

Structures and Electronic Properties of Peanut-Shaped Dimers and Carbon Nanotubes

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The structures and electronic properties of peanut-shaped dimers and carbon nanotubes constructed from C_{60} molecules are investigated using ab initio self-consistent field molecular and crystal orbital methods based on the density-functional theory. The calculations show that the formation of peanut-shaped structures without octagonal carbon rings is energetically favorable. The obtained band structures indicate that the peanut-shaped nanotube can be a semiconductor or a metal.

Introduction

The structural diversity of C_{60} oligomers and polymers has attracted great interest, because different structures may lead to different properties. The coalescence of two fullerene cages can lead to a peanut-shaped dimer which was first proposed by Strout et al.¹ and observed in 1999.² Recent research has shown that, under heating³ or electron-beam (EB) irradiation⁴ conditions, the C_{60} molecules encapsulated in single-wall carbon nanotubes (SWNTs) can coalesce to form peanut-shaped dimers as a main product at first time, and eventually can form peanut-shaped carbon nanotubes (PCNTs). C_{60} films can also form this type of structures. J. Onoe et al. found that EB-induced C_{60} film is a peanut-shaped carbon nanomaterial.^{5,6} By use of a four-probe measurement, they found that the peanut-shaped polymer exhibits metallic characters.

The experimental Raman³ or IR^{2,6} spectra and the related theoretical calculations² have provided significant information of the polymerized C_{60} . However, no X-ray data of the peanut-shaped dimer and PCNT are provided in experiments, and thus the detailed structures are still not so clear for the nanomaterials. Further theoretical exploration is useful for understanding the possible structures and electronic properties of these peanut-shaped materials. There have been some theoretical simulations^{1,2,7} on the peanut-shaped dimers and the PCNT with MNDO, tight binding (TB), and molecular dynamics (MD) methods, but further investigation is necessary for understanding more about the peanut-shaped structures, especially for the PCNT. The study of PCNT is just in the beginning. What structures and electronic properties the PCNTs have is not well understood. It is guessed that the metallic characters of the EB-induced peanut-shaped polymer are due possibly to the formation of a 3D network.⁵ Nevertheless, could a one-dimensional (1D) PCNT exhibit metallic characters? The TB and LDA pseudopotential plane-wave calculations showed that a PCNT resulting from the fusion process of C_{60} molecules without removing any atom is a semiconductor;⁷ however more possible PCNT structures are still needed to explore. Study of the structure–property relationship for PCNTs should be of benefit to the design of novel tubular carbon structures with specific functions.

In the present work, we have investigated several possible structures and electronic properties of the PCNTs as well as

the corresponding peanut-shaped dimers using ab initio self-consistent field molecular and crystal orbital (SCF-MO and SCF-CO) methods based on the density-functional theory (DFT). According to our knowledge, no ab initio SCF-CO calculation on the PCNTs is reported so far.

Models and Computational Details

Six peanut-shaped dimers (simply called P1–P6) are constructed as shown in Figure 1. Among them, P3 and P4 are obtained by fusion of two pentagons belonging to two different C_{60} cages, while P1, P2, P5, and P6 are constructed from coalescence of the two hexagons. The nomenclature of the peanut-shaped dimers follows ref 1, but we also add the symmetry for further structural division. For example, P56/66- C_{3v} denotes the peanut-shaped dimer derived from one C_{60} with pentagon–hexagon bonds broken and another with hexagon–hexagon bonds broken, and it has C_{3v} symmetry. These dimers had been proposed,^{1,8} except P2, which is studied for the first time.

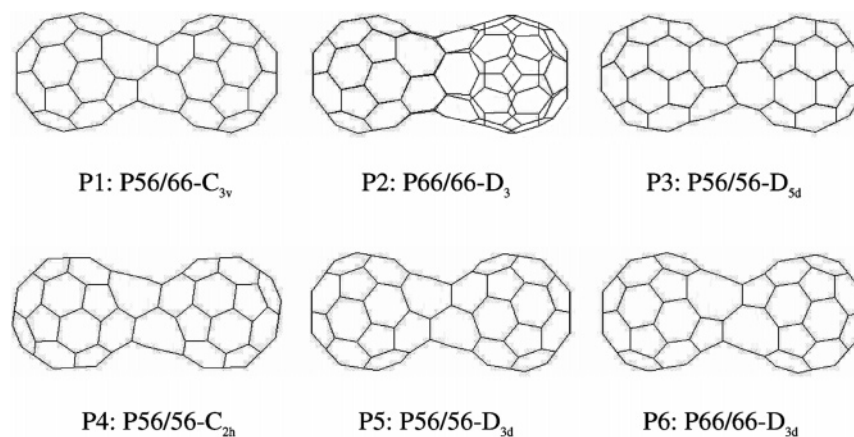
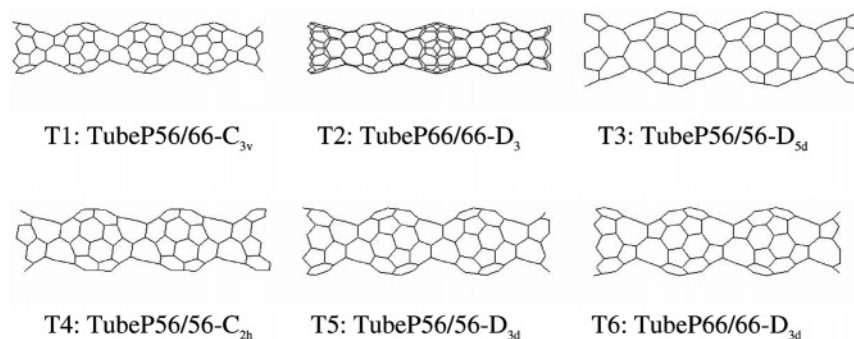
Six 1D PCNTs labeled with T1–T6 (see Figure 2) are constructed from the corresponding peanut-shaped dimers with the same symmetries. For T3–T6, the smallest repeating cell contains 60 carbon atoms. However each unit cell of T1 and T2 contains 120 carbon atoms for keeping the 1D periodic structures.

The structures of the six peanut-shaped dimers are fully optimized using the DFT-B3LYP^{9,10} functional at the 6-31G(d) level with the GAUSSIAN98 program.¹¹ This is also the first time to calculate the dimers by means of the B3LYP functional at 6-31G(d) level. Optimizations with and without symmetry constraints are both performed. The difference of the calculated results under the two conditions is very small. For example, the energy difference is the largest for P6 optimization but is only 0.8 kJ/mol for the two optimized P6 structures. Therefore, the following discussions are all based on symmetry-constraint calculated results.

To get the structural parameters of the unit cell of PCNTs, the middle parts composed of sixty carbon atoms in the corresponding peanut-shaped dimers are directly taken as the unit cell for T3–T6. As for T1 and T2, the unit cells containing 120 carbon atoms are built by coalescence of two middle parts of the corresponding dimers.

The band structures and density of states of the PCNTs are calculated using the B3LYP-SCF-CO method at the same level

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**Figure 1.** Structures of peanut-shaped dimers.**Figure 2.** Models of PCNTs.**TABLE 1: Energies, Electronic Properties (in eV), and Numbers of Non-Hexagons for the Peanut-Shaped Dimers**

dimer	E_b	N_5	N_7	N_8	HOMO	LUMO	E_g
P1	-0.17	21	3	3	-5.69	-3.41	2.28
P2	-0.42	18	6	0	-4.72	-3.90	0.82
P3	-0.76	22	10	0	-5.65	-3.26	2.39
P4	0.22	22	2	4	-5.55	-3.36	2.20
P5	-1.03	18	6	0	-5.78	-3.28	2.51
P6	0.55	24	0	6	-5.64	-3.60	2.04
C ₆₀	0	12	0	0	-5.99	-3.22	2.77

with CRYSTAL98 program.¹² It is pointed out that DFT has become a standard model in periodic system calculations,^{13–15} and the hybrid B3LYP functional has also been successfully utilized in the periodic systems.^{16–19} In the SCF-CO calculations, shrinking factors are set to 40, and default values of convergence criteria in CRYSTAL98 program are used.

Results and Discussion

A. Peanut-Shaped Dimers. The energies and electronic properties of peanut-shaped dimers are listed in Table 1. Here we define the binding energy E_b per 60 carbon atoms related to I_h C₆₀ cage for the dimers as

$$E_b = E_{\text{peanut}}/2 - E_{\text{C}_{60}}$$

From Table 1, we can see that formations of P1, P2, P3, and P5 dimers are energetically favorable, i.e., the coalescence of two C₆₀ molecules leads to more stable systems. On the other hand, the E_b is larger than zero for P4 and P6, hence the coalescence is endothermal for the two dimers. The order of stability is P5 > P3 > P2 > P1 > P4 > P6. This order for P1, P5, and P6 agrees with that of the MNDO calculation¹. The analysis in refs 2 and 6 gave that IR spectra of the polymerized C₆₀ perhaps reflected the vibration of peanut-shaped dimer P5/

66. According to previous theoretical study¹ and our DFT calculations here, forming this structure is favorable to the stability for the coalescence of two C₆₀ cages.

The carbon rings in these peanut-shaped dimers have pentagons, hexagons, heptagons, and octagons. The numbers of nonhexagon rings obey following rule

$$N_5 - N_7 - 2N_8 = 12$$

where N_5 , N_7 , and N_8 are the numbers of pentagons, heptagons, and octagons, respectively. Because of the existence of non-planar heptagons and octagons, the dimers are the systems with both positive and negative Gaussian curvatures, but C₆₀ is a structure with only positive Gaussian curvature. It seems that the stability of the dimers has something to do with the numbers of octagons. Those dimers with fewer octagons are more stable. Table 1 shows that the three most stable dimers P5, P3, and P2 have no octagonal rings, and the numbers of octagons increase with the decrease of the stabilities for P1, P4, and P6. Although P5 and P6 have the same symmetry D_{3d} , P5 is most stable but P6 most unstable. Hence, the coalescence pattern is very important to determine the stability of the dimers. The coalescence forming more octagonal rings seems unfavorable to the stability. Moreover, the stabilities of these dimers are also affected by the conjugation degree in coalescence region. For more stable structures, the bond lengths are more average and the angles are more closed to 120. For example, in the coalescence region of the most stable dimer P5, the bond lengths and bond angles are in the range of 1.384–1.480 and 118.3–124.8 Å, respectively. But in the most unstable dimer P6, they are 1.373–1.511 and 109.2–133.3 Å, respectively. The most unstable dimer has the most octagonal rings among the six dimers. The conjugation in octagonal rings is not as good as that in hexagons, which may lead to less stable structures.

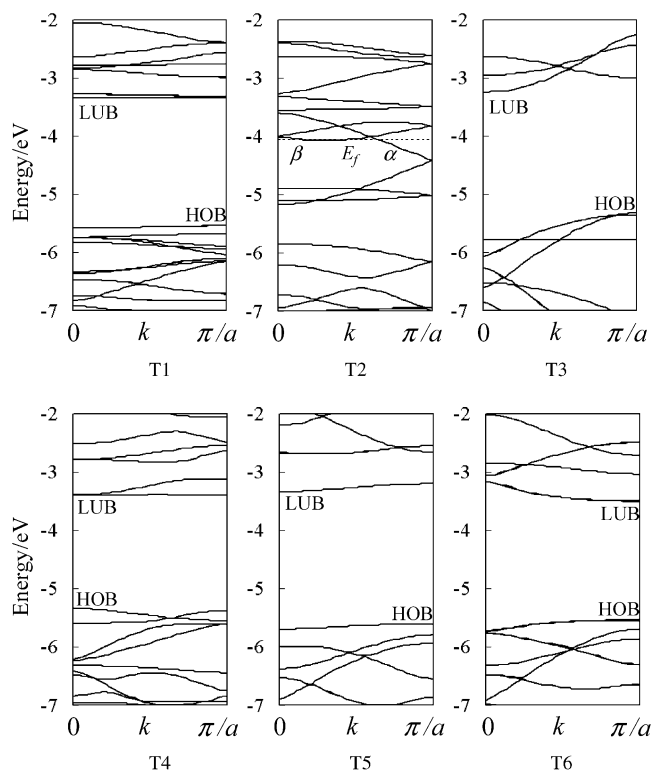


Figure 3. Band structures of the PCNTs.

TABLE 2: Energies (E) Per Sixty Carbon Atoms Related to a Single I_h C_{60} Molecule and Electronic Properties of PCNTs (in eV)

PCNT	E	HOCO	LUCO	E_g	HOB width	LUB width
T1	1.38	-5.54	-3.34	2.20	0.040	0.002
T2 ^a	-0.05	-4.05	-4.05	0	0.806	0.251
T3	-1.15	-5.33	-3.25	2.08	1.269	0.990
T4	0.90	-5.34	-3.40	1.94	0.215	0.002
T5	-1.67	-5.61	-3.34	2.28	0.081	0.137
T6	1.66	-5.54	-3.50	2.04	0.187	0.330

^a HOCO and LUCO energies of T2 are just the Fermi level, and HOB and LUB of T2 are the two partially filled bands.

From Table 1, we can see that the highest-occupied molecular orbitals (HOMOs) and the lowest-unoccupied molecular orbitals (LUMOs) for these dimers are all higher and lower than those of C_{60} , respectively. Hence the energy gaps between LUMO and HOMO levels become smaller after the coalescence. Generally, a large energy gap is unfavorable to the excitation of electrons, thus the dimers with larger energy gap may have higher kinetic stability. P5 has the largest energy gap and the lowest energy, and therefore P5 should be the most favorable to both thermodynamic and kinetic stabilities among the dimers studied. Although the Koopmans' theorem is not valid in DFT calculation, the rise of HOMO and the decline of LUMO should always favor the ionization and attraction of electrons, respectively. Hence, compared with C_{60} , the ability of losing and accepting an electron is increased for the peanut-shaped dimers, but the changes are small except for P2.

B. PCNTs. The calculated band structures and the obtained electronic properties for the PCNTs are shown in Figure 3 and listed in Table 2, respectively.

From Table 2, it can be seen that the energy order of PCNTs is $T5 < T3 < T2 < T4 < T1 < T6$. The 56/56 D_{3d} coalescence is always the most stable whether for a dimer or a polymer from the point of view of energy. The order of stabilities for the three most stable PCNTs is the same as that for the

corresponding dimers. Moreover, the extension along the tube axis is still energetically favorable for the three most stable PCNTs. Hence, it is confirmed again that the coalescence without producing an octagonal ring is exothermic. The Monte Carlo simulation⁷ for the three- C_{60} system led to a linking pattern similar to T3. Maybe T3 is easier to form than T5 from a point of view of dynamic process, though T5 is more stable than T3. Among the structures without octagons, P2 becomes unstable energetically in going to T2 in comparison with P3 and P5. Perhaps this is concerned with the change of the highest-occupied levels from P2 to T2. The crystal orbital analysis shows that the partially filled bands α and β for T2 in Figure 3 are mainly derived from the HOMO and LUMO of the P2 dimer, respectively. Also the bottom of the α band is -4.41 eV (at $k = \pi/a$), 0.31 eV higher than the HOMO of P2. The electrons in the β band have an even higher energy (about -4.05 eV). Therefore, the average energy of electrons in the α and β bands is quite higher than that in the HOMO of P2. Although the energies of the systems are not determined by the electronic energy of the highest-occupied levels, higher highest-occupied energy should be unfavorable to the stability.

Figure 3 shows that there exist band gaps (E_g) between the highest-occupied band (HOB) and the lowest-unoccupied band (LUB) in all PCNTs except T2. Therefore PCNTs are all semiconductors except T2. The LDA pseudopotential plane-wave calculations also gave that a PCNT similar to T5 is a semiconductor.⁷ For the five semiconductors, the energy gaps have no significant difference between the PCNTs and the corresponding dimers, which indicates that the extension of C_{60} molecules through the five coalescence types cannot reduce the energy gap greatly. Because the levels of HOCOs and LUCOs are close to those of the HOMOs and LUMOs of the corresponding dimers, the change of energy gaps is small for the five PCNTs. The EB-induced C_{60} polymer with metallic property was supposed to have a possible 3D network composed of peanut-shaped polymers similar to T1.⁵ Although the SCF-CO calculation shows that T1 exhibits semiconducting property, it cannot be sure whether the 3D network composed of T1 polymers is a semiconductor or a metal. Nevertheless, even a 1D PCNT can be a metal, such as the T2 structure. As a matter of fact, the energy gap of the P2 dimer is the smallest among the dimers studied. The bottom of the β band is about -4.07 eV, lower than the LUMO of P2, and consequently the difference between the bottoms of α and β bands is 0.34 eV and is smaller than the energy gap of P2. The calculated dispersion of the α band is 0.81 eV, thus wider than the difference between the bottoms of α and β bands, which leads to the cross of α and β bands. Hence, the extension from dimer to polymer through 66/66 D_3 coalescence causes overlap of the frontier bands in T2, which leads to partially filled bands and zero band gap. Moreover, formation of metallic T2 is energetically favorable. Therefore the PCNTs studied can be a semiconductor or a metal, which is similar to the usual carbon nanotube. It is very possible that these 1D PCNTs have also great potential for developing new nanoelectronic materials.

From Table 2, we can see that the frontier bandwidths of T3 are the widest, and those of T1 are the narrowest. The frontier bandwidths of the three most stable PCNTs are all larger than those of 1D C_{60} polymer with a [2 + 2] connection mode.^{20,21} The bandwidths are concerned with the atomic orbital overlap on the PCNT. From the obtained crystal orbitals, it can be found that the frontier orbitals of T3 are relatively continually distributed on the whole tube, but for T1, the atomic orbitals contribute little to the frontier crystal orbitals in the coalescence

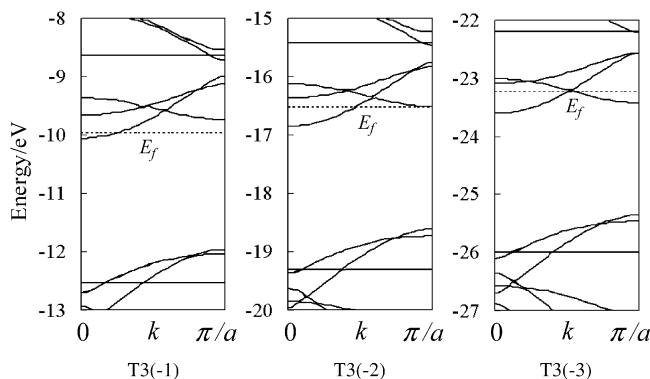


Figure 4. Band structures of the anionic T3. The charge numbers per unit cell are given in parentheses.

region, thus the orbital overlap is greatly decreased in the coalescence region, and it results in the very narrow bands. Because narrow bandwidth is unfavorable to the move of charge carriers, the PCNT with narrow bands should not be a good candidate for conducting material, such as T1 structure. For the metallic T2, the crystal orbitals of the α band show that the interaction of p_π orbitals in the coalescence region at middle of the unit cell is a strong antibonding interaction. Moreover, the crystal orbitals of the α band are also relatively continually distributed on the whole tube. Accordingly, the bottom of the α band is higher than the HOMO of the P2 dimer, and this band has relatively wider dispersion (0.81 eV). The α band is gradually increased from $k = \pi/a$ to $k = 0$ due to the increase of antibonding interaction of p_π orbitals in the coalescence region between the nearest neighbor unit cells, which leads to the overlap with β band.

Since doping with electron donors or acceptors is an important method to produce functional materials, we have also performed SCF-CO calculations on anionic PCNTs with 1–3 extra electrons per unit cell and the same geometric structures of the corresponding neutral PCNTs. In the calculations, because the unit cell of a periodic system must be neutral, the charges are compensated by adding a uniform background charge density in the CRYSTAL 98 program.¹² The calculations show that the extra electrons fill the unoccupied bands almost in a rigid-band manner, and the shape of bands changes little but the band levels decline with the filling of extra electrons. For T2, the filling of extra electrons does not change the metallic property due to the overlap of the partially filled bands. Since the filling with odd electrons always results in partially filled bands, the monovalent and trivalent anionic PCNTs are all metallic. For the bivalent anionic PCNTs, the situation is different for different polymers. The LUBs of neutral T1, T4, and T5 are not degenerate; thus the corresponding bivalent anionic tubes are semiconductors due to that the LUBs are completely filled. For T3 and T6, the LUBs are degenerate, two extra electrons make the LUBs half-filled, and therefore the bivalent anionic T3 and T6 are metals. Since the changes of band structures for all anionic PCNTs are similar, as an example, only the band structures of anionic T3 are shown in Figure 4. Selecting T3 is because it has degenerate LUBs and is energetically favorable. Compared with the band structures of the neutral T3 (see Figure 3), it is easy to understand that the rigid-band theory is valid in the PCNTs on condition that the geometrical structures are kept unchanged with the filling of extra electrons.

The calculated density of states (DOS) at fermi level for neutral T2 is 6 states/eV/spin/ C_{60} . The DOS for those metallic anionic PCNTs are in the range of 2–6 states/eV/spin/ C_{60} .

These values of DOS are not larger than those of alkali-metal-doped C_{60} crystals.^{22,23}

Conclusion

Several models of the peanut-shaped dimers and carbon nanotubes obtained from the coalescence of C_{60} cages are investigated using DFT-B3LYP functional at 6-31G(d) level. The geometric structures of the dimers are fully optimized. On the basis of the optimized structures of the dimers, the 1D PCNTs are constructed. It is found that the stabilities of the peanut-shaped structures are dependent on the coalescent patterns. The structures without the octagonal rings are energetically favorable.

According to the SCF-CO calculations, we found that the 1D peanut-shaped carbon nanotube can be a semiconductor or a metal, which is concerned with the coalescent structure. A 3D network is not a necessary condition to display metallic characters for the PCNTs. The filling of extra electrons is almost in a rigid-band manner. 1D conducting materials may be produced from the PCNTs. The obtained values of DOS for the neutral and anionic metallic PCNTs are in the range of 2–6 states per eV per spin per C_{60} , which are not larger than those for the alkali-metal-doped C_{60} crystals.

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