

Computations of Nanotubes as Agents for Molecular Electronics: Narrow Nanotubes Related to C_{36} , C_{32} , C_{20} , and C_{16}

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ABSTRACT

Very recently, narrow nanotubes have been observed with a diameter of 5 Å and even with a diameter of 4 Å. It has been supposed that the narrow nanotubes are closed by fragments of C_{36} and C_{20} fullerenes. The contribution reports computations on related model nanotubes with stoichiometries like C_{84} , C_{96} or C_{80} . Computations are carried out at the PM3, SAM1, HF/4-31G, and B3LYP/6-31G* levels, though the geometry optimizations are performed only at the semiempirical levels. Two C_{36} fullerenes are considered, D_{6h} and D_{2d} , and, for example, at the PM3 level and with the C_{84} nanotube stoichiometry the D_{2d} cage closure gives a lower energy (by 185 kcal/mol and diameter of 5.42 Å). There is another possible candidate, C_{32} cage with a D_{4d} symmetry. At the PM3 level and with the C_{96} nanotube stoichiometry the D_{4d} closure has the nanotube energy lower by 210 kcal/mol (with the nanotube diameter of 5.43 Å) compared to the D_{6h} nanotube closure. On the other hand, four-membered rings should not play a significant role in the narrow nanotubes with the diameter of 4 Å, where the dodecahedron-related closure should be exclusive as a four-membered ring containing structure is located already much higher in energy. Applicability of the new structures in the field of molecular electronics is briefly discussed.

Keywords: Narrow nanotubes; smaller fullerenes; four-membered rings; Jahn-Teller effect; molecular electronics.

1 INTRODUCTION

A new type of nanotubes, extremely narrow nanotubes, has very recently been discovered. Sun *et al.* [1] produced narrow nanotubes with a diameter of 5 Å. Later on, Qin *et al.* [2] and Wang *et al.* [3] reported even nanotubes with a diameter of only 4 Å. Incidentally, some smaller fullerenes were also prepared, first solid-state [4] C_{36} and then gas-phase [5] and solid [6] C_{20} . It has been suggested [1,2] that the narrow nanotubes are actually closed by fragments of the small C_{36} and C_{20} fullerenes. Our preliminary model calculations [7] support the suggestion. In this contribution, we report further computations on the model narrow nanotubes with stoichiometries: C_{84} , C_{96} , and C_{80} . Computations are carried out at the semiempirical PM3 and SAM1 levels,

and checked at the *ab initio* Hartree-Fock SCF HF/4-31G and density functional theory B3LYP/6-31G* levels. The paper aims at a better understanding of structural features of narrow nanotubes and their relationships to functional properties for materials science and molecular electronics.

2 COMPUTATIONS

The geometry optimizations were performed with the PM3 semiempirical method [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 symmetry constraints in Cartesian coordinates and with analytically constructed energy gradient. The harmonic vibrational analysis was also carried out, namely by numerical differentiation of the analytical energy gradient. The harmonic vibrational analysis offers a straightforward check if a local energy minimum was really reached as required by the physical nature of our problem. It can also simulate IR or Raman vibrational spectra.

Inter-isomeric energetics was further computed at *ab initio* level using the Gaussian package [12,13]. However, the advanced computations were only carried out in the fixed optimized PM3 geometry, i.e., no *ab initio* geometry optimizations. In the PM3 optimized geometry, the *ab initio* Hartree-Fock SCF calculations in the standard 4-31G basis set were first performed (HF/4-31G). Then, starting from the HF/4-31G 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 is really a local minimum in the wavefunction space). If the SCF stability check failed, the wavefunction was reoptimized in order to find a lower-energy solution.

3 RESULTS AND DISCUSSION

According to our recent B3LYP/6-31G* calculations [7], there are just two C_{36} fullerene structures that control the system at higher temperatures: the conventional (built from pentagons and hexagons only) fullerenes D_{6h} and D_{2d} . Although the D_{2d} structure (as the isomer lower in potential energy) has to prevail at very low temperatures, their stability order is reversed already below 500 K. Then, the conventional fullerene with the topo-

logical D_{6h} symmetry increases its relative fraction to a temperature maximum at about 1184 K with a yield of some 77.1 %. These computational findings agree well with the available solid-state NMR results [4].

There is a symmetric cut of the D_{6h} C_{36} cage with six pentagons, and we can derive a model nanotube with such caps (we shall call it D_{6h} -related nanotube, although even the C_{36} cage has the D_{6h} symmetry only in a topological sense, as it in fact undergoes a Jahn-Teller distortion and symmetry reduction). We can also cut the D_{2d} C_{36} cage and thus create another cap and a D_{2d} -related model nanotube (this patch could actually be obtained from the D_{6h} cage, too). The medium part of the nanotubes between the caps can have very different lengths, however, from a practical point of view, we are limited by computational demands.

Moreover, both model nanotubes should have the same number of carbon atoms so that we have an isomeric pair and thus, we can compare the energies directly. Thus, we have selected a C_{84} isomeric pair with topological symmetries D_{6h} and D_{2d} . In all the treatments the D_{6h} model nanotube is located considerably higher in the potential energy: 779, 906, 987, and 771 kJ/mol in the PM3, SAM1, HF/4-31G, and B3LYP/6-31G* approach, respectively. There is some qualitative difference between the semiempirical and *ab initio* treatments as the former refer to room temperature and the latter to the absolute zero temperature. Moreover, the PM3 and SAM1 terms are derived from the fully optimized molecular geometries, while the *ab initio* HF/4-31G and B3LYP/6-31G* terms are computed just in the fixed PM3 optimized geometries. In overall, the separation energies computed at different levels of theory agree reasonably well. The PM3 computed middle diameter of the D_{2d} -related model nanotube is about 5.42 Å (the D_{6h} -related model nanotube about 4.81 Å). This computed model geometry corresponds well with the observed value [1] of 5 Å.

With this computational knowledge, we can now also try a fragment with a four-membered ring. There is a relatively natural choice as the ground state for C_{32} is in fact a D_{4d} cage [14] with 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 have to satisfy [14] the binding condition: $2n_4 + n_5 - n_7 = 12$ (there are no heptagons in the D_{4d} C_{32} *quasi*-fullerene). Although thermodynamic treatment points [14] out five cages significantly populated at high temperatures, the D_{4d} C_{32} *quasi*-fullerene remains present. In fact, four-membered rings represent [15-17] an important alternative structural pattern for B-N hetero-fullerenes and nanotubes [18,19]. Such boron-nitride fullerenes with four-membered cycles have indeed been observed quite recently [20].

Hence, it makes sense to test computationally a C_{32} fragment with a four-membered ring as a cap for narrow nanotubes (though, four-membered rings have rarely [21,22] been considered with fullerenes so far). In order to get a pair of isomers, we can - for example - select the C_{96} stoichiometry. Although we have only a D_{4d}/D_{6h} pair, the results basically suggest that the D_{2d} C_{36} -related and D_{4d} C_{32} -related nanotubes should be comparable in energy. This conclusion follows from the finding that the conventional D_{6h} C_{36} -related model nanotube is placed above the D_{4d} C_{32} -related species

by some 877, 1192, 1153, and 931 kJ/mol in the PM3, SAM1, HF/4-31G, and B3LYP/6-31G* computations, respectively. Interestingly enough, the PM3 computed diameter of the D_{4d} C_{32} -related model nanotube is 5.43 Å, i.e., almost identical with that computed for the D_{2d} C_{36} -related model nanotube.

Finally, we can try narrow nanotubes capped with a fragment of the very recently prepared [5,6] C_{20} dodecahedron. The C_{20} species is the smallest conventional (classical) fullerene possible. Thus, it consists of twelve five-membered rings (and no six-membered ring). Its topological symmetry is I_h , i.e., the same as the icosahedral symmetry of C_{60} . Topologically, the structure is one of the Platonic solids - dodecahedron. But the frontier orbitals are degenerate and partially filled which requires a symmetry lowering [23-25] according to the Jahn-Teller theorem. At the HF/6-31G* level, for example, the symmetry of C_{20} is reduced to C_2 according to the computations of Raghavachari *et al.* [25].

As a structural alternative with 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} , it has never been isolated and also, in contrast [14] to C_{32} , there is no clear indication that it may be plausible. In order to get again an isomeric pair, we have selected the C_{80} stoichiometry. However, the computed energetics clearly rules the C_{16} -related model nanotube out. In fact, only the PM3, SAM1, and HF/4-31G energy estimations are available. The calculated B3LYP/6-31G* separation energy has unrealistically high value. It is probably caused by a jump to another solution [26] during the iteration procedure. Interestingly enough, a very high value is produced by both G94 and G98 programs, though not exactly the same term. It also happened with this structure that at the HF/4-31G level exhibited an unstable SCF solution so that a new search had to follow. In the B3LYP/6-31G* case, however, the wavefunction was stable with respect to the tried perturbations. Moreover, starts from other initial wave functions led to the same solution. Nevertheless, the other three separation energies are mutually consistent and so big 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, 2241, and 2275 kJ/mol in the PM3, SAM1, 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.

Nanotubes are formed [27] on a (catalytic) surface rather than in a simple gas phase like fullerenes. In the case of isomeric fullerenes, the high temperature gas-phase conditions should allow for inter-isomeric equilibria. There are several relatively well known systems that can illustrate the feature. For example, in C_{78} even four isomers have been observed [28-31] and the finding is reflected accordingly in computations [32-35]. For nanotubes localized on a surface, the concept of a partial thermodynamic equilibrium, and how to achieve it, is less clear and may not control the formation process. It could be however investigated what kind of predictions can be obtained from an approach based only on

the vibrational partition function, i.e. with the frozen translational and rotational degrees of freedom. Other approach could consider nanotubes attached to metal particles while the whole combined cluster is moving in gas phase. As the catalytical metal particles are probably not homogeneous, we deal with a considerably more complex scheme than in the case of gas-phase fullerene formation. Anyhow, catalytical actions have so far been simulated [36-38] only very rarely in fullerene science. Clearly enough, a full understanding and a complete modelling of nanotube distributions is much more remote task than elucidation of the fullerene formation mechanism.

Possible applications of fullerenes [39,40] and nanotubes [41-43] in molecular electronics have been studied vigorously. Three terminal devices for molecular electronics have been demonstrated [40] based on both fullerenes and nanotubes. It is not clear which of the two systems may be given preference in future. However, for the time being, production of a selected fullerene species is considerably simpler to control than a defined nanotube production. The narrow nanotubes themselves are very new species and their further studies are needed. Still, there is already one their application aspect of considerable interest. Superconductivity in 4 Å single-walled carbon nanotubes has been reported [44]. The narrow nanotubes were embedded in a zeolite matrix and exhibited superconductivity at temperatures below 20 K. Incidentally, measurements of superconductivity on ropes of single-walled carbon nanotubes have also been reported [45] though at considerably lower temperatures.

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 suggest also a possibility that some of them can have a four-membered ring at tips. Consequently they should exhibit somewhat different electronic features, this also being potentially significant for possible future applications in materials science and molecular electronics.

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