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Hypothetical toroidal, cylindrical, and helical analogs of C_{60}

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ABSTRACT

Toroidal, cylindrical, and helical analogs of C_{60} buckyball are theoretically constructed and analyzed. In these structures, pentagons and heptagons are separated compactly by hexagons in analogy to pentagons in C_{60} and heptagons in C_{168} proposed by Vanderbilt and Tersoff (1992) [2]. Specifically, all nonhexagons therein are surrounded by hexagons and hexagons are surrounded alternatively by hexagons and nonhexagons, i.e. these structures are polyhedra of Clar type with all their Clar rings nonhexagonal. Quantum chemical calculations have been carried out which show that they possess stabilities comparative to that of C_{60}. And their structural features are also investigated in detail. Buckled carbon nanotubes deriving from buckytori with periodically varying radii are suggested to be candidacies for the product of coalescing arrays of C_{60}. The helicity of the buckyhelices as a function of their characterizing shifting parameters is studied. In the limit of large shifting parameter, the buckyhelices adopt an unusual geometric form that has not been reported in the literature yet.

1. Introduction

In the early nineties, right after the discovery of carbon nanotubes (CNT) [1], Vanderbilt and Tersoff [2] proposed a negative-curvature analog of C_{60}, which is basically a triply periodic C_{168} structure composed of only hexagons and heptagons. While the pentagons in C_{60} are all surrounded by hexagons and the hexagons are surrounded by alternating hexagons and pentagons, the heptagons in C_{168} are surrounded by hexagons and the hexagons are surrounded by alternating hexagons and heptagons. The resulting structure for C_{168} is like replacing each carbon atom in a diamond lattice with hollowed carbon nanotetrapod (superatom), and the bonding between these superatoms with a suitable nanotube (superbond). Topologically speaking, C_{60} is isomorphic to a sphere and C_{168} is isomorphic to the D-type triply periodic minimal surface (TPMS) [3–7]. According to the Gauss–Bonnet theorem, each unit cell in C_{168} contains exactly 24 heptagons and every carbon atom in this structure belongs to a particular heptagon. This amazing analogy between the two molecular structures raises an immediate question: Is it possible to construct a graphitic structure, which may possess both positive and negative Gaussian curvatures at the same time, such that nonhexagons are completely surrounded by hexagons and hexagons are surrounded alternately by hexagons and nonhexagons? In the discussion made by Fowler and Pisanski [8], this is equivalent to asking for Clar type fullerenes with all their Clar rings nonhexagonal, where C_{60} and C_{168} are both solutions possessing positive and negative curvatures throughout, respectively.

In this paper, we provide a positive answer to the question. Three different solutions are suggested where they have the same shapes and topologies of a torus, a cylinder, and a helical tube, respectively. The latter two are singly periodic infinite structures and are derived from the torus case. All three graphitic structures proposed have pentagons and heptagons in equal numbers, and each pair of pentagon and heptagon comes together with four hexagons. In other words, the ratio between the numbers of polygons in these structures are $N_5 : N_6 : N_7 = 1 : 4 : 1$, where N_i is the number of i-gons. Quantum chemical calculations showed that the heat of formation of the toroidal and cylindrical structures are comparable to that of C_{60}. The structural properties and general geometric features of the three molecular structures are discussed.

2. Buckytori

It is well known that any toroidal carbon nanotube (TCNT) with all faces hexagonal can be formed by bending, and connecting the ends, of a finite straight carbon nanotube. The polyhex TCNT has been of theoretical interest especially on its magnetic response because of its curious topology and geometry [9–23]. It was found that for certain magic numbers of chiral vectors and the number of unit cells the polyhex TCNT may carry extremely large paramagnetic persistent current under an external magnetic field [9]. However, for the polyhex TCNTs to be stable without seriously distorting chemical bondings therein, the number of carbon atoms

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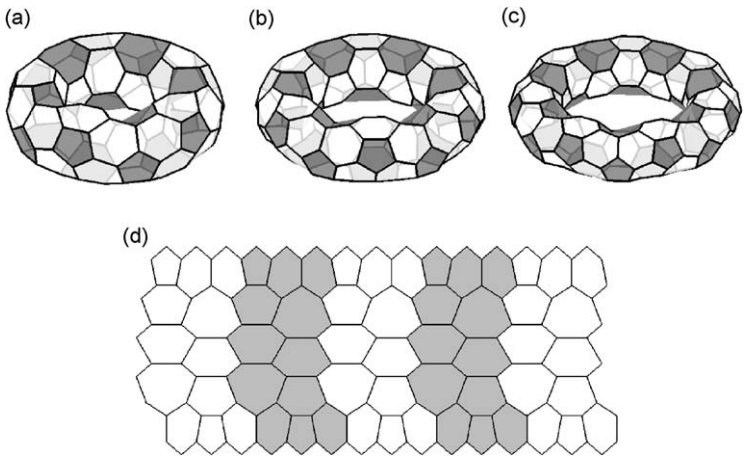

Fig. 1. The three proposed buckytori, where pentagons and heptagons are surrounded by one layer of hexagons. Each rotational unit cell contains 24 carbon atoms. (a) D_{5d} C_{120}. (b) D_{6d} C_{144}. (c) D_{7d} C_{168}. (d) The face representation of unfolded D_{5d} C_{120}, where the top and the bottom rows of atoms are repeated.

must be as large as thousands or more so each σ bond bears relatively small distortion. Experiments reporting the existence of giant ring-like TCNTs have been carried out [24,25], which are possible candidates of polyhex TCNTs.

Though not yet experimentally confirmed, quantum chemical calculation shows that TCNTs with nonhexagonal defects can be stable molecules, even if they contain only about a hundred of carbon atoms [26–31]. This is because by properly inserting pentagons (heptagons) at the outer-rim (inner-rim) of the torus, the deviations of bond lengths and bond angles from planar graphite are greatly reduced. A very general systematic construction and classification method for TCNTs with nonhexagonal rings that includes most of the existing construction methods for defect-containing TCNTs as a subset [29–34] was proposed by the present authors [35].

By carefully examining the topology and connectivity of these TCNTs, we found that one particular family of TCNTs precisely satisfies all requirements raised in the previously proposed question. These TCNTs belong to the D_{nd} point group, where n is the rotational symmetry number. In Fig. 1(a)–(c), we show three particular TCNTs with $n = 5, 6, 7$ cases, and the planar graph shown in part (d) corresponds to the unfolded TCNT with $n = 5$ based on its face representation. Each of the rotational unit cells contains 24 carbon atoms, so the resulting D_{5d}, D_{6d}, and D_{7d} TCNTs contain 120, 144, and 168 atoms, respectively. It is interesting to note that the number of carbon atoms in a D_{7d}-TCNT is the same as that in a single unit cell of C_{168}. As stated in the question and shown clearly by the three TCNTs in Fig. 1, the pentagons and heptagons are surrounded by hexagons while the hexagons, depending on their loci, are surrounded alternately by three hexagons plus three heptagons, or two heptagons and one pentagons, or one heptagons and two pentagons. In analogy to C_{168}, we deliberately call these TCNTs "buckytori", since they are the realization of buckyball on a torus. As discussed by Vanderbilt and Tersoff, C_{60} and C_{168} are derived from the *inflation* transformation of C_{20} (dodecahedron) and C_{56} parent molecules. The three TCNTs shown in Fig. 1, C_{120}, C_{144}, and C_{168}, can also be *deflated* to one third smaller molecules containing only $2n$ pairs of pentagons and heptagons. The deflation process in these cases can be seen as removing all the hexagons out of the parent structures or, as commented by Vanderbilt and Tersoff, as replacing each hexagon by a single carbon atom at the center of it.

The optimized positions of inequivalent atoms of the total five buckytori, with rotational symmetry number ranging from four to eight, based on the semi-empirical AM1 quantum chemical calculation [36] are given in Table 1. Since these TCNTs are D_{nd}-symmetric, we only report the coordinates of seven inequivalent atoms in the table. By applying the reflection with respect to yz-plane, one can obtain the other five coordinates for atoms with negative x values. The C_2 rotation about $(\cos(2\pi/n), \sin(2\pi/n), 0)$ can generate all 24 coordinates in a single unit cell. Finally the C_n rotation about z-axis will generate the total $24n$ atoms of the molecules.

In Table 2, we present some of the structural and physical information of these TCNTs using the AM1 method. It can be seen that the heat of formation per atom of the buckytori, depend on the rotational symmetry number, are comparable to that of C_{60}, although the deviations of bond lengths and bond angles from graphite are a little bit higher. The stabilities of general fullerenes can be explained by a continuum elastic theory [37–43], where the formation energies of curved graphitic structures are the summation of strain energy of bending planar graphene and the local energies of defects. The strain energy term is proportional to integration of the square of mean curvature over the surface of the structure. Since the buckytori possess curvature comparable to that of C_{60} meanwhile contain more nonhexagonal defects than

Table 1
AM1-optimized coordinates of inequivalent atoms of TCNT C_{120}, C_{144}, and C_{168}. See text for the generating method of the whole molecule.

Atom	C_{120}			C_{144}			C_{168}		
	x	y	z	x	y	z	x	y	z
1	0.651	−2.917	0.685	0.656	−3.605	0.688	0.664	−4.344	0.666
2	1.429	−3.125	1.915	1.514	−3.998	1.808	1.569	−4.860	1.703
3	1.353	−4.575	2.097	1.343	−5.435	1.990	1.334	−6.284	1.890
4	0	−5.168	1.792	0	−6.024	1.709	0	−6.875	1.625
5	0.769	−5.543	−1.548	0.747	−6.469	−1.528	0.733	−7.364	−1.537
6	1.227	−5.943	−0.214	1.197	−6.983	−0.223	1.167	−7.960	−0.255
7	0	−5.949	0.624	0	−6.929	0.631	0	−7.859	0.617