THE JOURNAL OF
PHYSICAL
CHEMISTRY A

VOLUME 106, NUMBER 19, MAY 16, 2002

LETTERS

Permanent Chiral Twisting of Nonchiral Carbon Nanotubes

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Received: February 18, 2002

Simulations of the solid-state structures of single-wall carbon nanotubes show that once a chiral twisting of a tube is included the interactions with the nearest tubes lock it in place. Comparison with experiments and implications for the catalytic activity of these new materials are discussed.

Introduction

The mechanical and electronic properties of carbon nanotubes are under scrutiny for a variety of applications.[1−10] Despite the flurry of activity, a large number of basic issues remain to be explored and settled before they become fully available for technological exploitation. Here we address, through computer simulations, a chemically appealing consequence of the inter-tube interactions.

Single-wall carbon nanotubes, SWCNT, can exist as insulators, as semiconductors, or even as conductors, and their structure can be chiral or nonchiral. These properties depend on the unit cell of the 2D graphite lattice that is rolled up to form the tube.[11,12] In particular, the so-called zigzag and armchair tubes are the only topologically nonchiral tubes. In the now popular (n, m) notation, $m = 0$ identifies zigzag tubes, and $n = m$ identifies armchair tubes. The great majority of chiral SWCNT are insulating. To date, the metallic, nonchiral (10, 10) armchair tubes have been the subject of a large number of theoretical studies,[11,12] although their experimental relative abundance is still open to debate.[13] Aggregation is one of the hurdles impeding the progress of work on single tubes and is caused by the formation of the $\pi-\pi$ stacking interactions that are repeated over the length of the tubes, which makes them form bundles that are not easy to pry apart (for instance, in solution, the solvent molecules can hardly percolate between the bundles). The bundles constitute one of the pristine forms of SWCNT, and the investigation of the inter-tube interactions is of fundamental theoretical and practical interest if one is to use them.

In this work, we investigate a special, chemically very important type of deformation: the chiralization of a nanotube through helicoidal twisting along its principal axis. In an isolated SWCNT, a twisting, once induced, would easily disappear, and the tube would bounce back to its original shape. In the solid, however, the large number of weakly binding inter-tube dispersion forces may lock the deformation into place permanently.

To test this hypothesis, we employed the so-called Brenner potential (set 1),[14] with the van der Waals interactions described by the MM3 potential[15] that was parametrized on a variety of organics and on graphite and was successful in the description of the subtle effects that lead to C_{60} spinning in the solid.[16] The cutoff for the interatomic potential was set to 12 Å after we verified that the procedure gave accurate results for graphite. Periodic boundary conditions, pbc, were used both axially and equatorially, Figure 1 provides a pictorial example.

Simulations were performed on isolated tubes having crystal structures with unit cells of 2 × 2 and 2 × 4 SWCNT with a length of up to ∼12 nm. A maximum of 76 800 atoms were treated explicitly (plus pbc). All the simulations were performed

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10.1021/jp025657g CCC: $22.00

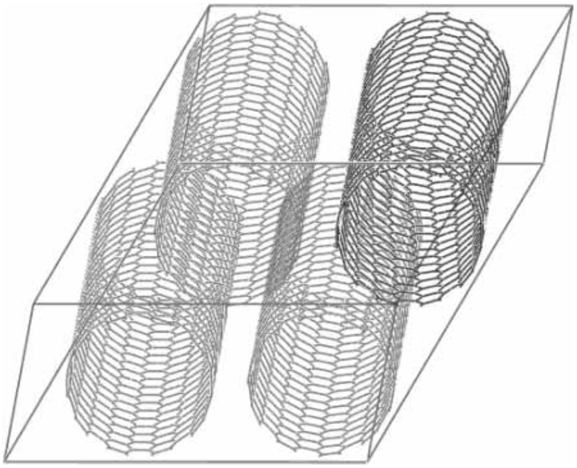

Figure 1. Pictorial representation of a cell with one chiralized nanotube.

TABLE 1: Summary of the More Significant Results for the Chiral Twisting of SWCNT[a]

Single Tube

length	24.6	49.2	98.4	196.8	393.7	590.5	1181.1
rings	20	40	80	160	320	480	960
atoms	400	800	1600	3200	6400	9600	19 200
E	853	533	334	180	90	60	30

2 × 2 Cell with One Chiral Tube

rings	40	80	160	320	640	960
atoms	3200	6400	12 800	25 600	51 200	76 800
energy	719	367	189	104	71	69
$E_{\text{intratube}}$	714	360	180	89	43	29
$E_{\text{intertube}}$	5	7	9	15	28	40

[a] Lengths are in Å and energies, E, in kcal mol^{-1}. Other results are discussed directly in the text.

on (10, 10) tubes. A single (10, 10) SWCNT without caps has a high 10-fold rotational symmetry along the axis with a periodicity of 36°. The successive rings/layers along the main axis of the tube are each made by 20 atoms. Chirality can be induced by in-phase twisting of the layers. The energy cost of the torsion depends on the length of the tube that the twisting insists upon. For the same angle of twisting, the longer the stretch, the lower the energy penalty to pay. To take advantage of the periodic boundary conditions present in our computer program, a simple approach is to apply an overall 36° rotation of the rings that are spread along the full length of the longitudinal axis, z, of the unit cell. In this way, the x and y coordinates of the atoms of the initial and final-plus-one layers are equivalent.

Initial simulations were performed on an isolated tube. The largest system was 120-nm long and comprised 19 200 atoms. The constrained twisting increased the energy of the systems (see Table 1).

Upon geometry optimization and from 3200 atoms, the distortion energy decreases linearly with the tube length to reach a chemically significant value of 30 kcal mol^{-1} for 19 200 atoms. Relaxing the constraint unwinds the tube back to the nonchiral structure. Table 1 also shows that a chiralized tube embedded in an environment of nonchiral tubes is energetically more costly than an isolated one. The increased energy cost reflects the combination of the inter-tube hexagon−hexagon mismatch, which decreases their van der Waals interaction energy and the intra-tube distortion energy. In shorter tubes, the distortion costs more than the energy of the hexagons' mismatch, and for the longest tube investigated here (960 rings), the van der Waals energy cost is 40 kcal mol^{-1} versus an intra-tube distortion energy of 29 kcal mol^{-1}.

A number of questions arise: (i) Is the chiral twisting permanent, or can it be made permanent? (ii) In the case of a stable twisted conformation, what is the length of distortion that SWCNT can support? (iii) Can left and right handedness be supported simultaneously, and how do the differently chiralized SWCNT interact? (iv) Is the induced conformational chirality actually present, or has it been detected in experiments? The first three questions were answered by further simulations in the solid phase and are discussed below.

(i) Stability of Chiral Twisting. The structure of a chiralized nanotube of 19 200 atoms embedded in a nonchiral nanotubes environment (2 × 2 cell) was optimized without boundary conditions along its main axis (i.e., axially uncoupled). The tube does not unwind to the nonchiral shape but relaxes to a local chiral minimum. The van der Waals interactions, therefore, keep the deformation in place and are able to lock the chirality. Once generated, conformational chiral twisting of SWCNT in crystals or in bundles may therefore be permanent (see discussion of ref 16 below).

(ii) Length of Chiral Twisting. The 36° torsion that was used throughout the computer experiments was applied to a 960-layers tube in a 2 × 2 (axially coupled) crystal for a varying number of rings. When the central 640 rings were twisted, the optimized energy of the system was 65 kcal mol^{-1} higher than that of the global, nonchiral minimum, but it was also 5 kcal mol^{-1} lower than when the twisting was spread over all 960 rings. Once induced, the conformational deformation must therefore have a finite length and may not spread over the entire tube length. Analogously, for a torsion of 775 out of 960 rings, the energy was 63 kcal mol^{-1} higher than the global minimum and 6 kcal mol^{-1} lower than when the torsion was spread over 960 rings, but when twisting 875 out of 960, the two energies were slightly smaller in the former and slightly larger in the latter. The optimal length for a 36° torsion is therefore between 800 and 900 layers.

(iii) Handedness of Chiral Twisting. Visual inspection of the SWCNT bundled structure generated in this work shows that two (10, 10) chiralized nanotubes of different handedness have the same inter-tube interactions as those of two chiralized tubes of the same handedness. In general, this is not the case: additional calculations performed on (12, 6) tubes proved that a small energy difference exists for the two possible handedness interactions (i.e., left−left equal to right−right and right−left equal to left−right). For (10, 10) SWCNT, however, it is interesting that two interacting left- or right-handed tubes are isoenergetic to a system composed of a right-handed tube interacting with a left-handed one. Optimization of 4 × 2 cells with two chiralized tubes gave an excess energy of 203 kcal mol^{-1}. This value is slightly less than twice the energy (104 kcal mol^{-1}) of a singly twisted tube and can further be compared with 390 kcal mol^{-1} of a set of four twisted tubes. The energy penalty for twisting does not increase linearly with the number of tubes.

(iv) Support for the Presence of Chiral Twisting. Scanning tunneling microscopy, STM, images of nanotube bundles is the most appropriate means to detect the presence of induced chiral twisting. Indeed, Clauss et al.[17] showed that their STM images may result from chiral nanotubes but are more consistently explained as resulting from a nonchiral armchair tube with a twist distortion. It is worth mentioning that direct comparison with STM or any scanning probing microscopy experiments may be carried out only partially because the number of tubes on a perfectly ordered surface is less than the number in the bulk (three versus six) and also because often the NT surface presents disorder, which implies even fewer neighbors. In the first case, a factor of 2 would apply to the inter-tube energies; in the second case, the torsional distortion could still be kept in place if the NT ends are embedded in a bundle where inter-tube interactions prevents their uncoiling.

Several conclusions about the existence of induced chirality in SWCNT may be made:

(i) The sizable energy penalty of the twisting ensures that it must appear in a high-energy regime, for instance, when the tubes are synthesized; alternatively, nanomanipulation based on atomic force microscopy devices may be used to induce this type of chiral twisting.

(ii) In the absence of a chiral catalyst in the synthesis, the amount of right handedness must equal the amount of left handedness; chiral areas of the same or different handedness can coexist on the same tube or, more likely, on different tubes on the basis of the energy.

(iii) Carbon nanotubes have been used as supports in heterogeneous catalysis,[18,19] with reaction yields that are twice as large as those obtained using amorphous carbon. If methods to separate tubes of different induced chirality can be devised, for instance, by using suitable chiral environments in the chamber in which they are prepared, it may be expected that the chiral and chirally twisted SWCNT used as a chiral support to metal catalysts will contribute to give enantiomeric excesses.

Although nanotubes can become chiral by the mechanism described before, permanently twisted tubes can also appear in conjunction with other solid-state conditions such as the aggregatation of tubes into ropes.[20]

In this work, (10, 10) SWCNT have been taken as a test case to evaluate the possible existence of permanent chiral twisting. The stability of the twisting is induced by a graphite-like hexagon−hexagon match between adjacent tubes and depends on the kind of tube and its environment. For instance, a semiconducting (17, 0) SWCNT rotates rigidly with a lower barrier than a (10, 10) barrier when it is surrounded by six metallic (10, 10) tubes. This behavior is due to the imperfect match of the two hexagon motifs. In general, the phenomenon is not expected to depend on the electronic nature of the SWCNT (metallic, semiconducting, or insulating), but it will depend on the pattern of tube−tube interactions.

Other static deformations induced by SWCNT aggregation will be reported elsewhere.

Acknowledgment. This work was carried out with partial support from the European Union, TMR Network USEFULL under contract FRMX-CT97-0126, the Human Potential Network FUNCARS under contract HPRN-1999-00011, and the CNR program Materiali Innovativi (legge 95/95).

References and Notes

(1) Rueckes, T.; Kim, K.; Joselevich, E.; Tseng, G. Y.; Cheung, C. L.; Lieber, C. M. *Science (Washington, D.C.)* **2000**, *289*, 94−97.

(2) Tans, S. J.; Verschueren, A. R. M.; Dekker, C. *Nature (London)* **1998**, *393*, 49−52.

(3) Frank, S.; Poncharal, P.; Wang, Z. L.; DeHeer, W. A. *Science (Washington, D.C.)* **1998**, *280*, 1744−1746.

(4) Kong, J.; Franklin, N. R.; Zhou, C.; Chapline, M. G.; Peng, S.; Cho, K.; Dai, H. *Science (Washington, D.C.)* **2000**, *287*, 622−625.

(5) Collins, P. G.; Bradley, K.; Ishigami, M.; Zettl, A. *Science (Washington, D.C.)* **2000**, *287*, 1801−1804.

(6) Inganäs, O.; Lundstroem, I. *Science (Washington, D.C.)* **1999**, *284*, 1281−1282.

(7) Baughman, R. H.; Cui, C.; Zakhidov, A. A.; Iqbal, Z.; Barisci, J. N.; Spinks, G. M.; Wallace, G. G.; Mazzoldi, A.; DeRossi, D.; Rinzler, A. G.; Jaschinski, O.; Roth, S.; Kertesz, M. *Science (Washington, D.C.)* **1999**, *284*, 1340−1344.

(8) Liu, C.; Fan, Y. Y.; Liu, M.; Cong, H. T.; Cheng, H. M.; Dresselhaus, M. S. *Science (Washington, D.C.)* **1999**, *286*, 1127−1129.

(9) Chen, P.; Wu, X.; Lin, J.; Tan, K. L. *Science (Washington, D.C.)* **1999**, *285*, 91−93.

(10) Kim, P.; Lieber, C. M. *Science (Washington, D.C.)* **1999**, *286*, 2148−2150.

(11) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: San Diego, CA, 1996.

(12) Harris, P. J. F. *Carbon Nanotubes and Related Structures*; Cambridge University Press: Cambridge, U.K., 1999.

(13) Colomer, J.-F.; Henrard, L.; Lambin, Ph.; Van Tendeloo, G. *Phys. Rev. B: Condens. Matter* **2001**, *64*, 125425-1−125425-7.

(14) Brenner, D. W. *Phys. Rev. B: Condens. Matter* **1990**, *42*, 9458−9471.

(15) Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551−8566.

(16) Deleuze, M. S.; Zerbetto, F. *J. Am. Chem. Soc.* **1999**, *121*, 5281−5286.

(17) Clauss, W.; Bergeron, D. J.; Johnson, A. T. *Phys. Rev. B: Condens. Matter* **1998**, *58*, R4266−R4269.

(18) Planeix, J. M.; Coustel, N.; Coq, B.; Brotons, V.; Kumbhar, P. S.; Dutartre, R.; Geneste, P.; Bernier, P.; Ajayan, P. M. *J. Am. Chem. Soc.* **1994**, *116*, 7935−7936.

(19) Rodriguez, N. M.; Kim, M. S.; Baker, R. T. K. *J. Phys. Chem.* **1994**, *98*, 13108−13111.

(20) Ausman, K. D.; O'Connell, M. J.; Boul, P.; Ericson, L. M.; Casavant, M. J.; Walters, D. A.; Huffman, C.; Saini, R.; Wang, Y.; Haroz, E.; Billups, E. W.; Smalley, R. E.; In *Roping and Wrapping Carbon Nanotubes*, Proceedings of the XVth International Winterschool on Electronic Properties of Novel Materials, Kirchberg, Austria, March 2001.