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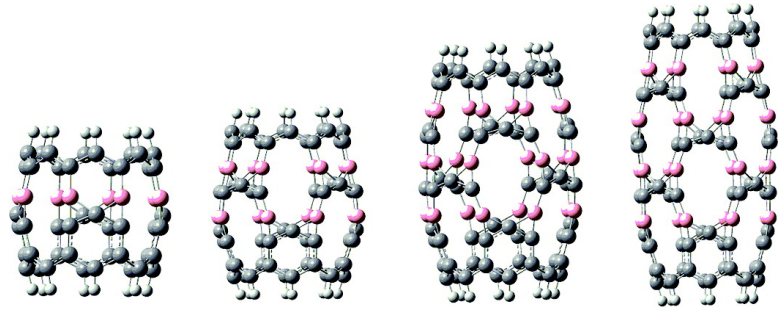

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Zigzag Boron−Carbon Nanotubes with Quasi-planar Tetracoordinate Carbons

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Since the discovery of the carbon nanotube by Iijima in 1991,[1] single-wall carbon nanotubes (SWNTs) have a standing interest in experimental and theoretical domains[2,3] owing to their potential applications in nanoscience and nanotechnology. It was well-known that the wall of SWNT consists of carbon hexagons and its two terminal caps contain the carbon pentagon. All of the carbon atoms in SWNTs adopt an approximate sp^2 hybrid. In 1970, Hoffmann and co-workers proposed a kind of novel bonding way of sp^2 carbon, that is, planar tetracoordinate carbon (ptC).[4] Stimulated by the ptC studies, a chemistry of the "hypercoordinate flat carbon" has received considerable attention recently.[5−24] In 2005, Li et al. found hydrometal complexes containing two ptC atoms to be stable.[9] Furthermore, multi-ptC (mptC) centers in organoboron compounds constructed by assembling three basic building blocks and carbon rings were predicted to be stable by Minyaev et al.[10] On the basis of such an assemble strategy, an effective route to construct novel structures with the ptC arrangements was proposed. More recently, we have investigated a series of belt-like and tubular boron and carbon clusters with mptC or multiquasi-ptC (mqptC), and these structures are predicted to be stable.[11] If the tubular segments with mqptC is embeded into the zigzag carbon nanotube, what would happen?

Here we consider four kinds of basic subunits (N1, N2, N3, and N4) with different numbers of the ptC layer as shown in Figure 1. Curling of the belt-like structure will yield the zigzag boron−carbon nanotube with mqptCs, and Figure 2 exhibits the formation process of nanotube from the belt-like structure comprising the N2 subunit. According to the general SWNT nomenclature, we add an index into (m, n), that is, (m, n, i), to denote the novel nanotube with mqptCs, where i is the number of the mqptC layer. For example, as Figure 2 displays, there are two mqptC layers in the (8, 0) nanotube, and it is denoted as (8, 0, 2).

The boron−carbon tubes of (m, 0, i) (m = 6, i = 1−3; m = 8, 10, and 12, i = 1−4) have been optimized at the B3LYP/6-31G* level. For (6, 0, 1), in consideration of the three C_2CB_2 arrangements, there are two isomers (see Figure 2S in Supporting Information). B3LYP calculations with the 6-31+G* and 6-31G* basis sets have performed to assess the stability of the two isomers of (6, 0, 1). The results show that the isomer with three C_2CB_2 units in same direction is more stable than that in any different direction. This indicates that the C_2CB_2 units toward the same direction may result in the lower-energy structure. As can be seen from the possible structures consisting of the N2 subunit in Figure 1, the different arrangements of two C_2CB_2 subunits result in three kinds of isomers B1, B2, and B3 (see Figure 3S in Supporting Information). The three isomers are in C_{4v}, D_{3d}, and D_{3d} symmetry, respectively. The energy order of the isomers is B1 < B2 < B3, and the less stable B2 and B3 have an imaginary frequency. The low-energy isomer B1 with the C_2CB_2 units in the same direction is predicted to be stable, and the relatively high stability of the same direction arrangement of C_2CB_2 units has been noticed in our previous studies.[11] Therefore, present calculations focus on the zigzag boron−carbon tubes containing the same-direction C_2CB_2 units, and all calculations have been performed by the Gaussian 03 program.[25]

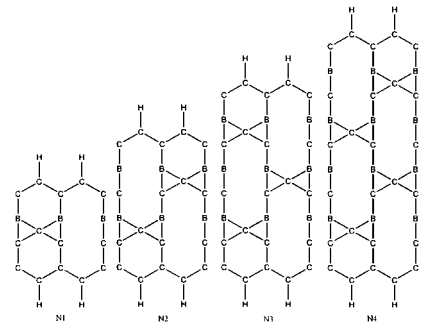

Figure 1. The subunits of the zigzag boron−carbon nanotubes with the ptC atoms (The subunit is about one-third of the whole tube).

The optimized bond distances of B-ptC and C-ptC in the (m, 0, 1) nanotube are about 1.56 and 1.41 Å, respectively. There are two kinds of C_2CB_2 units in the (m, 0, 2) nanotube, and corresponding B-ptC and C-ptC bond distances range from 1.57 to 1.59 Å and from 1.41 to 1.43 Å, respectively. In the (m, 0, 3) tube, the bond distance of B-ptC is intermediate between 1.59 and 1.61 Å, and the C-ptC separation changes from 1.42 to 1.44 Å. The (m, 0, 4) tube has similar B-ptC and C-ptC bond lengths in comparison with (m, 0, 3). The sum of the optimized four bond angles associated with the ptC atom in the (m, 0, i) tubes varies from 354° to 359° as the index i increases from i = 1 to i = 4, suggesting that the (m, 0, i) nanotubes contain multiquasi-ptC centers. At the B3LYP/6-31G(d) level, vibrational analyses of (m, 0, i) (m = 6, 8, 10, and 12; i = 1−2) show that these tubes are stable structures without imaginary frequency except for (8, 0, 2). However, B3LYP/6-31G calculations on the zigzag tubes of (8, 0, i) (i = 1−4) indicate that their optimized structures are almost unchanged and they are stable species without imaginary frequency. Such discrepancy in frequency calculation of (8, 0, 2) arises from the use of different basis sets.

In contrast with the zigzag SWNTs of $(12, 0)_k$,[26] the HOMO−LUMO gap of (m, 0, i) decreases monotonously with

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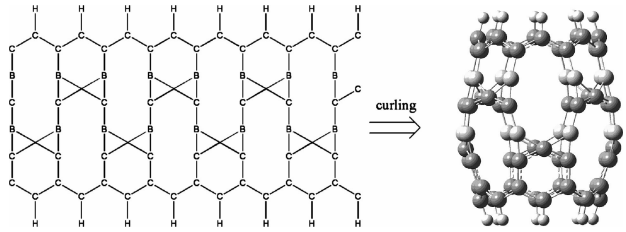

Figure 2. The formation scheme of the zigzag boron−carbon tube of (8, 0, 2).

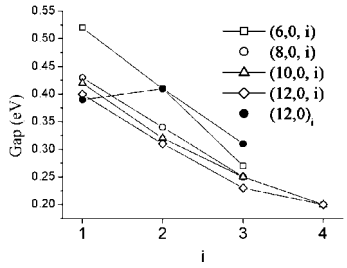

Figure 3. The HOMO−LUMO gaps of zigzag boron−carbon tubes (*m*, 0, *i*) vs *i*.

the increase of diameter and length of the nanotube as shown in Figure 3. The HOM−LUMO splitting of (*m*, 0, *i*) decreases from 0.52 to 0.20 eV as *m* and *i* increase. The novel boron−carbon tubes thus exhibit metal properties. Noted that the HOMO−LUMO gap and the HOMO energy of the nanotubes (12, 0)$_k$ and (12, 0, *i*) with almost the same atoms and lengths are comparable as shown in Figure 3. For example, the HOMO−LUMO gaps of (12, 0, 1) and (12, 0)$_2$ are 0.40 and 0.39 eV, respectively, and (12, 0, 2) and (12, 0)$_4$ have the same gaps of 0.31 eV.

The natural charge populations reveal that the electron charges on ptC in all structures are negative and they generally change from $-0.19e$ to $-0.31e$, whereas the charges on B are positive and they are about $0.75e$. The ptC atoms in the top layer in nanotube have almost the same charge populations while the charges on ptC in the same nanotube increase from top to bottom. For example, in (12, 0, *i*) the charges on the top layer are -0.304, -0.315, -0.305, and $-0.301e$ for $i = 1-4$, respectively, and charge populations from top to bottom for (12, 0, 4) are -0.301, -0.237, -0.193, and $-0.189e$. The selected orbitals of (6, 0, 1) indicate that there are conjugated π bonds within the C_2CB_2 unit and between the C_2CB_2 unit and its adjacent atoms in the tubular wall (see Supporting Information). Such extended π bonding may stabilize these nanotubes (*m*, 0, *i*). Since the most stable nanotubes (*m*, 0, *i*) are in C_{nv} point group, the all of structures have dipole moments. The dipole moments of nanotubes (*m*, 0, *i*) decrease with the increase of their length and diameter. Among these tubes, the nanotube (6, 0, 3) has the greatest dipole moment of 10.89 Debye, and the nanotube (12, 0, 1) has the smallest one of 1.63 Debye.

Unlike the structures of carbon nanotube, the wall of boron−carbon tube with ptC atoms contains the 10-membered ring comprising six carbon atoms and four boron atoms. The different series of nanotubes with the ptC atoms have different window sizes for their 10-membered rings. There are 1, 2, 3, and 4 kinds of 10-membered ring windows for the nanotubes (*n*, 0, *i*) ($i = 1-4$), respectively. And their sizes are about 2.9 $\times$ 5.6 Å^2 for $i = 1$, 3.2 $\times$ 5.3, 3.3 $\times$ 5.7 Å^2 for $i = 2$, 3.2 $\times$ 5.3, 3.8 $\times$ 5.3, 3.2 $\times$ 5.9 Å^2 for $i = 3$, and 3.2 $\times$ 5.3, 3.8 $\times$ 5.3, 3.7 $\times$ 5.5, and 3.2 $\times$ 6.0 Å^2 for $i = 4$. The size of 10-membered window increases with the increase of *i*. Such large windows allow relatively large atoms and small molecules to enter into the nanotubes, and thus such novel nanotubes with ptC may serve as potential storage or catalytic support materials.

In summary, we have constructed four kinds of novel zigzag boron−carbon nanotubes with ptC atoms. Their structures, stabilities, and bonding properties have been explored by DFT calculations. Calculations show that these novel zigzag tubes (*m*, 0, *i*) generally have very small HOMO−LUMO gaps and they behave as metals for enough long tubes. This differs from the conventional SWNTs of (*m*, *n*) which bear a character of metal as the $m - n$ difference is a multiple of 3.[27] Structurally, there are big windows on the walls of nanotubes and they are promising in design for functional materials.

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Supporting Information Available: Complete ref 25; relative energies, HOMO−LUMO gaps, optimized geometries, the sizes of the 10-membered ring windows of nanotubes (*m*, 0, *i*), the isomers of (6, 0, 1) and (6, 0, 2), electron charges populations of C_2CB_3 units in nanotubes (*m*, 0, *i*). This material is available free of charge via the Internet at http://pubs.acs.org.

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