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SYMMETRY OF A CAPPED NANOTUBE

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A Euclidean graph associated with a molecule is defined by a weighted graph with adjacency matrix $M = [d_{ij}]$, where for $i \neq j$, d_{ij} is the Euclidean distance between the nuclei i and j. In this matrix d_{ii} can be taken as zero if all the nuclei are equivalent. Otherwise, one may introduce different weights for distinct nuclei. In this article, the automorphism group symmetry of a capped nanotube is computed.

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1. Introduction

The development of applications to utilize the unique properties of carbon nanotubes (CNTs) is one of the key current issues in nanostructure research and computer simulations play an essential role in this area.[1]

Graph theory is a branch of discrete mathematics concerned with relation, between objects. From the point of the graph theory, all organic molecular structures can be drawn as graphs in which atoms and bonds are represented by vertices and edges, respectively. A graph G is called a weighted graph if each edge e is assigned a non-negative number w(e), called the weight of e.

The symmetry of a graph means the automorphism group symmetry and it does not need to be isomorphic to the molecular point group symmetry. However, it does represent the maximal symmetry which the geometrical realization of a given topological structure may posses.[2,3] Automorphisms have other advantages such as in generation nuclear spin species, NMR spectra, nuclear spin statistics in molecular spectroscopy, chirality and chemical isomerism.[4-6]

One of us (ARA) proved an algorithm to compute the automorphism group of weighted graphs.[7] In this paper, using this algorithm and a GAP program[8,9], we calculate the automorphism group of a capped nanotube.

An automorphism of a weighted graph G = (V,E) is a permutation g of V with the following properties: (i) for any u,v in V, g(u) and g(v) are adjacent if and only if u is adjacent to v. (ii) for each e in E, w(g(e)) = w(e). The set of all automorphism of a weighted graph G, with the operation of composition of permutations, is a permutation group on V(G), denoted Aut(G). A non-empty subset X of V(G) is called an orbit of G under the action of Aut(G), if there exists $x \in X$ such that $X = \{\alpha(x) \mid \alpha \in Aut(G)\}$. G is called vertex transitive or simply transitive, if it has a unique orbit.

A permutation of the vertices of a graph belongs to its automorphism group if it satisfies $P^tAP = A$, where P^t is the transpose of permutation matrix P and A is the adjacency matrix of the graph under consideration. There are n! possible permutation matrices for a graph with n vertices. However, all of them may not satisfy the mentioned equation.

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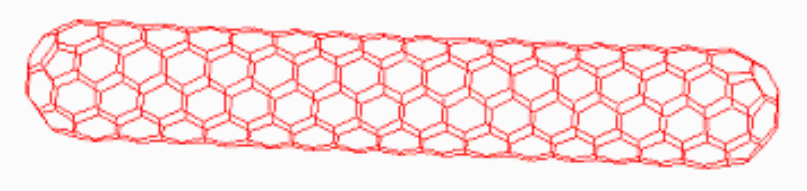

Fig. 1. A Capped (5,5) Nanotube.

2. Experimental

Since 1990, two new families of carbon allotropes have become available for experimental study, both prepared by the simple method of arc discharge. Fullerenes are molecular cages with diameters of a few Å composed of tens to hundreds of carbon atoms[10,11]. Nanotubes, on which are focused many hopes for the technological exploitation of the new forms of carbon, are of similar diameter but may be a micrometer or more in length. The first observation of nanotubes was by Iijima in 1991, who noticed fibrous structures in high-resolution electron micrographs of the deposit left on the cathode after arc discharge vaporization of graphite electrodes[12]. Calculations predict that the physical properties of the tubes will be sensitive functions of structure.

Real nanotubes are finite rather than infinite and must terminate in some way. Under the conditions of the synthesis, they may be attached to metal particles or end in amorphous carbon material, but many are observed to have polyhedral or hemi-spherical caps.

Single-walled tubes nucleate on a catalyst particle and then normally grow by adding carbon atoms to the base[13-15]. Miyauchi et al.[16] pointed out the importance of caps when studying small-diameter tubes grown by chemical vapor deposition. The structures of the nanotube caps at nucleation have an important role at the apparent preference for some nanotube chiralities in their growth method. The caps of carbon nanotubes and their interaction with the catalyst will be the key for controlling the chirality of single-walled carbon nanotubes during growth[17].

Capping clearly influences both physical and chemical properties of the tubes. Examples are easily found. Graph theory predicts that an infinite leapfrog tube has a vanishing band gap[18] whereas the geometrically closed leapfrog fullerene, however large, has a finite HOMO–LUMO gap which is relatively large for its atom count[19]. Similarly, any open tube of hexagons is a bipartite graph and thus has a symmetrical spectrum, but this symmetry is lost on capping, as a fullerene with pentagons is no longer bipartite. Curvature localizes steric strain and renders the caps vulnerable to chemical attack, allowing opening, capillary filling and re-sealing by suitable reagents[20].

Nanotube caps can have various structures, shapes and degrees of curvature. Tubes of the types (5,5) and (9,0) are of appropriate diameters to be capped by fullerene hemispheres[21]. However, caps can have different levels of sphericity and arrangements of atoms, and can also be nearly flat, conical or bill-like[21]. The one absolute requirement is that they satisfy Euler's theorem[22,23], which states that in order to achieve complete closure of a hexagonal lattice of any size or shape, it is necessary to incorporate a total of exactly twelve pentagons. In the case of nanotubes, this means that each cap, whatever its shape or structure, must include six pentagons.

A CNT consists of a rolled-up hexagonal planar lattice of carbon atoms which structure is uniquely defined by a chiral vector denoted by (**n,m**). Depending on the values of **n** and **m**, a variety of CNT with different chemical and physical properties can be produced. A Fortran program is written for generating desired length of different CNTs for any given set of the chiral vector (**n,m**). In this program, at first, a sheet of graphite is constructed. Then, a part of this sheet is selected (its shape is determined by **n** and **m** vectors, Fig. 1). Finally, the selected part is shifted row-by-row to the coordinate center followed by proper rotational transformations to produce the desired CNT.

Generation of a cap for an armchair CNT is started with a carbon hexagon as the core of the cap. Then, layers of hexagonal rings are added to this central hexagon until the diameter of cap

approaches diameter of the desired CNT. To suite the cap for the armchair CNT with radius of interest, the alternative hexagons of the last row which are facing the central hexagon via their gons are converted to pentagons. The cap produced in this way is called a *hexagon cap*. It is also possible to start with a pentagon as the core for the construction of a pentagon cap suitable for an armchair CNT using exactly the same procedure. Therefore, Examples of the caps produced in this procedure starting with hexagon and pentagon as the central core of the cap are illustrated in Fig. 2.

The overall symmetry of the obtained capped CNT depends on the way the cap is connected to the CNT as well as on the initial symmetries of the cap and CNT. In this work, we have used the eclipsed conformation for the two caps connected to the two ends of the CNTs. This conformation imposes a limitation on the length of the armchair CNT. The pentagon cap itself has a larger angular strain as compared to a free hexagon cap, while it has a smaller angular strain at the junction to CNT.

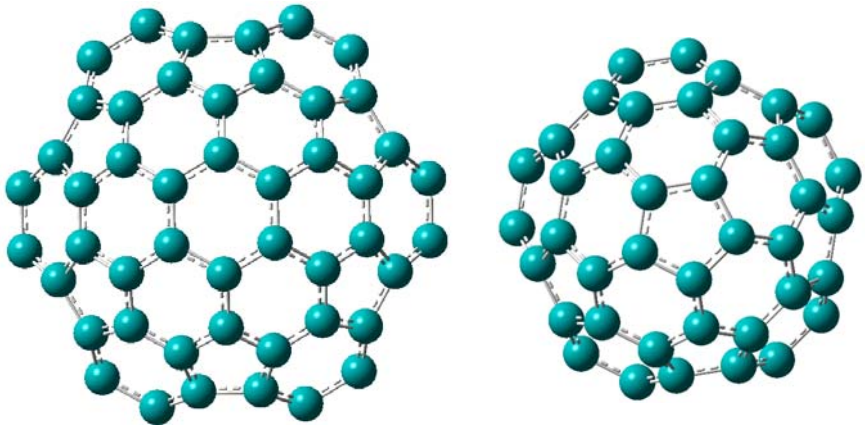

*Fig. 2. Two types of caps (left: hexagon, right: pentagon) constructed in this work, respectively for (**6**,**6**) and (**5**,**5**) CNT's.*

3. Main Results

In this section we first describe some notation, which will be kept throughout. Let G be a group and N be a subgroup of G. N is called a normal subgroup of G, if for any $g \in G$ and $x \in N$, $g^{-1}xg \in N$. Moreover, if H is another subgroup of G such that $H \cap N = \{e\}$ and $G = HN = \{xy \mid x \in H, y \in N\}$, then we say that G is a semidirect product of H by N denoted by $H \wedge N$. If H is also normal in G then $G \equiv H \times K$, the direct product of H an K. We now assume that D_{2n} denotes the dihedral group of order 2n, $n \geq 3$. This group can be presented by $D_{2n} = \langle x , y \mid x^n = y^2 = 1, y^{-1}xy = x^{-1}\rangle$. It is easy to see that D_{2n} is isomorphic to the semidirect product of a cyclic group of order 2 by a group of order n.

Consider an (**n,n**) capped nanotube T. We prove that the point group of this nanotube has dihedral type, when n is odd. To do this, we suppose that V_1, V_2, …, V_n are hexagons of the first row of 2-dimensional lattice of T and $\sigma = (1,2,\ldots,n)$. Then σ determines a permutation x of the molecular symmetry group G of T. On the other hand, there is a C_2 axial perpendicular to the C_n main axial but it does not have the horizontal plane. Now it is easy to see that the group G is generated by x and y. This group satisfies the relations $x^n = e$, $y^2 = e$ and $x^{-1}yx = x^{-1}$ and so it is a dihedral group of order 2n or its point group is D_{nd}, as desired.

We now assume that n is even. Then there is an additional symmetry element, i.e. the horizontal plane. This point group has D_{nh} structure containing some dihedral subgroup.

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