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Some Properties of Carbon Nanotubes and their Resonance Graphs

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Abstract

Carbon nanotubes were discovered more than 30 years ago and their unique structure explains their unusual properties such as conductivity and strength. Carbon nano-
tubes without caps are also called tubulenes. The resonance graph of a tubulene reflects the interaction between its Kekulé stuctures.

In this paper we prove some properties of tubulenes and their resonance graphs. We give the explicit proof that tubulenes are planar bipartite graphs what was observed in [14] but wasn't proved. Further, it is shown that the resonance graph of every tubulene is always bipartite. We also describe the structure and the length of a shortest path in the hexagonal lattice. This result is then used to give a condition under which the resonance graph of a tubulene is not connected.

1 Introduction

Benzenoid graphs are 2-connected planar graphs such that every inner face is a hexagon. Benzenoid graphs are generalization of *benzenoid systems*, also called *hexagonal systems*, which can be defined as benzenoid graphs that are also subgraphs of a hexagonal lattice. We refer to [11, 12] for more information about these graphs, especially for their chemical meaning as representation of benzenoid hydrocarbons.

The *resonance graph* $R(G)$ of a benzenoid graph G reflects the structure of perfect matchings of G. The concept is quite natural and has a chemical meaning since perfect matchings of a benzenoid graph are Kekulé structures of a corresponding hydrocarbon molecule, therefore it is not surprising that it has been independently introduced in the chemical literature [7,10] as well as in the mathematical literature [17] under the name *Z-transformation graph.* A survey of some basic properties of resonance graph of benzenoid systems can be found in [16].

If we embed benzenoid systems on a surface of a cylinder and join some edges we obtain structures called open-ended single-walled carbon nanotubes also called tubulenes (note that there are also closed-ended single-walled carbon nanotubes i.e. carbon nanotubes with caps). They were discovered in 1991 [13] and have been since then recognized as fascinating materials with nanometer dimensions, unusual electrical and mechanical properties. In 1996 Smalley group at Rice university successfully synthesized the aligned closed-ends single-walled carbon nanotubes [15], which have property of electrical conductivity and super-steel strength. In the same year some basic properties of tubulenes were observed and their Kekulé count was given in [14]. Beside that carbon nanotubes have attracted great attention in different research fields such as nanotechnology, artificial materials, and so on. For the details, see [5,6,19].

Topological indices of carbon nanotubes are quite well investigated; for example see [1, 2,4,8,9] but not much is known about the structure of their resonance graphs. Resonance graphs of some families of tubulenes were considered in [21–23] where the connection to Lucas cubes was established and in [3,18] the equality of the Zhang-Zhang polynomial of a tubulene and the cube polynomial of its resonance graph was shown.

In this paper the bipartiteness of tubulenes and their resonance graphs is proven. Further, with the use of shortest paths in the hexagonal lattice we give the condition under which the resonance graph of a tubulene is not connected.

2 Preliminaries

First we will formally define open-ended carbon nanotubes, also called *tubulenes* ([14]). Choose any lattice point in the hexagonal lattice as the origin O. Let $\overrightarrow{a_1}$ and $\overrightarrow{a_2}$ be the two basic lattice vectors. Choose a vector $\overrightarrow{OA} = n\overrightarrow{a_1} + m\overrightarrow{a_2}$ such that n and m are two integers and $|n| + |m| > 1$, $nm \neq -1$. Draw two straight lines L_1 and L_2 passing through O and A perpendicular to OA, respectively. By rolling up the hexagonal strip between L_1 and L_2 and gluing L_1 and L_2 such that A and O superimpose, we can obtain a hexagonal tessellation $\mathcal{HT}$ of the cylinder. L_1 and L_2 indicate the direction of the axis of the cylinder. Using the terminology of graph theory, a *tubulene* T is defined to be the finite graph induced by all the hexagons of $\mathcal{HT}$ that lie between c_1 and c_2, where c_1 and

c_2 are two vertex-disjoint cycles of $\mathcal{HT}$ encircling the axis of the cylinder. The vector $\overrightarrow{OA}$ is called the *chiral vector* of T and the cycles c_1 and c_2 are the two open-ends of T.

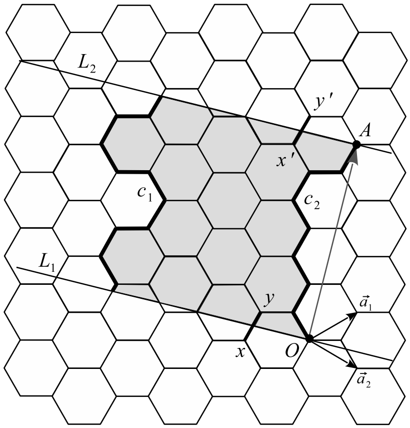

Figure 1. Illustration of a $(4, -3)$-type tubulene.

For any tubulene T, if its chiral vector is $n\overrightarrow{a_1} + m\overrightarrow{a_2}$, T will be called an (n, m)-type tubulene, see Figure 1.

An *1-factor* of a tubulene T is a spanning subgraph of T such that every vertex has degree one. The edges of the 1-factor form an independent set of edges i.e. a *perfect matching* of G (in the chemical literature these are known as Kekulé structures; for more details see [12]). Let M be a perfect matching of T. A hexagon h of T is M-*alternating* if the edges of h appear alternately in and off the perfect matching M. Such hexagon h is also called a *sextet*.

The *resonance graph* $R(T)$ of a tubulene T is the graph whose vertices are the perfect matchings of T, and two perfect matchings are adjacent whenever their symmetric difference forms the set of edges of some hexagon of T.

3 Some results about tubulenes and their resonance graphs

Every tubulene T is a planar graph since it can be drawn on a sphere. There exists such a planar drawing of T that cycle c_1 is a boundary of an interior face and cycle c_2 is a boundary of an exterior face of T.

It was mentioned in [14] that tubulenes are bipartite graphs but the explicit proof was not given, therefore we provide it.

Theorem 3.1 *Let T be a tubulene. Then T is a bipartite graph.*

Proof. We can color the hexagonal lattice with two colors (black and white), such that any two vertices with the same color are not adjacent. Let $\overrightarrow{a_1}$ and $\overrightarrow{a_2}$ be two basic vectors of the hexagonal lattice. It follows that the start point and the end point of $\overrightarrow{a_1}$ (or $\overrightarrow{a_2}$) have the same color since the distance between them is two. Let L_1 and L_2 be two straight lines from the definition of a tubulene. Consider the following:

(i) If v is a vertex on L_1, then there is exactly one vertex v' on L_2 such that $\overrightarrow{vv'} = \overrightarrow{OA}$ (in a tubulene T vertices v and v' are glued together). Without loss of generality we can assume that v is colored white. Since $\overrightarrow{OA} = n\overrightarrow{a_1} + m\overrightarrow{a_2}$ it follows from the above discussion that v and v' are colored with the same color. When we join v and v' to get a new vertex w of a tubulene T we can color it white and all its adjacent vertices are colored black.

(ii) Let $e = xy$ be an edge of the hexagonal lattice which intersects line L_1 in a point different from x and y. We can assume that vertex y lies between L_1 and L_2. Let x' and y' be such vertices that $\overrightarrow{xx'} = \overrightarrow{OA}$ and $\overrightarrow{yy'} = \overrightarrow{OA}$ (see Figure 1). As in (i) x and x' have the same color and the same is true for y and y'. But x and y have different colors. When we join lines L_1 and L_2 together we get a new edge yx' of a tubulene T where y and x' have different colors.

With this we have proved that a tubulene T can be colored with two colors such that any two vertices with the same color are not adjacent. This completes the proof. ■

The next goal is to show that the resonance graph of a tubulene is bipartite. We could have used Theorem 3.2 from [20], which says that the resonance graph of a plane bipartite graph is always bipartite, but the definition of the resonance graph in [20] is not completely the same as in this paper since we do not allow rotation of the cycles c_1 and c_2. However, in the resonance graph obtained with our definition only some edges from the resonance graph in [20] may be missing. And since the second graph is bipartite, so is also the first graph. For the sake of completeness we give the proof adapted for tubulenes.

Theorem 3.2 *Let T be a tubulene with a perfect matching. Then its resonance graph $R(T)$ is bipartite.*

Proof. We know that $R(T)$ is bipartite if and only if $R(T)$ does not contain an odd cycle.

Let $C = M_0 M_1 \dots M_t$ be a cycle in $R(T)$, where $M_0 = M_t$. Hence there exists a sequence of hexagons $h_1, h_2, \dots, h_t$ such that $E(h_i) = M_{i-1} \oplus M_i$ for every $i \in \{1, 2, \dots, t\}$. For every hexagon h of a tubulene T we define $\delta(h)$ to be the number of times h appears in the sequence $h_1, h_2, \dots, h_t$. We will show that $\delta(h)$ is an even number for every hexagon h of T. We consider two options:

(i) Let h be a hexagon with an edge e lying on a cycle c_1 or c_2. We know that $M_0 = M_0 \oplus E(h_1) \oplus E(h_2) \oplus \dots \oplus E(h_t)$, hence there must be an even number of terms in the sequence $h_1, h_2, \dots, h_t$ containing the edge e. Since h is the only hexagon of T that contains e, $\delta(h)$ must be even.

(ii) Now suppose that no edge of h lie on c_1 or c_2. Let e be an edge of h and the other hexagon containing the edge e be h'. Similar as in (i) we can see that $\delta(h) + \delta(h')$ is even. Assume that $\delta(h)$ is odd. Then $\delta(h')$ must be odd. Let e' be any edge of h' different from e and let the other hexagon containing e' be h'' – see Figure 2 (there is such a hexagon h'' since $\delta(h')$ is odd). But $\delta(h'')$ is odd too since $\delta(h') + \delta(h'')$ is even. If we repeat this discussion we can reach a hexagon h^* (if we carefully select the next hexagon on every step) such that h^* contains an edge lying on c_1 or c_2 and $\delta(h^*)$ must be odd. But $\delta(h^*)$ must be even since h^* contains an edge lying on c_1 or c_2 - a contradiction. This contradiction shows that $\delta(h)$ is even.

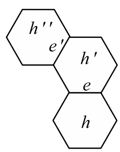

Figure 2. Hexagons h, h' and h''.

We have proved that $\delta(h)$ is an even number for every hexagon h of T. Hence $t = \sum_{h \in T} \delta(h)$ is even, i.e. C is an even cycle. ■

From examples in [3, 21–23] it is obvious that the resonance graph is not necessarily connected. We want to give a condition for T such that $R(T)$ will not be connected. But to do this, some preparation is needed. In the following discussion we will describe shortest paths in the hexagonal grid.

It is obvious that there are 6 different types of paths of length 2 in the hexagonal lattice. We can see them in Figures 3 and 4. Let paths in Figure 3(a) be called path P_1, paths in Figure 3(b) path P_2 and paths in Figure 4 path P_3.

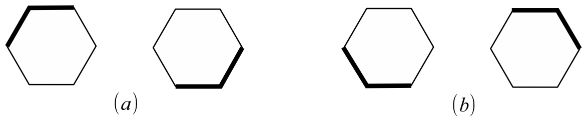

Figure 3. Paths P_1 and P_2.

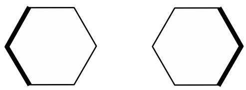

Figure 4. Path P_3.

In the preliminaries we introduced two basic vectors of the hexagonal lattice. But there is also the third basic vector, this is $\overrightarrow{a_3} = \overrightarrow{a_1} - \overrightarrow{a_2}$. These vectors represent three different directions in which we can move in the hexagonal lattice. Note that P_1 represents a move for vector $\overrightarrow{a_1}$, P_2 represents a move for vector $\overrightarrow{a_2}$ and P_3 represents vector $\overrightarrow{a_3}$.

Let C and D be two vertices of the hexagonal lattice such that $\overrightarrow{CD} = n\overrightarrow{a_1} + m\overrightarrow{a_2}$, where $\overrightarrow{a_1}$ and $\overrightarrow{a_2}$ are two basic vectors of the hexagonal lattice and n, m are integers. We will determine the length and a structure of a shortest path between C and D. Consider the following cases.

1. $m, n \geq 0$.

   Now we introduce a hexagonal coordinate system, which has two main directions – one is the direction of $\overrightarrow{a_1}$ and the other is the direction of $\overrightarrow{a_2}$ – such that C is a vertex on hexagon $(0,0)$, see the dark grey area in Figure 5. We can say that C has coordinates $(0,0)$ and that every vertex, which has the same position on hexagon (i,j) as C has on $(0,0)$, has coordinates (i,j). Let A be the set of all vertices of the hexagonal lattice to which the coordinates have been assigned. If V is the set of all vertices, then every edge of the hexagonal lattice has one vertex in A and one vertex in $V - A$. It is clear that with this notation D has coordinates (n,m) and every path between C and D contains an even number of edges and its vertices alternately belong to A and $V - A$. Thus, every path from C to D is constructed from paths P_1, P_2 and P_3.

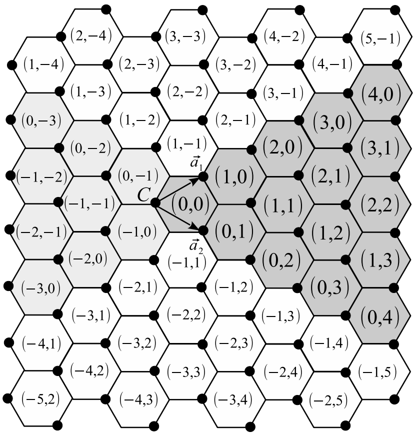

Figure 5. A hexagonal coordinate system in cases 1 and 2 (vertices in A are denoted with black dots).

If we want to construct a shortest path from vertex $C = (0,0)$ to vertex $D = (n,m)$ we should make n moves with vector $\overrightarrow{a_1}$ and m moves with vector $\overrightarrow{a_2}$. If we make a move with vector $\overrightarrow{a_3}$, two coordinates are changed and the resulting path will not be the shortest. For vector $\overrightarrow{a_1}$ we need path P_1 and for vector $\overrightarrow{a_2}$ we need path P_2. Any shortest path is obtained if we use just paths P_1 and P_2, n and m times, respectively. Hence the length of a shortest path from C to D is $2|n| + 2|m|$.

In Figure 6 we can see two examples of shortest paths between vertices C and D, where $n = 3$ and $m = 2$. Every move for vector $\overrightarrow{a_1}$ is colored black and every move for $\overrightarrow{a_2}$ is grey.

2. $m, n \leq 0$

This case is very similar to 1 since the only difference is the direction of vectors $\overrightarrow{a_1}$, $\overrightarrow{a_2}$. We consider a hexagonal coordinate system in the directions of $-\overrightarrow{a_1}$ and $-\overrightarrow{a_2}$, see the light grey area in Figure 5.

3. $n > 0, m < 0$ and $|n| \geq |m|$

In this case the third basic vector of the hexagonal lattice is important, this is $\overrightarrow{a_3} = \overrightarrow{a_1} - \overrightarrow{a_2}$. We introduce a hexagonal coordinate system with the directions of

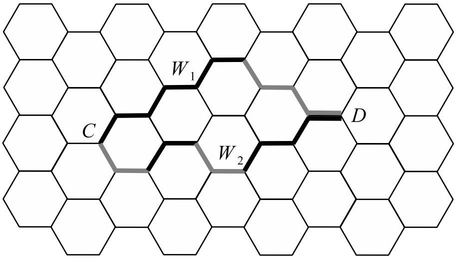

Figure 6. Shortest paths W_1 and W_2.

vectors $\overrightarrow{a_1}$ and $\overrightarrow{a_3}$, see the dark grey area in Figure 7.

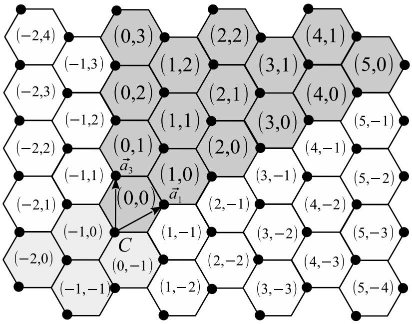

Figure 7. A hexagonal coordinate system in cases 3 and 4.

For a move in the direction of vector $\overrightarrow{a_3}$ we need path P_3. Hence every shortest path from C to D is constructed from paths P_1 and P_3. The length of every shortest path is $2|m| + 2|n + m|$ since $\overrightarrow{CD} = (-m)(\overrightarrow{a_1} - \overrightarrow{a_2}) + (n + m)\overrightarrow{a_1}$.

4. $n < 0, m > 0$ and $|n| \geq |m|$

   Consider a hexagonal coordinate system in the directions of $-\overrightarrow{a_1}$ and $-\overrightarrow{a_3}$, see the light grey area in Figure 7. By similar arguments as before we can see that every shortest path from C to D is constructed from paths P_1 and P_3. Its length is again $2|m| + 2|n + m|$ since $\overrightarrow{CD} = m(\overrightarrow{a_2} - \overrightarrow{a_1}) + (-n - m)(-\overrightarrow{a_1})$.

5. $n > 0, m < 0$ and $|n| < |m|$

   In this case a hexagonal coordinate system is constructed with vectors $-\overrightarrow{a_2}$ and $\overrightarrow{a_3}$, see the dark grey area in Figure 8.

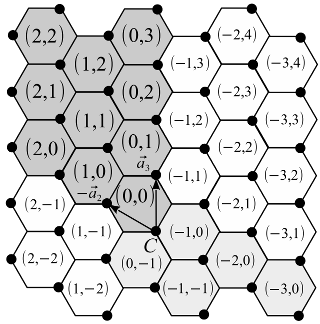

Figure 8. A hexagonal coordinate system in cases 5 and 6.

Hence every shortest path is obtained if we use just paths P_2 and P_3. Since $\overrightarrow{CD} = n(\overrightarrow{a_1} - \overrightarrow{a_2}) + (-n-m)(-\overrightarrow{a_2})$, its length is $2|n| + 2|m+n|$.

6. $n < 0, m > 0$ and $|n| < |m|$

   Similar as in Case 5, a shortest path is constructed just from paths P_2 and P_3 (i.e. with vectors $\overrightarrow{a_2}$ and $-\overrightarrow{a_3}$), see the light grey area in Figure 8. Its length is $2|n| + 2|m+n|$ since $\overrightarrow{CD} = (-n)(\overrightarrow{a_2} - \overrightarrow{a_1}) + (n+m)\overrightarrow{a_2}$.

Let T be a (n,m)–type tubulene and c a shortest cycle encircling the axis of the cylinder. Let C be a point (not necessarily a vertex) on L_1 and on a cycle c and let D be a point on L_2 such that $\overrightarrow{CD} = n\overrightarrow{a_1} + m\overrightarrow{a_2}$. Then c (drawn in the hexagonal lattice) is obviously a shortest path from C to D and without loss of generality we can assume that C (and D) is a vertex of the hexagonal lattice (if it is not, then C lies on an edge xy – such that y is between L_1 and L_2 – and D lies on $x'y'$ and we can consider a path between x and x', see Figure 1). If c is a shortest cycle encircling the axis of cylinder then c is called a *min-cycle*.

Theorem 3.3 *Let T be a tubulene where c_1 and c_2 are min-cycles. Then T has at least 4 perfect matchings and one of the components of the resonance graph $R(T)$ is an isolated vertex.*

Proof. There are three types of edges in the hexagonal lattice. First are parallel to the edge e_1, second to the edge e_2 and third to the edge e_3 (see Figure 9).

Let T be a (n,m)-type tubulene. We will consider cases 1 to 6 from the previous discussion:

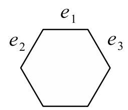

Figure 9. Edges e_1, e_2 and e_3.

- Cases 1 and 2

  Cycles c_1 and c_2 contain just paths in Figures 3(a) and 3(b) (paths P_1 and P_2). Hence, every second edge on c_1 and c_2 is parallel to e_1. Let M be the set of all edges of a tubulene T (drawn in the hexagonal lattice) that are parallel to e_1. Then M is a perfect matching of a tubulene T with no sextet. Thus, M is an isolated vertex in $R(T)$.

- Cases 3 and 4

  In this case, every second edge on c_1 and c_2 is parallel to e_2. For M we can take the set of all edges of a tubulene T (drawn in the hexagonal lattice) that are parallel to e_2. M is again an isolated vertex in the resonance graph.

- Cases 5 and 6

  Let M be the set of all edges of a tubulene T (drawn in the hexagonal lattice) that are parallel to e_3. M is an isolated vertex of the resonance graph.

Edges in M that are also on c_1 can be replaced with edges on c_1 that are not in M and we get a new perfect matching of T. Similar can be done for cycle c_2. Since there are two options for c_1 and c_2, we get four different perfect matchings of T. We have proved that a tubulene has a perfect matching which is an isolated vertex of the resonance graph, thus, $R(T)$ is not connected. ■

Theorem 3.3 claims that in the case when cycles c_1 and c_2 of a tubulene T are min-cycles, the resonance graph $R(T)$ is not connected. In Figure 10 there is an example of a tubulene where c_1 and c_2 are not min-cycles, but the resonance graph is not connected anyway. We assume that for every tubulene its resonance graph is not connected, hence we conclude the paper with the conjecture.

Conjecture 3.4 *Let T be a tubulene with a perfect matching. Then the resonance graph $R(T)$ is not connected.*

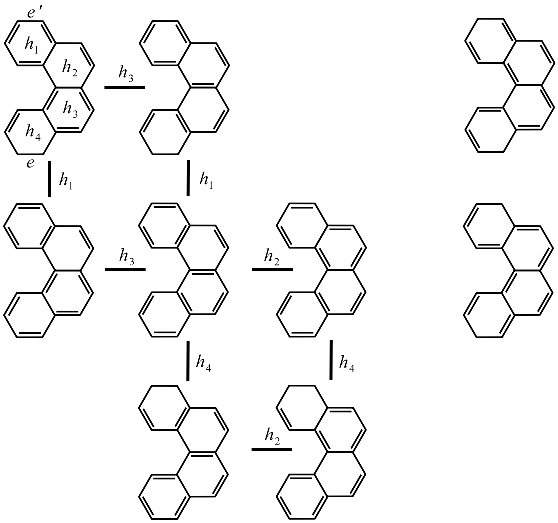

Figure 10. Resonance graph of a $(3,-3)$-type tubulene where c_1 and c_2 are not min-cycles. Edges e and e' are joined together.

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