

The Two-Layer ONIOM Technique in the Studies of Chemical Reactions on Carbon Nanotube Tips

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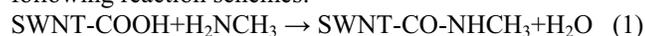
ABSTRACT

We studied theoretically the interaction of simple aliphatic amines with carboxylated zigzag and armchair SWNT models. Amidation reactions are extremely important in carbon nanotube derivatization, solubilization and purification. Our recent theoretical studies revealed energetic preferences of amide formation on the armchair nanotubes as compared to their zigzag counterparts. In the present work, we used single-level MM+ molecular mechanics and AM1 semi-empirical method to study non-covalent interactions. To study the amidation reaction, the two-level ONIOM technique was employed where the higher level was treated with B3LYP/6-31G(d) DFT, and the lower level was described with either UFF molecular mechanics or AM1. We found that the use of AM1 for the lower-level description has serious limitations. To study theoretically chemical reactions on carbon nanotube tips with the ONIOM technique, where the higher level is treated with B3LYP, we recommend UFF molecular mechanics.

Keywords: carbon nanotubes, derivatization, amidation, ONIOM, B3LYP, UFF

1 INTRODUCTION

In continuation of our combined quantum mechanics/molecular mechanics (QM/MM) studies of selective amidation [1,2] and esterification [3] of monocarboxy-substituted tips of zigzag and armchair single-walled carbon nanotube (SWNTs), according to the following reaction schemes:



we studied theoretically the interaction of simple aliphatic amines with carboxylated zigzag and armchair SWNT models. These reactions are extremely important in carbon nanotube derivatization, solubilization and purification. Our recent theoretical studies [1-3] revealed energetic preferences of amide and ester formation on the armchair nanotubes as compared to their zigzag counterparts. In the present work, we used single-level MM+ molecular mechanics and AM1 semi-empirical method to study non-covalent interactions. To study reaction 1, the two-level

ONIOM technique was employed where the higher level was treated with B3LYP/6-31G(d) DFT, and the lower level was described with either UFF molecular mechanics or AM1.

2 THEORETICAL METHODS

SWNT models and notations used are shown in Figure 1. For the simplest single-level molecular mechanics calculations of interaction of aliphatic amines with monocarboxy-substituted SWNT fragments, we used three (Z(*n*,0)-3R and A(*n*,*n*)-3R) and five (Z(*n*,0)-5R) aromatic ring-belt models of variable diameter. Dangling bonds at the nanotube edges were filled with hydrogen atoms. MM+ force field implemented in HyperChem version 5.1 package (by HyperCube Inc., Canada) was used. Geometry optimization was performed with the Polak-Ribiere conjugate gradient algorithm and a root mean square (RMS) gradient of 0.001 kcal Å⁻¹ mol⁻¹. For similar single-level AM1 semi-empirical calculations, we used the two and three aromatic ring-belt zigzag models, with AM1 method implemented in the Gaussian 98W suite of programs [4].

The reactions with CH₃NH₂ were studied with the nanotube models similar to those described in our previous studies [1-3], using a two-level ONIOM approach [5,6] implemented in the Gaussian 98W suite of programs. The higher, quantum mechanics level included the atoms belonging to CH₃NH₂ and the terminal carboxylic group, together with their adjacent C and H-atoms (dark atoms in Figure 1). The Becke's three-parameter hybrid method [7] with the exchange functional of Lee, Yang and Parr [8] (B3LYP) was used for the higher-level description, in conjunction with the 6-31G(d) basis set by Pople et al. [9-11]. The remaining nanotube atoms were treated with UFF molecular mechanics [12] (for Z(10,0)-2R, A(5,5)-2R, Z(16,0)-3R and A(10,10)-3R models) or AM1 semi-empirical method (for Z(10,0)-2R, A(5,5)-2R, Z(16,0)-2R and A(10,10)-2R models).

The stationary point geometries were fully optimized and characterized as minima (0 imaginary frequencies; for reactants, reaction complexes and products) or first-order saddle points (1 imaginary frequency; for transition states) by vibration frequency calculations. All the optimizations met the default convergence criteria set in Gaussian 98W.

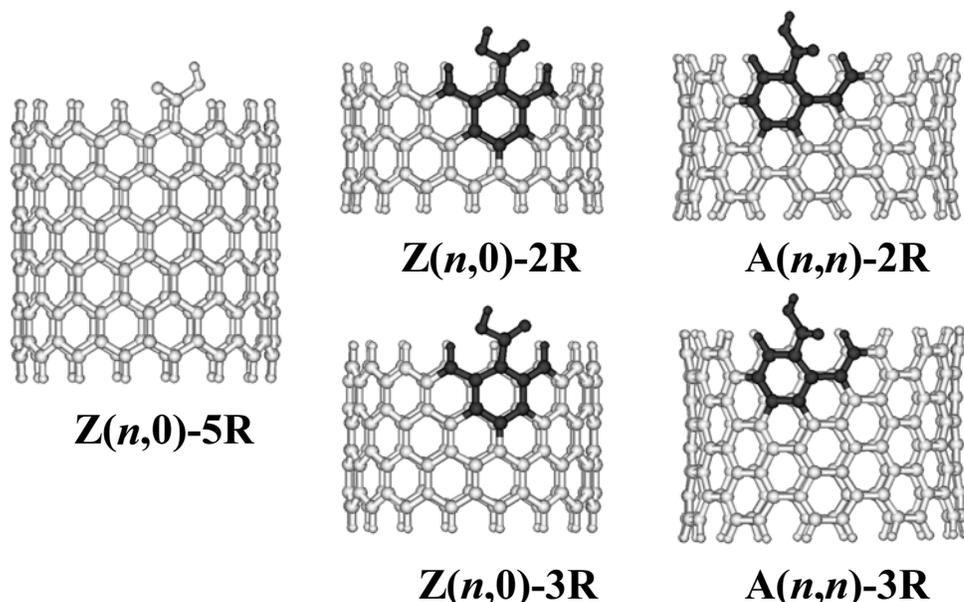


Figure 1: Models of monocarboxy-substituted SWNTs used for MM, QM/MM and QM/QM calculations. Z=zigzag, A=armchair. $Z(n,0)$ -2R, $Z(n,0)$ -3R and $Z(n,0)$ -5R are exemplified by the models with $n=16$; $A(n,n)$ -2R and $A(n,n)$ -3R, by the models with $n=10$. The 2R and 3R models were used for two-level ONIOM calculations; the highlighted (dark) atoms and those belonging to methylamine molecule were treated at the higher (B3LYP) level, and the remaining SWNT atoms were treated with UFF molecular mechanics or AM1 semi-empirical method.

3 RESULTS AND DISCUSSION

We performed single-layer MM+ molecular mechanics and AM1 semi-empirical modeling of interactions of simple amines with monocarboxy-substituted SWNT fragments of variable diameter and length, to estimate the lower level contribution. We were interested in whether there is an energetic difference between adsorption outside and inside the nanotube cavity [1]. From common considerations, the smaller the SWNT diameter, the bigger this difference should be. At the same time, there must be a lower diameter limit, where amine molecule does not fit the nanotube cavity anymore. On the contrary, increasing the nanotube diameter should result in decreasing the energy difference.

For MM+ modeling, we used monocarboxy-substituted $Z(n,0)$ -3R, $A(n,n)$ -3R and $Z(n,0)$ -5R nanotube models (Figure 1), whereas ammonia, methylamine, n -propylamine and n -nonylamine were tested as adsorbates. The nanotube length was sufficient to accommodate one RNH_2 or NH_3 molecule. Since a conformation and exact position of amine molecule (especially for n -propylamine and n -nonylamine) with respect to the nanotube model can noticeably influence the interaction energy calculated, to obtain more uniform and comparable results, in all simulations we chose the same starting geometry, where the following three criteria were met: (1) NH_2 group was placed close to the SWNT's COOH, (2) the two molecules were parallel to each other;

(3) the carbon chain plane (for the case of n -propylamine and n -nonylamine) was parallel to the closest SWNT wall. We found that for narrower zigzag SWNTs ($n = 7$ to 13), which are more strained due to a stronger distortion from the plain graphite sheet, the calculated total energies were positive; the values become negative starting with (14,0) SWNT. For the armchair models, the MM+ energies were positive for $n = 4$ to 9, and negative starting with $n = 10$. NH_3 molecule fits inside the nanotube starting with $n = 9$; here the energy difference $\Delta E_{out/in}$ has the highest value, than it rapidly decreases and does not show notable changes after $n = 20$. CH_3NH_2 has a slightly bigger molecule size, fitting inside $Z(10,0)$ (highest $\Delta E_{out/in}$ value) and wider SWNTs; after ca. $n = 20$, the energy difference does not show significant changes.

Bigger nanotube diameters are required to accommodate longer-chain amines (n -propylamine and n -nonylamine) inside the cavity, $Z(12,0)$ and $A(6,6)$ (the highest $\Delta E_{out/in}$ value). The biggest energetic difference (of ca. 28 kcal mol⁻¹) between adsorption outside and inside SWNT, was obtained for nonylamine at $Z(12,0)$ -5R SWNT; then $\Delta E_{out/in}$ drops rapidly with increasing n up to approximately 20, and its further decrease becomes very slow: even for $Z(30,0)$ -5R nanotube, $\Delta E_{out/in}$ is almost 5 kcal mol⁻¹. Thus, the energetic difference $\Delta E_{out/in}$ should be significant for a wide size range of CNTs, and the preferential sites for adsorption of long-chain amines are inside the nanotubes.

The amines inside and outside narrower SWNTs tended to remain parallel. With increasing SWNT diameter, the amine gradually rotated with respect to the nanotube axis. For example, the angle between nonylamine and Z(30,0)-5R axis was as much as 30°, and for even higher n values it increased further. The angle between methylamine and SWNT axis (for n values of up to 80 in Z(n ,0)-3R models) reached 60°, with the amino group turned to an arbitrary direction with respect to the position of COOH group. These observations lead to a conclusion that van der Waals interactions make a major contribution into amine adsorption on carboxy-substituted SWNTs, as modeled by MM+, whereas the interaction between the polar NH₂ and COOH groups does not manifest at all. The latter follows from very long NH⁺⋯O separations, of ca. 5 Å in many cases, which cannot be qualified as hydrogen bonds, whereas the shortest distance between the molecules CH⁺⋯C_{wall} was less than 3 Å.

Semi-empirical calculations with AM1 method produced totally different results. Since AM1 is much more computationally demanding than molecular mechanics, the nanotube models (all zigzag) themselves were reduced to two or at best three belts of aromatic rings, with a maximum n value of 15. The pattern of amine interaction with carboxylated nanotube fragments completely changed. In particular, amino group of nonylamine molecule placed inside Z(15,0)-3R SWNT, was strongly attracted to the carboxylic group, forming a hydrogen bond with NH⁺⋯O=C separation of 2.42 Å. This interaction made nonyl radical deviate from the coaxial position and adopt a slightly bent conformation. This bending was not observed if nonylamine molecule was initially placed outside the nanotube cavity. The molecule remains aligned, forming hydrogen bond between the NH₂ and COOH groups, and showing no sign of interaction between the hydrophobic nonyl radical and SWNT wall. Both H atoms of the amino group participated in hydrogen bonding with the carbonyl group, with slightly different NH⁺⋯O=C separations, of 2.39 and 2.54 Å. We found that H-bonding with the OH group instead of C=O is possible as well. However the general feature, that is no manifestation of interaction between the hydrophobic nonyl radical and SWNT wall, did not change. Thus, contrary to MM+ molecular mechanics, AM1 semi-empirical method accounts well for hydrogen bonding between the NH₂ and COOH groups, but completely neglects interaction between the hydrophobic fragments.

Based on the above observations only, it is difficult to give a preference to molecular mechanics or AM1 quantum mechanics for the lower-level description in ONIOM calculations. An important factor is cost-efficiency, and from this point of view the use of molecular mechanics seems more attractive. We performed a series of ONIOM calculations for the amidation reaction 1, using UFF molecular mechanics and AM1 semi-empirical method for the lower level. The higher level was treated at the B3LYP/6-31G(d) level of theory in all cases. In the chemical models employed the high level included the

atoms belonging to methylamine molecule and the terminal carboxylic group, together with their adjacent C and H-atoms (dark atoms in Figure 1). The remaining part of the nanotube was variable in diameter and length. For B3LYP/6-31G(d):UFF calculations, we tested narrow and short SWNTs Z(10,0)-2R and A(5,5)-2R [1,2], as well as wider and longer models Z(16,0)-3R and A(10,10)-3R [3]. For B3LYP/6-31G(d):AM1 calculations, the use of wider models with three complete belts of aromatic rings was not possible due to limited computational resources, and short SWNT models were considered only, that is Z(10,0)-2R, A(5,5)-2R, Z(16,0)-2R and A(10,10)-2R.

We analyzed the calculated energies (relative to the level of separated reactants) for reaction complexes (RC), transition states (TS), hydrogen-bonded products (P) as well as sums of energies of separated products (amidated nanotube and water molecule; P(sep)). The values analyzed were B3LYP, ONIOM and zero-point energy-corrected ONIOM values (ZPE-ONIOM). Similarly to the single-level MM+ and AM1 calculations, we tested different orientations of methylamine with respect to the nanotube.

It turned out that with AM1 lower-level description, not all the calculations can be successfully performed: while the optimization itself was completed smoothly (and B3LYP and ONIOM energies were retrieved), force-constant and frequency calculations usually failed due to self-consistency problems. This prohibited transition state optimizations, which often require force-constant calculation at every step.

The choice of lower-level description influences mutual orientation of the amine and nanotube components as well. A general trend here was similar to the one found in the single-level calculations. At the B3LYP/6-31G(d):UFF level of theory, CH₃ group of methylamine was strongly attracted to the nanotube, and its N—C bond was turned towards SWNT's center of mass. It was not the case at the B3LYP/6-31G(d):AM1 level of theory: since attraction between the hydrophobic moieties is very weak (if any), both 'inside' and 'outside' starting geometries produced very similar reaction complexes, with N—C bond turned outwards the nanotube. Correspondingly, their energies differed insignificantly, by less than 0.1 kcal mol⁻¹. In the amide products, the freedom of methylamine moiety is restricted, and the 'inside' and 'outside' isomers were distinct, as expected, in terms of both geometry and energy.

As regards the selectivity of amidation reaction 1 at carboxylated tips of zigzag and armchair nanotubes [1,2], this conclusion remained valid at the B3LYP/6-31G(d):AM1 theoretical level. Taking into consideration all the energies calculated (B3LYP, ONIOM and ZPE-ONIOM), in both series of calculations (Z(10,0)-2R versus A(5,5)-2R, and Z(16,0)-2R versus A(10,10)-2R), amidation of the armchair SWNT tips is more preferable than in the case of their zigzag counterparts. This was especially clearly seen for the B3LYP energies, where the difference was ca. 10 kcal mol⁻¹. In addition, reaction complexes were much more stable for the zigzag than for armchair

nanotubes, by >6 kcal mol⁻¹. Furthermore, their energies turned to be much lower with respect to the corresponding products: this fact makes amidation of the carboxylated SWNT tips a prohibited reaction at all.

Due to the deficiencies in the results of B3LYP/6-31G(d):AM1 ONIOM calculations for our systems, we further focus on molecular mechanics description of the lower level. A detailed inspection of the geometry of hydrogen-bonded reaction complexes [1,2], revealed that within narrow carboxylated SWNTs, surrounding SWNT walls attract methylamine molecule, making it equilibrate close to the nanotube axis. In principle, this might dramatically influence its position with respect to COOH group, resulting in unrealistically long N—H^{··}O separations, which are supposed to be hydrogen bonds, and apparently producing significant errors in energy estimates for RCs. In particular, such long separations were observed for Z(10,0)-2R model, when calculated at the B3LYP/4-31G:UFF and B3LYP/6-31G(d):UFF theoretical levels [1,2]. However, increasing the nanotube diameter to $n = 16$ (calculated diameter of ca. 1.25 nm approaching realistic, commonly observed SWNT diameters) fixed this problem: the values of N—H^{··}O separation in RCs were quite reasonable, of 2.411 and 2.306 Å, respectively. A similar positive result was obtained with the same SWNT model for esterification reaction 2 [3].

The conclusion on the selectivity of amidation reaction remains valid at the present level of theory for bigger SWNT models. Regardless of the energy values considered (B3LYP, ONIOM and ZPE-ONIOM), in case of the 'inside' isomers the reaction on carboxylated A(10,10)-3R nanotube was exothermic, and endothermic for its zigzag counterpart. The difference in energies of the products exceeded 10 kcal mol⁻¹ for B3LYP energies to more than 25 kcal mol⁻¹ for ONIOM and ZPE-ONIOM energies. The transition state energies were much lower for the armchair nanotube as well, by ca. 13 kcal mol⁻¹ (B3LYP values) to 28 kcal mol⁻¹ (ONIOM and ZPE-ONIOM energies). The armchair reaction complex had a slightly higher B3LYP energy than the zigzag reaction complex has (-1.9 vs. -2.4 kcal mol⁻¹), but laid by ca. 7 kcal mol⁻¹ lower according to ONIOM and ZPE-ONIOM energy values. The latter observation, however, did not affect the reaction selectivity.

Contrary to the results of B3LYP/6-31G(d):AM1 ONIOM calculations, there were big differences in the geometric and energetic parameters for the 'inside' and 'outside' isomers computed at the B3LYP/6-31G(d):UFF level of theory. N—C bonds in all the reaction complexes, transition states and products were always directed towards the nanotube, hampering in this way free rotation around C—C(=O)O bond and consequently inter-conversion of the isomers. This account for van der Waals interactions between the nanotube walls and methyl radical is a substantial argument for the use of UFF molecular mechanics for the lower-level description. It turned out that most energy values calculated for the 'outside' RCs, TSs and Ps are lower than the respective energies for the

'inside' species, to a different extent; the exceptions were energies for transition state and hydrogen-bonded products in the case of A(10,10)-3R model. But even accounting for this fact, the reaction selectivity remained the same. Although it changed to exothermic for the zigzag nanotube, exothermicity for the armchair model was higher by ca. 8 kcal mol⁻¹ (B3LYP energy) to more than 20 kcal mol⁻¹ (ONIOM and ZPE-ONIOM energies). The transition state energies were lower for the armchair nanotube as well, by ca. 6 kcal mol⁻¹ (B3LYP values) to 20 kcal mol⁻¹ (ZPE-ONIOM energy).

The dependence of reaction parameters on mutual spatial orientation of the nanotube and the second reactant, as well as on CNT diameter, is natural and logic, especially if the second reactant contains a hydrophobic fragment. Thus, it is inferred mandatory that the chemical model selected for theoretical description accounts for such steric factors, having realistic cylindrical shape and diameter, whereas bidimensional sheet models ignore the nanotube walls and curvature effects, and should be avoided.

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