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Energetic trends of single-walled carbon nanotube ab initio calculations

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Abstract Hartree–Fock (HF) calculations for a variety of single-walled carbon nanotube (SWCNT) systems indicate linear relationships between electronic energies and changes in length and circumference for both armchair and zigzag type nanotubes. A simple protocol to predict energies for large SWCNT (C atoms >500) is developed through a set of structural parameters and AM1 optimized geometries from small SWCNTs. The energetic trends shown by the calculations are used to support the theory of SWCNT nucleation from a preformed carbon, or graphene with six 5-member rings, cap.

Introduction

Single-walled carbon nanotubes (SWCNTs) are a conceptually simple material: a sheet of graphene rolled into a tube. However, they have attracted the interest of research scientists, industry and governments because of their large number of potential applications. While Tibbets [1] grew carbon nanotubes as early as 1984, Ijima [2] first documented the carbon nanotube in 1991 by high resolution TEM; fifteen years later the United States government is contributing 1.2 billion dollars towards research and production of nanotechnology, with carbon nanotubes (CNTs) as the flagship nanomaterial [3].

SWCNTs are the perfect example of structure defining properties. Gao and Herndon [4] and Dresselhaus et al. [5] were among the first to show that these structures have four distinct geometries: zigzag, armchair, chiral zigzag and chiral armchair. Hamada et al. developed an indexing system that is used to describe the helicity of a nanotube [6]. It has been observed that the different structures (type and diameter) dictate the energy and band gap characteristics of the material [7–11]. The carbon nanotube cap or endcap plays an important role in modeling techniques, since the specific placements of hexagons and pentagons in the end cap will create an array of nanotubes with predictable geometries [12]. Since, carbon nanotubes (single-walled or multi-walled) are always capped, as shown in Figs. 1–3; it has been proposed that end caps act as a nucleus for SWCNT growth, either with a metal catalyst [13] or without [12]. Nucleation occurs when a cap forms homogenously. In some cases, this occurs in order to satisfy a minimum energy configuration; a tube will heterogeneously grow from the end cap rather than closing off into a fullerene capsule.

The size of this nanomaterial is not only what elicits interest, but also what causes difficulty in characterizing the growth processes and properties. With current manufacturing techniques, controlling the diameter, length, number of concentric walls or concentric tubes and chirality of CNTs is difficult if not possible. By understanding how tubes form and which structures are more favorable, it may be possible to control and optimize growth in order to use CNTs to their full

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Fig. 1 TEM bright-field image of MWCNTs produced by pyrolized tire in a DC arc in air

potential. Determining which tube configurations are more likely to form during growth will allow for an easier transition between conceptual or theoretical devices and manufactured devices.

This research seeks to demonstrate which configurations of SWCNTs are more energetically favorable by comparing total and atomic energies as the length, circumference and type change. This information is then used to determine a quantitative structure property relationship. Simple structural parameters are used in combination with AM1 and electronic energies to determine an equation used to correlate the electronic energies of smaller SWCNT systems with larger SWCNTs. This is useful since calculations for larger (>500 atom) tubes become computationally cumbersome, but nonetheless more practical. Due to the difficulty in achieving self-consistent field convergence and the long computational times involved in modeling systems with large atomic numbers it is virtually impracticable to model MWCNTs. Studying SWCNTs and double-walled carbon nanotubes (DWCNTs) may allow growth parameters to be established for MWCNT system. That is, specific SWCNTs may provide a fundamental epitaxial nucleation unit, which would presumably determine the MWCNT structural features.

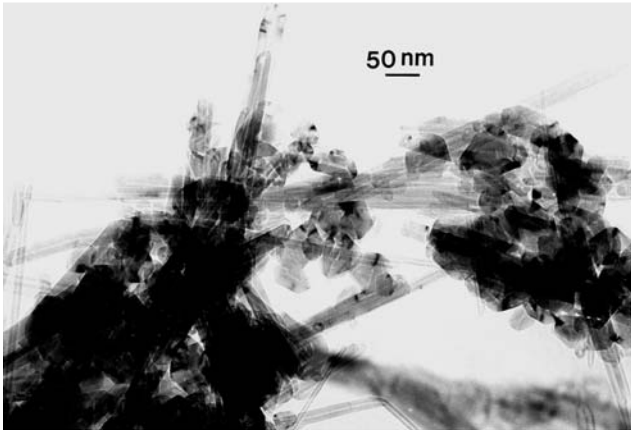

Fig. 2 TEM bright-field image of MWCNTs produced by pyrolized tire in a DC arc in helium

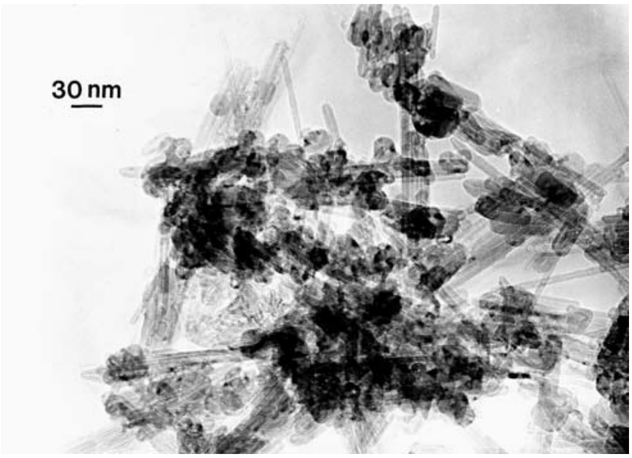

Fig. 3 TEM bright-field image of MWCNTs produced by a propane flame

Homogenous nucleation is most easily described as self-solidification; a solid phase nucleates from the liquid or vapor phase with no catalyst or impurities acting as initial nucleation sites. Heterogeneous nucleation occurs when a catalyst or impurity acts as an initial nucleation site. A variety of nucleation mechanisms have been proposed for SWCNT growth. The more common theories and practices include heterogeneous nucleation in the form of catalytic growth by the tip or root methods, but it has also been proposed that end caps play a significant role in nucleation. Reich et al. [13] proposed that cap growth on a catalyst allows for epitaxial type growth of nanotubes. They propose that if cap growth can be controlled then the chirality of the nanotube can be controlled, since a finished cap will grow only one (*n*,*m*) nanotube. This work is similar to our previous theories (Lair et al.

[12]) except that nucleation of the cap occurs homogenously from the gas or vapor phase followed by heterogeneous growth of the tube body. These findings are supportive of earlier proposals of fullerene-related nucleation as presented by Liu and Cowley [14]. Guo et al. [15] also described carbon nanotubes in the form of multi-walled fullerenes in the context of self-assembly by homogeneous carbon condensation in the gas phase. They concluded that carbon multi-walled tube growth was inherent in the condensation of pure carbon vapors.

The formation of an end cap provides a unique, critical nucleus for nanotube growth because as a homogeneous nucleus forms in carbon vapor, there is no corresponding volume free energy term since the critical nucleus is a hemispherical shell. The CNT, which grows from this hemispherical nucleus, can then be considered to grow heterogeneously (or auto catalytically). Consequently, carbon nanotube growth represents a unique growth phenomena in the vapor phase because only the incipient end cap nucleus growth is homogeneous, while subsequent tube growth and opposite cap formation, as well as subsequent growth of concentric layers to produce MWCNTs can be considered heterogeneous (or autocatalytic) growth [12]. From this theory, the proposed method of MWCNT growth would occur with a SWCNT acting as a *seed* or initial nucleus for subsequently layers.

Computational details

All calculations in this work were performed using the Gaussian 03W suite of software [16]. Geometries were optimized using semi-empirical AM1 calculations and electronic energies were determined with the Hartree-Focke (HF) 6-31G level of theory. It should be noted that all energies are give in atomic units (au) also known as Hartrees (1 au = 1 Hartree = 627.5095 kcal/mol). These basis sets and models were used to optimize the time and accuracy required for the large number of calculations needed for this study. Density functional theory (DFT) calculations (LSDA/STO-3G//B3LYP/3-21G) were performed on some of the systems in order to compare accuracy. It has been shown that LSDA/STO3-G optimizations give similar results to higher-level calculations [17] and the B3LYP/3-21G calculation has been shown to give very accurate heat of formations for hydrocarbons and nanotubes [18]. Calculations were run on an IBM eServer pSeries 590 SMP system with 24 POWER5 1.67 GHz processors and 96 GB of main memory.

Results and discussion

Experimental data

Transmission electron microscope (TEM) bright-field images showing a variety of carbonaceous materials including SWCNTs, MWCNTs and multi-layer fullerenes are shown in Figs. 1–3. These samples were produced from pyrolized tire powder injected into a 50 amp, DC arc in air, a pyrolized tire powder injected into a 130 amp, DC arc in helium and from a propane flame exhaust, respectively, as described by Murr et al. [19]. The inner diameters (ID) of CNTs in the images were measured and the average ID was found to be 3 nm (Fig. 4). Producing this size SWCNT would require greater than 500 atoms and would take a considerable amount of computational time to model. It has been shown that there is a possibility for formation of sub-nanometer size tubes [18], but our interest was to study the energetic trends of tubes that are most likely to form, and shown for example in Figs. 1–3. In this work, armchair tubes from 0.8 nm diameter (6,6) thru 2.44 nm diameter (18,18) and zigzag tubes from 0.5 nm diameter (6,0) thru 1.6 nm diameter (19,0) were studied in order to extrapolate the electronic energies for larger tubes (~3 nm) (Fig. 4). It should also be noted that the inner diameter of these MWCNT is what we will call the diameter of the *seed* SWCNT. We are interested in this size nanotube so that the growth characteristics of MWCNT systems (Figs. 1–3) can be better understood.

Carbon nanotube length

Increasing the length of a SWCNT requires the addition of benzenoids (6-member rings) to the body of the tube. There are no structural changes in the

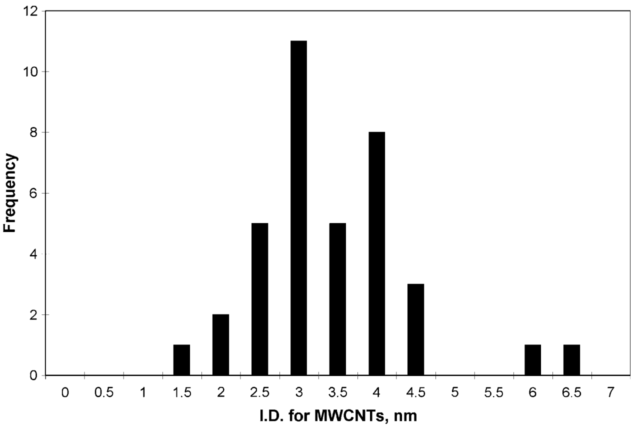

Fig. 4 Histogram of the inner diameters of collected MWCNTs

atomic arrangement of atoms, there is only the addition of atoms. It seems intuitive then that the energy changes between nanotubes of different lengths would be dependent only on the number of additional atoms.

Computations were performed for zigzag (12,0) (0.94 nm diameter) and armchair (6,6) (0.81 nm diameter) SWCNTs, with double-capped ends only containing carbon atoms, a single capped end with the opposite end terminated in hydrogen atoms and no end caps with both extremities terminated in hydrogen, as the length of the tube increased. Figure 5 and 6 show how the structure of a zigzag and armchair nanotube change as the length of the tubes increase. The zigzag tubes shown in Fig. 5 show a tube with one interior row of benzenes capped at both ends and a tube with three interior rows of benzenes capped at both ends. Figure 6 shows the progression of an armchair tube as the length increases. Figure 7 shows the end caps used for the (12,0) and (6,6) SWCNTs.

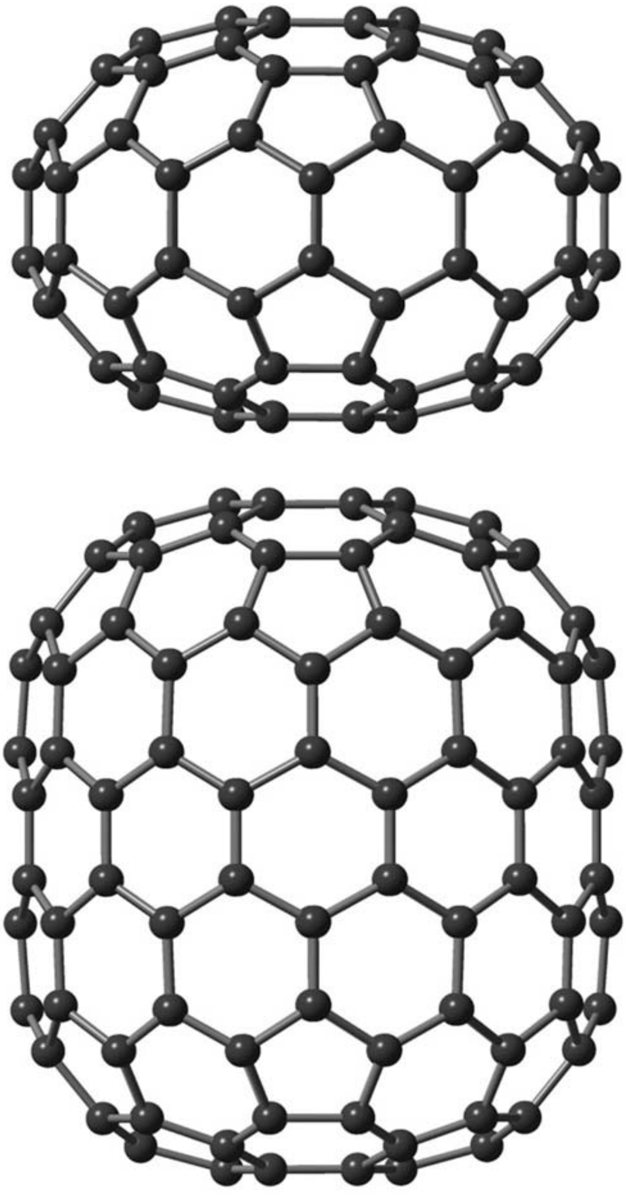

Fig. 5 Zigzag SWCNT composed of one interior row of benzenoids (top) and three interior rows (bottom)

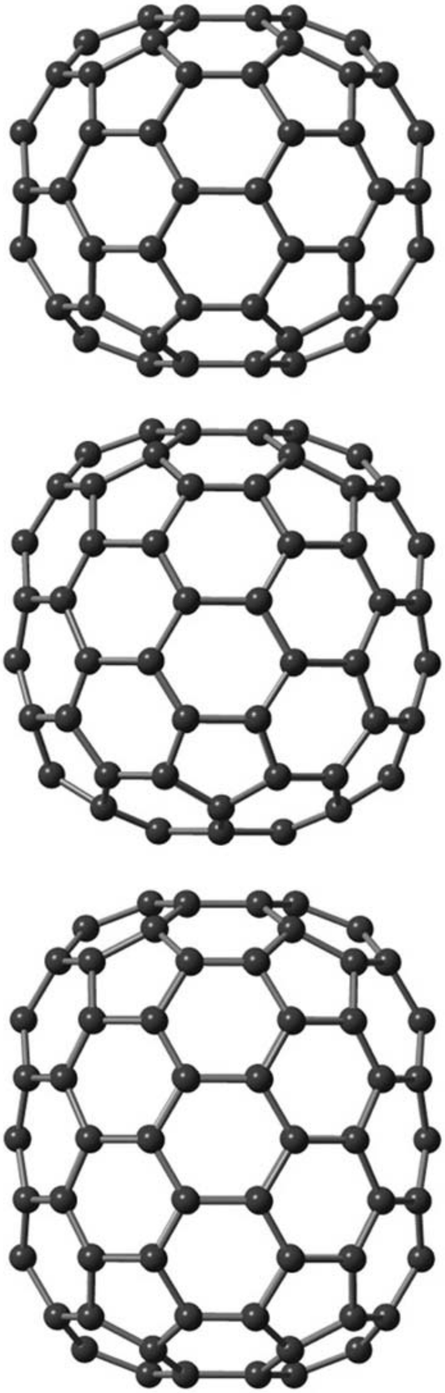

Fig. 6 Progression of armchair SWCNTs length from one (top) to three (bottom) interior rows of benzenoids

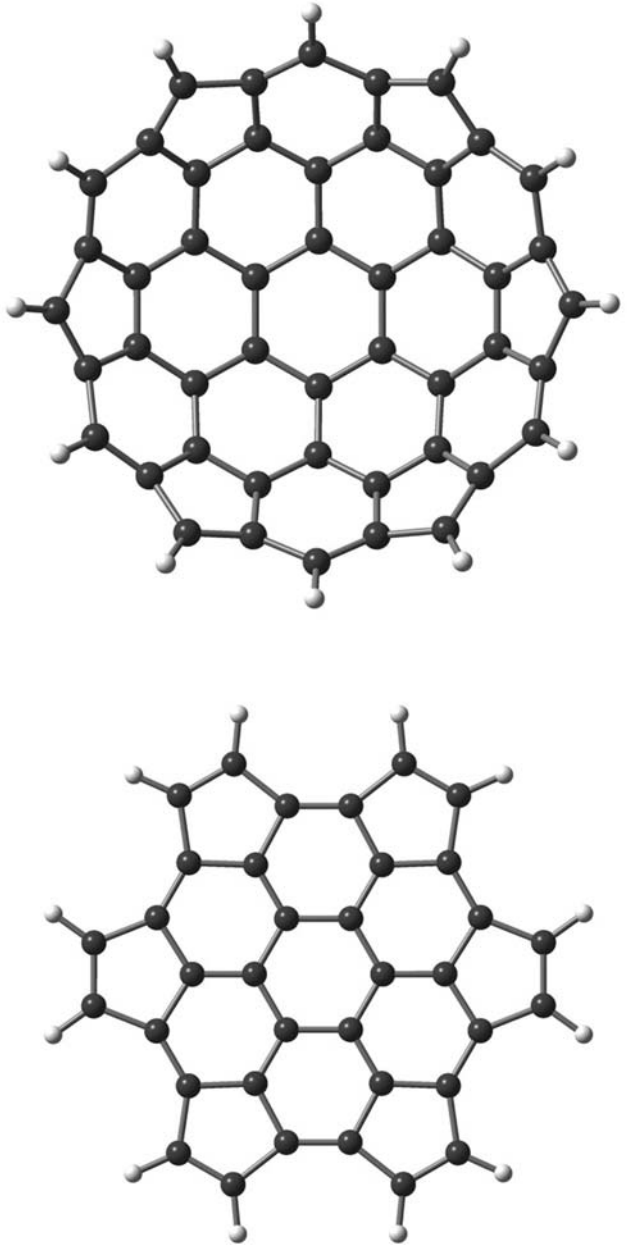

Fig. 7 End caps of the (12,0) zigzag (top) and (6,6) armchair (bottom) SWCNTs

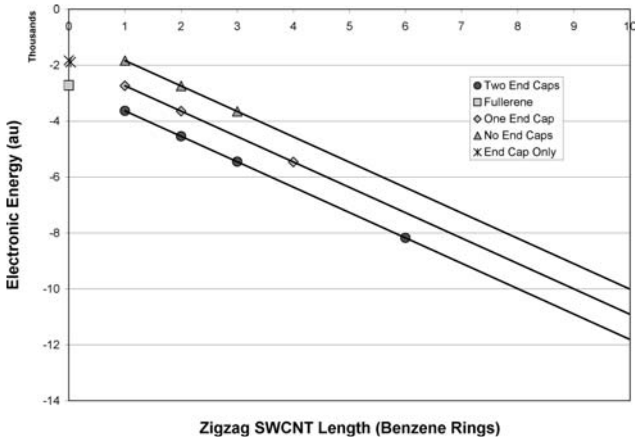

Fig. 8 Electronic energy of the (12,0) zigzag SWCNTs as tube length increases

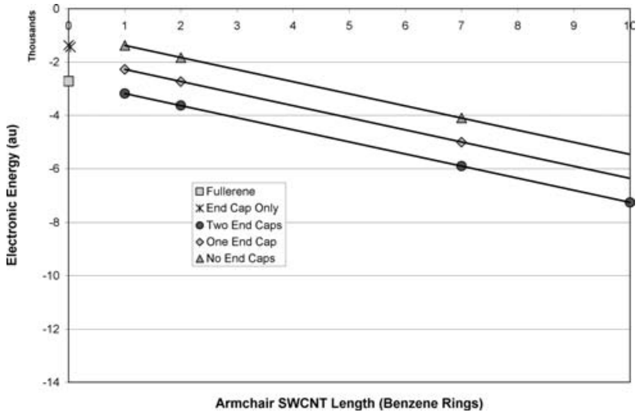

Fig. 9 Electronic energy of the (6,6) armchair SWCNTs as tube length increases

Figures 8 and 9 show the changes in electronic energy, of the (12,0) and (6,6) nanotubes respectively, as the length of the tube increases. The energy of the tubes (or total atomic energy) has a linear relationship with the length. This means that electronic energies for very long CNTs could be extrapolated from data of smaller CNTs. It should also be noted that the slope for the armchair tubes is approximately double that of the zigzag tubes. This occurs due to differences in the structural characteristics; in order to add one additional row of length to the zigzag tube it is necessary to add 24 carbon atoms, but for the armchair tube, only 12 carbon atoms are needed. This implies that the slope of the line is dependent on the number of carbon atoms in the circumference of the tube. In Figs. 10 and 11, the electronic energy per atom is plotted for the same systems, in order to understand which capping configuration is more energetically favorable. It can be seen that for both types (zigzag and armchair), double-capped tubes have the same energy per atom while single and uncapped tubes have less stable energies that appear to exponentially decay. The graphs also show that single capped tubes are more stable then uncapped tubes, confirming that it is energetically favorable for tubes to be capped, as seen in experimental results like those in Figs. 1–3. As far as determining which type of tube is more energetically favorable isomers of double capped, zigzag and armchair SWCNTs, containing only carbon atoms were compared. The only structural similarity between these

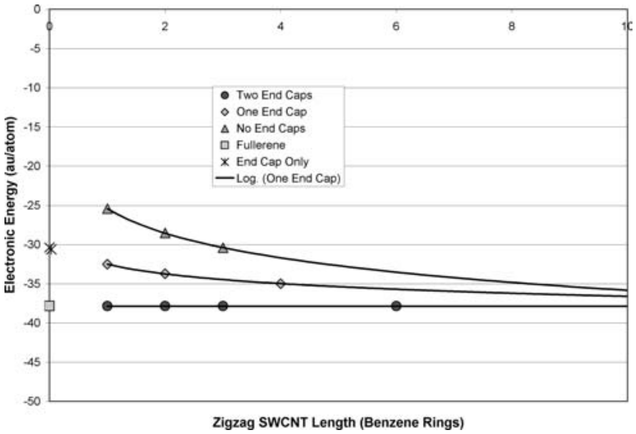

Fig. 10 Electronic energy per atom of the (12,0) zigzag SWCNTs as tube length increases

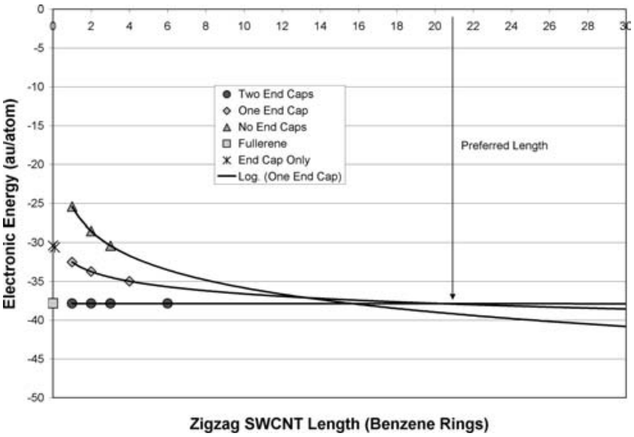

Fig. 12 The intersection of the single-capped and double-capped data represents the optimal length of the (12,0) zigzag SWCNT

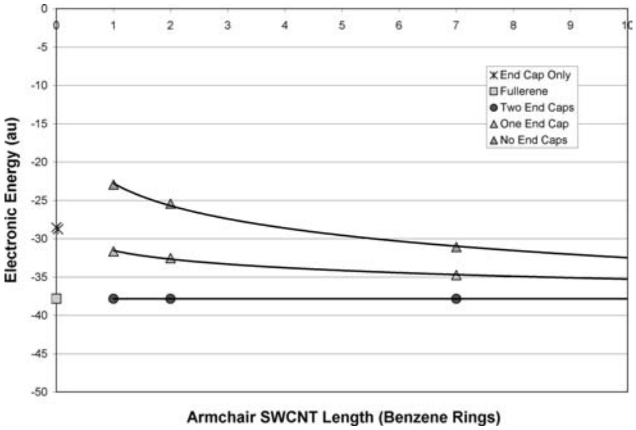

Fig. 11 Electronic energy per atom of the (6,6) armchair SWCNTs as tube length increases

isomers was the number of carbon atoms. It was found that the armchair tubes had a slightly more stable energy than the zigzag tubes. The difference in energy between the armchair and zigzag isomers was approximately 0.3 kcal/mol·atom for double-capped tubes. Figure 12 shows how the predicted behavior of the nanotube changes for longer tubes. If a cap formed, and acted as a nucleus for nanotube growth the drive for growth is the decrease in energy per atom as the tube length increases. According to Fig. 12, the optimal length would occur at the intersection of the single and double-capped curves. At this point a second end cap could form, after the tube is capped at both ends, it can then act as a *seed* SWCNT for additional subsequent layers.

Carbon nanotube circumference

The data from the length computations showed that the energy increases linearly with length. Therefore, it is possible to perform computations on nanotubes with increasing circumferences by using only one row of benzenoids between the end caps; this keeps the systems to a smaller number of atoms, while still offering a valid comparison. Figures 13 and 14 show some of the end caps used as the circumference increases for zigzag and armchair SWCNTs, respectively.

Figure 15 shows how the calculated electronic energies change with increasing circumference, for zigzag (6,0) (0.47 nm diameter) thru (19,0) (1.63 nm diameter) SWCNTs containing two end caps with one interior row of benzene rings. As the systems grow in circumference the electronic energy increases linearly. Jumps in energy occur where large numbers of atoms are added to the caps. These jumps are a structural feature of the nanotubes caused by the outward movement of five-member rings; this concept is further explained in previous research [12]. It should be noted that the most symmetric end caps for each circumference were used in these experiments. Figure 16 shows similar results for changes in energy for armchair (6,6) (0.81 nm diameter) thru (11,11) (1.49 nm diameter) SWCNTs containing two end caps and one interior row of benzenoids.

The electronic energy per atom remains constant as the circumference increases, for zigzag and armchair capped SWCNT systems. In fullerenes, pentagon proximity decreases the stability of a system because of the effect on both the steric strain and π electronic structure [20], but the ab initio calculations reveal that this does not occur in nanotubes. As the circumference increases, the pentagons are sited further away from each other, but the electronic energy per atom stays constant. The energy per atom for both zigzag and armchair

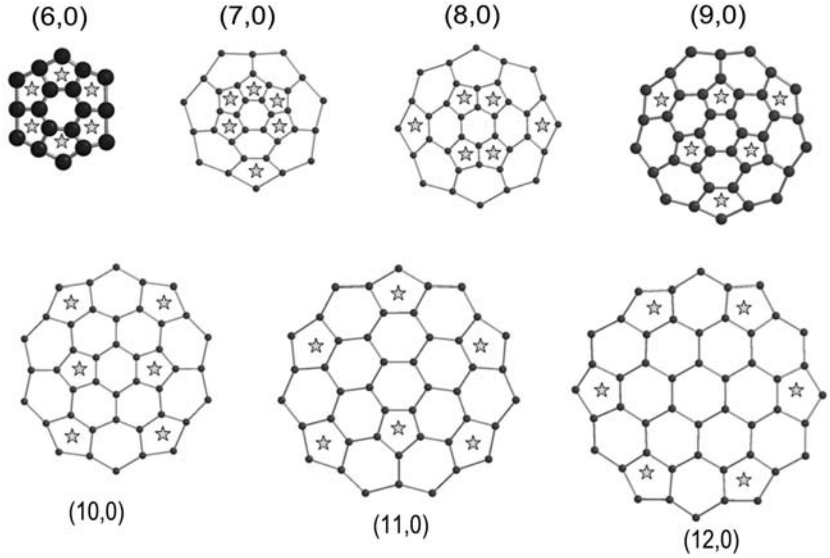

Fig. 13 Examples of end caps used as the circumference increases for zigzag SWCNTs, the stars indicate the location of 5-member rings

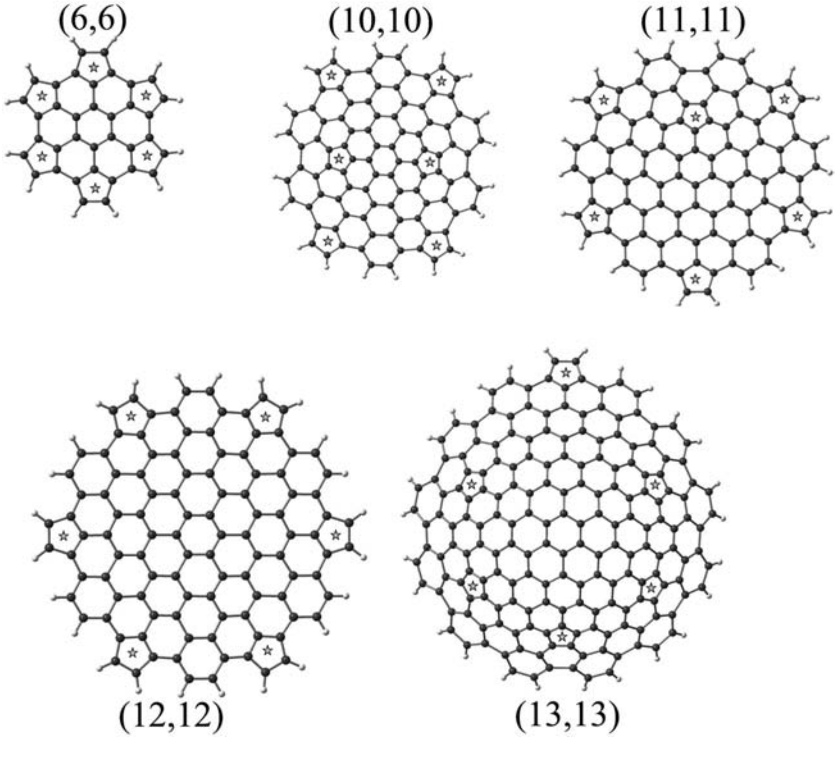

Fig. 14 Examples of end caps used as the circumference increases for armchair SWCNTs

SWCNTs ranges from –37.83 to –37.86 au/atom, a difference of approximately 18 kcal/mol·atom.

In order to confirm the accuracy of the AM1//HF/6-31G calculations some DFT calculations were performed on the zigzag SWCNT. The basis sets chosen for the DFT calculations were the LSDA/STO3-G for geometric optimization and B3LYP/3-21G for single point energy calculations. Table 1 shows a comparison of the results from the calculations. It can be seen that the HF and DFT give similar electronic energies for these systems.

Prediction of SWCNT Electronic Energies

The linear behavior of the electronic energies and previous work correlating electronic energies of small hydrocarbon structures to larger structures and to heats of formation [21–23] suggest that a multiple variable linear equation could be used to describe the energetics of SWCNTs. Structural parameters and AM1 energies were used as independent variables and the electronic energy as the dependent variable in a multi-variable linear regression. The eleven

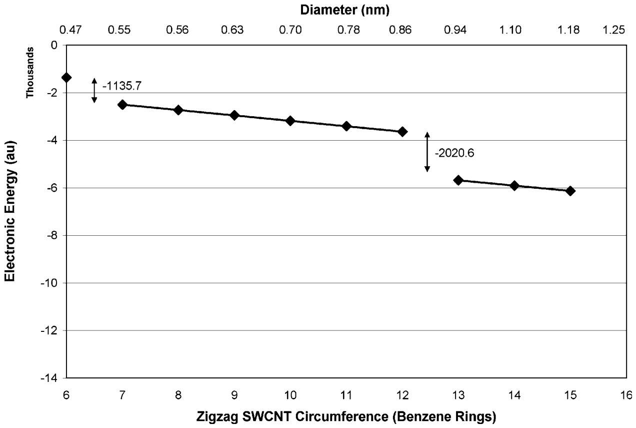

Fig. 15 Changes in energy for zigzag (6,0) thru (15,0) SWCNTs containing two end caps and one interior row of benzenoids

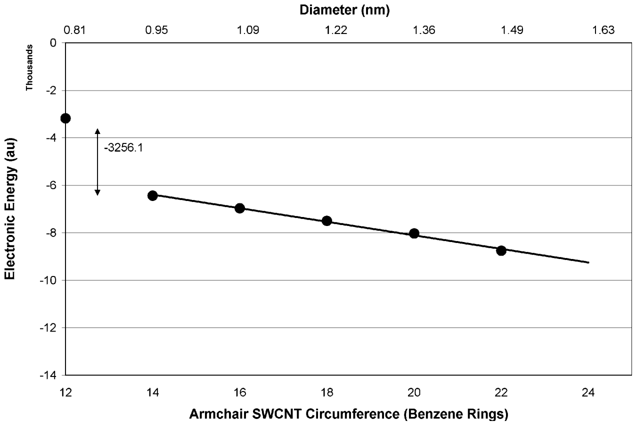

Fig. 16 Changes in energy for armchair (6,6) thru (18,18) SWCNTs containing two end caps and one interior row of benzenoids

Table 1 Comparison of HF and DFT calculations, all calculations are given in Hartrees

SWCNT	AM1//HF/6-31G	LSDA/STO-3G// B3LYP/3-21G	% Difference
(6,0)	–1361.9532	–1363.6790	0.13%
(7,0)	–2497.6503	–2500.5801	0.12%
(10,0)	–3179.6133	–3183.1177	0.11%
(13,0)	–5678.4818	–5684.6324	0.11%
(15,0)	–6132.8915	–6139.4554	0.11%

Table 2 Independent variables used to describe the structural parameters and AM1 energies of SWCNTs

#	Variable	Parameter	Description
1	*Q*	C atoms	The total number of carbon atoms in the SWCNT.
2	*R*	H atoms	The total number of hydrogen atoms in the system.
3	*S*	AM1 Energy	The heat of formation predicted by optimized AM1 calculations
4	*T*	Benzenoids in caps	The total number of benzene rings in the caps.
5	*U*	Benzenoids in body	The total number of benzene rings in the body of the tube.
6	*V*	Total Benzenoids	The total number of benzene rings in the SWCNT.
7	*W*	Pentagonal Rings	The number of pentagonal rings in the SWCNT (a defect free tube has 12).
8	*X*	Type	The cosine of the chiral angle (cos 0° = Zigzag, cos 30° = Armchair).
9	*Y*	Diameter	The diameter of the SWCNT in angstroms.
10	*Z*	Pentagon Proximity 1	The number of pentagonal rings directly connected.
11	AA	Pentagon Proximity 2	The number of pentagonal rings seated 1 benzenoid or less from another pentagonal ring.

structural parameters used to describe the various SWCNTs in this study can be found in Table 2; of these, two parameters were found to be statistically significant. Some of the eleven parameters included the number of benzenoids in the tube body, cosine of the chiral angle (cos 0°= zigzag, cos 30°= armchair) and tube diameter. In order to confirm the insignificance of pentagon proximity two parameters used to describe pentagon proximity were also tested. These parameters were found to have larger standard errors than their coefficient values and found not to be significant in the calculation. The regression was calculated again using only the significant parameters; the number of carbon atoms and AM1 energy. A reference set of 19 double-capped SWCNTs of less than 500 atoms were used. Table 3 summarizes the statistical results for the analysis of the electronic energies of small SWCNT

Table 3 Statistical results for the multi-variable linear regression of structural parameters for small SWCNTs

Standard Error	0.0075	
Multiple *R*	1.0000	
R^2	1.0000	
Largest calc error	0.0132	
Ind. Variable	Coefficients	Standard Error
Q (Total C Atoms)	–37.8749	2.0907E–04
S (AM1Energy)	1.1953	2.2893E–02

systems. While this equation does significantly reduce the time involved in computing electronic energies for large SWCNTs, it is still necessary to perform an AM1 optimization calculation on the structures.

Summary and conclusions

It has been shown that the electronic energies for all types of SWCNTs grows linearly as both the circumference and length of the SWCNT increases. The ab initio calculations suggest that no tube type is preferred (zigzag, chiral or armchair) since all induce the same electronic energy per atom (~ –37.8 au/atom). It has been suggested that pentagon proximity in fullerenes causes an increase in heats of formation [20]; however, according to these preliminary studies this does not seem to be true for CNTs since both smaller circumference tubes (more pentagon proximity) and larger circumference tubes (less pentagon proximity) have similar electronic energies per atom. The experimental data (Figs. 1–3) showing a variety of carbonaceous materials including various sizes and types of manufactured capped MWCNT and capped SWCNT confirms the computational results that SWCNT are more stable when capped on both ends. The computational data also showed that it takes less energy to begin to form a nanotube (an end cap connected with one row of benzenoids) then it does to form a similar sized fullerene (two joined end caps containing twelve, 5-member rings).

Reich et al. [13] used ab initio calculations to show that the chirality of a CNT can be controlled by growth of a specific cap on a catalyst substrate (Ni). While this work agrees with the use of a cap to control the structural parameters of a CNT, a solid metal catalyst is not used to initiate growth of the end cap; instead, it is proposed that homogenous gas-phase nucleation occurs as previously described by Lair et al. [7]. Guo et al. [15], found that self-assembly of MWCNTs occurred in gas-phase conditions due to chemisorbed carbon atoms between tube layers, which kept the open end of the CNT from closing. We have shown that it is energetically more favorable for a SWCNT to continue its growth than to close into fullerenes, but further study is needed to understand the growth mechanisms of MWCNTs as well as the initial growth or extension of SWCNTs. This work has also shown how it is possible to relate the energies of smaller tubes to large tubes with a simple multiple coefficient linear equation.

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