

Computations of model narrow nanotubes closed by fragments of smaller fullerenes and *quasi*-fullerenes

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Abstract

New type of carbon nanotubes—narrow nanotubes—has recently been observed with diameters of 4–5 Å. It has been postulated that the narrow nanotubes are closed by fullerene fragments of C₂₀ and C₃₆. This paper presents computational results on related model nanotubes with stoichiometries such as C₈₀, C₈₄, C₉₆, C₁₀₈, or C₁₂₀. The computations were carried out at the PM3, AM1, SAM1, HF/3-21G, HF/4-31G, and B3LYP/6-31G* levels. Two C₃₆ fullerenes were considered, D_{6h} and D_{2d}. At the PM3 level and with the C₈₄ nanotube stoichiometry, the D_{2d} cage closure gave a lower energy (by 185 kcal/mol and a diameter of 5.42 Å). There is another possible candidate, a C₃₂ cage with D_{4d} symmetry (two four-membered rings). At the PM3 level and with the C₉₆ nanotube stoichiometry, the D_{4d} closure (with a diameter of 5.43 Å) had energy lower by 210 kcal/mol than that of the D_{6h} nanotube closure. On the other hand, four-membered rings should not play a significant role for narrow nanotubes with a diameter of 4 Å, where the dodecahedron-related closure should be exclusive. Still narrower nanotubes are briefly discussed.

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1. Introduction

A new type of extremely narrow nanotubes has very recently been discovered. Sun et al. [1] produced narrow nanotubes with a diameter of 5 Å. Qin et al. [2] and Wang et al. [3] reported even narrower nanotubes with a diameter of only 4 Å. Recently, some smaller fullerenes were prepared, first solid-state [4] C₃₆ and then gas phase [5] and solid [6] C₂₀. It has been suggested [1,2] that the narrow nanotubes are actually closed by fragments of the small C₃₆ and C₂₀ fullerenes. Our preliminary model calculations [7] supported this hypothesis. In this contribution, we present further computational results on model narrow nanotubes with stoichiometries of C₈₀, C₈₄, C₉₆, C₁₀₈, and C₁₂₀. Computations were carried out at the semiempirical PM3, AM1, and SAM1 levels and further verified at the ab initio Hartree–Fock SCF HF/3-21, HF/4-31G and density functional theory B3LYP/6-31G* levels.

2. Calculations

The geometry optimizations were performed with the PM3 and AM1 semiempirical methods [8] and with the newer SAM1 semiempirical method [9]. The computations were carried out primarily with the AMPAC [10] and SPARTAN [11] program packages. The geometry optimizations were performed with no preselected symmetry constraints in Cartesian coordinates and with an analytically constructed energy gradient. Harmonic vibrational analysis was also carried out, namely by numerical differentiation of the analytical energy gradient. The harmonic vibrational analysis offers (through the number of imaginary vibrational frequencies) a straightforward check if a local energy minimum was really achieved as required by the physical nature of our problem. The vibrational frequencies can also be used for spectral simulation and construction of partition functions for stability evaluations based on the Gibbs function (high temperatures in fullerene syntheses stress importance of the entropy contribution).

Inter-isomeric energetics were further computed at selected ab initio levels using the Gaussian package [12,13]. However, the advanced computations were only carried out

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in the fixed optimized PM3 geometry, i.e. with no *ab initio* geometry optimizations (as dictated by computational feasibility). In the PM3 optimized geometry, the *ab initio* Hartree–Fock SCF calculations in the standard 3-21G and 4-31G basis sets were first performed (HF/3-21G and HF/4-31G). The PM3 method is known [14] to reproduce well the available observed data, especially bond lengths, for fullerenes. Selection of these two smaller basis sets is a computational intermediate in order to allow reasonable treatment. The basis sets also exhibited good SCF convergency properties. Then, starting from the HF/4-31G SCF solution, the B3LYP density functional computations with the standard 6-31G* basis set were carried out (B3LYP/6-31G*). In the HF/4-31G computations, the stability of the wavefunction was checked (i.e. if it was really a local minimum in the wavefunction space).

3. Results and discussion

According to our recent B3LYP/6-31G* calculations [7], there are just two C₃₆ fullerene structures that are dominant at higher temperatures: the conventional D_{6h} and D_{2d} fullerenes (i.e. that are built from pentagons and hexagons only). Although the D_{2d} structure (as the isomer lower in potential energy) dominates at very low temperatures, the D_{2d}/D_{6h} stability order is already reversed at temperatures below 500 K. At this point, the conventional fullerene with the topological D_{6h} symmetry increases its relative fraction to a temperature maximum at approximately 1184 K with a computed yield of 77.1%. These computational results are based on enthalpy–entropy interplay and agree well with the available solid-state NMR spectra [4].

If a symmetric cut is made of the D_{6h}-C₃₆ cage with six pentagons, a model nanotube with such caps can be derived (we shall call it D_{6h}-related nanotube, although even the C₃₆ cage has the D_{6h} symmetry only in a topological sense, as it in fact undergoes a Jahn–Teller distortion and symmetry reduction). The D_{2d}-C₃₆ cage can be cut in a similar fashion

to create another cap and a D_{2d}-related model nanotube. (Note that this patch could actually be obtained from the D_{6h} cage as well.) The central body of the tubes between the caps can have very different lengths. However, from a practical point of view, we are limited by computational resources. Moreover, both model nanotubes should have the same number of carbon atoms to deal with an isomeric pair for comparison of their energies directly.

There is a clear difference in the energies of the two model nanotubes as reported in Table 1 for the C₈₄ isomeric pair (Fig. 1). The energy difference reflects both the differences in the cap structures and in the body arrangements. The D_{2d}-related model nanotube is lower in energy than the D_{6h} structure and has an inner diameter of about 5.42 Å (the D_{6h}-related model nanotube has a diameter of approximately 4.81 Å). This computed model geometry corresponds well with the observed value [1] of 5 Å. The energy differences computed at different levels of theory agree reasonably well (Table 1). The HF/4-31G term comes somewhat higher and may be related to the unbalanced character of the basis set.

With these results, we can also attempt a four-membered ring. A natural choice is the ground state of C₃₂—a D_{4d} cage [15] which contains two four-membered rings (together with eight pentagons and eight hexagons). In such generalized fullerenes, called *quasi*-fullerenes, the numbers of four-, five-, and seven-membered rings must satisfy [15] the following condition: $2n_4 + n_5 - n_7 = 12$ (there are no heptagons in the D_{4d}-C₃₂ *quasi*-fullerene). Although a thermodynamic treatment with partition functions suggests [15] that also other two cages are significantly populated at higher temperatures, the D_{4d}-C₃₂ *quasi*-fullerene is still present. In fact, four-membered rings represent [16–18] an important alternative structural pattern for B–N hetero-fullerenes and nanotubes [19,20], and such boron nitride fullerenes with four-membered cycles have been observed quite recently [21].

Therefore, it is interesting to test computationally a C₃₂ fragment with a four-membered ring as a cap for narrow nanotubes even though four-membered rings have rarely

Table 1

Computed characteristics^{a,b} of model narrow nanotubes related to the D_{2d}-C₃₆, D_{6h}-C₃₆, D_{4d}-C₃₂, I_h-C₂₀, and D_{4d}-C₁₆ cages

Model ^c	ΔE^a (kJ/mol)						ϕ^b (Å)
	PM3	AM1	SAM1	HF/3-21G	HF/4-31G	B3LYP/6-31G*	PM3
C ₈₄ /D _{6h} -C ₃₆	779	821	906	728	987	771	4.81
C ₈₄ /D _{2d} -C ₃₆	0	0	0	0	0	0	5.42
C ₉₆ /D _{6h} -C ₃₆	877	968	1192	766	1153	931	4.79
C ₉₆ /D _{4d} -C ₃₂	0	0	0	0	0	0	5.43
C ₈₀ /D _{4d} -C ₁₆	2004	2265	2241	2015	2275	— ^d	3.45
C ₈₀ /I _h -C ₂₀	0	0	0	0	0	0	3.93

^a The semiempirical PM3, AM1, and SAM1 terms represent the fully optimized relative heats of formation $\Delta H_{f,298,r}^\circ$ at room temperature, the *ab initio* HF/3-21G, HF/4-31G and B3LYP/6-31G* terms are relative potential energies computed in the PM3 optimized geometries.

^b ϕ denotes the diameter of a model nanotube, measured in its middle part.

^c Symmetry labels refer to the topological symmetries of the cages used for nanotube capping.

^d An SCF failure.

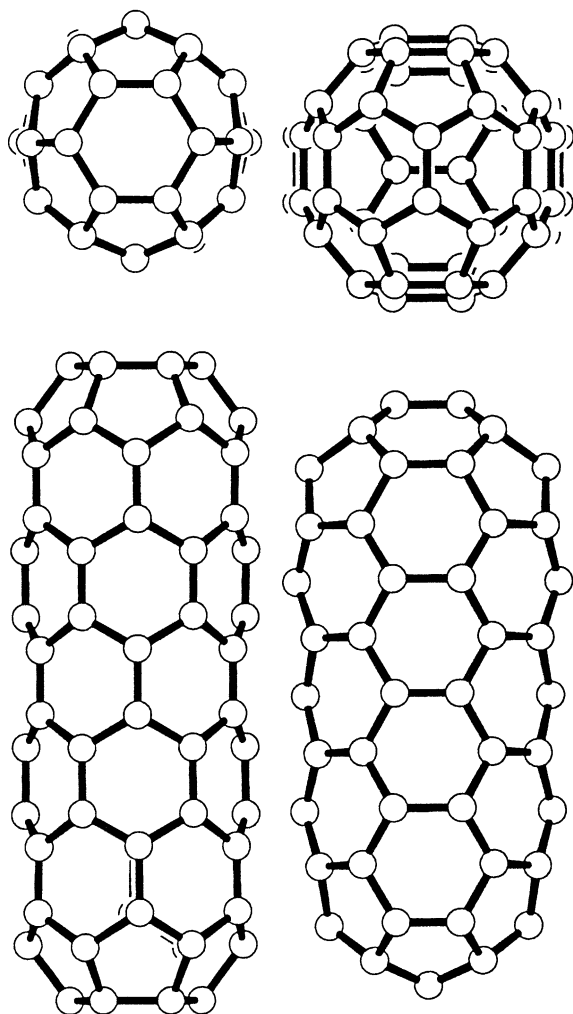


Fig. 1. PM3 structures of C_{84} model nanotubes capped with fragments of D_{6h} - and D_{2d} - C_{36} .

[14,22] been considered with fullerenes to this point. In order to have a pair of isomers, we utilized the C_{96} stoichiometry (see Fig. 2). Although we have only the D_{4d}/D_{6h} isomeric pair, the results in Table 1 basically suggest that the D_{2d} - C_{36} -related and D_{4d} - C_{32} -related nanotubes should be comparable in energy. Interestingly enough, the diameter of the D_{4d} - C_{32} -related model nanotube is 5.43 Å, which is almost identical with that of the D_{2d} - C_{36} -related model.

The inter-cap distances in our models are relatively short as dictated by computational feasibility. Changes in energetics are shown in Table 2 where model nanotubes are extended by 24 carbon atoms. Although the relative term, $\Delta\Delta H_{f,298}^\circ/n$ (the isomeric difference in heats of formation related to one carbon atom) is somewhat different for these systems, the changes actually stress the conclusions derived from the shorter models. However, it is presently beyond our computational ability to enlarge these models further.

Finally, we have attempted to calculate nanotubes which are capped with a very recently prepared [5,6] C_{20} dodecahedron fragment. As a structural alternative which contains

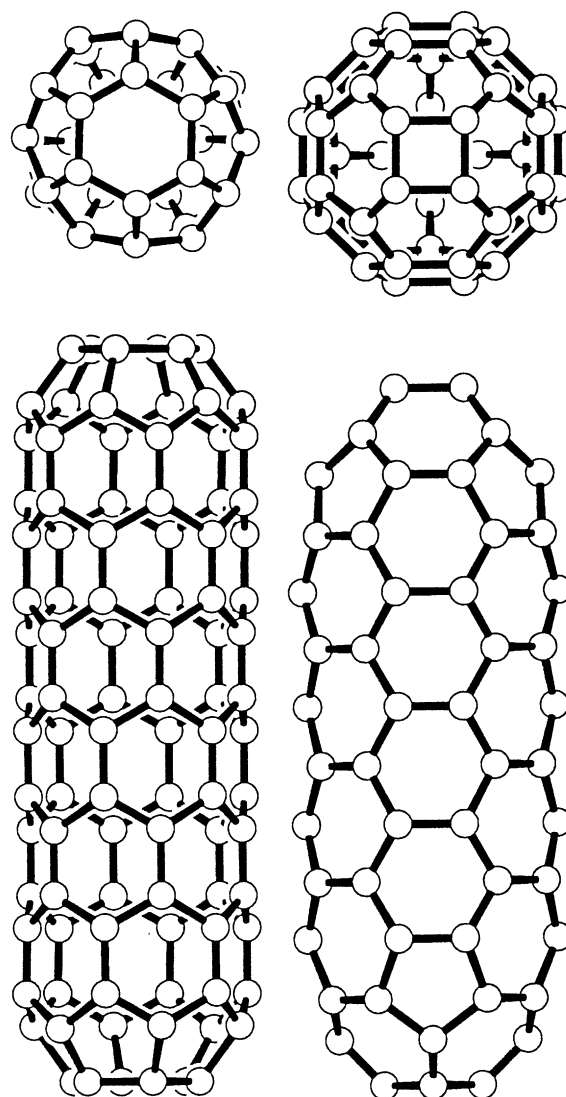


Fig. 2. PM3 structures of C_{96} model nanotubes capped with fragments of D_{6h} - C_{36} and C_{32} .

Table 2

Changes in the PM3 computed energetics^a for model narrow nanotubes related to the D_{2d} - C_{36} , D_{6h} - C_{36} , and D_{4d} - C_{32} cages with an increase of their length

C_n model ^b	D_{2d} - C_{36}	D_{6h} - C_{36}	$\Delta\Delta H_{f,298}^\circ$	$\Delta\Delta H_{f,298}^\circ/n$
C_{84}	5138	5917	779	9.28
C_{108}	6043	7066	1023	9.47
C_n model ^b	D_{4d} - C_{32}	D_{6h} - C_{36}	$\Delta\Delta H_{f,298}^\circ$	$\Delta\Delta H_{f,298}^\circ/n$
C_{96}	5594	6471	877	9.13
C_{120}	6392	7623	1231	10.3

^a The PM3 values refer to the fully optimized heats of formation $\Delta H_{f,298}^\circ$ at room temperature (in kJ/mol).

^b Symmetry labels refer to the topological symmetries of the cages used for nanotube capping.

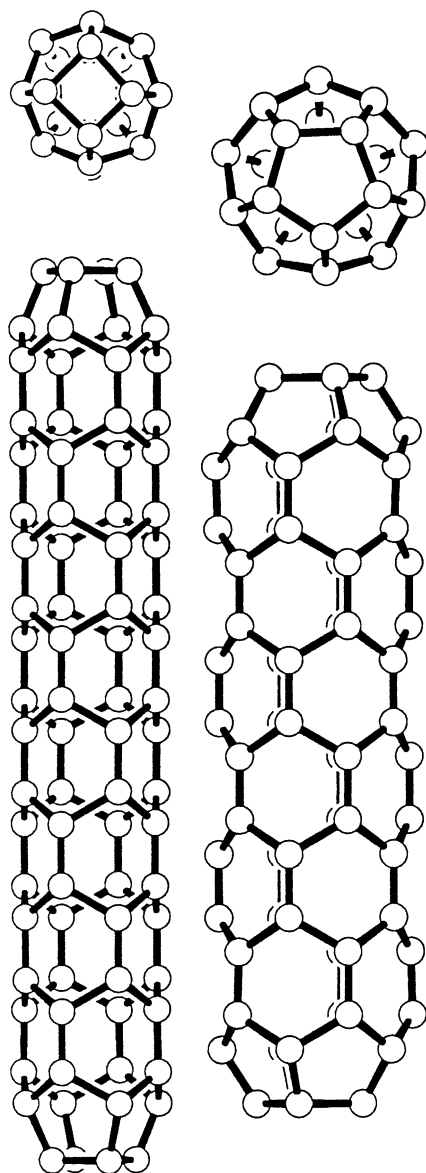


Fig. 3. PM3 structures of C_{80} model nanotubes capped with fragments of C_{16} and C_{20} .

a four-membered ring, one can recall a C_{16} cage built from two four-membered rings and eight pentagons. However, the latter cage is somewhat virtual as compared [4–6] to C_{36} and C_{20} , and it has never been isolated. In contrast [15] to C_{32} , there is no clear indication that it may be a plausible structure. In order to attain an isomeric pair, we calculated the C_{80} stoichiometry (Fig. 3). However, the computed energetics clearly rule out the C_{16} -related model nanotube (see Table 1).

In fact, only the PM3, AM1, SAM1, HF/3-21G, and HF/4-31G energy estimations are available for the C_{80} stoichiometry. The calculated B3LYP/6-31G* separation energy is unrealistically high. It is probably caused by a jump to another SCF solution during the iteration procedure. Interestingly enough, a very high energy is produced

by both G94 and G98 programs, though not exactly the same value. It is coincidental for this structure that at the HF/4-31G level it exhibited an unstable SCF solution so that a new search had to follow. In the B3LYP/6-31G* case, however, the wavefunction was still stable with respect to the attempted perturbations. Moreover, repeated starts from other initial wave functions led to the same solution. Nevertheless, the other five separation energies are mutually consistent and large so that they can be considered conclusive even without the related B3LYP/6-31G* calculation. The D_{4d} - C_{16} -related model nanotube with two four-membered rings is located above the conventional C_{20} fullerene-related nanotube by 2004, 2265, 2241, 1015, and 2275 kJ/mol in the PM3, AM1, SAM1, HF/3-21G, and HF/4-31G computational treatments, respectively. Consequently, for the narrow nanotubes of the 4 Å gauge the capping with the conventional C_{20} fullerene fragment seems to be the only plausible option. The C_{20} -related C_{80} PM3 model nanotube has 3.93 Å diameter.

In principle, one can imagine still narrower nanotubes. For example, a triangle combined with three pentagons can be used as a cap. Such a nanotube model with, for example, the stoichiometry of C_{90} is isomeric with the 4.0 Å wide model nanotube closed by fragments of C_{20} dodecahedron. The species with two triangles at its ends is computed at the PM3 level to be just 2.7 Å wide. However, the PM3 energetics suggests it is out of any consideration as it is some 7000 kJ/mol higher than the dodecahedron-based C_{90} model nanotube.

Nanotubes are formed [23] on a (catalytic) surface rather than in the gas phase as are fullerenes. In the case of isomeric fullerenes, high temperature gas-phase conditions should allow for inter-isomeric equilibria. There are several relatively well known systems that can illustrate this feature. For example, with C_{78} four isomers have been observed [24–28] and the experimental results are reflected accordingly in computations [29–32]. For nanotubes localized on a surface, the concept of a partial thermodynamic equilibrium [33,34], and how to achieve it, is less clear and actually may not control the formation process. It should be, however, investigated as to what type of predictions can be obtained from an approach based only on the vibrational partition function.

In this paper, the PM3 geometry is given preference as it is the best tested semiempirical method with fullerenes [14,34]. The PM3 method reproduces [14,34–36] (basically within the experimental error bars and the differences between different measurements) the observed bond lengths in C_{60} and C_{70} . For example, the PM3 lengths of the two types of bonds in C_{60} are 1.384 and 1.458 Å while their NMR measured values are [37] 1.40 ± 0.015 and 1.45 ± 0.015 Å. At the semiempirical level, the harmonic vibrational analysis is also computationally feasible, and as there are no imaginary frequencies in the computed vibrational spectra, the analysis shows that all the optimized structures are local energy minima. However, it would be still interesting to re-optimize the structures at some ab initio HF or density

functional level when computationally possible to us. The jumps in some SCF iteration cycles likely indicate low lying excited states [38], which itself is a topic which deserves a deeper investigation.

In conclusion, the reported computations support the C₃₆ and C₂₀ caps in the nanotubes 5 and 4 Å wide, respectively. However, for the 5 Å wide nanotubes, the computations also suggest a possibility that some can have four-membered ring caps at the tips, and consequently, they should exhibit different material and electronic properties. The computations do not support existence of nanotubes with diameters smaller than 4 Å.

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