé structure K such that both the outer and inner perimeters of G are $K-$alternating cycles.

Before continuing, we need some more definitions.

Definition 4 An edge e of a coronoid G is said to be a boundary edge if e lies on the inner or outer perimeter of G.

Definition 5 A hexagon of a coronoid is said to be a thin hexagon if it possesses some boundary edges which do not form a path.

Definition 6 A thin hexagon s of a coronoid G is said to be a cut-hexagon if the boundary edges of s lie on the same perimeter of G.

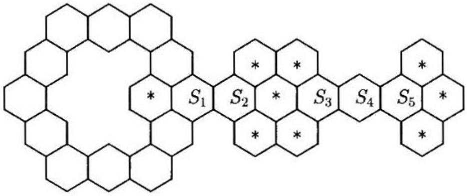


Fig. 3 An illustration for thin and cut hexagons.

In Fig.3, all the hexagons of G except those each of which has a star are thin hexagons, among them $s_1, s_2, \cdots, s_5$ are cut-hexagons. One can check that deleting of a cut hexagon from G will disconnect G.

Definition 7 A regular coronoid G is said to be reducible if there is a normal tearing down such that $G - s$ is still regular, where s is the deleted hexagon.

Definition 8 A regular coronoid is said to be minimal if it is not reducible (cf. the regular coronoid depicted in Fig.4).

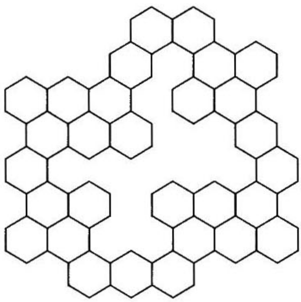


Fig. 4 A minimal regular coronoid.

Lemma 9 Let G be a regular coronoid. Hexagons $s_1, s_{11}, \cdots, s_{1n_1}, s_2, s_{21}, \cdots, s_{2n_2}, s_3, \cdots \cdots, s_{t-1}, s_t$ are along the same perimeter C of G, where $s_1, s_2, \cdots, s_{t-1}$ and s_t are hexagons of mode L_5 and other hexagons s_{ij} are of mode P_4 (cf. Fig.5). Let K be a Kekulé structure of G such that the outer and inner perimeters of G are $K-$alternating cycles. If edges e'_1 and e'_t belong to K, G is reducible.

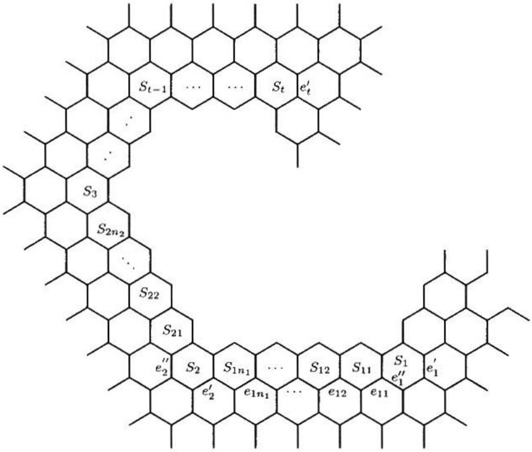
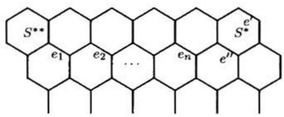
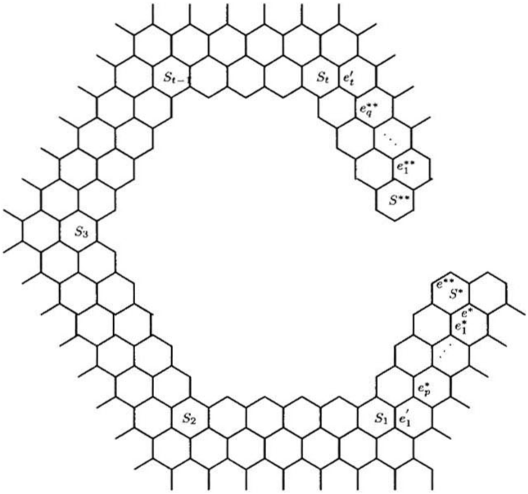


Fig.5 An illustration for the conditions of Lemma 9.

Proof. If e''_1 belongs to K, then $G' = G - s_1$ is a coronoid such that the outer and inner perimeters of G' are $K-$alternating cycles (cf. Fig.5, where the edges of K are denoted by double lines). Thus G' is still regular (Theorem 3). G' is obtained from G by a normal tearing down. Therefore, G is reducible by definition 7. If e''_1 does not belong to K, then the edges $e_{11}, e_{12}, \cdots, e_{1n_1}$ and e'_2 belong to K. Let $K^* = K \triangle E(C) = (K \cup E(C)) - (K \cap E(C))$. It is evident that the outer and inner perimeters of G are also K^*-alternating cycles. Since e'_2 belongs to K and does not lie on the perimeter C of G, e'_2 also belongs to K^*. Consider the edge e''_2. If e''_2 belongs to K^*, then $G'' = G - s_2$ is a coronoid such that the outer and inner perimeters of G'' are K^*-alternating cycles. Thus G'' is still regular . G'' is obtained from G by a normal tearing down. Therefore, G is reducible. Now suppose that e''_2 does not belong to K^*. We can discuss as above, and find a hexagon $s_i (i \leq t)$ such that the outer and inner perimeters of $G^* = G - s_i$ are $K-$ or K^*-alternating cycles. Thus G^* is regular and G is reducible.



A: m=0



B: $m \geq 1$

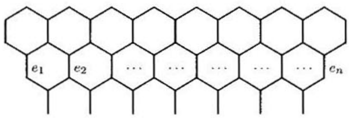
Fig. 6 Illustrations for the proof of Lemma 10.

Lemma 10 Let G be a regular coronoid with a hexagon s^* of mode L_3 and a hexagon s^{**} of mode P_2 on the same perimeter C of G. If there is no thin hexagon between s^* and s^{**} along C (clockwise or anti-clockwise), then G is reducible.

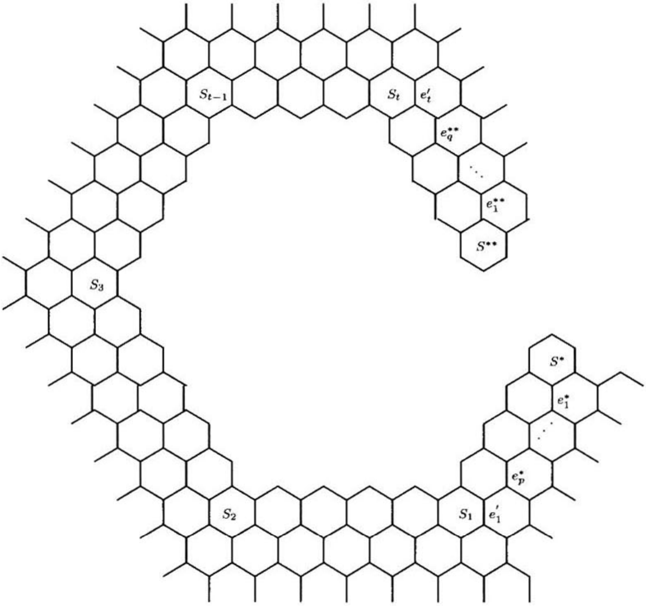
Proof. Denote by C^* the section of the perimeter C between s^* and s^{**} along which there is no thin hexagon. Without loss of generality, we may assume that s^* and s^{**} are the nearest in the sense that there is no other hexagon of mode L_3 or P_2 along C^*. Consider the number t of hexagons of mode L_5 along C^*. First, suppose that $m = 0$ (cf. Fig.6 A). Let K be a Kekulé structure of G such that the outer and inner perimeters of G are $K-$alternating cycles and the edge $e^{'}$ belongs to K. Evidently, the edges $e_1, e_2, \cdots, e_h$ and $e^{''}$ belong to K. Let $K' = K - \{e^{'}\}$. Then K' is a Kekulé structure of $G' = G - s^*$ such that the outer and inner perimeters of G' are $K'-$alternating cycles, which implies that $G^{'}$ is regular. Hence G is reducible. Now assume that $m \geq 1$. Let K^* be a Kekulé structure of G such that the outer and inner perimeters of G are K^*-alternating cycles and the edge e^{**} belongs to K^* (cf. Fig.6 B). If the edge e^* belongs to K^* too, then the outer and inner perimeters of $G^* = G - s^*$ are $K^{''}-$alternating cycles, where $K^{''} = K^* - \{e^{**}\}$. Hence G^* is regular. Therefore, G is reducible. If the edge e^* does not belong to K^*, then the edges $e_1^*, e_2^*, \cdots, e_p^*$ and e_1' belong to K^*. On the other hand, s^{**} is of mode P_2, the edges $e_1^{**}, e_2^{**}, \cdots, e_q^{**}$ and e_t' belong to K^*. By the definition of C^*, there is no thin hexagon along C^* . Thus all the hexagons along C^* except $s_1, s_2, \cdots, s_t$ are of mode P_4. Now by Lemma 9, G is reducible.

Lemma 11 Let G be a regular coronoid. G possesses two hexagons s^* and s^{**} of mode P_2 on the same perimeter C of G. If there is no thin hexagon between s^* and s^{**} along the perimeter C (clockwise or anti-clockwise), then G is reducible.

Proof. Denote by C^* the section of the perimeter C between s^* and s^{**} along which there is no thin hexagon. Without loss of generality, we may assume that s^* and s^{**} are the nearest in the sense that there is no other hexagon of mode P_2 along C^* . If there is a hexagon of mode L_3 along C^* , then G is reducible by Lemma 10. Now assume that there is no hexagon of mode L_3 along C^* . If there is no hexagon of mode L_5 along C^* (cf. Fig.7 A), one can check that all the edges $e_1, e_2, \cdots, e_n$ are fixed single bonds (cf. Ch 8 in [7]), contradicting that G is regular and possesses no fixed bonds. Hence there must be some hexagons of mode L_5 along C^* (cf. Fig.7 B). Let K be a Kekulé structure of G such that the outer and inner perimeters of G are $K-$alternating cycles. Since s^* is of mode P_2, the edges $e_1^*, e_2^*, \cdots, e_p^*$ and e'_1 belong to K. Similarly, the edges $e_1^{**}, e_2^{**}, \cdots, e_q^{**}$ and e'_t belong to K as s^{**} is of mode P_2. By the definition of C^*, all the hexagons along C^* except $s_1, s_2, \cdots, s_t$ are of mode P_4. Now by Lemma 9, G is reducible.



A: there is no hexagon of mode L_5 on C^*



B: there are some hexagons of mode L_5 on C^*

Fig. 7 Illustrations for the proof of Lemma 11

Lemma 12 Let G be a regular coronoid. Hexagons $s^*, s_1, \cdots, s_n, s^{**}$ are along the same perimeter C of G, where s^* and s^{**} are hexagons of mode L_3 and the other hexagons are of mode P_4 (cf. Fig.8). Then G is reducible.

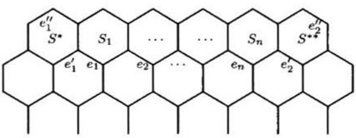


Fig. 8 An illustration for the conditions of Lemma 12.

Proof. Let K be a Kekulé structure of G such that the outer and inner perimeters of G are K−alternating cycles, and the edge e_1'' belongs to K. If the edge e_1' belongs to K, then the outer and inner perimeters of $G' = G - s^*$ are K'−alternating cycles, where $K' = K - \{e_1''\}$. Hence G' is regular. Therefore, G is reducible. If the edge e_1' does not belong to K, then the edges $e_1, e_2, \cdots, e_n$ and e_2' belongs to K. Thus the outer and inner perimeters of $G'' = G - s^{**}$ are K''−alternating cycles, where $K'' = K\triangle E(C) - \{e_2''\} = (K \cup E(C)) - (K \cap E(C)) - \{e_2''\}$. Hence G'' is regular. Therefore, G is reducible.

Lemma 13 Let G be a regular coronoid. G possesses two hexagons s^* and s^{**} of mode L_3 on the same perimeter C of G. If there is no thin hexagon between s^* and s^{**} along the perimeter C (clockwise or anti-clockwise), then G is reducible.

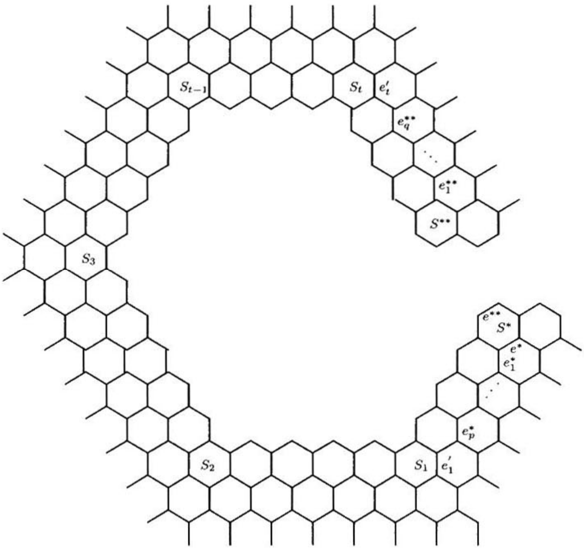


Fig. 9 An illustration for the proof of Lemma 13.

Proof. Denote by C^* the section of the perimeter C between s^* and s^{**} along which there is no thin hexagon. Without loss of generality, we may assume that s^* and s^{**} are the nearest in the sense that there is no other hexagon of mode L_3 along C^*. If there is a hexagon of mode P_2 along C^*, then G is reducible by Lemma 10. Now assume that there is no hexagon of mode P_2 along C^*. If there is no hexagon of mode L_5 along C^*, then all the hexagons along C^* between s^* and s^{**} are of mode P_4 (cf. Fig.8). By Lemma 12, G is reducible. Now assume that there are some hexagons of mode L_5 along C^* (cf. Fig.9). Let K be a Kekulé structure of G such that the outer and inner perimeters of G are K−alternating cycles and the edge e^{**} belongs to K. If the edge e^* belongs to K too, then the outer and inner perimeters of $G^* = G - s^*$ are K^*−alternating cycles where

$K^* = K - \{e^{**}\}$. Hence G^* is regular, and G is thus reducible. If the edge e^* does not belong to K, then the edges $e_1^*, e_2^*, \cdots, e_p^*$ and e_1' belong to K. Now consider the hexagon s^{**}. By discussing in a similar way as above, either $G^{**} = G - s^{**}$ is regular and G is thus reducible; or the edges $e_1^{**}, e_2^{**}, \cdots, e_q^{**}$ and e_t' belong to K. Now the conditions that e_t' and e_1' belong to K and there is no thin hexagon along C^* satisfy the Lemma 9. Therefore, G is reducible.

Lemma 14 Let G be a regular coronoid with a hexagon s of mode L_1. Then G is reducible.
Proof. One can check that $G - s$ is still regular. Hence G is reducible.

Lemma 15 Let G be a regular coronoid with a cut-hexagon s. Then G is reducible.
Proof. By Lemma 14, we may assume that G has no hexagon of mode L_1. We only consider the case when the cut-hexagon s lies on the outer perimeter C of G. For the case when s lies on the inner perimeter, it can be dealt in a quite similar way. By the definition of cut-hexagons, $G - s$ is disconnected and has a component which is a benzenoid. Without loss of generality, we may assume that s is a cut-hexagon such that one of the components of $G - s$, say G_1, is a benzenoid without cut-hexagons (cf. the hexagon s_5 of the coronoid depicted in Fig.3). Note that there are six possible positions for G, in each of which some of the edges of G are vertical. If for some position the top row of G_1 does not contain the hexagon s and has more than two hexagons, then G has a hexagon of

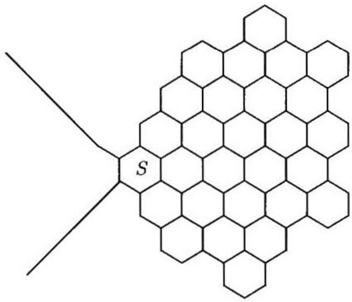


Fig. 10 An illustration for the proof of Lemma 15

mode L_3 and a hexagon of mode P_2 (cf. Fig.6 A), or G has two hexagons of mode L_3 (cf. Fig.8). Then by lemma 10 or Lemma 12 , G is reducible. If for each of the six possible positions, the top row of G_1 has only one hexagon, which must be a hexagon of mode P_2 (cf. Fig.10), G is also reducible by Lemma 11 .

Definition 16 Let G be a regular coronoid. A section U of G is said to be a unit of G if U has at least three hexagons and has exactly two thin hexagons which are not cut-hexagons and have no edge in common.

Definition 17 A unit U of G is said to be a parallelogram if U has exactly two hexagons of mode P_2, and all the other hexagons except the two thin hexagons are of mode P_4.

In Fig.11 , a regular coronoid with three units is given, where the top one is a parallelogram, the other two units have an edge e in common.

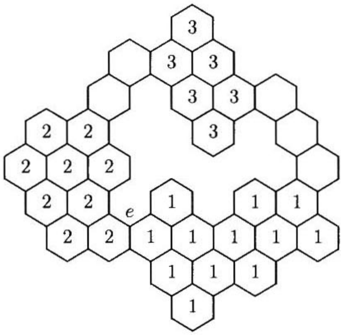


Fig. 11 A regular coronoid with three units.

Lemma 18 Let G be a regular coronoid. If G possesses a unit U which is not a parallelogram, G is reducible.

Proof. Let the two thin hexagons of U be denoted by s^* and s^{**}. There are six possible positions for G, in each of which G has some vertical edges. If for each of the six possible positions the top row of U contains either s^* or s^{**}, U is as depicted in Fig.12. Let K be a Kekulé structure of G such that the outer and inner perimeters of G are $K-$alternating cycles and the edge e belongs to K. Note that the edge e' belongs to K. Hence the outer and inner perimeters of $G - s$ are $K'-$alternating cycles, where $K' = K - \{e\}$. Therefore, $G - s$ is regular which implies that G is reducible. In the following we assume that for some position, the top row of U does not contain any of s^* and s^{**}. We distinguish two cases:

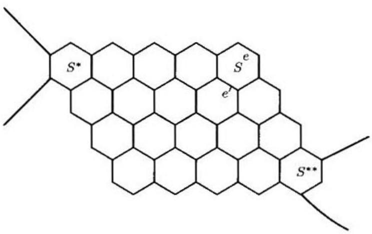


Fig. 12 An illustration for the proof of Lemma 18.

Case 1. For some of the six possible positions, the top row of U does not contain any of s^* and s^{**} and has more than two hexagons. Then G has a hexagon of mode L_3 and a hexagon of mode P_2 (cf. Fig.6 A), or G has two hexagons of mode L_3 (cf. Fig.8). By lemma 10 or Lemma 12 , G is reducible.
Case 2. For each of the six possible positions, the top row which contains neither s^* nor s^{**} has only one hexagon. Such hexagon must be of mode P_2. The perimeter of U is divided by s^* and s^{**} into two sections C'_U and C''_U. If one of C'_U and C''_U contains two hexagons of mode P_2, then G is reducible by Lemma 11 . The case, in which both C'_U and C''_U contain exactly one hexagon of mode P_2, or one of C'_U and C''_U contains exactly one hexagon of mode P_2 and the other contains no hexagon of mode P_2, can not occur. Otherwise, G is non-Kekuléan since there is an isolated vertex (one of the black vertices as shown in Fig.13).).

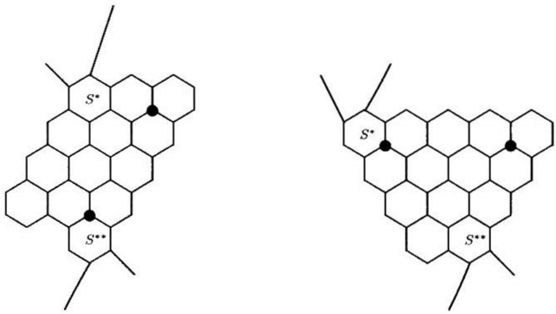


Fig.13

We are now in the position to formulate our main result.
Theorem 19 Let G be a regular coronoid. G is minimal if and only if G satisfies: 1. each unit (if any) of G is a parallelogram; 2. each hexagon of G not belonging to any unit is a thin hexagon which is not a cut-hexagon.
Proof. Suppose that G is a regular coronoid satisfying 1. each unit (if any) of G is a parallelogram; 2. each hexagon of G not belonging to any unit is a thin hexagon which is not a cut-hexagon. One can check that G has no hexagon of mode L_1, or L_3, or L_5. No normal tearing down can be applied to G. Hence G is minimal.
On the other hand , if G is minimal, G must contain some thin hexagons. Otherwise, G possesses two hexagons of mode P_2 or L_3, or one hexagon of mode P_2 and one hexagon of mode L_3, satisfying the condition of Lemma 11, or Lemma 13, or Lemma 10, and is reducible, which is a contradiction. For a hexagon of G, if it belongs to a unit of G, then it belongs to a parallelogram (Lemma 18). If it does not belong to any unit of G, it is a thin hexagon which is not a cut-hexagons (Lemma 15).

References

[1] I.Gutman, S.J.Cyvin, Introduction to the Theory of Benzenoid Hydrocarbons, Springer-Verlag(1989).

[2] S.J.Cyvin, J.Brunvoll, B.N.Cyvin, Theory of Coronoid Hydrocarbons, Lecture Notes in Chemistry 54, Springer-Verlag(1991).

[3] S.J.Cyvin, I.Gutman, Kekulé Structures in Benzenoid Hydrocarbons, Lecture Notes in Chemistry 46, Springer-Verlag(1988).

[4] B.N.Cyvin, J.Brunvoll, S.J.Cyvin, In: Advances in the Theory of Benzenoid Hydrocarbons, Topics in Current Chemistry 162, Springer-Verlag(1992).

[5] S.J.Cyvin, B.N.Cyvin, I.Gutman, Z.Naturforsch, 40a(1985), 1253.

[6] S.J.Cyvin, J.Brunvoll, B.N.Cyvin, J.Chem.Inf.Comput.Sci. 29(1989),79.

[7] S.J.Cyvin, J.Brunvoll, Chen Rong Si, B.N.Cyvin, Zhang Fu Ji, Theory of Coronoid Hydrocarbons *II*, Lecture Notes in Chemistry 62, Springer-Verlag(1994).

[8] WC He, WJ He, Match 25 (1990) 237.

[9] Zhang Fu Ji, Chen Rong Si, Discrete Applied Mathematics 30(1991),63.

[10] Zhang Fu Ji, Zheng Mao Lin, Discrete Applied Mathematics 36(1992),67.