Nanotubes

Side-Wall Opening of Single-Walled Carbon Nanotubes (SWCNTs) by Chemical Modification: A Critical Theoretical Study[**]

Zhongfang Chen,[*] Shigeru Nagase, Andreas Hirsch,
Robert C Haddon, Walter Thiel, and
Paul von Ragué Schleyer[*]

Dedicated to Professor Henry F. Schaefer III
on the occasion of his 60th birthday

Single-walled carbon nanotubes (SWCNTs) have unique electronic, mechanical, and structural characteristics; consequently, promising applications derived from these materials, such as chemical sensors or nanometer-scale electronic devices,[1] can be expected. Structurally altered nanotubes with appropriate addends should facilitate their use by improving solubility, processability, and ease of dispersion, as well as by providing sites for chemical attachment to surfaces and polymer matrices.[2]

A vexing problem is ascertaining the detailed structures of nanotube derivatives after their preparation. The characterization of functionalized SWCNTs is difficult; all experimental attempts to determine the precise location and mode of addition of newly attached groups have failed. SWCNT adducts with possible three-membered rings (3MRs) that result from oxygen, methylene, and NH additions are simple but very important side-wall functionalized derivatives. Oxidation reactions are used widely to purify nanotubes,[3] and the electrical properties of carbon nanotubes are extremely sensitive to oxygen exposure.[4] Methylene and NH adducts are the prototypes of the recently synthesized covalently bonded dichlorocarbene[5] and nitrene[6] adducts. The available theoretical studies on the structures of nanotube oxide[7] and dichlorocarbene adducts[8] that involve either armchair[7a,8] or zigzag tube[7b–f] models, employed rather unsatisfactory methodology (see below).

Owing to the large size of nanotubes, carefully chosen truncated models, appropriate for the problem being investigated, are required. One approach uses small nanotube fragments to simulate a full nanotube, but carries out computations at a relatively high level.[7b,9] The other approach uses the ONIOM technique,[10] which treats part of the system at a high theoretical level but the rest of the system at a lower level. This strategy allows larger systems to be simulated at a practical computational cost.[7a–c,11] Thus, a recent ONIOM(B3LYP/6-31G*:AM1) study employed a C_{16} fragment (Figure 1a) for the high-level computation to simulate the side-wall chemistry of the armchair SWCNTs.[7a,11a–11f] However, no systematic validation of the ONIOM approach for such applications is available.

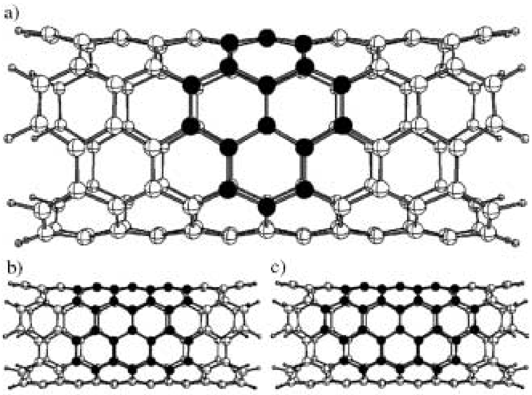

Figure 1. Thirteen-layered (5,5) tube model ($C_{130}H_{20}$), in which the highlighted a) 16, b) 28, and c) 32 atoms are used for the high-level treatment in the two-level ONIOM computations.

Herein we report B3LYP/6-31G* computations[12] on the O, CH_2, and NH nanotube derivatives, as well as the hypothetical SiH_2 adduct, for both (5,5) and (8,0) SWCNTs. In addition, several combinations of methods in the two-level ONIOM approach are evaluated.

(5,5) Armchair SWCNT Derivatives**:** The optimized structure of the NH adduct of the 13-layered tube model is shown in Figure 2 as an example (see the Supporting Information for others). The separations between the two C atoms at the site at which the O, CH_2, SiH_2, and NH addends are attached to the (5,5) armchair SWCNT models are all over 2 Å (Table 1). Regardless of the addend and of the length of the the (5,5) model, all the modified nanotubes have opened structures rather than 3MRs. We have obtained the

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[*] Dr. Z. Chen, Prof. Dr. A. Hirsch, Prof. Dr. P. von R. Schleyer
Institut für Organische Chemie
Universität Erlangen-Nürnberg
Henkestrasse 42, 91054 Erlangen (Germany)
Fax: (+49) 9131-85-26864
E-mail: chen@organik.uni-erlangen.de
schleyer@chem.uga.edu

Prof. Dr. S. Nagase
Department of Theoretical Studies
Institute for Molecular Science
Okazaki 444-8585 (Japan)

Prof. Dr. R. C. Haddon
Departments of Chemical and Environmental Engineering and
Chemistry and Center for Nanoscale Science & Engineering
University of California
Riverside, CA 92521 (USA)

Prof. Dr. W. Thiel
Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr (Germany)

Dr. Z. Chen, Prof. Dr. P. von R. Schleyer
Department of Chemistry and
Center for Computational Quantum Chemistry
University of Georgia
Athens, GA 30602 (USA)

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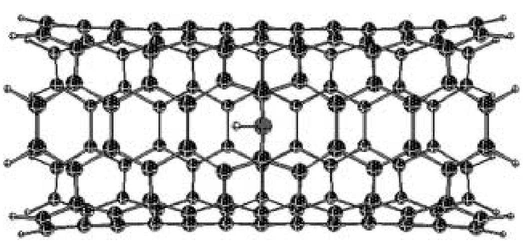

Figure 2. B3LYP/6-31G* optimized NH adduct of the 13-layered (5,5) SWCNT model.

Table 1: Distances (in Å) between two C atoms attached to the addend in *n*-layered (5,5) SWCNT derivatives (B3LYP/6-31G*).

n	O	CH_2	SiH_2	NH
5	2.141	2.250	2.542	2.179
7	2.049	2.142	2.379	2.086
9	2.139	2.231	2.478[a]	2.086
13	2.096	2.186	2.417	2.131

[a] Another minimum with a CC bond length of 1.723 Å is 16.8 kcal mol^{-1} higher in energy.

same result for the oxygen and methylene adducts of (10,10) SWCNTs that have typical nanotube diameters (see Supporting Information). The strain of the 3MR alternatives and their diminished aromaticity, as in the bridged 1,6-X-[10]annulenes,[13] is responsible for these open structures. These findings contradict earlier theoretical studies with the ONIOM method[7a,11f] and with GGA (general gradient approximation) exchange-correlation functionals by using a plane-wave basis set.[7g,14]

(8,0) zigzag SWCNTs: There are two sets of C–C bonds in zigzag SWCNTs (see Figure 3). Though no literature on the structures of CH_2, NH, and SiH_2 adducts with zigzag SWCNTs is available, oxygen adducts of such tubes have been well investigated. With the exception of the work reported in reference [7e], the C–C bond parallel to the tube axis was used as the site to model the reactions.[7b,d,f,g] We find that all the (8,0) tube oxides in this addition pattern (**I**) favor closed 3MRs (C–C bond lengths 1.464, 1.468, and 1.473 Å for Figure 3a–c, respectively). However, the parallel C–C bonds in the zigzag SWCNTs have greater single-bond character, whereas the diagonal C–C bonds are more double-bond-like. Indeed, computations confirm our expectation that the oxide **3d** with addition-pattern **II** not only is 25.6 kcal mol^{-1} more stable than **3a**, but, as in the (5,5) adducts, also has an opened structure (2.126 Å) rather than a 3MR, in agreement with reference [7e]. This conclusion holds true for CH_2, NH, and SiH_2 adducts (see Supporting Information), whose addition-pattern **II** is more stable than **I** by 30.7, 29.5, and 20.4 kcal mol^{-1}, respectively.

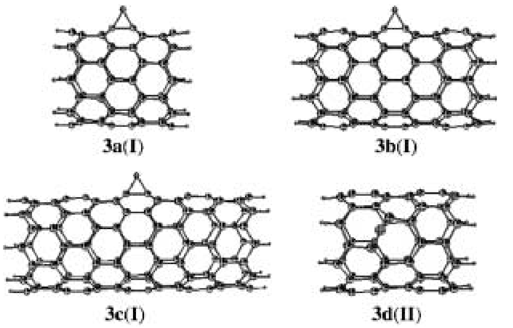

Figure 3. B3LYP/6-31G* optimized structures of (8,0) SWCNT oxide. (a)–(c) are 8-, 12- and 16-layered model with addition pattern **I**, and (d) is the 8-layered model with addition pattern **II**.

ONIOM evaluation**:** Does the ONIOM model give reliable results for nanotubes? Table 2 summarizes a critical evaluation that involves different combinations in the two-level ONIOM method for the 16-, 28-, and 32-atom high-level models (Figure 1). The B3LYP/6-31G* results on the adducts of the full $C_{130}H_{20}$ systems are used as reference; HF/3-21G and AM1 data on these full systems are included for comparison.

Table 2: Distances (in Å) between the two C atoms where the addend in *n*-layered (5,5) SWCNT derivatives is attached.

13-layer	N_{high}[a]	O	CH_2	SiH_2	NH
B3LYP/6-31G*	full	2.096	2.186	2.417	2.131
HF/3-21G	full	2.133	2.140	2.314[b]	2.140
AM1[c]	full	2.216	2.224	2.366	2.174
ONIOM	16	1.586	1.694	1.719	1.636
(B3LYP/6-31G*	28	1.585	1.687	1.593	1.634
:AM1)	32	1.590	1.706	1.706	1.646
ONIOM	16	2.084	2.176	2.402	2.120
(B3LYP/6-31G*	28	2.090	2.182	2.411	2.126
:B3LYPSTO-3G)	32	2.083	2.176	2.398	2.118
ONIOM	16	1.559	1.651	1.669	1.599
(B3LYP/6-31G*	28	1.570	1.682	2.580	1.622
:HF/3–21G)	32	1.581	1.712	1.622	1.639

[a] Number of atoms at the high level in ONIOM approach. [b] Another minimum with a 1.789 Å bond length is 2.5 kcal mol^{-1} higher in energy. [c] Higher energy minima with closed 3MRs also were located (see Supporting Information).

The full B3LYP/6-31G* results are reproduced at the full HF/3-21G and full AM1 levels: all the (5,5) tube adducts favor opened structures rather than 3MRs. However, higher-energy closed 3MR minima also were located for all the adducts at AM1 and for the SiH_2 adduct at HF/3-21G. But these closed 3MR forms did not survive further optimization at B3LYP/6-31G*.

In contrast, only the ONIOM(B3LYP/6-31G*:B3LYP-STO-3G) combination reproduces all the results from density functional theory. The combination of B3LYP/6-31G* with AM1 and with HF/3-21G fail since they predict closed 3MRs. This is surprising as both AM1 and HF/3-21G methods by themselves give opened structures (see Table 2). When the opened B3LYP geometry for the oxide was used as the starting structure for ONIOM optimization for the latter two combinations, only closed 3MRs resulted. The often-employed ONIOM(B3LYP:AM1) model as implemented in Gaussian 98[12] is thus not reliable, at least for the systems we studied. This underlines the need for careful validation of the ONIOM approach for any given application. The S-value test[15] (see Supporting Information) may be helpful in this regard.

In summary, the (5,5) armchair SWCNT derivatives investigated here have opened structures instead of 3MRs. Furthermore, the addends prefer attachment to the diagonal C−C bonds in (8,0) zigzag tubes, and also are prone to adopt opened rather than 3MR structures. Since armchair and zigzag tubes are two extremes for SWCNT structures, evidently the side-wall of SWCNTs can be opened by chemical modifications. As the often-used ONIOM(B3LYP:AM1) approach is not appropriate for the systems studied in this paper, serious limitations in the ONIOM approach to computational nanotube chemistry are apparent. Our computational results, that SWCNT derivatives favor opened rather than 3MR structures, may be verified experimentally with new advances in SWCNT solubilization and spectroscopic analysis. Experiments aimed at this purpose are under way.

Supporting Information available**:** AM1 results, optimized structures of (10,10) SWCNT adducts, S-value test, B3LYP/6-31G* structures for (5,5) and (8,0) SWCNT adducts.

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