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Resonance Graphs of Armchair Nanotubes Cyclic Polypyrenes and Amalgams of Lucas Cubes

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Abstract

Carbon nanotubes have become interesting object of research because of unusual properties such as conductivity and strength. Our interest is in a class of armchair carbon nanotubes, called cyclic polypyrenes and their resonance graphs. The resonance graph reflects the structure of perfect matchings (t.i. Kekulé structures) of a carbon nanotube. We show the connection of the resonance graph of a cyclic polypyrene to Lucas cubes; these are graphs with a vertex set of all binary strings of a given length without consecutive 1's and 1 in the first and the last bit, where two vertices are adjacent if their strings differ in exactly one bit.

The main result of this paper is that the resonance graph of a cyclic polypyrene is an amalgam of two Lucas cubes together with a box P_3^n and one isolated vertex. The direct corollary of this result is the number of Kekulé structures of a cyclic polypyrene.

1 Introduction

We continue with the research on the structure of resonance graphs of some carbon nanotubes started in [25, 26]. We focus on structures called cyclic polypyrenes. Pyrene is a hexagonal system consisted of 4 hexagons. By superimposing pyrene hexagonal systems and embedding them on a surface of a cylinder, we obtain a cyclic structure called cyclic polypyrene. They belong to very interesting structures chemically known as carbon nanotubes. Carbon nanotubes vere discovered in 1991 [11] and can be imagined as a C_{70} fullerene with many thousands of carbon rings inserted across its equator, giving a tiny tube with about 1.5 nm of diameter and a length of several microns. In 1996 Smalley group at Rice university successfully synthesized the aligned single-walled nanotubes [22], which are carbon nanotubes with the almost alien property of electrical conductivity and super-steel strength. Carbon nanotubes have attracted great attention in different research fields such as chemistry physics, artificial materials, and so on. For the details, see [2, 3, 24].

The resonance graph of a graph G reflects the structure of perfect matchings of G. The resonance graph of a cyclic polypyrene is strongly connected to Lucas cubes [1, 5, 12, 14, 18], which are subgraphs of well known Fibonacci cubes [9, 10, 13]; both of them were introduced as models for interconnection networks.

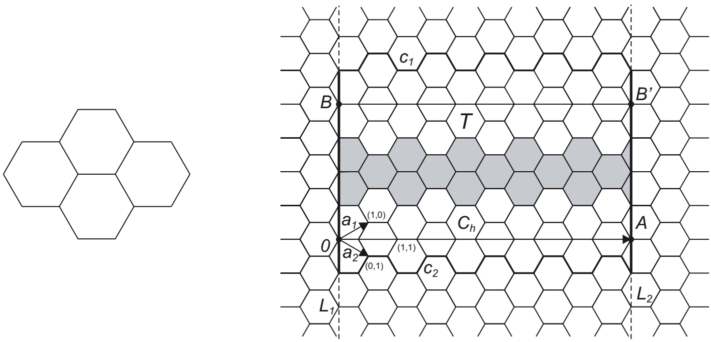
Our main result explains the structure of the resonance graph of a cyclic polypyrene; it is the union of the amalgam of two Lucas cubes together with a box P_3^n and one isolated vertex.

In the next section we give all the necessary definitions. In the third section, we state and proof the main theorem, fromm which we obtain a corollary concerning the Kekulé count of a cyclic polypyrene.

2 Preliminaries

Benzenoid graphs are 2-connected planar graphs such that every inner face is encircled by a 6-cycle (hexagon); for details see survey [8]. Benzenoid graphs are generalization of *benzenoid systems*, also called *hexagonal systems*. Pyrene is a hexagonal system consisting of 4 hexagons; see Figure 1 a). Superimposing several pyrene hexagonal systems through a hexagon we obtain a polypyrene. Further, if embedded on a surface of a cylinder we obtain a cyclic structure which belongs to the class of well known carbon nanotubes; let us define them more precisely.

Choose any lattice point in the hexagonal lattice $\mathcal{H}$ as the origin O. Let $\vec{a_1}$ and $\vec{a_2}$ be the two basic lattice vectors. Choose a vector $\vec{OA} = n\vec{a_1} + m\vec{a_2}$ such that n and m are two integers and at least one of them is not zero. Draw two straight lines L_1 and L_2 passing through O and A perpendicular to OA, respectively. By rolling up the hexagonal



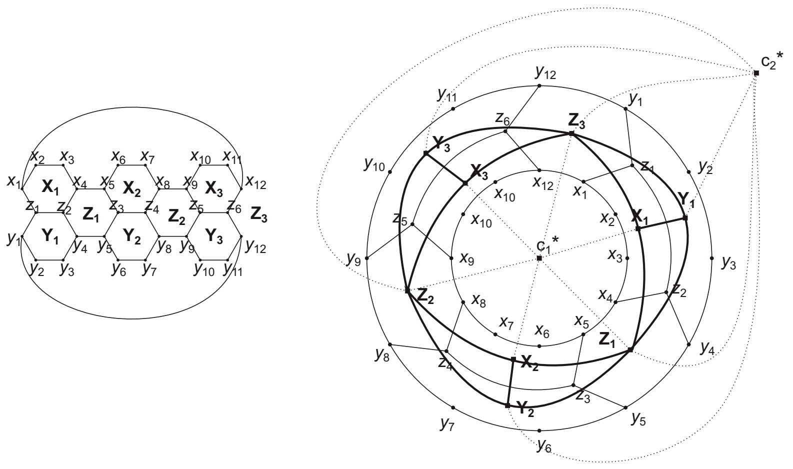
(a) (b)

Figure 1: a) A hexagonal system pyrene, b) a $(5,5)$-type nanotube T_5 called cyclic polypyrene.

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 $\mathcal{H}$ of the cylinder; see Figure 1 b). L_1 and L_2 indicate the direction of the axis of the cylinder. Using the terminology of graph theory, a *nanotube* T is defined to be the finite graph induced by all the hexagons of $\mathcal{H}$ that lie between c_1 and c_2, where c_1 and c_2 are two vertex-disjoint cycles of $\mathcal{H}$ encircling the axis of the cylinder. The vector $\vec{OA}$ is called the *chiral vector* of T. The cycles c_1 and c_2 are the two open-ends of T. If e is an edge of cycle c_1 or c_2 then it is a *peripheral* edge of T.

For any nanotube T, if its chiral vector is $\vec{OA} = n\vec{a_1} + m\vec{a_2}$, T will be called an (n,m)-type nanotube, see Figure 1 b). If $n = m$, nanotube is an *armchair nanotube* and if exactly one of n or m is zero, then it is a *zigzag nanotube*.

For $n \geq 1$ a *cyclic polypyrene* T_n is a (n,n)-type armchair nanotube consisting of n overlapping pyrene molecules as seen on Figure 1 b). Let c_1 and c_2 be the cycles encircling T_n. It is clear, that T_n is a bipartite planar graph, see Figure 2 a) and b) (note that hexagons of T_n are 6-cycles in the planar drawing of T_n). Let T_n^* be the dual graph of T_n, and let c_1^*, c_2^* be the vertices of T_n^* corresponding to cycles (faces) c_1, c_2 of T_n, respectively. Then the hexagons of T_n can be divided into three disjoint subsets denoted $\mathcal{X}, \mathcal{Y}$ and $\mathcal{Z}$. The set $\mathcal{X}$ is formed of hexagons whose corresponding vertices in a graph induced on set $V(T_n^*) - \{c_1^*, c_2^*\}$ are of degree 3 and are also incident to the vertex c_1^* in T_n^*. The set $\mathcal{Y}$ is defined analogously; the corresponding vertices are now adjacent to the vertex c_2^* in T_n^*. All other hexagons of T_n form a set $\mathcal{Z}$ (the corresponding vertices in a graph induced on $V(T_n^*) - \{c_1^*, c_2^*\}$ are of degree 4). Note that cardinalities of all three sets of hexagons for T_n are equal to n.



(a) (b)

Figure 2: a) A planar drawing of a cyclic polypyrene T_3 with labeled hexagons, b) T_3 with the dual graph T_3^*.

The following definitions are well known for hexagonal systems and can be extended to nanotubes.

A *1-factor* or a *perfect matching* of a graph G is a spanning subgraph with every vertex having degree one (in the chemical literature these are known as Kekulé structures, see [7]). Let M be a perfect matching of a graph G. A cycle c of G is M*-alternating* if the edges of c appear alternately in and off the perfect matching M.

Let P be a set of hexagons of a nanotube T. The subgraph of T obtained by deleting from T the vertices of the hexagons in P is denoted by $T - P$. It is clear that $T - P$ can be the empty graph.

Let P be a set of hexagons of a nanotube T with a perfect matching. Then the set P is called a *resonant set* of T if the hexagons in P are pair-wise disjoint and there exists such a perfect matching of T that contains a perfect matching of each hexagon in P. A resonant set is *maximal* if it is not contained in another resonant set. A resonant set P such that $T-P$ is empty or has a unique perfect matching is called a *canonical* resonant set.

The *resonance graph* $R(T)$ of a nanotube T is the graph whose vertices are the perfect matchings of T, and two perfect matchings are adjacent whenever their symmetric difference is the edge set of a hexagon of T. The concept is quite natural and has a chemical meaning, therefore it is not surprising that it has been independently introduced in the chemical literature [4, 6] as well as in the mathematical literature [23] under the name *Z-transformation graph.*

Let H_1 be a subgraph of a graph G_1 and H_2 a subgraph of G_2, where H_1 and H_2 are graphs isomorphic to a given graph H. Then the *amalgam* of G_1 and G_2 is obtained from G_1 and G_2 by identifying their subgraphs H_1 and H_2. The graph operation is called *amalgamation.*

The *Cartesian product* $G\Box H$ of two graphs G and H is the graph with the vertex set $V(G)\times V(H)$ and $(a,x)(b,y)\in E(G\Box H)$ whenever $ab\in E(G)$ and $x=y$, or, if $a=b$ and $xy\in E(H)$. The Cartesian product of n copies of a graph G is G^n.

The vertex set of the n-dimensional *hypercube* Q, $n\geq 0$, consists of all binary strings of length n, two vertices being adjacent if the corresponding strings differ in precisely one place.

The *Fibonacci cubes* are for $n\geq 0$ defined as follows. The vertex set of Γ_n is the set of all binary strings $b_1b_2\ldots b_n$ containing no two consecutive 1's. Two vertices are adjacent in Γ_n if they differ in precisely one bit.

A *Lucas cube* Λ_n is very similar to the Fibonacci cube Γ_n. The vertex set of Λ_n is the set of all binary strings of length n without consecutive 1's and also without 1 in the first and the last bit. The edges are defined analogously as for the Fibonacci cube. Both, Fibonacci and Lucas cubes are subgraphs of hypercubes. The vertices of the Lucas cube Λ_n, $n\geq 1$, are *Lucas strings* of length n and the number of all such strings is a *Lucas number* $L_n=|V(\Lambda_n)|$. The following closed formula is known as the *Binet formula* for the Lucas numbers $L_n=\left(\frac{1+\sqrt{5}}{2}\right)^n+\left(\frac{1-\sqrt{5}}{2}\right)^n$ and the first Lucas numbers are $1,3,4,7,11,18,35,\ldots$

Finally, for $X\subseteq V(G)$ let $G[X]$ denotes the subgraph of G induced by the set X.

3 Main result

The resonance graph structure of some nanotubes has been already discussed; for a single strip nanotubes called cyclic polyphenantrenes in [25] and for more general case, cyclic fibonacenes in [26]. Our main result explains the structure of the resonance graph of some related molecules, t.i. cyclic polypyrenes.

Theorem 3.1 *For a cyclic polypyrene T_n, $n \geq 1$, the resonance graph $R(T_n)$ is isomorphic to the disjoint union of an amalgam of two Lucas cubes Λ_{2n}, P_3^n and K_1.*

Proof.

Let T_n be a cyclic polypyrene and let c_1 and c_2 be the cycles encircling T_n. Further, let $\mathcal{X}, \mathcal{Y}, \mathcal{Z}$ be the sets of hexagons of T_n as described above; with $\mathcal{X} = \{X_1, X_2, \ldots, X_n\}$, $\mathcal{Y} = \{Y_1, Y_2, \ldots, Y_n\}$ and $\mathcal{Z} = \{Z_1, Z_2, \ldots, Z_n\}$, where for each $i = 1, 2, \ldots n$ any triple of vertices corresponding to hexagons X_i, Y_i, Z_i forms a 3-cycle in the dual graph T_n^*.

Let $\mathcal{M}(T_n)$ be the set of perfect matchings of T_n. $\mathcal{M}(T_n)$ can be divided into three (not disjoint) sets $\mathcal{M}_1(T_n)$, $\mathcal{M}_2(T_n)$ and $\mathcal{M}_3(T_n)$. $\mathcal{M}_1(T_n)$ is consisted of all perfect matchings of T_n that contains edges of c_1 with end-vertices of degree 2 and similarly in $\mathcal{M}_2(T_n)$ are all those perfect matchings that contain edges of c_2 with end-vertices of degree 2. And in the set $\mathcal{M}_3(T_n)$ there are perfect matchings without peripheral edges of hexagons from $\mathcal{Z}$. By the name Z-peripheral edges we mean peripheral edges of hexagons from $\mathcal{Z}$.

Let us start with the resonance graph induced on vertices from $\mathcal{M}_3(T_n)$. Since none of the Z-peripheral edges takes part in any perfect matching from $\mathcal{M}_3(T_n)$, the induced resonance graph is isomorphic to the resonance graph of n (disjoint) copies of a benzenoid graph with two hexagons, that is a naphtalene. The resonance graph of the naphtalene is a path on three vertices P_3. By the decomposition theorem from [15] the resonance graph of n copies of naphtalene is isomorphic to the Cartesian product P_3^n (see Figure 3) and therefore

$$R(T_n)[\mathcal{M}_3(T_n)] = P_3^n \, .$$

Let us proceed with the resonance graph of T_n induced with the vertex set $\mathcal{M}_1(T_n)$. Every perfect matching from $\mathcal{M}_1(T_n)$ is fixed on peripheral edges with ends of degree two on c_1. Let this set of fixed vertices be V_1. Then the subgraph of T_n induced on the vertex set $V(T_n) - V_1$ is isomorphic to a carbon nanotube called cyclic polyphenantrene (see [25]) or more general case to a cyclic fibonacene (see [26]). We know from [26] that

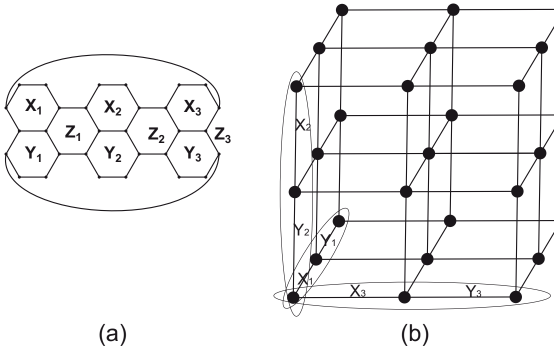


Figure 3: The resonance graph of T_3 induced with perfect matchings from $\mathcal{M}_3(T_3)$.

the resonance graph of a cyclic fibonacene with $2n$ hexagons is isomorphic to the union of Lucas cube Λ_{2n} and two isolated vertices. In the same paper the structure of Λ_{2n} is well explained; it is consists of two maximal hypercubes of dimension n, one induced with the maximal resonant set $\mathcal{Y}$ and the other with the maximal resonant set $\mathcal{Z}$. Let the first hypercubes be Q^1_Y and the other Q^1_Z; see Figure 5 a). From the structure of Lucas cube we know that they share exactly one vertex which is also a center vertex of a Lucas cube; let it be vertex u_1 (note that it is labeled with 0^{2n}). Beside that there are some other maximal hypercubes of smaller dimensions, each of them containing vertex u_1 (for more details see [26]). Let us denote the two isolated vertices in the resonance graph induced on $\mathcal{M}_1(T_n)$ with M_1 and M_1'. In one of them, say M_1, both cycles c_1 and c_2 are alternating cycles, such that every Z-peripheral edge is in M_1, see Figure 4. The other perfect matching M_1' is without Z-peripheral edges and therefore $M_1' \in \mathcal{M}_3(T_n)$. Note that this is the only perfect matching in $\mathcal{M}_1(T_n)$ without Z-peripheral edges and therefore $\mathcal{M}_1(T_n) \cap \mathcal{M}_3(T_n) = \{M_1'\}$.

Similarly, the resonance graph induced on $\mathcal{M}_2(T_n)$ is isomorphic to the Lucas cube Λ_{2n} together with two isolated vertices. The two maximum cardinality hypercubes of Λ_{2n} are now induced with the maximal resonant sets $\mathcal{X}$ and $\mathcal{Z}$ sharing a center vertex u_2, so let the first one be Q^2_X and the other one Q^2_Z; see Figure 5 a). The two isolated vertices in the resonance graph induced on $\mathcal{M}_2(T_n)$ are now M_2 and M_2', where in the perfect matching M_2 both cycles c_1 and c_2 are again alternating cycles containing every Z-peripheral edge, so $M_2 = M_1 = M$ belongs to $\mathcal{M}_1(T_n) \cap \mathcal{M}_2(T_n)$ (again see Figure 4). Since M is without

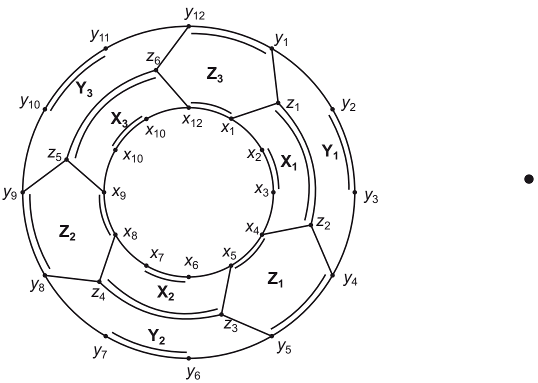


Figure 4: A perfect matching $M_1 = M_2 = M$ of T_3 that is an isolated vertex in $R(T_3)$.

alternating hexagons, it is an isolated vertex in $R(T_n)$. The other perfect matching M_2' is without Z-peripheral edges and therefore $M_2' \in \mathcal{M}_3(T_n)$ (note that $M_1' \neq M_2'$). Like before, this is the only such perfect matching and therefore $\mathcal{M}_2(T_n) \cap \mathcal{M}_3(T_n) = \{M_2'\}$.

Next we consider the resonance graph induced on the set $\mathcal{M}_1(T_n) \cup \mathcal{M}_2(T_n) - \{M, M_1', M_2'\}$ (perfect matchings M_1' and M_2' are excluded since both of them belong to $\mathcal{M}_3(T_n)$ and M is an isolated vertex in $R(T_n)$). Hypercube Q_Z^1 is a maximal hypercube of the Lucas cube Λ_{2n} and from [26] follows that the corresponding resonant set in T_n, t.i. $\mathcal{Z}$, is a canonical resonant set. Since Q_Z^2 is also a maximal hypercube of Λ_{2n} induced by a canonical resonant set $\mathcal{Z}$, hypercubes Q_Z^1 and Q_Z^2 coincide and are isomorphic to n-dimensional hypercube Q_n. Any other perfect matching from $\mathcal{M}_1(T_n)$ has at least one alternating hexagon from $\mathcal{Y}$, and perfect matchings from $\mathcal{M}_2(T_n)$ have always at least one alternating hexagon from $\mathcal{X}$. Thus we can conclude that the subgraph of $R(T_n)$ induced on perfect matchings from the intersection $\mathcal{M}_1(T_n) \cap \mathcal{M}_2(T_n)$ is isomorphic only to Q_n. Further, no perfect matching from $\mathcal{M}_1(T_n) - \mathcal{M}_2(T_n)$ is adjacent to any perfect matching from $\mathcal{M}_2(T_n) - \mathcal{M}_1(T_n)$ since in any perfect matching from the first set hexagons from $\mathcal{X}$ are not alternating and in the second case hexagons from $\mathcal{Y}$ do not alternate. Therefore the resonance graph induced on the set of perfect matchings $\mathcal{M}_1(T_n) \cup \mathcal{M}_2(T_n) - \{M, M_1', M_2'\}$ is isomorphic to the amalgam of two Lucas cubes Λ_{2n}, as seen on Figure 5 b) (note that the amalgamation is determined with the isomorfizem f between Q_Z^1 and Q_Z^2; $f(u_1) = v_2\,, f(v_1) = u_2$ where v_1, v_2 are antipodal vertices of u_1, u_2 in Q_Z^1, Q_Z^2, respectively).

$\square$

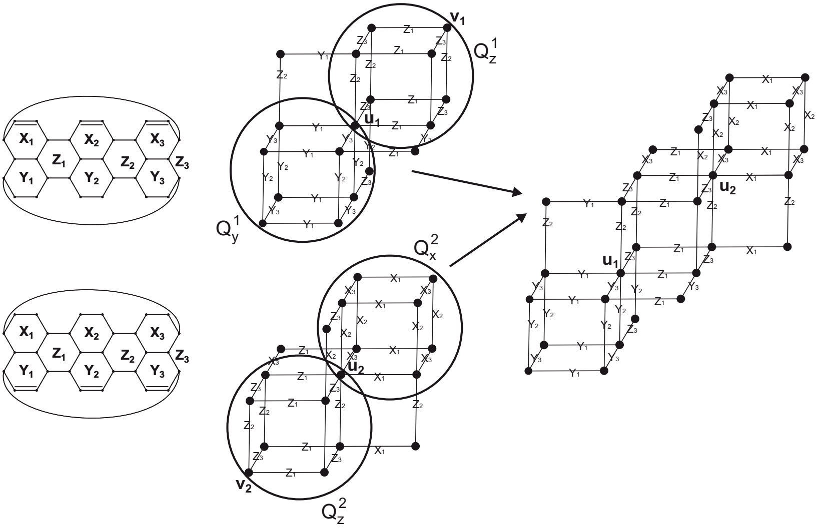


Figure 5: a) The resonance graphs induced with hexagons from $\mathcal{Y}$, $\mathcal{Z}$ and $\mathcal{X}$, $\mathcal{Z}$ b) the amalgam of two Lucas cubes.

Let $K(G)$ be the number of perfect matchings (t.i. Kekulé structures) of a graph G. The number of Kekulé structures is known only for some cases. Significant work on the topic was done in [21], followed by many others. For example, the recurrence relation for K of some capped zig-zag nanotubes was established in [16]. The Kekulé count of cyclic variants of naphtalene and benzo[*c*]phenantrenes were obtained in [17]. Some other results were obtained in [19] and [20] using the techniques of the transfer matrix. Using Theorem 3.1 and the Binet formula for the Lucas numbers we can directly get the number of Kekulé structures for a cyclic polypyrene.

Corollary 3.2 *The number of perfect matchings of a cyclic polypyrene T_n, $n \geq 1$, is*

$$K(T_n) = 2L_{2n} - 2^n + 3^n + 1,$$

where $L_{2n} = \left(\frac{1+\sqrt{5}}{2}\right)^{2n} + \left(\frac{1-\sqrt{5}}{2}\right)^{2n}$.

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