Direct Amidation of Terminal Carboxylic Groups of Armchair and Zigzag Single-Walled Carbon Nanotubes: A Theoretical Study

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ABSTRACT

Using a two-level ONIOM approach, we performed a theoretical study of the direct amidation of mono-carboxyl-derivatized fragments of zigzag (10,0) and armchair (5,5) single-walled carbon nanotubes (SWNTs) with the simplest aliphatic amine, methylamine. Our results suggest that the direct formation of amides is much more energetically preferable on armchair SWNT tips than on the zigzag nanotube tips. This might open a new route to selective derivatization of different forms of carbon nanotubes.

One of the much-promising ways to expand application areas of carbon nanotubes (CNTs) is their chemical derivatization.[1−18] In the studies of interaction of CNTs with organic compounds, amines gained special attention. Applications of particular interest are the covalent functionalization of CNT probe tips for chemical force microscopy,[2,3] increasing the solubility of single-walled CNTs (SWNTs),[1,4,9,14] their self-assembly on gold substrates,[11] plasma activation of CNTs for chemical modification,[15] and chemical gating of individual semiconducting and metallic SWNTs.[16] The most extensively explored is the formation of amide derivatives between carboxylic groups on oxidized CNT tips and long-chain amines.[1−4,9] The reaction is usually performed through a chemical activation of the carboxylic groups with thionyl chloride or carbodiimides in an organic solvent medium.[1−4,9,11] More recently, we suggested an alternative approach to the amide derivatization: direct treatment of carboxylated CNTs with vaporous amines under reduced pressure and temperatures of ca. 200 °C,[19] according to the following general scheme:

$$SWNT-COOH + HNR^1R^2 \rightarrow$$
$$SWNT-CO-NR^1R^2 + H_2O \quad (1)$$
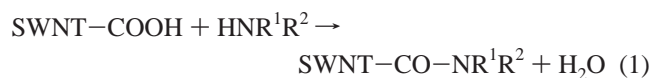
where R^1 = H or Alk and R^2 = Alk.

CNTs can be considered polyfunctional macromolecules, where, from common considerations, every particular reaction can take place at different sites with different efficiencies: this refers to both the tips and walls. Another important aspect of CNT reactivity is the existence of different forms on the nanotubes by themselves: zigzag, armchair, and chiral forms. All of these species are apparently present in CNTs grown by most methods. For the particular case of direct amidation reaction 1, one can expect that the reactivity of carboxylic groups toward amines might be different depending on whether the nanotubes have an armchair or zigzag structure. Studying the specificity of such a sort can be considered as a possible pathway to selective derivatization of different forms of CNTs, and to their further separation: for example, due to different solubility of derivatized and nonderivatized nanotubes. However, this goal seems to be very complicated from the experimental point of view and requires further sophistication of the methods of handling and observing individual CNTs.

In the meantime, some insight can be obtained by using theoretical approaches. Various model chemistries were already used to study structural, physical, and chemical properties of CNTs. Among quantum chemical methods employed for the nanotubes, one can mention pure semiempirical,[20−24] Hartree−Fock,[22] and density functional theory (DFT) calculations.[22,25] While semiempirical methods proved to be a very useful and accessible tool to describe some CNT properties semiquantitatively, they are obviously unable to

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provide reliable estimates for reaction mechanisms and energetics. On the other hand, the ab initio procedures (including DFT) so far are too expensive to allow routine calculations of such large molecular systems as even small SWNTs are.

An elegant solution for this problem came with the development of the ONIOM approach,[26,27] consisting of dividing the whole molecular system into two or three levels: a relatively small section, essential for a CNT property of interest, is treated at a higher theoretical level (ab initio), whereas the remaining one or two serve mostly to constrain the general geometry and are described by a computationally less demanding method (molecular mechanics or semiempirical).[26,27] Recently, the ONIOM approach was employed to study the addition of hydrogen and fluorine atoms to zigzag (10,0) and armchair (4,4) SWNT side walls.[28–30] In those works, the high-level description of the reaction site was performed with the B3LYP DFT method in conjunction with the 4-31G, 6-31G(d), or 6-311G(d) basis set, and the low level was treated with the universal force field[31] (UFF) molecular mechanics method.

Using the same computational procedure, in the present paper we tried to address the following question: how different can the reactivity of carboxylic groups be toward amines in the direct amidation reaction (1) depending on whether the nanotubes have an armchair or zigzag structure?

As model reaction systems, we used monocarboxylated short fragments of (10,0) zigzag and (5,5) armchair SWNTs (shown in Figure 1) interacting with the simplest aliphatic amine, methylamine. Reaction mechanisms were studied using a two-level ONIOM approach[26,27] implemented in the Gaussian 98W suite of programs.[27,32] UFF[31] was used for the low-level treatment, and the Becke's three-parameter hybrid method[33] with the exchange functional of Lee, Yang, and Parr[34] (B3LYP) was used for the high-level description, in conjunction with the 6-31G(d) basis set by Pople et al.[35–37] A search for transition states was first carried out using the QST2 procedure: in this case, whole molecular systems were treated with the AM1 semiempirical method. Then the results obtained were refined with the ONIOM procedure, using the TS option for the search of transition state. The stationary point geometries were fully optimized and characterized as minima (0 imaginary frequencies) or first-order saddle points (1 imaginary frequency) by calculations of vibration frequencies. All the optimizations met the default convergence criteria set in Gaussian 98W. As in refs 28 and 29, we discuss the calculated B3LYP energies, using the molecular mechanics only to constrain the geometry of the high-level fragment.

For the reactants, the high level included a methylamine molecule and carboxylic groups along with their adjacent C and H atoms, as shown in Figure 1. Although the total number of atoms (and nanotube length) did not coincide in the two (armchair and zigzag) SWNT models, important characteristics such as the number of B3LYP-treated atoms and of terminal hydrogen atoms was kept the same.

Total optimized geometries and fragments treated at the B3LYP/6-31G(d) theoretical level of the reaction complexes, transition states, and products for the gas-phase reaction of
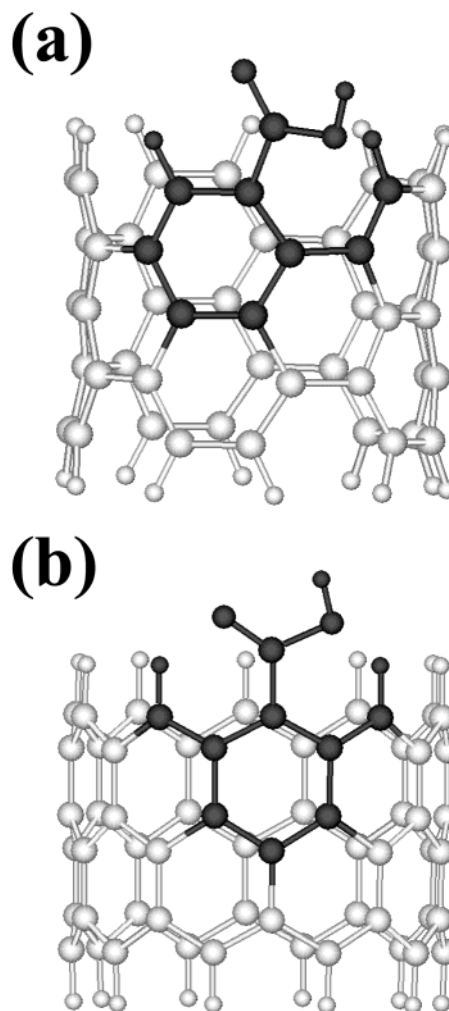

Figure 1. Monocarboxyl-substituted fragments of (5,5) armchair (a) and (10,0) zigzag (b) SWNTs used for two-level ONIOM calculations of the model gas-phase reaction with methylamine. The highlighted (dark) atoms and those constituting methylamine molecule were treated at the B3LYP/6-31G(d) level of theory; the remaining SWNT atoms were treated with UFF molecular mechanics.

(5,5) armchair and (10,0) zigzag SWNT with methylamine are presented in Figures 2 and 3, respectively. As could be expected, there are noticeable differences in the geometries at every stationary point. For example, for the reaction (van der Waals) complexes, in the case of armchair (5,5) SWNT there is a very weak hydrogen bond between the amino and carboxylic groups, with $O(2)\cdots H(2)$ distance of 2.321 Å (Figure 2a and Table 1), whereas the corresponding $O(2)\cdots H(3)$ distance of 3.731 Å in the zigzag (10,0) nanotube (Figure 3a and Table 1) is far too long to consider it a H-bond. [We attempted to refine the calculations with the 6-31++G(d,p) basis set to enhance the van der Waals interactions, but the geometry obtained does not differ significantly from the one obtained with the 6-31G(d) basis set ($O(2)\cdots H(3)$ distance slightly increased, from 3.731 to 3.780 Å).] Both observed $NH\cdots H$ distances (elongated as compared to common H bonds) along with the trend of the methyl group to keep close to the nanotube axis well agree with our earlier suggestion,[19] that hydrophobic forces con-
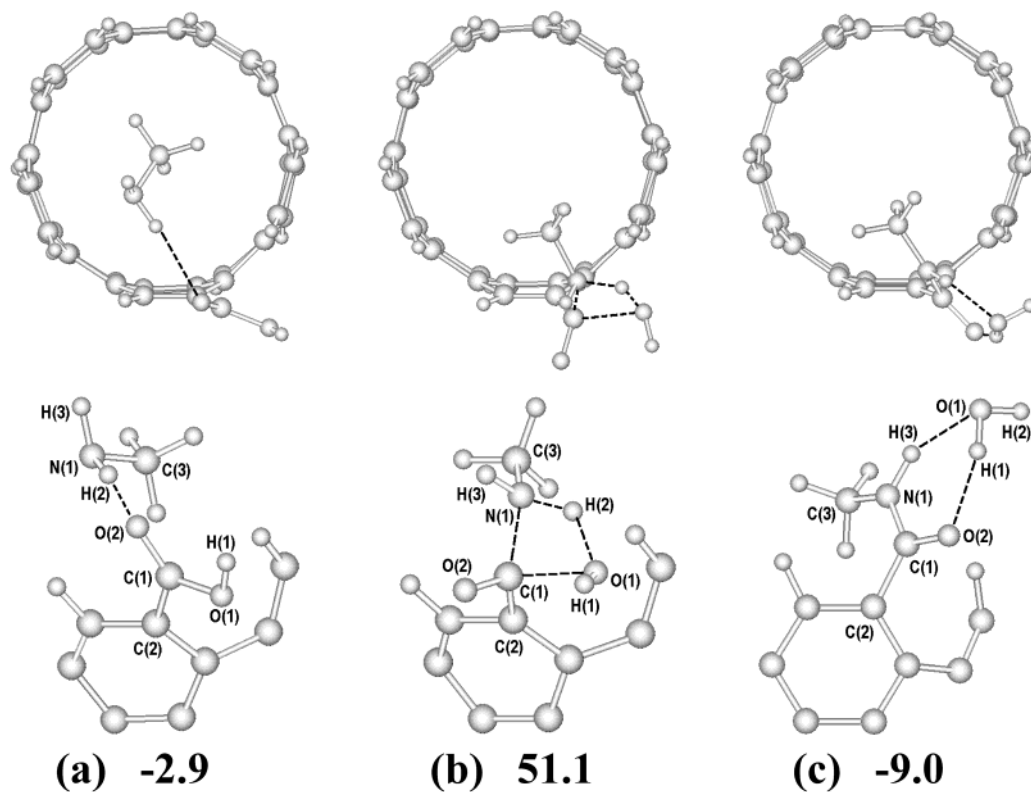
Figure 2. Total optimized geometries (top row) and fragments treated at the B3LYP/6-31G(d) theoretical level (bottom row) of the reaction complex (a), transition state (b), and products (c), with calculated B3LYP energies (in kcal mol^{-1}; relative to the reactant level) for the model gas-phase reaction of (5,5) armchair SWNT (Figure 1a) with methylamine.
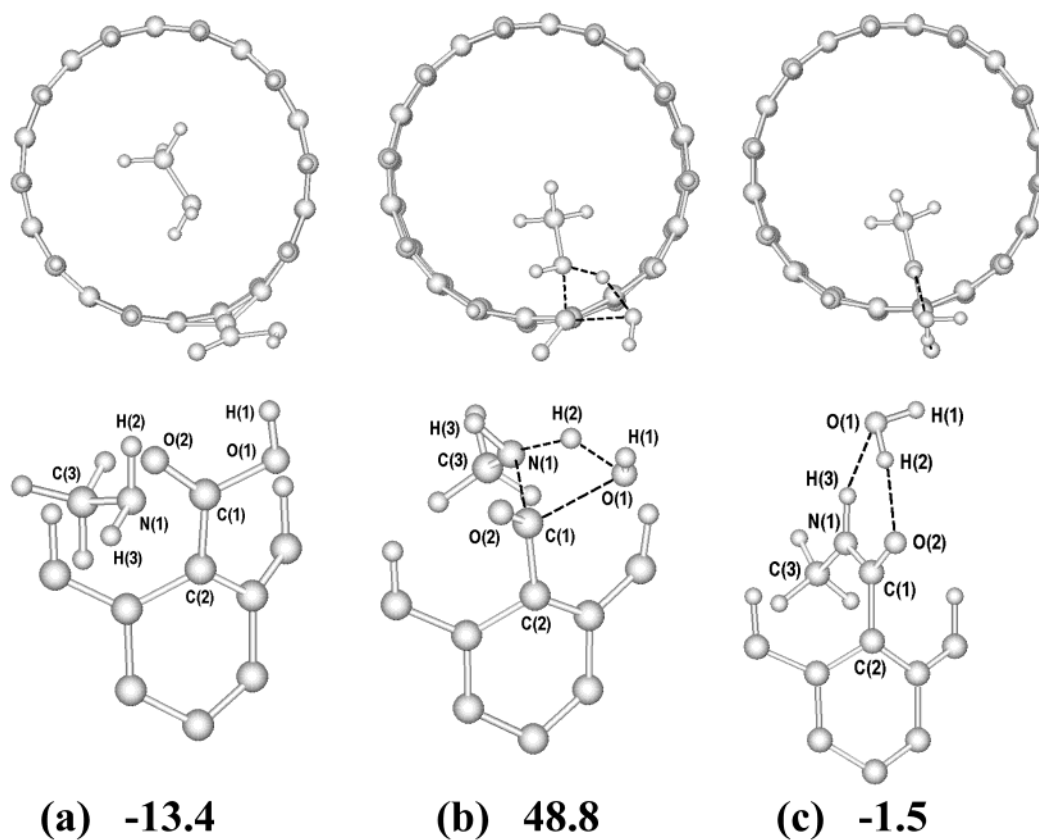

Figure 3. Total optimized geometries (top row) and fragments treated at the B3LYP/6-31G(d) theoretical level (bottom row) of the reaction complex (a), transition state (b), and products (c), with calculated B3LYP energies (in kcal mol^{-1}; relative to the reactant level) for the model gas-phase reaction of (10,0) zigzag SWNT (Figure 1b) with methylamine.

Table 1. Selected Interatomic Distances (Å) for the Reaction Complexes (RC), Transition States (TS), and Products (P) Shown in Figures 2 and 3

	(5,5) armchair			(10,0) zigzag		
	RC	TS	P	RC	TS	P
N(1)−C(3)	1.463	1.474	1.456	1.463	1.471	1.455
N(1)−H(2)	1.019	1.219		1.019	1.166	
N(1)−C(1)		1.603	1.362		1.637	1.360
N(1)−H(3)	1.018	1.021	1.025	1.019	1.020	1.023
O(2)−H(2)	2.321					1.835
O(2)−H(3)				3.731		
C(1)−O(2)	1.220	1.222	1.240	1.234	1.218	1.241
C(1)−C(2)	1.484	1.524	1.504	1.428	1.489	1.501
C(1)−O(1)	1.355	1.859		1.387	1.987	
O(1)−H(1)	0.976	0.973	0.986	0.974	0.972	0.969
O(1)−H(2)		1.304	0.969		1.368	0.988
O(1)−H(3)			1.967			2.008
O(2)−H(1)			1.869			

tribute more significantly into aliphatic amine interactions with SWNTs than the attraction between the polar NH_2 and COOH groups does. For the transition states and products, the differences in terms of interatomic distances between the respective armchair and zigzag species are less manifested and do not exceed 0.128 Å.

The energies presented in Figures 2 and 3 are relative to the level of separated reactants. If one compares the energies of the transition states to those of the reactant level, their values do not differ significantly: 51.1 and 48.8 kcal mol^{-1} for the armchair and zigzag SWNTs, respectively (Figures 2b and 3b). Much bigger differences can be found for the reaction complexes and products. Energy for the armchair reaction complex (−2.9 kcal mol^{-1}) is by 10.5 kcal mol^{-1} higher than that for its zigzag counterpart (−13.4 kcal mol^{-1}). [This can be interpreted as stronger methylamine adsorption on zigzag SWNT; further detailed studies are desirable to verify whether this can be generalized for other aliphatic amines.] The situation is opposite for the amidation products: the armchair products (−9.0 kcal mol^{-1}) are lower by 7.5 kcal mol^{-1} as compared to the zigzag products (−1.5 kcal mol^{-1}). This shows the direct formation of amides on armchair SWNT tips according to reaction 1 to be much more advantageous than that on zigzag SWNT tips. Moreover, since for the latter the reaction complex appears to lie below the products, the amidation as a whole is energetically unfavorable (though it can be facilitated by pumping out water formed, as contemplated in the gas-phase derivatization technique[19]).

Another strong argument supporting the conclusion is evident if one compares the transition state energies not to the reactant level, but to the level of the reaction complexes. Barrier heights calculated in this way are 54.0 (armchair) and 62.2 kcal mol^{-1} (zigzag), which is a significant difference, of 8.2 kcal mol^{-1}.

In summary, our results of two-level ONIOM quantum mechanics/molecular mechanics calculations suggest that the direct formation of amides according to reaction 1 is much more energetically preferable on armchair SWNT tips than on the zigzag nanotube tips. It is too premature to discuss

practical implications of the data obtained (and besides, as any theoretical results, they have to be taken with a certain precaution). Nevertheless, one can envision the use of this or other chemical reactions for selective derivatization of different forms of CNTs (armchair, zigzag, or chiral). In the case of amidation reaction 1[19] with long-chain amines,[1−4,9] the derivatized nanotubes would acquire a higher solubility than underivatized CNTs, which would open a route to their facile separation.

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