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k-resonance of open-ended carbon nanotubes

Fuji Zhang *

Department of Mathematics, Xiamen University, Xiamen, Fujian, 361005, People's Republic of China

Lusheng Wang

Department of Computer Science, City University of Hong Kong, Kowloon, Hong Kong, People's Republic of China

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An open-ended carbon nanotube or a *tubule* is a part of some regular hexagonal tessellation of a cylinder. A tubule T is said to be k-resonant if for every k (or fewer) pairwise disjoint hexagons, the subgraph obtained from T by deleting all the vertices of these hexagons must have a Kekule structure (perfect matching) or must be empty. The 1-resonant tubules can be constructed by an approach provided in H. Zhang and F. Zhang, Discrete Appl. Math. 36 (1992) 291. In this paper, we give the construction method of $k(k \geqslant 3)$-resonant tubules. The lower bound of its Clar number of $k(k \geqslant 3)$-resonant tubules is also given. Note that the present paper does not consider the capped species.

1. Introduction

Iijima observed the multiwall carbon nanotube in 1991 [1]. Two years later, two groups independently discovered the single-wall carbon nanotubes [2,3]. In 1996 Smalley's group synthesized the aligned single-wall nanotubes [4]. As point out by Smalley, a carbon nanotube is a carbon molecule with the almost alien property of electrical conductivity, and super-steel strength. It is expected that carbon nanotubes can be widely used in many fields. Due to this reason, carbon nanotubes have attracted great attention in different research communities such as chemistry physics and artificial materials. For the details, see [5,6].

In general, a single-wall carbon nanotube has two hemispherical caps connected by a carbon atoms skeleton of a tubular hydrocabon or the open-ended nanotube. In fact, tubules (the graphs of open-end nanotubes) are the basis for many researches in physics and chemistry. For example, the problem of recognizing the metallic carbon nanotubes and semicondicting nanotubes has been shown to be depend on the size and geometry of the tubule [6] (some more general criteria have been comprehensively explicated in [7] originally). On the other hand, though most nanotubes discussed in the

* Corresponding author.
E-mail: fjzhang@jingxion.xmu.edu.cn

literature have closed caps, open-ended tubules have also been reported [8–11]. Along this line Sachs, Hansen and Zheng discussed the enumeration of the number of Kekule structures (perfect matchings) of tubules. They provided an approach to consider their asymptotic behavior [12]. This too has been comprehensively treated in [13]. Erkoc and Turker [14] investigated the electronic structure of small tubules by using the AMI-RHF semiempirical molecular orbital method.

This paper considers the k-resonant theory of tubules. The inspiration of k-resonant structure comes from Clar's aromatic sextet theory [15–19] and the conjugated circuit theory of Herndon and Randic [20–22]. In Clar's theory, the mutually resonant sextets (hexagons) play an important role in the definitions of Clar's formula and the generalized Clar's formula. In Randic's theory, the conjugated hexagon (i.e., there is a Kekule structure M such that the perimeter of the hexagon is an M-alternating cycle) has the largest contribution to the resonant energy among all $4n + 2$ conjugated circuits. Based on this fact, one can define the k-resonant benzenoid systems and coronoid systems. In [23], Gutman first proposed the concept of 1-resonant benzenoid system and raised the problem of how to characterize them. This problem was solved by Zhang and Chen in [24]. Later, it was generalized to coronoid system in [25] and planar bipartite graphs in [26]. Zheng characterized $k(k \geqslant 2)$-resonant benzenoid system and gave a systematic method to construct all $k(k \geqslant 3)$-resonant benzenoid systems [27,28]. In [29], Chen and Guo solved the same problem for coronoid systems and the result was extended by Lin and Chen to multiple coronoid systems [30].

In this paper, we consider the k-resonant tubules. The paper is organized as follows: the basic notations and terminologies are given in section 2. In section 3, we deal with the 1-resonant tubules and 2-resonant tubules. We point out that a linear algorithm is known to check whether or not a tubule is 1-resonant, when we know one of its Kekule structure of this tubule. In section 4, we give a procedure for the construction of 3-resonant tubules. We also prove that if a tubule is 3-resonant, then it is also k-resonant for $k > 3$. A lower bound of Clar number of 3-resonant tubules is also given in section 4. Note that the k-resonant tubules characterized in this paper are different from the nanotubes refer to polyhex structures which extend a long way along the cylinder and the boundaries at the two ends are caps (see [1–10]). We will discuss our results in section 5.

2. Basic concept

It is well known that any hexgonal tessellation cylinder can be consider as a strip of regular hexagonal tessellation of the plane between two parellel straight line L_1 and L_2, where points of opposit (othogonal) positions on L_1 and L_2 are identified [5,6,12] (see figure 1). Without loss of generality, we can assume that L_1 and L_2 pass through the lattice points O of hexagons. (In fact, we can take any straight line parallel to the axis of the cylinder to be L_1.) If we unrolled the cylinder, then O and its oposite position A determine a vector $OA = C_h$. Suppose that the vectors a_1 and a_2 are shown as in figure 1. Then one of them, say, a_1, has the smaller angle between C_h and a_i. The chiral angle θ is defined as the angle between the vectors C_h and a_1.

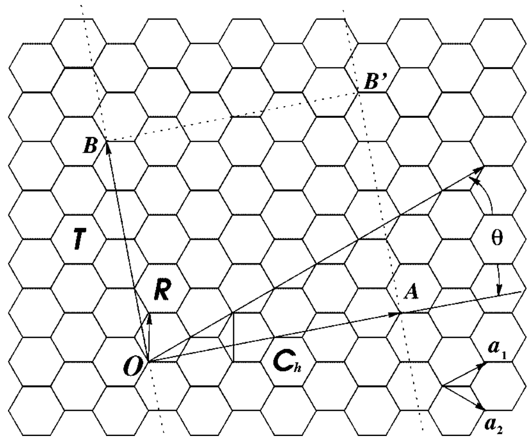


Figure 1. A tubule is unrolled onto the plane. When we identify O and A, and B and B', a tubule can be constructed. OA defines the chiral vector C_n. The angle between C_n and a_1 is the chiral angle θ.

From the hexagonal symmetry of the lattice [5,6], $0 \leqslant \theta \leqslant 30°$. The two extreme cases $\theta = 0°$ and $\theta = 30°$ (called *zigzag* and *armchair* hexagonally tessellated cylinders, respectively) are of special interest.

As pointed out in [12], the natural counterpart of the tubular hydrocabon is its carbon atom skeleton which forms a (open-ended) tubule. Note that we will not distinguish a tubule from its skeleton. Using the language of graph theory, a tubule T is defined to be a finite section of a hexagonally tessellated cylinder produced by two disjoint edge cuts such that each edge of T belongs to at least one hexagon of T. Clearly, for each edge cut, the line segments connecting the centers of two edges of the edge cut in a same hexagon will surround the axis of the cylinder. In the following, we assume that a tubule T is drawn in such a way that its axis is vertical. Denote the top and bottom perimeter of T to be c_1 and c_2, respectively.

In the rest part of the section, we introduce Clar formulas (a set of Clar aromatic sextets) for tubules. The concept was originally given by Clar in the study of benzenoid hydrocarbons [15–19]. (For benzenoid hydrocarbons, its carbon atom skeleton graph is a 2-connected planar graph whose every interior face is bounded by a regular hexagon of side length 1. This graph is called the *benzenoid system*.)

A Clar *formula* (a set of Clar aromatic sextets) for a tubule is a set of hexagons on the tubule selected (by drawing circles) as follows:

(1) draw circles in disjoint hexagons;

(2) the remainder of the tubule obtained by deleting the vertices of the circled hexagons must have a Kekule structure or must be empty;

(3) circles are drawn as many as possible subject to (1) and (2).

A set of selected hexagons satisfying rules (1) and (2) is called a *generalized Clar formula*. The number of selected hexagons in a Clar formula is called the *Clar number*.

Based on some experiments, Clar's aromatic sextet theory claims that for two isometric benzenoid hydrocabons, the one having a larger Clar number should be more stable. It is an inevitable trend to extend Clar's aromatic sextet theory to the study of tubules. The extended theory can also be used to explain why the armchair carbon nanotube is more stable than others.

3. 1-resonant and 2-resonant tubules

Any hexagonal tessellation of the cylinder is an infinite bipartite graph. As its subgraph, a tubule is also a bipartite graph. Moreover, a tubule is also a planar graph when we take the face surrounded by c_1 or c_2 to be infinite [12].

Definition 1. A tubule T is said to be *k-resonant*, if for every k (or fewer) pairwise disjoint hexagons, the graph obtained from the tubule by deleting the vertices of the hexagons has a Kekule structure or is empty.

In other words, T is k-resonant, iff any k (or fewer) pairwise disjoint hexagons of T form a generalized Clar formula. By definition, if T is k-resonant, then T is also k'-resonant for any $k' < k$. This concept can be extended to planar graphs when hexagons are replaced by interior faces.

Now we recall some basic concepts of matching theory [31]. A Kekule structure of a molecular graph G corresponds to a perfect matching of G. An edge of a graph G is said to be allowed if it is in some perfect matching of G and forbiden, otherwise. If an edge is in *every* perfect matching of G, then it is called a *fixed double bond*. A connected bipartite graph G is *elementary*, if each edge in G is allowed. For a graph G with perfect matchings, a cycle c of G is *nice* if $G - c$ has a perfect matching.

The following concepts and lemmas can be found in [26]. We first give the definition of the *ear decomposition*. Let x be an edge. Joining its end vertices by a path P_1 of odd length, we get the so-called "first ear". We proceed inductively to build a sequence of bipartite graphs as follows: if $G_{r-1} = x + P_1 + P_2 + \cdots + P_{r-1}$ has already been constructed, add the rth ear P_r (of odd length) by joining any two vertices with different colors in the bipartite graph G_{r-1} such that P_r has no internal vertices in common with the vertices of G_{r-1}. The decomposition $G_r = x + P_1 + P_2 + \cdots + P_r$ will be called an (bipartite) *ear decomposition* of G_r.

Definition 2 [26]. An ear decomposition $(G_1, G_2, \ldots, G_r = G)$ (equivalently, $G = x + P_1 + P_2 + \cdots + P_r$) of a planar elementary bipartite graph G is called a reducible face decomposition, if G_1 is the boundary of an interior face of G and the ith ear P_i is exterior to G_{i-1} such that P_i and a part of the periphery of G_{i-1} surround an interior face of G for all $2 \leqslant i \leqslant r$.

Theorem 3 [26]. Let G be a planar elementary bipartite graph other than K_2. Then G has a reducible face decomposition starting with the boundary of any interior face of G.

Corollary 4 [26]. Let G be a planar bipartite graph other than K_2. Then G is elementary if and only if G has a reducible face decomposition.

When we begin to consider the tubule, the first thing to our mind is the coronoid system which is the carbon atom skeleton graph of coronoid hydrocarbons. In fact, a coronoid system G can be obtained from a benzenoid system by deleting at least one interior vertex and/or at least one interior edge such that each edge of G belongs to at least one hexagon of G and a unique non-hexagon interior face emerges. Several papers and two books are devoted to this topic [32]. It is natural to think that coronoid systems and tubules have almost the same properties. In fact, it is not conjecturable and some results are not valid simutaniously for these two types of graphs. We will find the first example in this section.

The following general theorem can be used to recognize 1-resonant tubules.

Theorem 5 [26]. Let G be a planar bipartite graph with more than two vertices. Then each face (including the infinite face) of G is 1-resonant iff G is elementary.

Corollary 6. A tubule T is 1-resonant iff T is elementary.

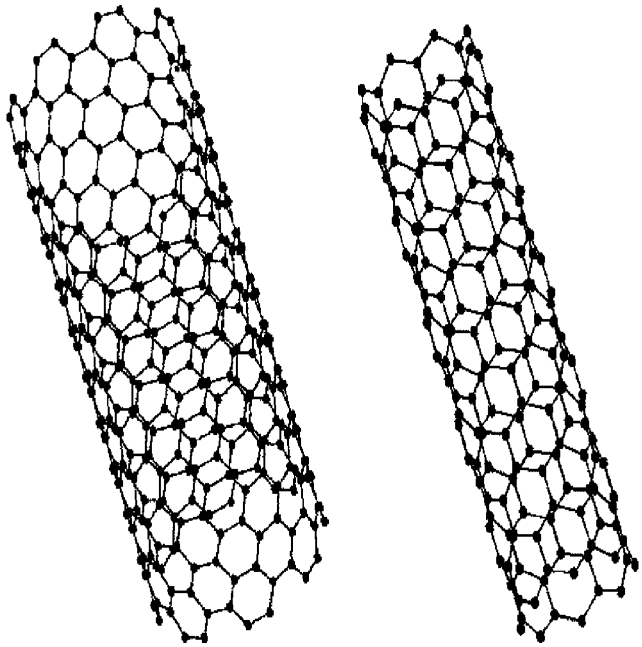
Proof. Let T be a 1-resonant tubule. Since each edge e of T is on the perimeter of a hexagon s and T is 1-resonant, $T - s$ has a perfect matching and e is allowed. Thus T is elementary. The inverse is clear by theorem 5. □

For the coronoid system, there is a stronger result: a coronoid system G is 1-resonant iff the outer and inner perimeters of G are nice cycles [25]. However, the statement is not true for tubules. The counter-example is zigzag tubules with the zigzag type of ends of figure 2(b). In fact, for this type of tubules all the edges which are parallel to the axis of the zigzag tubule are not allowed (see figure 2(b)). Hence, it is not an elementary graph. By theorem 6, it is not 1-resonant, though its two perimeters are nice cycles. In general, whether or not a zigzag nanotube is 1-resonant depends on its ends c_1 and c_2. Fortunately, we have a good algorithm to recognize the planar elementary graph. If a perfect matching of G [33] is known, the running time is linear. So we can use corollary 4 efficiently to recognize the 1-resonant tubules.

As pointed out in [12], tubules are planar bipartite graphs. By corollary 6 and theorem 3, it is easy to give a constructive procedure to construct 1-resonant tubules face by face. We omit the details here.

As for the 2-resonant tubules, up to now, there is no simple procedure to recognize them and the constructive procedure has not been found, either. It seems to be a very challenging problem in the study of 2-resonant tubules as well as for benzenoid systems.

Now we will give an example of 2-resonant tubule (see figure 3). We claim that all the armchair tubules are 2-resonant. Figure 3 shows that any pair of disjoint hexagons are resonant. In other words, the graph obtained from the tubule by deleting the vertices of each pair of disjoint hexagons has a Kekule structure.



(a) (b)

Figure 2. Armchair tubule (a) and zigzag tubule (b).

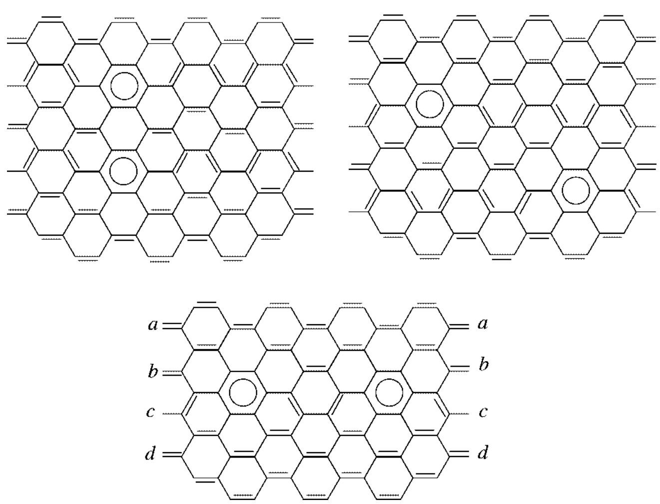


Figure 3. Any pair of disjoint hexagons of the armchair tubule are resonant. Note that the dangling edges with the same label are identified.

4. $k(k \geqslant 3)$-resonant tubules

Now we turn to the $k(k \geqslant 3)$-resonant tubules. Let us give an example of small $k(k \geqslant 3)$-resonant tubules (see figure 4). We consider A_3, the smallest armchair tubule,

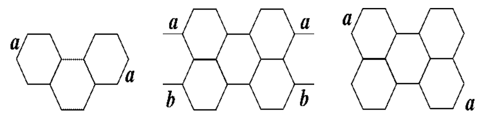


Figure 4. Three small tubules: (a) A_3, (b) $\overline{T}_3$ and (c) $\overline{T}_4$. The edges or dangling edges with the same label are identified.

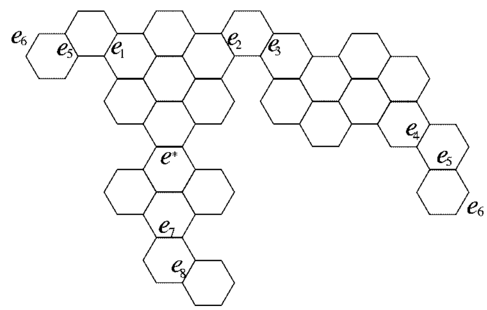


Figure 5. A tubule formed by identifying two edges with label e_6, in which $e_0, e_1, \ldots, e_6$ are chords of type II, e^* is a maximal chord of type I, e_7 and e_8 are chords of type I.

where the edges with the same label are overlayed. Note that A_3 has no disjoint hexagon and each hexagon is resonant. Thus A_3 is $k(k \geqslant 1)$-resonant. $\overline{T}_3$ and $\overline{T}_4$ are also $k(k \geqslant 1)$-resonant tubules, where the edges with the same label are overlayed. In fact, each hexagon and each pair of disjoint hexagons of $\overline{T}_3$ and $\overline{T}_4$ are resonant, and $\overline{T}_3$ and $\overline{T}_4$ have at most two disjoint hexagons.

An edge of a tubule T is a *chord* if its two ends are on the outer-perimeters c_1 and/or c_2 of T but $e \notin c_1 \cup c_2$. A chord e of a tubule T is of *type II* if one end is on c_1 and the other is on c_2. A chord e of a tubule T is of *type I* if its both ends of e are on the same perimeter c_1 or c_2.

Given a chord e of type I, T is seperated by e into two parts. One is a tubule, say, $T(e)$. The other is a benzenoid system, say, $B(e)$. The concept of a chord of a tubule is similar to the concept of a chord of a coronoid system. As in the later case, a chord e^* of type I is *maximal* if for any chord $e \neq e^*$ of type I, $B(e^*)$ is not the subgraph of $B(e)$ (see figure 5).

From the result of [29, section 3], we can see that for a $k(k \geqslant 3)$-resonant coronoid system there are at least two chords. But in our case, there are 3-resonant tubules having no chord (T_n' and $\overline{T}_6$ in figure 6) and there are 3-resonant tubules having exactly one chord (T_n'' in figure 6). This fact shows the difference between the coronoid systems and tubules again.

A tubule without a chord of type I is a *pure* tubule. We now give the construction method of 3-resonant pure tubules. If a pure tubule has more than one chord arranged clockwise as follows:

$$e_1, e_2, \ldots, e_t, \quad t > 1,$$

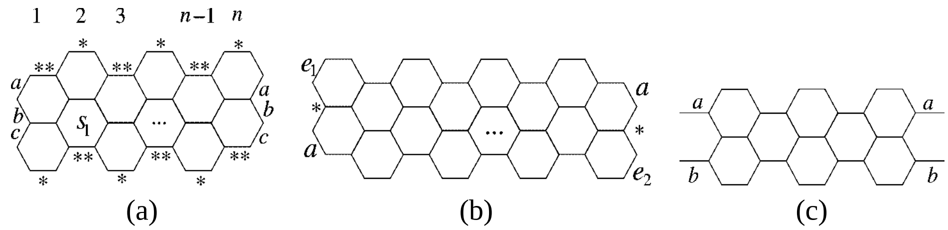


Figure 6. Three types of tubules formed by identifying the edges with the same label. (a) T'_n, $n \geqslant 4$, n is even; (b) T''_n, $n \geqslant 2$, n is even; (c) $\overline{T}_6$. T'_n and $\overline{T}_6$ have no chord, T''_n has exactly one chord a.

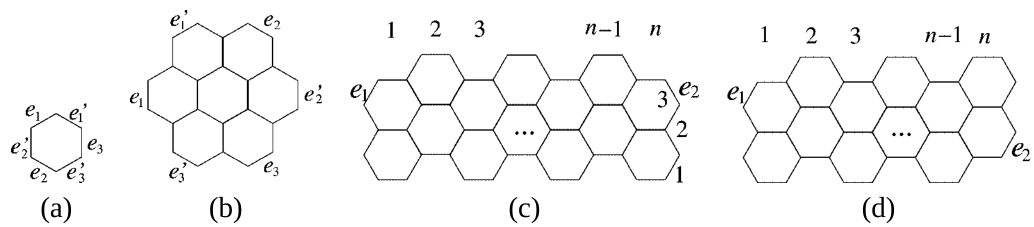


Figure 7. Building block of 3-resonant tubules $\{e_1, e_2, e_3\}$, $\{e'_1, e'_2, e'_3\}$ and their subsets with two elements are attachable combinations of a crown or a single hexagon. $\{e_1, e_2\}$ is an attachable combination of T_n. (a) A single hexagon; (b) a crown; (c) T_n, $n \geqslant 1$, n is odd; (d) T_n, $n \geqslant 2$, n is even.

denote the section between chord e_i and e_{i+1} (inclusive of e_i and e_{i+1}) by $T(e_i, e_{i+1})$ where $i+1$ is taken modulo t. In fact, if we split the edge $e_1, e_2, \ldots, e_r$, some benzenoid systems $T(e_i, e_{i+1})$ ($i = 1, 2, \ldots, t$) are obtained. We call them building blocks of T. For a tubule with chords of type I, we can easily split its chord in a similar way.

We will show that the benzenoid systems showing in figure 7 are all building blocks of 3-resonant tubules.

For each building block, the set(s) of attachable edges are specified in figure 7. For the single hexagon and crown, the six edges on the perimeter with two end vertices of degree 2 are divided into two sets $\{e_1, e_2, e_3\}$ and $\{e'_1, e'_2, e'_3\}$. We will see that in the spliting of 3-resonant pure tubule, two or three edges in the same set are spliting edges. We call them an attachable combination. For T_n, e_1 and e_2 form an attachable combination. For example, in a crown e'_1 and e_3 are not an attachable combination. The following lemma is valid for 3-resonant coronoid systems which is also true in the case of 3-resonant tubule. The proof is the same, so we will omit its details (see [30, lemma 2.1]).

Lemma 7. Let T be a 3-resonant tubule. Then

(1) T cannot have three consecutive vertices on its perimeter such that the first and last ones are of degree 3 and the second one is of degree 2;

(2) T has no subgraph as shown in figure 8;

(3) any two internal hexagons of T are disjoint;

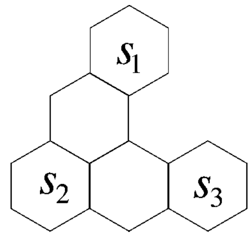


Figure 8. A forbiden subgraph of 3-resonant tubules.

(4) the vertices on the perimeter of any crown which is a subgraph of T are on the perimeter of T.

Note that conclusion (5) of lemma 2.1 in [30] asserts that a coronoid G has no such external hexagon that has exactly two parallel edges on the perimeter of G. But this fact is not true for tubules. In fact tubules $\overline{T}_4$ and $\overline{T}_6$ are counterexamples (see figures 4 and 5).

Now we are in the position to prove the following theorem.

Theorem 8. Let T be a 3-resonant pure tubule. Then

(1) if T has no chord, then T is T'_n, $\overline{T}_6$ or $\overline{T}_4$;

(2) if T has exact one chord, then T is T''_n or $\overline{T}_3$;

(3) if T has more than one chord (of type II) arranged clockwise as $e_1, e_2, \ldots, e_n$, then T can be splitted into sections: $T(e_i, e_{i+1})$, $i = 1, 2, \ldots, n \pmod n$, such that each section is either T_n, or a crown, or a hexagon, and the attachable edges e_i and e_{i+1} of which constitute an attachable combination.

Proof. Taking a hexagon s of T, we will show that s is contained in a subgraph of T which is one of $\overline{T}_3$, $\overline{T}_4$, $\overline{T}_6$, T'_n, T_n, or a crown or a hexagon, and has exactly two attachable edges e_i and e_{i+1} that constitute an attachable combination.

Case 1. None of the vertices of s lies on c_1 or c_2. By lemma 7(4) all the vertices on the outer perimeter of the crown containing s as its internal hexagon are on c_1 or c_2. Thus, at least one edge in the two sets $\{e_1, e_2, e_3\}$ and $\{e'_1, e'_2, e'_3\}$ is a chord of T (say e_1). It is not difficulty to see that, for the 3-resonant pure tubules, exactly two edges in the two sets $\{e_1, e_2, e_3\}$ and $\{e'_1, e'_2, e'_3\}$ are chords of T. Now we will prove that if one of e_i (say e_1) is a chord of T, then e'_i, $i = 1, 2, 3$, can not be a chord of T. Otherwise, we can find three hexagons of T: the hexagon s and the two hexagons of T which do not belong to the crown and contain the edges e_1 and e'_i, respectively. When we delete these three hexagons from T, an odd connected component is created, contradicting that T is 3-resonant (see figure 7).

Case 2. Hexagon s has exactly two vertices on c_1 or on c_2.

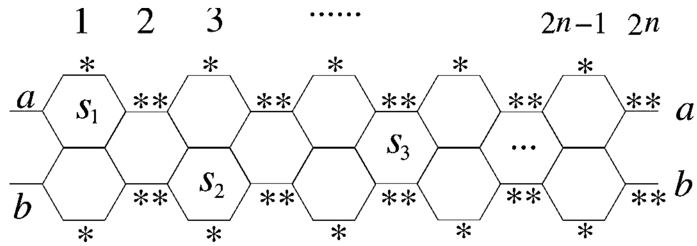


Figure 9. $\overline{T}_n$, $n \geqslant 4$, formed by identifying the dangling edges with the same label.

Subcase 2.1. s is contained in a subgraph of T which is a T_n' with $n \geqslant 4$ being even. By lemma 7(2), there is no hexagon on the positions, for which each has a star. By lemma 7(4), there is no hexagon on the positions, each of which has a double star. Thus T is just a T_n' and T has no chord (see figure 6).

Subcase 2.2. s is contained in a subgraph of T which is a T_n''. Then T is just T_n''. In fact, by the same discussion in the proof of subcase 2.1, we only need to show that there is no hexagon of T on the positions, where each of which has a star in T_n'' of figure 6. This fact can be seen by lemma 7(1).

Subcase 2.3. In the other case, s is contained in a maximal subgraph T_n of T in the sense that no other $n' > n$ such that $T_{n'}$ is a subgraph of G containing T_n. By the proof of subcase 2.1, we only need to consider the positions 1 and 2 (see figure 7). In fact, there is no hexagon of T on the position 1 (by lemma 7(1)). If there is a hexagon on position 2, there must be a hexagon on position 3 (by lemma 7(1)). This fact contradicts the maximality of n. Thus e_2 is either a chord of T or an edge on c_1 or c_2. Analogously, the same is true for edge e_1. Furthermore, if e_1 (e_2) is on c_1 or c_2, then e_2 (e_1) must be of type I, contradicting that T is a pure tubule. Clearly the section $T(e_1, e_2)$ is T_n and e_1 and e_2 are its attachment edges.

Case 3. Hexagon s has exactly three vertices on the perimeter of T. By lemma 7(1), it is impossible.

Case 4. A hexagon has exactly four vertices on c_1 or c_2 of T.

Subcase 4.1. The four vertices on c_1 or c_2 are end vertices of two parallel edges of s.

Subsubcase 4.1.1. s is contained in a subgraph of T which is a $\overline{T}_n$, $n \geqslant 4$ (n is even) (see figure 9).

By lemma 7(2), there is no hexagon of T on the positions with a star. By lemma 7(1), if there is a hexagon on a position with a double star, then each position which has a double star has a hexagon of T, contradicting the condition of subcase 4.1. Thus T can only be $\overline{T}_n$, $n \geqslant 4$ (n is even). When $n = 4$, $\overline{T}_4$ is 3-resonant, as point out at the begining of this section. When $n > 6$, T_n is not 3-resonant, since we can find three pairwise disjoint hexagons s_1, s_2 and s_3 which are not resonant (see figure 9). Thus the only remaining possibility is $n = 6$. It is not difficulty to check that $\overline{T}_6$ is 3-resonant. Thus s is contained in $\overline{T}_6$ or $\overline{T}_4$.

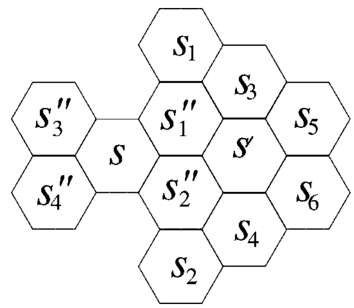


Figure 10. In case 4, S is the rightmost hexagon of $\overline{T}_n$.

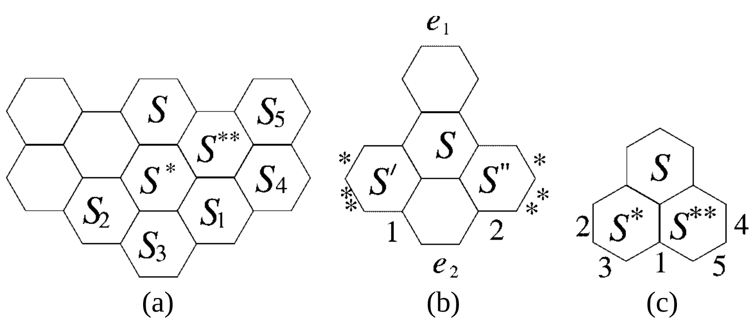


Figure 11. (a) subcase 4.2; (b) subcase 4.3; (c) case 5.

If s is contained in a maximal subgraph of T which is a $\overline{T}_n$, $n \leqslant 3$. Clearly, s is in a $\overline{T}_3$.

Subsubcase 4.1.2. s is not contained in a subgraph $\overline{T}_n$ of T. Then we may assume that s is the rightmost one fulfiling the condition of case 4 in the sense that s' does not belong to T or s' belongs to T but s_5 or s_6 does not (see figure 10). Similar to subsubcase 4.1.1, none of s_1 and s_2 belongs to T (by lemma 7(2)) and none of s_3 and s_4 belongs to T (by lemma 7(1)). If s' is not in T, then s is not resonant, a contradiction. Hence s' must be in T. Since s_1'' and s_4'' are resonant in T, at least one of s_5 and s_6 belongs to T. By lemma 1(1), they must both be in T, contradicting the selection of s.

Subcase 4.2. s has exactly three consecutive edges on the perimeter of T (see figure 11(a)).

Subsubcase 4.2.1. Both s_1 and s_2 belong to T. If s_3 belongs to T too, then s is in a crown with the center s^* and the conclusion valid by the discussion in case 1. Otherwise, s_3 does not belong to T. Then s^* is a hexagon having exactly two vertices on c_1 or c_2. By the discussion of case 2, s^* and also s is in a section which is one of T_n, T_n', and T_n''.

Subsubcase 4.2.2. At least one of s_1 and s_2 (say s_1) does not belong to T. If both s_4 and s_5 are in T, then, s^{**} is a hexagon of T with two parallel edges which belong to c_1 and c_2, respectively. This reduces to subcase 4.1. By the discussion of subcase 4.1, s^{**} (and also s) is in $\overline{T}_4$ or $\overline{T}_6$. Note that, by lemma 7(1), it is impossible that exactly one of s_4 and s_5 is in T. Thus, we need only to deal with the case when s_4 and s_5 are not in T. In this case, a chord of type I of T must exist, a contradiction.

Subcase 4.3. Hexagon s has exactly two non-parallel and non-incident edges on c_1 or c_2 (see figure 11(b)). By lemma 7(2), there is no hexagon on the positions, where each has a star. By lemma 7(1), there is no hexagon on the positions, where each has a double star. If there is a hexagon of T on one of the positions 1 and 2, then s' or s'' will be a hexagon fulfilling the condition of subcase 4.2. By the discussion there, s' (or s'') and therefore s are contained in a section which is either a T_n, or a crown, or T_n', or T_n'', or $\overline{T}_3$, or $\overline{T}_4$, or $\overline{T}_6$. If there is no hexagon of T on positions 1 and 2, it is clear that s is contained in a T_2. Then e_1 and e_2 must be chords of type II in T which forms a attachable combination.

Case 5. Hexagon s has five vertices on c_1 or c_2. If there is no hexagon of T on the position 1 (see figure 11(c)), then by lemma 7(1), there is no hexagon only on one of the positions 2, 3, 4 and 5. If there are two hexagons of T on the positions 2 and 3 (4 and 5) then there is no hexagon on the position of 5 (3) (by lemma 7(2)) and 4 (2) (by lemma 7(1)). Then s^{**} (s^*) is not resonant, again a contradiction. Thus T has only three hexagons. This means that T is not a tubule, a contradiction. Hence, there must be a hexagon on position 1. Now s^* is a hexagon with at most four vertices on c_1 or c_2 and s and s^* are in a same section. When s^* has exactly two vertices on c_1 or c_2, by the discussion in the previous cases, s^* and therefore s are contained in a T_n, $n > 1$. But the fact $n > 1$ implies that T has a chord of type I, contradicting the fact that T is pure. When s^* has exactly four vertices on c_1 or c_2, by the discussion of subcases 4.2 and 4.3, our conclusion is valid.

Case 6. Hexagon s has six vertices on c_1 or c_2. It is not difficulty to see that s has two attachable edges which constitute an attachable conbination of s.

Now we complete our proof. □

In general case, a 3-resonant tubule T may have chords of type I. Let T be a tubule with maximal chords of type I: $e_1^*, e_2^*, \ldots, e_n^*$. It is clear that $\hat{T} = T(e_1^*) \cap T(e_2^*) \cap \cdots \cap T(e_n^*)$ is a pure tubule and $B(e_i^*)$ is a 3-resonant benzenoid system. Thus, we can give a construction method of 3-resonant tubules based on 3-resonant benzenoid systems and 3-resonant pure tubules.

Now we give a construction method of 3-resonant pure tubule with at least two chords. Let A_0 be the set of crown, hexagon and T_n ($n = 2, 3, \ldots$) with attachable edges forming an attachable combination.

Construction procedure.

(1) Benzenoid system B_n with attachable edges are defined recursively as follows. Let us choose a benzenoid system H with attachable edges from A_0 and define H to be B_1. H is also defined to be the end section. If B_{n-1} with end section and its attachable edges is defined, choosing H_n from A_0. B_n can be obtained from B_{n-1} by identifying an attachable edge of H_n and an attachable edge of

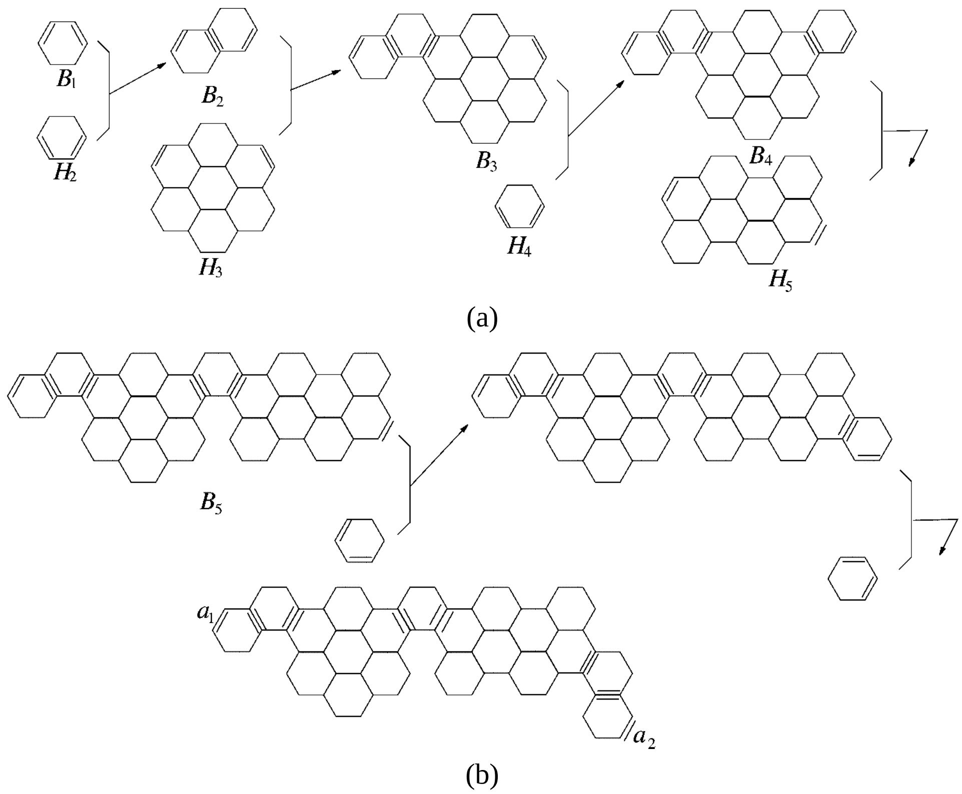


Figure 12. An illustration of the construction procedure (the last step (see (b)) is to identify a_1 and a_2).

the end section H_{n-1} of B_{n-1}. We define the end sections of B_n to be H_1 and H_n and attachable edges of B_n to be attachable edges of H_1 and H_n lying on the perimeter of B_n.

(2) If in B_n there are two attachable edge e_1 and e_n belonging to H_1 and H_n, respectively, and e_1 and e_2 are parallel, when we identify e_1 and e_2, so that a 3-resonant pure tubule are obtained (see figure 12).

The following simple lemma can be found in [29].

Lemma 9. Let T_n^- (T_n^{--}) denote the hexagonal system obtained from T_n by deleting one (two) attachable edge(s) together with its end vertices. Let C denote the crown, and C^- (C^{--}) are obtained from C by deleting one (two) edge(s) together with their end vertices which form an attachable combination of C. Then T_n, T_n^{--}, T_n^-, C, C^-, C^{--} are $k(k \geqslant 3)$-resonant.

Theorem 10. T is a $k(k \geqslant 3)$-resonant pure tubule with at least two chords of type II, iff T can be produced by the constructing procedure.

Proof. Let T be produced by the constructing procedure. Then T is a pure tubule with at least two chords of type II: $e_1, e_2, \dots, e_t$ such that each section $T(e_i, e_{i+1})$, $i = 1, 2, \dots, t \pmod t$, is either a T_n, or a crown, or a hexagon, which has exactly two attachable edges e_i and e_{i+1} constituting an attachable combination. Let $K = \{s_1, s_2, \dots, s_k\}$ be a set of pairwise disjoint hexagons of T. $K_i = K \cap T(e_i, e_{i+1})$, $i = 1, 2, \dots t$.

For each section $T(e_i, e_{i+1})$, $i = 1, 2, \dots, t$, if e_i (e_{i+1}) belongs to a hexagon in K not in the section, then delete end vertices of e_i (e_{i+1}). If e_{i+1} does not belong to any hexagon in K, then delete end vertices of e_{i+1}. The resultant graph is denoted by $T'(e_i, e_{i+1})$. It is clear that $T'(e_i, e_{i+1})$ is either a $T_n(C)$ or a $T_n^-(C^-)$ or a $T_n^{--}(C^{--})$, or an edge or a 3-path, and any two $T'(e_i, e_{i+1})$ are disjoint, and $\bigcup T'(e_i, e_{i+1})$ covers all vertices. By lemma 9, $T'(e_i, e_{i+1})$ is $k(k \geqslant 3)$-resonant. Hence K_i are resonant in the $T'(e_i, e_{i+1})$. Thus K is resonant in T and T is $k(k \geqslant 3)$-resonant.

Conversly, if a pure tubule T is $k(k \geqslant 3)$-resonant, then T is 3-resonant. By theorem 8, if we split a chord e, we obtain a benzenoid system with the form B_n and the two edges obtained from e need to be parallel. Thus T can be constructed by our procedure. □

Theorem 11. A pure 3-resonant tubule must be $k(k \geqslant 3)$-resonant.

Proof. If T has at least two chord, T can be produced by the construction procedure. Thus T fulfils the condition of theorem 10 and T is $k(k \geqslant 3)$-resonant. Now we need to show that T_n' and T_n'' ($n \geqslant 4$, n is even) are $k(k \geqslant 3)$-resonant.

(1) Taking a set K of disjoint hexagons of T_n'. If there is a hexagon s_1 in K containing exactly two vertices on c_1 or c_2 (see figure 6), then the graphs consisting of all the hexagons of $T_n' - s$ is isomorphic to a T_{n-3}. One can see that, these graphs are $k(k \geqslant 3)$-resonant (see also [28]). Thus K is resonant in T_n'. On the other hand, all hexagons of T having exactly four vertices on c_1 or c_2 are resonant. Thus, if all the hexagons in K have exactly four vertices on c_1 or c_2, they are also resonant. Therefore, T_n' is $k(k \geqslant 3)$-resonant.

(2) Taking a set of disjoint hexagons K of T_n''. If a hexagon s_1 in K contains the chord of T_n'' (see figure 6), then the graph consisting of all the hexagons of $T_n'' - s_1$ is $k(k \geqslant 3)$-resonant (see also [28]). If there is a hexagon s_3 in K containing exactly two vertices on c_1 or c_2, then clearly the graph consisting of the all the hexagons of $T_n'' - s_3$ is $k(k \geqslant 3)$-resonant (see also [28]). Thus K is resonant in T_n''. On the other hand, clearly all hexagons of T having at least four vertices on c_1 or c_2 are resonant. Thus, if all the hexagons in K have at least four vertices on c_1 or c_2, they are also resonant. Therefore $T_n'' - s_1$ is $k(k \geqslant 3)$-resonant.

For the cases of $\overline{T}_3$, $\overline{T}_4$ and $\overline{T}_6$, we can check them straightforwardly. □

A parallel result in benzenoid systems is the following.

Theorem 12 [28]. A 3-resonant benzenoid system must be $k(k \geqslant 3)$-resonant.

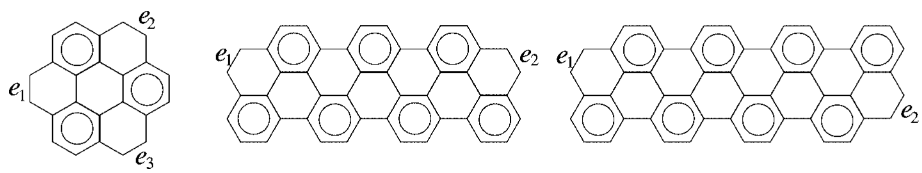


Figure 13. A Clar formula of a crown and two T_n's.

In general, we have

Theorem 13. Let T be a tubule with chord of type I, $e'_1, e'_2, \dots, e'_m$ be maximal chords of type I. Then T is $k(k \geqslant 3)$-resonant, iff $B(e'_i)$, $i = 1, 2, \dots, m$, is a $k(k \geqslant 3)$-resonant benzenoid system and $\hat{T} = T(e'_1) \cap T(e'_2) \cap \cdots \cap T(e'_n)$ is a $k(k \geqslant 3)$-resonant pure tubule.

Proof. The proof is similar to that of theorem 10. We omit its details. □

By theorems 11–13, we have

Corollary 14. A 3-resonant tubule must be $k(k \geqslant 3)$-resonant.

For $k(k \geqslant 3)$-resonant tubules, a trivial upper bound of Clar number is $n/6$, where n is the number of vertices of the tubule. This upper bound is reached by T'_n, since all the hexagons of T'_n with exactly four vertices on the perimeter of T'_n form a Clar formula of T'_n which has $n/6$ hexagons. Similarly, the Clar number of T''_n is $\lfloor n/6 \rfloor$.

The lower bound for the Clar number of the $k(k \geqslant 3)$-resonant tubules is $n/8$, where n is the number of vertices of the tubules.

The fact is based on the following two observations and our construction procedure.

(1) For the crown and T_n, we have a Clar formula K in which a set of attachable combinations do not belong to any hexagon in K (see figure 13).

(2) Deleting all the sections isomorphic to T_n and crown, we obtain some chains of hexagons. Any centers of any three consecutive hexagons of the chain are not on a straight line.

We can also check that the Clar number of $\overline{T}_3$, $\overline{T}_4$, $\overline{T}_6$ and A_3 is 2, 2, 3 and 1, respectively.

We omit the details of their proof.

5. Conclusion remark

In the experimental observation of carbon nanotubes, all the molcules have a large size and two caps [1–10]. But how about the nanotube with small size? This paper characterizes some open-ended tubules which are more stable from Clar's point of view.

For example, T_n' and T_n'' have the maximal Clar numbers $n/6$ and $\lfloor n/6 \rfloor$, respectively, where n is the number of carbon atoms. The tubules $\overline{T}_4$ and $\overline{T}_6$ have nice resonant property. We think that the corresponding tubular hydrocarbons are good candidates for synthesis, and the rolling up of multiple zigzag benzenoids or thin prolate rectanglar benzenoids is an efficient way to theoretically construct them. As for A_3 and T_3, since the curvature is large, it may be difficult to synthesize them.

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