

On the ordering of benzenoid chains and cyclo-polyphenacenes with respect to their numbers of Clar aromatic sextets

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Based on Clar aromatic sextet theory [Clar, *The Aromatic Sextet* (Wiley, New York, 1972)] and the concept of sextet polynomial introduced by Hosoya and Yamaguchi [*Mathematical Concepts in Organic Chemistry* (Springer, Berlin, 1986)], we define a new ordering of benzenoid systems. For two isomeric benzenoid systems B_1 and B_2 , we say $B_1 > B_2$ if each coefficient of sextet polynomial of B_1 is no less than the corresponding coefficient of sextet polynomial of B_2 . In this paper, we consider the ordering of the benzenoid chains. The maximal and second maximal benzenoid chains as well as the minimal, the second minimal up to the fourth minimal benzenoid chains are determined. Furthermore, under this ordering, we determine the maximal and second maximal cyclo-polyphenacenes as well as the minimal, the second minimal, and up to the seventh minimal cyclo-polyphenacenes.

1. Introduction

Since many benzenoid hydrocarbons have been found from the high-temperature carbonization coal tar, these plane compounds with condensed benzene rings have been extensively studied in the last centenary. After the first monograph of Clar [1], several books and papers were published (see [2–6] and the references cited therein). The simplest benzenoid hydrocarbons are benzenoid chains (polyphenacenes). Up to now, many benzenoid chains have been prepared [1, 7] and many theoretical and computational work has been done [8–10].

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After the discovery of carbon nanotube [11], the nonplane compounds with condensed benzene rings became an attractive topic for chemists and physicians, since it is expected that the carbon nanotube as an artificial material has nice electrical conductivity and strength. For details, (see [12] and the references cited therein). Stimulated by this fact, many researchers considered the tubulene [13–15]. The carbon skeleton of a tubulene is a benzenoid system embedded in a cylinder with two open ends (all its dangling bonds at both ends saturated with hydrogen atoms). The simplest tubulene is said to be *prim* which can be considered as a benzenoid chain embedded around a cylinder. To our knowledge the synthetic attempts have failed to prepare a monomeric *prim* tubulene. Although a similar type of hydrocarbons *prim* coronenes (*prim* coronoids) is prepared many years ago [16]. On the other hand, the theoretical interest has been high in recent years. For details see [17–19] and references cited therein. As pointed out by some authors these molecules exhibit a renewed interest owing to their close similarity to short carbon nanotubes". In fact *prim* tubulene is the simplest compounds with condensed benzene ring on the cylinder. In most of these studies the structures were built by optimization and *ab initio* calculation were carried out by advanced programs. It is natural to expect that the results obtained in this way is accurate enough comparing with the experimental data available and could be a useful aid in the broader field of chemistry in the future. Along this line the results of cyclo-polyphenacenes (a wide type of molecules including *prim* tubulenes and *prim* coronenes) are obtained by Dobrowolski [20], the results of cyclo-polyacenes are obtained by Honk *et al.* [17], Choi and Kim [18] and Turker [19]. Note that all of these authors only considered cyclo-polyphenacenes with small number of hexagons.

Another approach is to study the cyclo-polyphenacenes by using some invariant. For example, Misra and Klein introduced the invariant combinatorial curvature and considered its plausible relation to structural stresses, as manifested in thermodynamic stability [21]. Different from the other authors, Misra and Klein considered the case of cyclo-polyphenacenes with arbitrary number of hexagons, which is the case we are interested in.

In this paper, we will consider the application of Clar's aromatic sextet theory (see [1]) and the concept of sextet polynomial [22] which has been examined in different ways (see [23] and references cited therein) in recent years. In order to compare the stability we introduce a new quasiordering to rank benzenoid chains and cyclo-benzenoids with respect to their number of Clar aromatic sextets.

The problem of defining orderings according to some chemical or physical properties has attracted attention of a number of chemists, since it concerned a basic problem – the structure-property relations in chemistry. For details, see two surveys [24,25] which published in recent years.

The main task of this paper is to consider the benzenoid chains and cyclo-polyphenacenes. We determine the maximal and second maximal benzenoid

chains as well as the minimal, the second minimal up to the fourth minimal benzenoid chains under our ordering. We also solve the extreme problem for cyclo-polyphenacenes and determine the maximal and second maximal cyclo-polyphenacenes as well as the minimal, the second minimal, and up to the seventh minimal cyclo-polyphenacenes.

2. Benzenoid chains

Benzenoid systems are the graph representation of benzenoid hydrocarbons using the language of graph theory which is a finite connected plane graph without cut vertices in which every interior face is bound by a regular hexagon of side length one. A benzenoid chain is a benzenoid system whose each hexagon is adjacent to at most two hexagons. Clearly, benzenoid chain is the simplest type among all benzenoid hydrocarbons.

Now we recall the concept in Clar's aromatic sextet theory [1]. Let B be a benzenoid system with Kekule structures (perfect matching). A Clar aromatic sextet is a set of disjoint hexagons such that the remainder of the benzenoid system obtained by deleting the vertices of these hexagons must have a Kekule structure or must be empty. A set of Clar aromatic sextets is said to be a Clar formula if it has the maximum number of hexagons which is called the Clar number. Clar's theory asserts that for two benzenoid systems B_1 and B_2 , if the Clar number of B_1 is greater than that of B_2 , then B_1 is more stable. Since many isomers of benzenoid chains have the same Clar number, the accuracy is not enough to order the benzenoid chains (in general) with respect to their Clar numbers. We will denote the number of Clar aromatic sextets of B having i hexagons by $s(B, i)$ and denote the Clar number of B by $C(B)$. The following sextet polynomial has been defined by Hosoya and Yamaguchi (see [22] and the excellent survey in [5] p. 255) for benzenoid system:

$$S(B, x) = \sum_{i=0}^{C(B)} s(B, i)x^i,$$

where $S(B, 0) = 1$.

Stimulated by the concept of the Clar aromatic sextet theory and sextet polynomial, for a benzenoid system, Herndon and Hosoya [26] calculated the resonance energies by using the number of Clar aromatic sextets. Hence, it is natural to define a quasi-order which will have better accuracy as follows.

If for two benzenoid systems B_1 and B_2 , $s(B_1, k) \geq s(B_2, k)$, $k = 0, 1, \dots$, then we say B_1 is s -greater than B_2 and write $B_1 > B_2$. If both $B_1 > B_2$ and $B_2 > B_1$ hold, then B_1 and B_2 are said to be equivalent. If neither $B_1 > B_2$ nor $B_2 > B_1$ holds then B_1 and B_2 are incomparable. Clearly two s -equivalent has the same sextet polynomial, but need not to be isomorphic (see for example B_4 and B_5 in figure 4). All our work is based on this ordering.

Now we consider another quasi-ordering of graphs with respect to their matching number introduced by Hosoya [27] and Gutman [28]. Let $m(G, i)$ be the number of i -matching of G that is the number of selections of i independent edges in G . As usual we define $m(G, 0) = 1$ for all G . The counting polynomial of i -matching is called matching polynomial which can be defined as follows:

$$M(G, x) = \sum_{k=0}^{m(G)} m(G, i)x^{n-2k},$$

where $m(G)$ is the size of maximum matching of G .

If for two graphs G_1 and G_2 the relations $m(G_1, i) \geq m(G_2, i)$ are fulfilled for all k , then we say that G_1 is m -greater than G_2 and write $G_1 \succ G_2$ or $G_2 \prec G_1$. If both $G_1 \succ G_2$ and $G_2 \succ G_1$ hold, then G_1 and G_2 have the same matching polynomial but need not to be isomorphic (for example triangle and star with four vertices) and we say G_1 and G_2 are m -equivalent. If G_1 and G_2 are not m -equivalent and $G_1 \succ G_2$, then we say G_1 is greater than G_2 strictly. If neither $G_1 \succ G_2$ nor $G_2 \succ G_1$ holds, then G_1 and G_2 is said to be incomparable.

Many years ago, Gutman found an interesting relation between sextet polynomial of a benzenoid chain and the matching polynomial of its corresponding Gutman (caterpillar) tree (see [29]). Based on this relation, we can order the benzenoid chains with respect to their Clar aromatic sextets.

In graph theory a caterpillar tree T is defined to be the graph when all its end vertices are deleted the residual is a path. In other words, let v_1, v_2, \dots, v_m be a path if we join each of n_i new vertices to the vertex v_i by an edge, $i = 1, 2, \dots, m$, then a caterpillar tree is obtained. Let B be a benzenoid chain its corresponding Gutman tree is defined as follows: For each end hexagons and annulated hexagons and end hexagons of B , an edge is corresponded which joins to be a path successively. If there are n_i (linear annulated) hexagons between the hexagon corresponding to the successive edge $v_{i-1}v_i$ and $v_i v_{i+1}$, then we join n_i new vertices to v_i each by an edge (see figure 1). Let B be a benzenoid chain and G its corresponding Gutman tree (see [29] and the excellent survey in [5] pp. 273–289) showed that

$$S(B, k) = m(G, k),$$

where $m(G, k)$ is the number of k -matching of G .

Thus we have

Theorem 2.1. Let B_1 and B_2 be two benzenoid chains with the same number of hexagons and G_1 and G_2 are the Gutman trees of B_1 and B_2 , respectively. Then $B_1 \succ B_2$ if and only if $G_1 \succ G_2$.

Since the characteristic polynomial of a tree is also its matching polynomial, in [28] Gutman determined the extremal trees with respective their matching

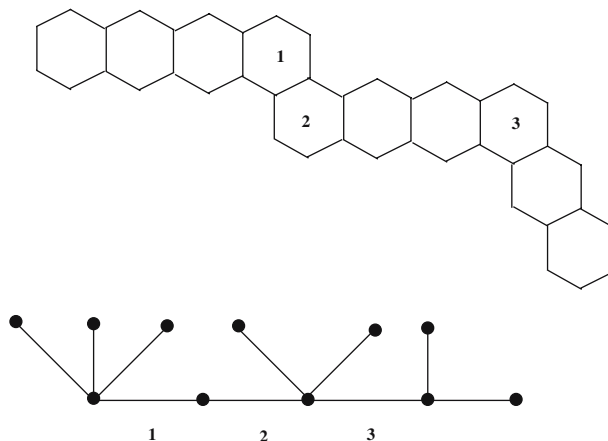


Figure 1. A benzenoid chain and its corresponding Gutman tree.

number. Fortunately, all the extremal trees are caterpillar trees, thus we give the following lemma.

Lemma 2.2. Let Γ_n be the set of caterpillar trees with n edges. If we order Γ_n with respect to their matching number, then

1. the maximal tree is P_n (n path) the second maximal tree is P'_n showing as in figure 2.
2. the minimal tree is $\text{star}(T_2)$ the second, ... forth minimal trees are T_2, \dots, T_4 as showing in figure 2.

Now we need some further concepts. Let G be a connected graph with perfect matchings. G is said to be k -cycle resonant if G contains at least k (≥ 1) disjoint cycles and, for $1 \leq t \leq k$, any t disjoint cycles in G are mutually resonant, that is, there is a perfect matching M of G such that the t disjoint cycles are M -alternating cycles. For a 2-connected graph G , a path P in G is said to be a chain if the degree of any end vertex of P is greater than two and the degree of any middle vertex of P is equal to two in G . In [17], X.Guo and one of the present author gave the following lemma.

Lemma 2.3. Let B a benzenoid system and k^* be the maximal number of the disjoint cycles in B . B is k^* -cycle resonant if and only if B is catacondensed benzenoid system with no chain of even length (catacondensed benzenoid is the benzenoid system – as a plane graph – without internal vertices).

In [30], it has been pointed out that k^* -cycle resonant systems have the greatest resonance energies than the other benzenoid systems. This is true for

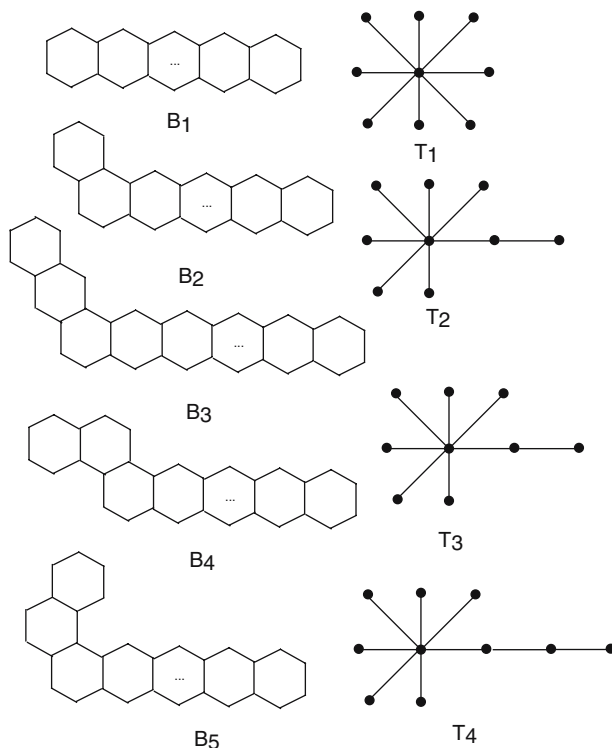


Figure 2. Some Gutman trees and their corresponding benzenoid chains.

the logarithmic model [31] and the Randić's conjugated circuit model [32]. Thus the first conclusion of the following theorem is not surprise.

By lemmas 2.2 and 2.3 we have

Theorem 2.4. Let Ψ_n be the set of benzenoid chains with n hexagons. If we order Ψ_n with respect to their Clar aromatic sextet, then

1. The maximal benzenoid chains are k^* -cycle resonant benzenoid systems. The second maximal benzenoid chains are the benzenoid chains with only two chains of even length located on the third hexagon and the other chains are of odd length.
2. The minimal benzenoid chain is a linear chain B_1 . The second and third minimal benzenoid chains are B_2 and B_3 respectively. Two s -equivalent benzenoid chains B_4 and B_5 are the fourth as showing in figure 2.

Now we give two remarks.

1. The result in this paper agrees with our previous results [33,24] obtained by comparing the *HMO* π -energy. But now we get more minimal benzenoid chains. The further advance quantum chemistry calculation is invited to check the general mathematical results obtained by Clar's theory.
2. Our approach for ordering the maximal benzenoid chain is not unique, the result weaker than [34]. But we can find two kinds of benzenoid chains which are more stable. This is the new information.

3. Cyclo-Polyphenacenes

The cyclo-polyphenacenes can be obtained by identifying two edges in two end hexagons respective where each hexagon is adjacent to exactly two hexagons. In this section we will use the code of Misra and Klein [21] to represent the cyclo-polyphenacenes and the graph corresponding to its carbon skeleton. We first mark a common vertex with degree 3 of the first and second hexagons and then intracing along the boundary of the cyclo-polyphenacenes locate the number of vertices with degree two before the third hexagon. Clearly, when the second hexagon is angular annulated the number is 0 or 2 and when the second hexagon is linear annulated the number is 1 (say $a_1 = 0, 1, 2$, respectively). Starting from the second hexagon, we can define a_2 in a similar way. Furthermore, a_i ($i = 1, 2, \dots, n$) can be defined inductively, where n is the number of hexagons of the cyclo-polyphenacenes. Since any hexagon can be chosen as the first and two directions of the upper and lower $2n$ cycle (two sides of the polyphenacenes) can be chosen, it is seen that up to $4n$ codes are conceivable. We view the $4n$ string of digits as ternary numbers and choose the smallest to correspond to the canonical code [21]. It is easy to see that the code of a cyclo-polyphenacene is $11\dots 1$ and a cyclo-polyphenathrene has the code $0202\dots 02$ (see figure 3).

Now we extend the concept in Clar's aromatic sextet theory [1] to cyclo-polyphenacenes. All the concepts (Clar number, sextet polynomial...) are the same as in section 2. In fact, we only need to change the words benzenoid system to cyclo-polyphenacenes in all definitions.

Our quasi-ordering can be introduced as follows: if for two cyclo-polyphenacenes B_1 and B_2 , $s(B_1, k) \geq s(B_2, k)$ are fulfilled for all k , where $S(B_i, k)$ is the number of i -matchings of B_i , then we say that B_1 is s -greater than B_2 and write $G_1 > G_2$ or $G_2 < G_1$. If both $B_1 > B_2$ and $B_2 > B_1$ hold then B_1 and B_2 are said to be s -equivalent, $G_1 \sim G_2$. If B_1 and B_2 are not s -equivalent and $B_1 > B_2$, then we say that B_1 is s -greater than B_2 strictly. Note that two s -equivalent cyclo-polyphenacenes have the same sextet polynomial but need not to be isomorphic. We will see that example later. Extending Clar's theory to cyclo-polyphenacenes, we assert that if two cyclo-polyphenacenes $B_1 > B_2$

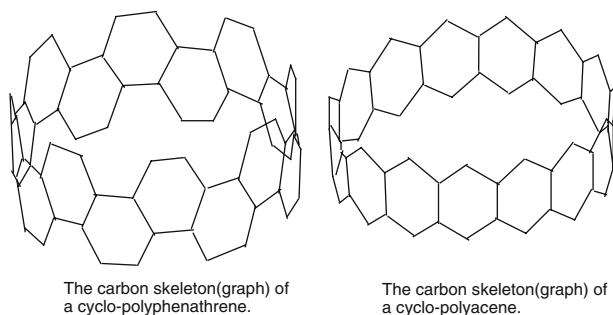


Figure 3. Two cyclo-polyphenacenes. For the sake of brevity, we do not distinguish a cyclo-polyphenacene, its carbon skeleton and its graph.

strictly, then B_1 is more stable. As the case of benzenoid systems, this ordering has better accuracy than simply to compare the Clar number of isomers.

Now we define the generalized crown corresponding to a cyclo-polyphenacenes. A generalized crown C is a graph when all its end vertices (the vertices with degree 1) are deleted, the residual is a cycle. In other words, let v_1, v_2, \dots, v_n be the vertices of a cycle. If we join each of m_i new vertices by an edge to the vertices v_i , for $1 \leq i \leq n$, then a generalized crown is obtained. For a cyclo-polyphenacenes B , using the code of Klein we can define a corresponding crown as follow: each of the hexagons with code 0 or 2 corresponding to an edge which join to be a cycle successively (say v_1, \dots, v_n). For all i , if there are sole n_i (where n_i may be zero) hexagons with code 1 lying between the hexagons corresponding the edge $(v_{i-1}v_i)$ and (v_i, v_{i+1}) then we take n_i new vertices and join each of them to v_i by an edge (see figure 4).

Inspiring by the results of Zhang et al. [35] we have the following lemma.

Lemma 3.1. Let B be a cyclo-polyphenacenes and G be its corresponding generalized crown. The number of Clar aromatic sextets having precisely i hexagon of B is equal to the number of i -matching of G .

The details of the proof of this lemma see appendix A.

Bearing in mind the quasi-ordering “ $>$ ” of graphs with respect to their matching numbers (see [36]), by lemma 3.1 we have:

Theorem 3.2. Let B_1 and B_2 be two cyclo-polyphenacenes with the same number of hexagons and C_1 and C_2 are their corresponding generalized crown, respectively. Then $B_1 > B_2$ (strictly) if and only if $C_1 > C_2$ (strictly).

Theorem 3.2 reduces the ordering problem of cyclo-polyphenacenes with respective to their number of Clar aromatic sextets to the ordering problem of general crown

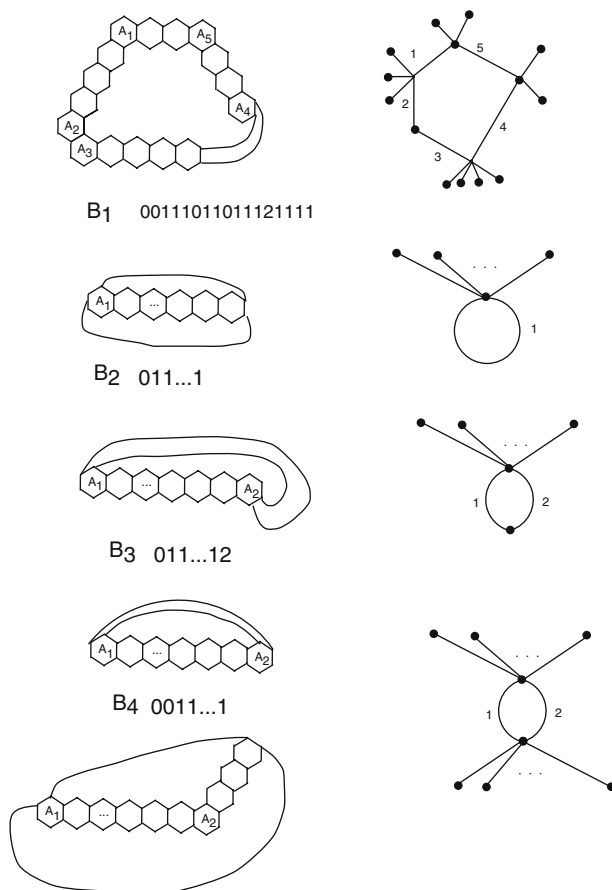


Figure 4. Five cyclo-polyphenacenes and their corresponding generalized crowns.

with respect to their matching numbers. Now, we need some further preparations about the second problem.

Let u and v be two vertices of the graph G , then $G(u, v)(m, n)$ denotes the graph obtained from G by joining m new pendant vertices to the vertex u and by joining n additional new pendant vertices to the vertex v .

Two vertices u and v of the graph G will be called equivalent if the subgraphs $G-u$ and $G-v$ are isomorphic. The following result is proved by Gutman and one of the present authors [36].

Lemma 3.3. If the vertices u and v of graph G are equivalent, then

$$G(u, v)(0, n) \prec G(u, v)(1, n - 1) \prec \dots \prec G(u, v)(\lfloor n/2 \rfloor, n - \lfloor n/2 \rfloor),$$

where $\lfloor \cdot \rfloor$ is the floor function.

Lemma 3.4. Let C be a generated crown, u is a pendant vertex of C and (u, v) an edge of C (v is on the cycle of C). C' is the crown obtained from C by deleting the vertex u and split the vertex v to an edge (v, v') to enlarge the cycle of C . Then $C' \succ C$.

Proof. Let us consider the k -matchings of C and C' . We claim that the number of k -matchings of C containing the edge (u, v) is equal to the number of k -matchings of C' containing the edge (v, v') . In fact $C - \{u\} - \{v\}$ (the graph obtained by deleting the vertices u and v in C) is isomorphic to $C' - \{v\} - \{v'\}$ and the other edges of these two k -matching are taken from $C - \{u\} - \{v\}$ and $C' - \{v\} - \{v'\}$ respectively. Note that the other k -matchings of C are all the k -matchings of $C - \{(u, v)\}$ (the graph obtained by deleting the edge (u, v) in C) and the other k -matchings of C' are all the k -matchings of $C' - \{(v, v')\}$. Since $C - \{(u, v)\}$ can be obtained from $C' - \{(v, v')\}$ by identifying the vertices v and v' and adding an isolated vertex, then each k -matching of $C - \{(u, v)\}$ can be considered as a k -matching of $C' - \{(v, v')\}$. Thus the number of k -matching of $C - \{(u, v)\}$ is no more than the number of k -matching of $C' - \{(v, v')\}$. Combining this result with the previous claim, the lemma 3.4 is proved.

Denote by Φ_n the set of cyclo-polyphenacenes with $n (\geq 4)$ hexagons using the codes, we have

Theorem 3.5. If the elements of Φ_n are ordering with respect to their number of Clar aromatic sextet then the minimal, second minimal, and third minimal element are

$$111 \dots 1 < 011 \dots 1 < 011 \dots 12 \sim 0011 \dots 1$$

the first two elements are unique and the inequalities hold strictly.

Proof. The cyclo-polyacenes with no Clar sextets are unique which is the minimal element of Φ_n with the code $11 \dots 1$ (see figure 3). Note that in Φ_n the element B_2 with the code $011 \dots 1$ is the unique cyclo-polyphenacenes with only one angular annulated hexagon (see figure 4). B_2 has $n - 1$ Clar aromatic sextet with one hexagon and has no other Clar aromatic sextets. But the other elements in Φ_n has exactly n Clar aromatic sextets. Thus B_2 is the second minimal element in Φ_n . Considering the corresponding crown, by lemma 3.4, the element B_3 with the code $011 \dots 12$ and B_4 with the code $0011 \dots 1$ are the minimal elements in Φ_n with two angular annulated hexagons (see figure 4). B_3 and B_4 have n Clar aromatic sextets and no other Clar aromatic sextets. But in $\Phi_n - \{B_1, B_2, B_3, B_4\}$ each element has n Clar aromatic sextet, and at least one Clar aromatic sextets has two hexagons. In fact their corresponding general crowns have either $k (> 2)$ -cycle or 2-cycle in the second case the minimum degree of the vertices on the cycle is 3. Therefore they have at least a 2-matching. Thus B_3 or B_4 is the third minimal elements in Φ_n . Obviously the inequalities hold strictly.

Lemma 3.6. If Φ_n are ordering with respect to their number of Clar aromatic sextet (see figure 3), then

1. the corresponding generalized crown of the fourth minimal elements in Φ_n are $C_2(u, v)(n - 3, 1)$ and $C_3(u, v)(n - 3, 0)$;
2. the corresponding generalized crown of the fifth minimal element in Φ_n is $C_2(u, v)(n - 4, 2)$;
3. the corresponding generalized crown of the sixth minimal element in Φ_n is $C_3(u, v)(n - 4, 1)$;
4. the corresponding generalized crown seventh minimal element in Φ_n is $C_4(u, v)(n - 4, 0)$

and the following inequalities hold strictly:

$$C_2(u, v)(n - 3, 1) \sim C_3(u, v)(n - 3, 0) < C_2(u, v)(n - 4, 2) < C_3(u, v)(n - 4, 1) < C_4(u, v)(n - 4, 0).$$

Proof. By theorem 3.2 we need to compare the coefficients of the matching polynomials of the elements in $\Phi_n - \{B_1, B_2, B_3, B_4\}$. Recall that the matching polynomial can be defined as follows:

$$M(G, x) = \sum_{k=0}^{m(G)} (-1)^k m(G, k) x^{n-2k},$$

where $m(G, k)$ is the number of k -matchings that is the number of selections of k independent edges in G and $m(G)$ is the size of maximum matching of G . From the proof of Theorem 3.5, we can see that the fourth minimal element of Φ_n have at least two angular annulated hexagons. Thus their corresponding generalized crowns have a $k(k > 1)$ -cycle. Now we have the following claims.

Claim 1. The matching polynomials of corresponding generated crowns of the elements in Φ_n with 2-cycle except B_3 are

$$\begin{aligned} C_2(u, v)(n - 3, 1) &: x^n - nx^{n-2} + (n - 3)x^{n-4}, \\ C_2(u, v)(n - 4, 2) &: x^n - nx^{n-2} + (2n - 8)x^{n-4}, \\ C_2(u, v)(n - 5, 3) &: x^n - nx^{n-2} + (3n - 15)x^{n-4}. \\ &\dots \end{aligned}$$

By theorem 3.2 and lemma 3.3 the other elements in Φ_n with two angular annulated hexagons are greater than the first three.

Claim 2. The matching polynomials of corresponding generated crowns of elements in Φ_n with 3-cycle are

$$\begin{aligned} C_3(u, v)(n - 3, 0) &: x^n - nx^{n-2} + (n - 3)x^{n-4}, \\ C_3(u, v)(n - 4, 1) &: x^n - nx^{n-2} + (2n - 7)x^{n-4}, \\ C_3(u, v)(n - 5, 2) &: x^n - nx^{n-2} + (3n - 13)x^{n-4}. \end{aligned}$$

By theorem 3.2 and lemma 3.3 the other elements in Φ_n with three angular annulated hexagons are greater than the first three.

Claim 3. The matching polynomial of the corresponding generalized crown of the minimal element in Φ_n with four angular annulated hexagons are $C_4(u, v)(n - 4, 0)$ and its matching polynomial is $x^n - nx^{n-2} + (2n - 6)x^{n-6}$.

By theorem 3.2, lemmas 3.3 and 3.4 the other elements with more than four angular annulated hexagons are greater than $C_4(u, v)(n - 4, 0)$.

Lemma 3.6 is now an immediate consequence of our claims.

Theorem 3.7. If Φ_n is ordering as lemma 3.6 then

1. the codes of the forth minimal elements of Φ_n are (see figure 5)

$$01011 \dots 1 \sim 011 \dots 121 \sim 00011 \dots 1 \sim 011 \dots 102 \sim 0011 \dots 12$$

2. the codes of the fifth minimal elements of Φ_n are (see figure 5)

$$011011 \dots 1 \sim 011 \dots 1211;$$

3. the codes of the sixth minimal elements of Φ_n are (see figure 5)

$$001011 \dots 1^* \sim 0011 \dots 121^* \sim 01011 \dots 12 \sim 011 \dots 1012;$$

4. the codes of the seventh minimal elements of Φ_n are (see figure 5)

$$0011 \dots 122 \sim 00011 \dots 12 \sim 0011 \dots 102 \sim 000011 \dots 1$$

$$\sim 00211 \dots 12 \sim 011 \dots 1202.$$

Furthermore, in four sets in 1–4, any pair of elements in different sets are not s -equivalent.

Proof. By lemma 3.6, we need only to consider the following cases:

1. 01011 ... 1 and 011 ... 121 are the codes of elements in Φ_n corresponding to the generalized crown $C_2(u, v)(n - 3, 1)$. The other elements in case 1 corresponding to the generalized crown $C_3(u, v)(n - 3, 0)$.

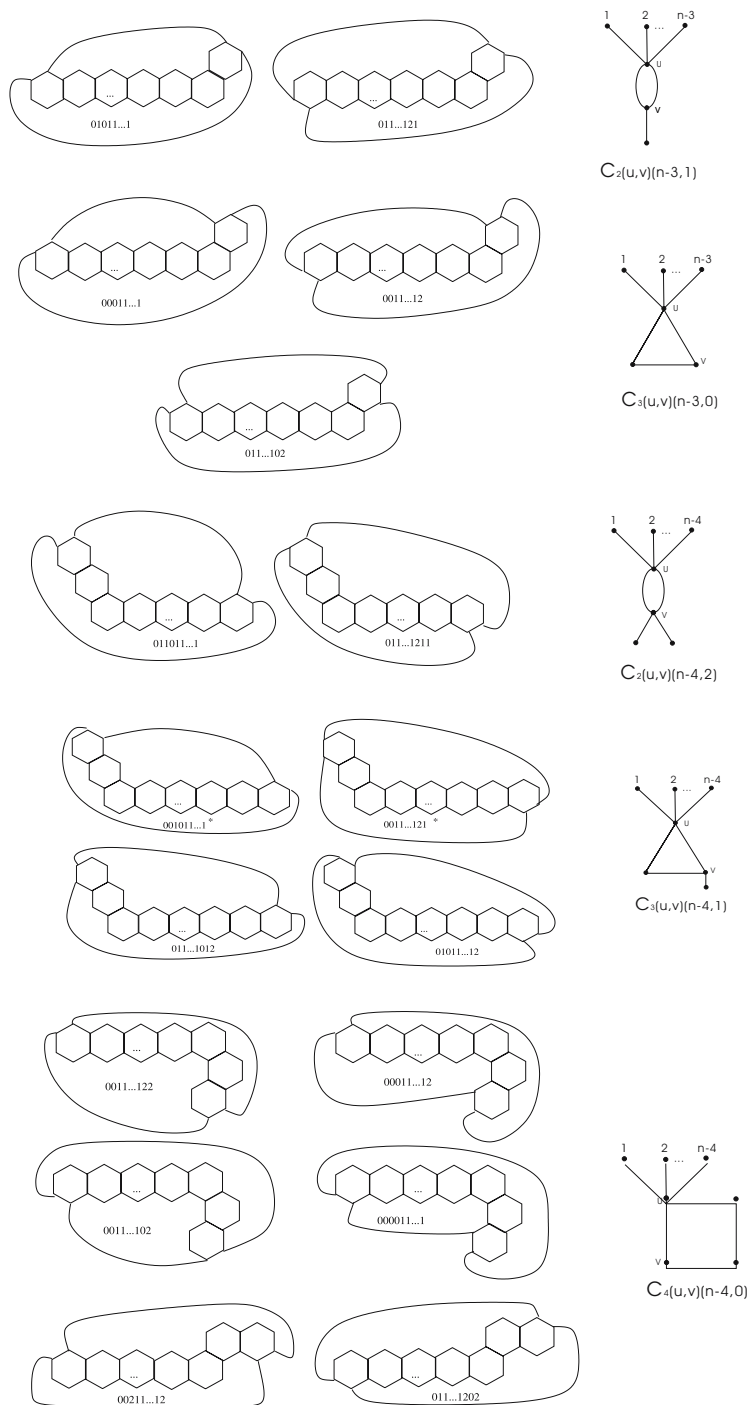


Figure 5. Five generalized crows and their corresponding cyclo-polyphenacenes.

2. Two elements in case 2 corresponding to $C_2(u, v)(n - 4, 2)$.
3. Four elements in case 3 corresponding to $C_3(u, v)(n - 4, 1)$.
4. All elements in case 4 corresponding to $C_4(u, v)(n - 4, 0)$. The first four elements are obtained by identifying two edges each in an end hexagon of the same benzenoid chain. The other elements are obtained by another benzenoid chain in a similar way.

The last conclusion follows from the last conclusion of lemma 3.6. The theorem is thus proved.

Theorem 3.8. If Φ_n is ordering as theorem 3.5, then

1. the corresponding generalized crown of maximal element in Φ_n is a n -cycle. The set of maximal elements of Φ_n are the cyclo-polyphenacenes whose digits of codes can only be 0 or 2.
2. the corresponding generalized crown of second maximal element of Φ_n is obtained by joining a pendant vertex to a $n - 1$ cycle. The set of second maximal elements of Φ_n are the cycle-polyphenacenes whose digits of codes can only be 0 or 2 except a 1.

Proof. It is a immediate consequence of lemma 3.4 and theorem 3.2.

Our results agree with some known results such as

1. The cyclacenes (cyclo-polyacenes) no longer have aromatic bond lengths but rather structures resembling two weakly interacting schleyer "trannulenes" which are circular, all-trans cyclic polyene ribbons [17]. In our theorem 3.5 cyclo-polyacene has no Clar acromatic sextex. It is the minimal element of Φ_n in our ordering.
2. The armchair carbon nanotube is the most stable one among the others. The cyclo-polyphenatheren is closely similar to the shortest armchair carbon nanotube. By theorem 3.8 it is in the set of maximal elements in our ordering.

Note that if we order the cyclo-polyenacenes with respective to their Clar number, we can not distinguish the second and third minimal elements in Φ_n since their Clar number are both 1. We can not distinguish the forth up to seventh minimal elements also, since all their Clar number are 2.

How to distinguish the maximal elements in Φ_n ? This is a further problem. Of course, we need to introduce another new ordering with better sensibility. We suggest to compare the HMO π -energy (the sum of absolute values of the graph of a molecule) of cyclo-polyphenacenes. Inspiring by our previous result of benzenoid chains (see [33,34]), the following conjecture is proposed:

Conjecture. In the set of cyclo-polyphenacenes with n hexagons the cyclo-polyacene has the minimal π -energy and the cyclo-polyphenathrenes has the maximal energy.

We believe that to compare the HMO π -energy can distinguish more elements in Φ_n . On the other hand, to prove any conclusion mathematically is more difficult.

Appendix A. The proof of lemma 3.1.

Lemma A.1. Let B be a cyclo-polyphenacenes and G be its corresponding generalized crown. The number of Clar aromatic sextets having precisely i hexagon of B is equal to the number of i -matching of G .

Proof. Note that the inner-dual of B has as its vertices the centers of hexagon of B where two vertices of B are connected by an edge if and only if the corresponding hexagons are adjacent in B . When B has at least three angular annulated hexagons, it is not difficult to see that the inner-dual of B is isomorphic to a subdivision of a polygon whose vertex is the centers of angular annulated hexagons. We claim that a Clar aromatic sextet is a set of pairwise disjoint hexagons such that there is at most one hexagon whose center is on a side of the polygon. In fact if there are two such hexagons s_1 and s_2 whose centers are lying on a side of the polygon then the hexagons intersected by the side and between s_1 and s_2 together with s_1 and s_2 form a benzenoid chain L which has Clar number two which is a contradiction.

On the other hand, for the corresponding generalized crown C each vertex of C with degree greater than 1 and its neighbors induce a star. Thus in any matching of C there is at most one edge in a star can be chosen. By the definition of corresponding crown, each side of the previous polygon corresponding to a star. From this fact we can easily to see that for any Clar aromatic sextets in B with i hexagons the corresponding i edges in C is a matching and vice versa. Thus there is a bijection between the Clar aromatic sextets in B with i hexagons and the i -matching in C . The degenerated cases are:

- B has no angular annulated hexagon, then B is a cyclo-polyacenes which has no Clar aromatic sextets, B corresponds to an empty graph which has no k ($k > 0$)-matching (see the polyacene in figure 4).
- B has exactly one angular annulated hexagon, then B is corresponding to a 1-cycle (loop) attaching some pendant vertices (a degenerated crown). It is no difficulty to see that all the hexagons except the angular annulated one, say A_1 , are Clar aromatic sextet. Thus the number of Clar aromatic sextet of B having 1 hexagon is equal to $n - 1$ which is the number of the 1-matching of the corresponding degenerated crown. Furthermore,

there is neither other Clar aromatic sextets in B nor $k(> 1)$ -matching in the corresponding degenerated crown. Thus the lemma is true in this case (see figure 4).

- B has exactly two angular annulated hexagons and another hexagons form two disjoint linear benzenoid chains (one of them may be empty). The corresponding crown of B is a 2-cycle attaching some pendent vertices to the vertices of the cycle respectively. It is no difficulty to see that each hexagon of B is a Clar aromatic sextet and each pair of linear annulated hexagons taking from the two linear benzenoid chains respectively are Clar aromatic sextets with two hexagons. Furthermore, there is no other Clar aromatic sextets. Comparing this fact with the number of 1-matching and 2-mathing of corresponding crown, the lemma is proved in the case (see figure 4).

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