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Published on Web 06/21/2002

Electronic Structures and Energetics of [5,5] and [9,0] Single-Walled Carbon Nanotubes

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Received December 10, 2001

Abstract: Standard enthalpies of formation, ionization potentials, electron affinities, and band gaps of finite-length [5,5] armchair and [9,0] zigzag single-walled carbon nanotubes (SWNTs) capped with C_{30} hemispheres obtained by halving the C_{60} fullerene have been computed at the B3LYP/6-311G* level of theory. Properties of SWNTs are found to depend strongly on the tube length and, in the case of the [9,0] zigzag species, on the relative orientation of the caps. The metallic character of an uncapped infinite-length [5,5] armchair SWNT manifests itself in the oscillatory dependence of the properties of capped finite-length tubes on their size. An infinite-length [9,0] zigzag SWNT is predicted to be a semiconductor rather than a metal irrespective of the presence of caps. The present results underscore the slow convergence of SWNT properties with respect to the tube length and uncover small but significant radial distortions along the long axes of SWNTs.

Introduction

Since their seminal discovery by Iijima,[1] there has been a flurry of theoretical and experimental research on carbon nanotubes. In particular, the single-walled nanotubes (SWNTs) appear to hold great promise of being practical solutions[2] to problems as diverse as, to name a few, sorption of toxic substances,[3] storage of hydrogen,[4,5] and template-mediated growth of crystals.[6] However, the greatest potential of SWNTs stems from their anticipated use in nanoelectronic devices.[7] With regard to this and other applications, reliable prediction of metallic vs semiconducting behavior of SWNTs is of critical importance.

Classification of SWNTs is facilitated by the observation that any infinite-length carbon tube is uniquely defined by a construction that involves rolling of a single graphite layer (a graphene sheet) in such a way that the end of the vector (conveniently represented by an [*n*,*m*] pair of numbers) connecting two centers of hexagons is superimposed on its origin.[8−13] SWNTs are chiral unless *m* equals either *n* or 0. In the former case, the armchair [*n*,*n*] SWNTs consist of layers of hexagons with long axes perpendicular to the tube axis, whereas in the case of [*n*,0] zigzag SWNTs the axes are parallel (Figure 1).

Simple considerations based upon the band structure of graphene lead to the conclusion that an infinite-length SWNT is metallic if $n - m = 0$, has a narrow band gap if $n - m$ is a multiple of 3, and is a moderate-gap semiconductor otherwise.[10−14] Indeed, early scanning tunneling spectroscopy (STS) experiments have confirmed a great variation in band gaps of SWNTs with diverse diameters and helicities.[15,16] However, the question of whether the [*n*,*n*] and [3*n*,0] tubes are indeed metallic as predicted by the aforementioned simple theory has been addressed only very recently by direct STS measurements of band gaps in the, [9,0], [12,0], and [15,0] zigzag SWNTs that have yielded the values of 80 ± 5, 42 ± 4, and 29 ± 4 meV, respectively.[17] These results are in qualitative agreement with predictions of simple models that attribute the band gaps to curvature effects scaling as R^{-2}, where R is the radius of a [3*n*,0] zigzag tube.[17,18] On the other hand, the pseudogaps observed in armchair SWNTs[17] have been found to originate entirely from inter-tube interactions.[19]

In the context of these new developments, the understanding of the influence of diameter, helicity, length, and capping of

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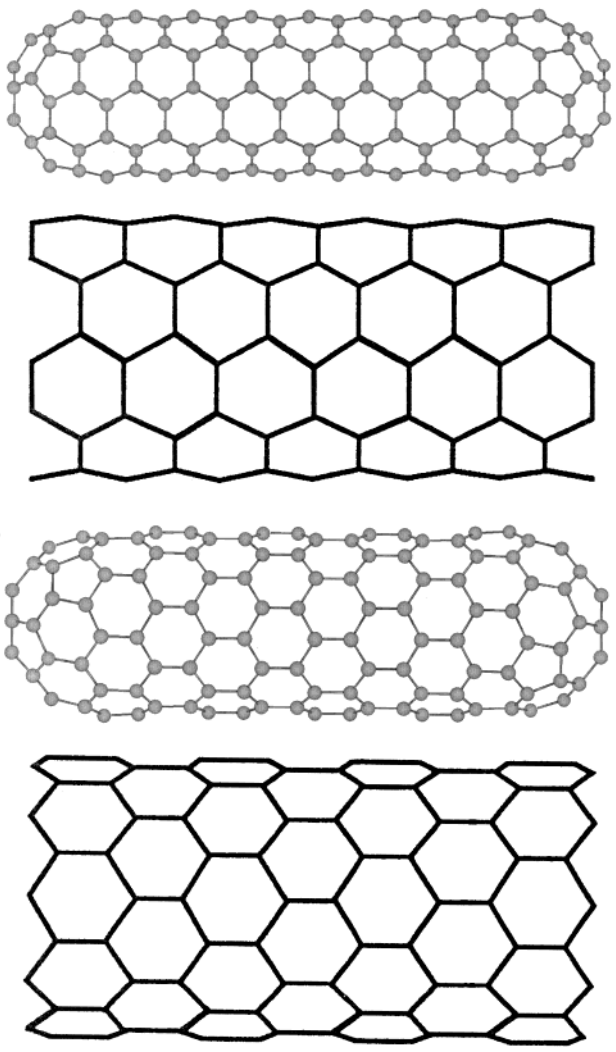

Figure 1. Carbon skeletons of (a) [5,5] armchair and (b) [9,0] zigzag SWNTs.

SWNTs on their electronic structures is becoming even more important than before. Unfortunately, with only a few notable exceptions thus far,[9,19−23] quantum-mechanical studies of SWNTs have been the domain of tight-binding model Hamiltonians[11,12,14,18,24−29] and all-electron semiempirical methods[30−32] that have often produced conflicting results. Therefore, there is an urgent need for benchmark electronic structure calculations on SWNTs employing reliable ab initio methods of modern quantum chemistry. Such calculations are described in this paper.

Details of Calculations

Full geometry optimizations (subject to symmetry constraints) were carried out at the B3LYP/6-311G* level of theory with the NWCHEM 3.3.1[33] suite of programs. The following grid definitions (obtained by issuing the "grid lebedev 75 5" input directive) were used: the Euler−MacLaurin radial quadrature with 57 shells, the Lebedev angular quadrature with 302 points, Becke spatial weights, grid pruning on. In test calculations on the C_{60} fullerene, such a grid was found to yield energies within less than 10^{-3} au (or 0.6 kcal/mol) from those obtained with a practically exact quadrature that was computationally too demanding for production runs.

The computed energies were converted (under the well-founded[34] assumption of transferable atomic contributions to zero-point energies and thermal corrections) to standard enthalpies of formation with the help of the (N/60) $C_{60} \rightarrow C_N$ isodesmic reaction.[35] Equating the negative HOMO energy with ionization potential (IP) yields $IP(C_{60}) = 6.40$ eV, which is significantly lower than the $IP(C_{60}) = 7.56 \pm 0.06$ eV average of experimental data equaling 7.54 ± 0.04,[36] 7.57 ± 0.01,[37] $7.58^{+0.04}_{-0.02}$,[38] and 7.59 ± 0.02 eV.[39] Similarly, the negative LUMO energy yields the estimate of the electron affinity $EA(C_{60}) = 3.66$ eV, which is significantly higher than the $EA(C_{60}) = 2.68 \pm 0.02$ eV average of the 2.666 ± 0.001[40] and 2.689 ± 0.008 eV[41] experimental values. Thus, the experimental band gap in gas-phase C_{60} exceeds the difference in the B3LYP/6-311G* HOMO and LUMO energies by 2.14 ± 0.06 eV. In light of these discrepancies, the IPs and EAs of SWNTs were estimated from the equations

$$IP(C_N) = IP(C_{60}) + \epsilon_{HOMO}(C_{60}) - \epsilon_{HOMO}(C_N) = 1.16 - \epsilon_{HOMO}(C_N) \quad (1)$$

and

$$EA(C_N) = EA(C_{60}) + \epsilon_{LUMO}(C_{60}) - \epsilon_{LUMO}(C_N) = -0.98 - \epsilon_{LUMO}(C_N) \quad (2)$$

The corrected band gaps in Tables 1 and 2 refer to differences between IPs and EAs estimated from these equations. Note that, since these differences are always larger than 2.14 eV, the corrected band gaps are clearly overestimated for longer SWNTs.

Discussion

[5,5] Armchair Single-Walled Carbon Nanotubes. The [5,5] armchair SWNTs can be capped with two hemispheres obtained by cutting the C_{60} shell along the equator, resulting in

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Table 1. The B3LYP/6-311G* Standard Enthalpies of Formation, HOMO and LUMO Energies, and Band Gaps of the [5,5] Armchair SWNTs Capped with C_{30} Hemispheres

species	symmetry	ΔH_f^0 [kcal/mol]	$-\epsilon_{HOMO}$ [eV]	IP [eV]	$-\epsilon_{LUMO}$ [eV]	EA [eV]	ΔE [eV] uncorrected	ΔE [eV] corrected
C_{70}	D_{5h}	660.7	6.34	7.50	3.66	2.67	2.68	4.82
C_{80}	D_{5d}	731.8	5.34	6.50	4.29	3.31	1.04	3.19
C_{90}	D_{5h}	772.4	5.71	6.87	3.77	2.79	1.95	4.09
C_{100}	D_{5d}	826.0	5.86	7.02	3.65	2.67	2.21	4.35
C_{110}	D_{5h}	891.0	5.21	6.37	4.14	3.16	1.06	3.20
C_{120}	D_{5d}	936.7	5.36	6.52	3.92	2.93	1.45	3.59
C_{130}	D_{5h}	987.9	5.57	6.73	3.72	2.74	1.85	3.99
C_{140}	D_{5d}	1049.1	5.10	6.26	4.09	3.11	1.01	3.15
C_{150}	D_{5h}	1099.2	5.15	6.31	4.00	3.02	1.15	3.29
C_{160}	D_{5d}	1150.4	5.36	6.52	3.77	2.79	1.59	3.73
C_{170}	D_{5h}	1209.5	5.03	6.19	4.07	3.09	0.96	3.10
C_{180}	D_{5d}	1262.2	5.01	6.17	4.07	3.09	0.94	3.08
C_{190}	D_{5h}	1313.3	5.19	6.35	3.84	2.86	1.35	3.49
C_{200}	D_{5d}	1370.5	4.98	6.14	4.06	3.07	0.92	3.06
C_{210}	D_{5h}	1425.9	4.90	6.06	4.12	3.14	0.79	2.93

Table 2. The B3LYP/6-311G* Standard Enthalpies of Formation, HOMO and LUMO Energies, and Band Gaps of the [9,0] Zigzag SWNTs Capped with C_{30} Hemispheres

species	symmetry	ΔH_f^0 [kcal/mol]	$-\epsilon_{HOMO}$ [eV]	IP [eV]	$-\epsilon_{LUMO}$ [eV]	EA [eV]	ΔE [eV] uncorrected	ΔE [eV] corrected
C_{78}	D_{3h}	732.6	6.07	7.23	3.62	2.64	2.45	4.59
	D_3	718.3	5.71	6.87	4.09	3.11	1.62	3.76
C_{96}	D_{3d}	806.2	5.82	6.98	3.74	2.76	2.08	4.22
	D_3	823.1	5.51	6.67	4.05	3.07	1.46	3.60
C_{114}	D_{3h}	904.7	5.62	6.78	3.73	2.75	1.89	4.03
	D_3	911.9	5.33	6.49	4.09	3.11	1.24	3.38
C_{132}	D_{3d}	996.7	5.46	6.62	3.82	2.84	1.64	3.78
	D_3	1002.1	5.22	6.38	4.07	3.09	1.15	3.29
C_{150}	D_{3h}	1087.8	5.34	6.50	3.82	2.84	1.52	3.66
	D_3	1094.2	5.12	6.28	4.09	3.11	1.03	3.17
C_{168}	D_{3d}	1180.3	5.25	6.41	3.87	2.89	1.37	3.51
	D_3	1185.4	5.05	6.21	4.09	3.11	0.96	3.10
C_{186}	D_{3h}	1272.7	5.17	6.33	3.88	2.90	1.28	3.42
	D_3	1277.4	4.99	6.15	4.10	3.12	0.89	3.03
C_{204}	D_{3d}	1364.6	5.10	6.26	3.91	2.93	1.19	3.33
	D_3	1369.0	4.94	6.10	4.10	3.12	0.84	2.98

C_{60+10j} tubes that possess D_{5d} (D_{5h}) symmetry for j even (odd). The D_{5d} SWNTs have the valence electron configurations of $(j + 10 + m_1(j))a_{1g}$ $(j + 4 - m_2(j))a_{1u}$ $(j + 2 - m_1(j))a_{2g}$ $(j + 8 + m_2(j))a_{2u}$ $(4j + 24)e_{1g}$ $(4j + 24)e_{1u}$ $(4j + 24)e_{2g}$ $(4j + 24)e_{2u}$, where $m_1(j)$ and $m_2(j)$ are the integer parts of $(j+1)/3$ and $(j+2)/3$, respectively, whereas the valence electron configurations of the D_{5h} SWNTs read $(j + 10 + m_1(j))a_1'$ $(j + 3 - m_2(j))a_1''$ $(j + 3 - m_1(j))a_2'$ $(j + 8 + m_2(j))a_2''$ $(4j + 26)e_1'$ $(4j + 22)e_1''$ $(4j + 26)e_2'$ $(4j + 22)e_2''$.

An infinite-length [5,5] armchair SWNT is predicted to be destabilized with respect to graphite by ca. 5.54 kcal/mol per carbon atom (Figure 2). This estimate is in a reasonable agreement with the strain energy of 0.18 eV (or 4.2 kcal/mol) obtained previously from LDA calculations.[9] It is important to note that this limiting value is approached in a highly oscillatory manner (Figure 2 and Table 1). Such strong oscillations, which are also conspicuous in the computed HOMO and LUMO energies (Figure 3 and Table 1), constitute a signature of metallic character at the bulk limit with periodic boundary conditions,[42] i.e., for an uncapped infinite-length tube. In fact, the observed oscillation period of approximately 3 is consistent with the wave vector $k_F \approx 2\pi/3$ at which the band crossing responsible for

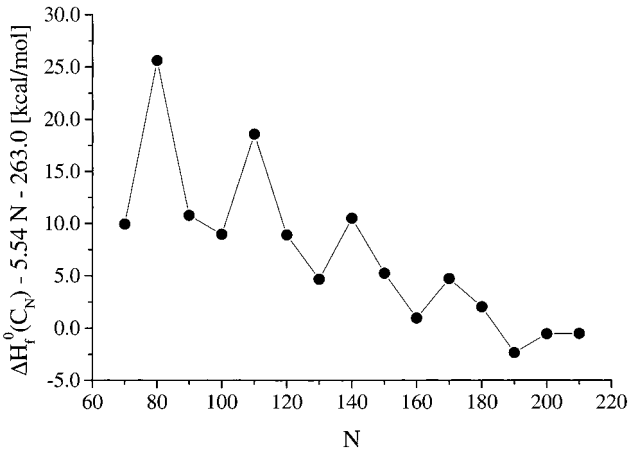

Figure 2. The dependence of the B3LYP/6-311G* standard enthalpies of formation of the [5,5] armchair SWNTs capped with C_{30} hemispheres on the number of carbon atoms.

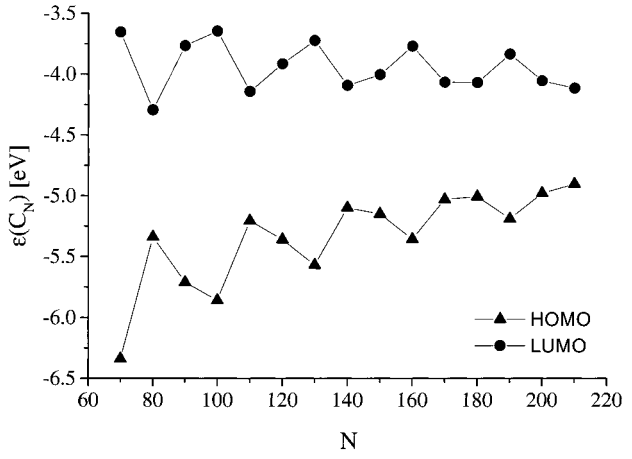

Figure 3. The dependence of the B3LYP/6-311G* HOMO and LUMO energies of the [5,5] armchair SWNTs capped with C_{30} hemispheres on the number of carbon atoms.

the metallic character of infinite-length [n,n] armchair SWNTs occurs (note that a simple theory predicts $k_F = 2\pi/3$[11,12] and the introduction of electron−electron repulsion affects k_F only slightly[22]).

The aforedescribed oscillations have been previously observed (but not explained) in the Hückel band gaps of both uncapped and capped [5,5] armchair SWNTs[29] and in the band gaps of

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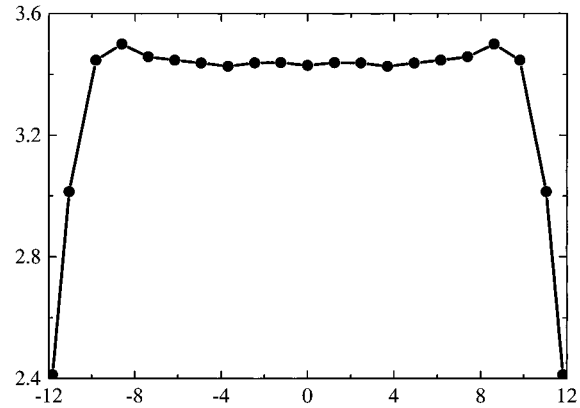

Figure 4. The outline of the C_{210} [5,5] armchair SWNT.

the [6,6] armchair SWNTs capped with hydrogen atomscalculated at the HF/STO-3G level of theory as well as withthe DFT, PM3, and EHMO approaches.[23] However, the corresponding oscillations in the computed energies have apparently escaped attention of the authors of those studies. The HF/STO-3G, DFT, and PM3 band gaps have not appeared to vanish at the bulk limit, in agreement with the conclusions of a PM3 investigation of open-ended finite [5,5] armchair SWNTs.[31]

The present benchmark calculations indicate that finite-length [5,5] armchair SWNTs capped with C_{30} hemispheres possess substantial band gaps, even when the corrections given by eqs 1 and 2 are not taken into account (Table 1). The band gaps are strongly dependent on the tube length. Most likely, the transition to metal takes place at the bulk limit but the number of carbon atoms required for a sufficient narrowing of the band gap eludes precise estimation. The presence of a residual band gap due to capping, observed in Hückel calculations on the [5,5] armchair SWNTs,[29] remains a possibility.

One interesting aspect of SWNT geometries uncovered by the present study is the slight mismatch between the diameters of the caps and the main body of the tube. The resulting termini swelling by as much as 0.08 Å confers a "dog biscuit" outline upon SWNTs (Figure 4).

[9,0] Zigzag Single-Walled Carbon Nanotubes. Capping of the [9,0] zigzag SWNTs with two C_{30} hemispheres produces two families of C_{60+18j} tubes. The members of the first family possess D_{3d} (D_{3h}) symmetry for j even (odd).[8] The D_{3d} SWNTs have the valence electron configurations of $(7j/2 + 14)a_{1g}$ $(5j/2 + 8)a_{1u}$ $(5j/2 + 6)a_{2g}$ $(7j/2 + 12)a_{2u}$ $(12j + 40)e_g$ $(12j + 40)e_u$, whereas the valence electron configurations of the D_{3h} SWNTs read $(7j + 29)/2)a_1'$ $((5j + 13)/2)a_1''$ $((5j + 15)/2)a_2'$ $((7j + 23)/2)a_2''$ $(12j + 44)e'$ $(12j + 36)e''$. The members of the second family, related to the D_{3d}/D_{3h} SWNTs by a $\pi/3$ rotation of one of the caps,[20] possess D_3 symmetry and the $(7j + 21 - 2m(j))$-a_1 $(5j + 19 + 2m(j))a_2$ $(24j + 80)e$ valence electron configurations, where $m(j)$ is the integer part of $(n + 1)/2$, for both even and odd j.

Except for the C_{78} species, the D_3 SWNTs are predicted to be less stable than their D_{3d}/D_{3h} counterparts (Figure 5 and Table 2), the difference of standard enthalpies of formation approaching ca. 4 kcal/mol for long tubes. Among the C_{150} capped SWNTs, the D_3 [9,0] tube is 6.4 kcal/mol less stable than the D_{3h} [9,0] one, whereas the D_{5h} [5,5] tube is 11.4 kcal/mol less

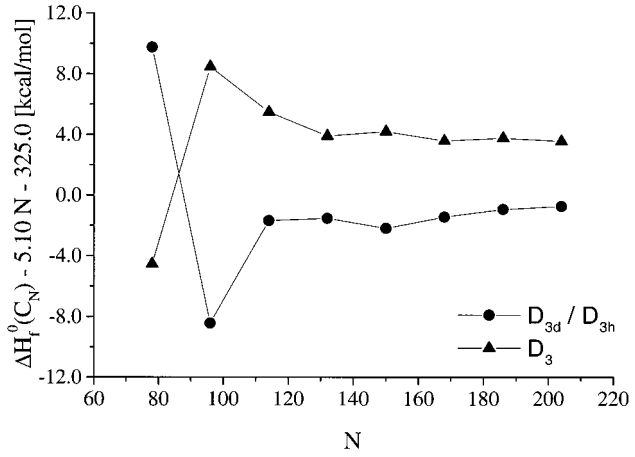

Figure 5. The dependence of the B3LYP/6-311G* standard enthalpies of formation of the [9,0] zigzag SWNTs capped with C_{30} hemispheres on the number of carbon atoms.

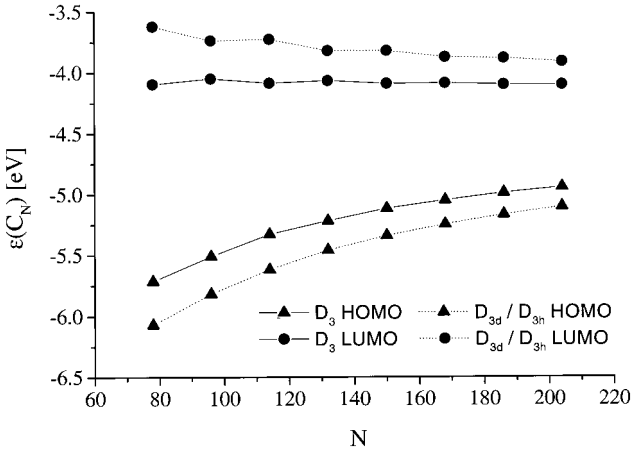

Figure 6. The dependence of the B3LYP/6-311G* HOMO and LUMO energies of the [9,0] zigzag SWNTs capped with C_{30} hemispheres on the number of carbon atoms.

stable, reflecting larger strain due to increased curvature. These values are somewhat smaller than the previously published HF/6-31G* relative energies of 10.0 and 14.4 kcal/mol, respectively.[20] An infinite-length [9,0] zigzag SWNT is predicted to be destabilized with respect to graphite by ca. 5.10 kcal/mol per carbon atom (Figure 5). As expected from a simple theory,[9] the ratio of strain energies of the infinite-length [9,0] and [5,5] SWNTs is close (0.92 vs 0.91) to the reciprocal square of the ratio of the corresponding tube radii.

The band gaps of the [9,0] zigzag SWNTs decrease with the tube lengths, the gaps of the D_3 species being always significantly narrower than those of their D_{3d}/D_{3h} counterparts (Figure 6 and Table 2). As expected from the lack of significant oscillations in the $\Delta H_f^0(C_N)$ vs N and $\epsilon(C_N)$ vs N plots, the band gaps do not appear to vanish at the bulk limit. Thus, irrespective of the presence of caps, an infinite-length [9,0] zigzag SWNT is not metallic, in agreement with the experimental data[17] and the results of tight-binding[12,21,24] and LDA[21] calculations but in contradiction with the predictions of the Su−Schrieffer−Heeger model.[25]

One should mention that the termini swelling observed in the geometries of the [5,5] armchair SWNTs is also present in the [9,0] zigzag tubes.

Conclusions

Standard enthalpies of formation, ionization potentials, electron affinities, and band gaps of finite-length [5,5] armchair and [9,0] zigzag single-walled carbon nanotubes (SWNTs) capped with C_{30} hemispheres obtained by halving the C_{60} fullerene have been computed at the B3LYP/6-311G* level of theory. Properties of SWNTs are found to depend strongly on the tube length and, in the case of the [9,0] zigzag species, on the relative orientation of the caps. The metallic character of an uncapped infinite-length [5,5] armchair SWNT manifests itself in the oscillatory dependence of the properties of capped finite-length tubes on their size. An infinite-length [9,0] zigzag SWNT is predicted to be a semiconductor rather than a metal irrespective of the presence of caps. The present results underscore the slow convergence of SWNT properties with respect to the tube length and uncover small but significant radial distortions along the long axes of SWNTs.

We believe that this study will stimulate further experimental research on the influence of diameter, helicity, length, and capping of SWNTs on their electronic properties and will serve as a benchmark for calculations that employ computationally less demanding approaches.

Acknowledgment. The research described in this publication has been supported by the Office of Energy Research, Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under the grant DE-FG02-97ER14758.

JA0126879