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A theoretical study of functionalized single-wall carbon nanotubes: ONIOM calculations

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Abstract

In this study, we employed ONIOM calculations to study functionalized single-wall carbon nanotubes (SWCNTs), for assessing an appropriate level of theory for accurate binding energies calculations, particularly by considering ozone adsorption and arylation. Although ONIOM models reproduced the binding energies and geometries in relatively good agreement with the density functional theory B3LYP/6-31G* values in some cases, the 'same level different basis set' (SLDB) protocol, was shown to be more appropriate for studying SWCNTs, as the π-network was preserved. We also found that sidewall functionalization deforms the tube significantly, and the use of any lower level methods could not describe bond breaking/forming appropriately.

1. Introduction

Applications of single-wall carbon nanotubes (SWCNTs) are still limited by the inability to carefully control, for example, the separation of metallic and semiconducting tubes. Chemical functionalization [1,2], including direct attachments of functional groups to the sidewall of SWCNTs using diazonium reagents [3], solvent free functionalization [4], fluorination and subsequent derivatization [5], functionalization by strong oxidizing agents [6], or ozonation [7], have therefore been carried out. Furthermore, functionalized SWCNTs also hold promise for applications in areas such as medicinal chemistry [8], or could enhance solubility [9].

An accurate determination of the mechanisms of SWCNTs functionalization is computationally extremely demanding due to the size of such nanosystems. ONIOM, introduced by Morokuma et al. [10], and recently reviewed [11], is a computationally efficient tool for the study of chemical reactions involving large molecular systems, by allowing a partitioning of the molecule (*real*) into two or three different regions, where a high-level calculation on a small region (*model*) is performed, and the effects of the remainder spectator regions are included at a low-level of theory. The dangling bonds of the *model* fragment at the boundary between different levels are saturated with hydrogens as link atoms. Selection of the atoms in the *model* and the level of theory in that part of the system (high-level), as well as the level of theory for the *real* system (low-level), are the limiting factors regarding the accuracy of the results.

Several theoretical studies of SWCNTs functionalization by applying ONIOM were previously reported, including interactions with N and O atoms [12,13], O_2/N_2 [14–16], hydrogen and fluorine [17], cycloaddition of several 1,3-dipolar molecules [18,19], epoxidation [20], Diels–Alder cycloaddition [21] and [2+3] cycloaddition [22] onto the sidewall of nanotubes. Mostly B3LYP/6-31G* at the high-level, and a unified force field (UFF) or a semiempirical AM1 approach for the low-level *real* SWCNT, was applied. However, it has been previously noted that by employing UFF for the low-level, relaxation effects could not be included due to local minima, and binding energies (BE) had to be estimated from the high-level of theory part [14,15,17]. Indeed, the importance of the layers partitioning in the application of

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ONIOM for the investigation of the sidewall functionalization of SWCNTs, was recently pointed out [23,24].

In this study, we examined several *model* sizes within ONIOM, as well as levels of theory, in order to assess an appropriate level of theory in modeling sidewall functionalization of SWCNTs. Specifically, ozone (O_3) adsorption, for comparison with previous ONIOM results [18], and 2-phenyl-1 *H*-imidazole functionalization, previously also studied as an infinite extended model [25], were investigated. Most recently, the effects of –COOH functionalization on the electronic structure of SWCNTs were studied for a periodic system [26]. Note that although ozone adsorption enhances the propensity for functionalization, and could alter the field emission properties, for example, an enhancement upon exposure of O_3 to the sample was observed, decaying as the exposure time increases, indicating degradation by etching [27], the effects of O_3 were not explored extensively theoretically thus far [28].

2. Methods

Calculations were carried out for a C(5,5) SWCNT ($C_{130}H_{20}$), with the high-level *models* (including link atoms) consisting of C_2H_4 (2C), C_6H_8 (6C), $C_{10}H_8$ (10C) and $C_{16}H_{10}$ (16C) (Fig. 1). The binding energies of O_3 and 2-phenyl-1 *H*-imidazole (L) (Scheme 1) bonded to $C_1{=}C_2$ on a SWCNT sidewall, were estimated by applying B3LYP/6-31G* at the high-level in all calculations, and UFF, AM1 and B3LYP/3-21G low-levels for the *real* system. In all cases, geometries were fully optimized without any symmetry constraints [29]. All results were compared to the B3LYP/6-31G* binding energies, which was the highest level of theory applied.

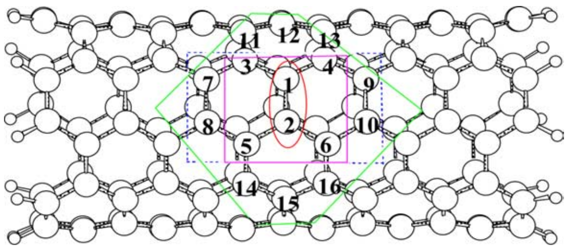
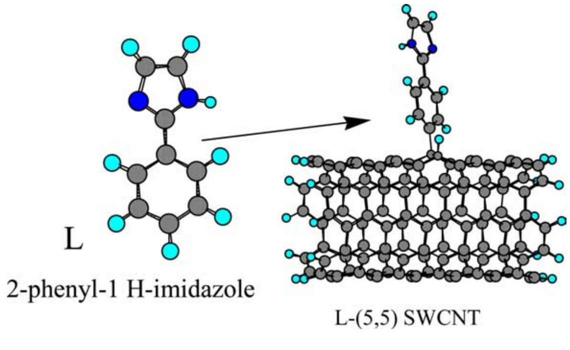


Fig. 1. Carbon atoms considered in different two-layer ONIOM models of a C(5,5) SWCNT: 2C (red), 6C (pink), 10C (blue) and 16C (black).



Scheme 1.

3. Results and discussion

The B3LYP/6-31G* binding energy of O_3 adsorbed at an armchair C(5,5) SWCNT was shown to be exothermic by ca. 19 kcal/mol, which is larger than a value of about 9 kcal/mol calculated for an extended system, where the unit cell included 80 °C atoms and one O_3 molecule [30]. The addition of diffuse functions for the oxygen had a negligible effect (Table 1). While the binding energies obtained using ONIOM (B3LYP/6-31G*:B3LYP/3-21G) for the 10C and 16C *models*, were in relatively good agreement with the B3LYP/6-31G* result, the application of the UFF or AM1 for the low-level, mostly used in previous work, resulted in unrealistic values. The discrepancies when applying a 2- vs. 16-atom model within ONIOM, as well as in using different levels of theory for the low-level, emphasize the importance of an appropriate partitioning of the molecular model. Note that the C(5,5) ($C_{130}H_{20}$) SWCNT functionalization with 2-phenyl-1 *H*-imidazole was shown to be endothermic, because functionalization of SWCNTS is known to require special conditions for reactions to take place. ONIOM (10C and 16C/B3LYP/6-31G*:B3LYP/3-21G) BE values are within 2 kcal/mol of the reference result.

As an alternative, we estimated the effects of applying the “same level different basis” (SLDB) technique without partitioning the SWCNT. *Models* comprising of 2C, 6C, 10C and 16C carbon *atoms* (Fig. 1) were treated at the B3LYP/6-31G* level, while a B3LYP/3-21G basis set was used for the rest of the SWCNT (Table 1). It is encouraging to note that the SLDB results, even with a small number of atoms at the high-level, are in excellent agreement with the values calculated with the large basis set throughout, and also show an improvement on using a smaller basis set for the whole system.

Moreover, the SLDB calculations preserve conjugation, and any number of atoms may be considered at the high-level without the problem of encountering local minima in those cases where broken six-membered rings are examined. In applying ONIOM, conjugation and aromaticity could be broken, as shown by Montoya et al. [31], in studying adsorption on a carbonaceous surface. The problem of locating local minima could also be encountered in ONIOM. This may be due to the disruption of the π-network of the aromatic

Table 1
BEs[a] obtained using different theoretical methods

Methods[b]	BE (kcal/mol)			
	Ozonation		Arylation (L-SWCNT)	
AM1//AM1	−0.26		17.02	
6-31G*//AM1	−23.84		50.91	
3-21G//3-21G	−48.70		29.85	
6-31G*//3-21G	−23.51		43.57	
6-31G*//6-31G*	**−19.13**		**39.68**	
6-31+G*//6-31G*	−18.44			
ONIOM (*Model*//A:B)[c]	ONIOM	B3LYP[d]	ONIOM	B3LYP[d]
2C/6-31G*:UFF	−34.32	−59.60	−43.60	−20.81
2C/6-31G*:AM1	−10.16	−72.91	20.77	−35.12
2C/6-31G*:3-21G	−28.54	−72.71	[e]	
10C/6-31G*:UFF	−1.83	14.83	36.77	68.17
10C/6-31G*:AM1	−11.36	15.06	43.85	63.52
10C/6-31G*:3-21G	−19.36	17.77	38.14	69.30
16C/6-31G*:UFF	−13.40	−7.17	−7.90	35.85
16C/6-31G*:AM1	−31.34[f]	−15.64	21.93	38.59
16C/6-31G*:3-21G	−20.17	17.77	38.14	41.94
SLDB (L-*n*/B1+B2)[g]				
2C/6-31G*+3-21G	−15.94		39.88	
6C/6-31G*+3-21G[h]	−18.57		40.25	
10C/6-31G*+3-21G	−18.47		38.26	
16C/6-31G*+3-21G	−18.52		39.85	

A negative (positive) BE value indicates an exothermic (endothermic) reaction.

[a] BE = $E(O_3/L\text{-nanotube}) - E(\text{nanotube}) - E(O_3/L)$.

[b] B3LYP in all QM methods.

[c] Fig. 1 for different *models*; A and B represent methods used for the *model* and *real* systems, respectively.

[d] B3LYP BE for *model* system only.

[e] Local minimum not achieved.

[f] Also reported in [17].

[g] SLDB; L = B3LYP and *n* atoms treated at basis-1 (B1) and rest of the tubes at basis-2 (B2).

[h] Local minimum for the 6C *model* were not found for other ONIOM models, and may be due to the disruption of the π-network of the aromatic six-membered rings.

six-membered rings and the use of too many link-atoms. For example, in the 6C (C_6H_8) model (shown in Fig. 1), eight C=C bonds are replaced by an equal number of C–H bonds in the high-level calculation. The geometries summarized in Table 2 further support the accuracy of the SLDB application.

A significant structural deformation of the C(5,5) SWCNT upon O_3 adsorption was observed, as shown in Fig. 2, by superimposing the positions of the carbon atoms of the pristine SWCNT and the O_3-SWCNT, and a similar deformation was noted also for the 2-phenyl-1 *H*-imidazole functionalization. Note that the overall deformation of the SWCNT (length of ~1.4 nm) requires 42.1 and 49.9 kcal/mol for O_3, and 2-phenyl-1 *H*-imidazole functionalization, respectively, estimated from the energy difference between the pristine tube and the deformed functionalized tube. Such a deformation has been reported earlier by Morokuma and coworkers [13], for oxidized nanotubes. Thus, the pyramidalization angle in the O_3-SWCNT neighboring the adsorption has increased, indicating a reactive site, which could assist in the characterization of these chemical processes [32].

4. Conclusion

In this study, we report the results of ONIOM calculations to study functionalized SWCNTs. Because there is an extensive rearrangement of electron density, methods not able to describe charge transfer, polarization, and bond breaking/forming in chemical reactions, should be avoided. For weakly bound systems, upon physisorption, where the SWCNTs are not very distorted, the application of the ONIOM method with AM1 may be useful [33]. However, a systematic and thorough investigation would be necessary prior to any definite conclusion.

Although several ONIOM models and methods reproduced the binding energies and geometries close to the B3LYP/6-31G* values, the SLDB protocol could be more appropriate for studying SWCNTs as the π-network is preserved. Further developments to study larger tubes, and of differing lengths [23], are under investigation. Our results provided insight into the significant structural deformation, which occurs upon sidewall functionalization.

Table 2
Selective B3LYP/6-31G* bond lengths and their changes[a] predicted by different methods

Methods[b]	Ozonation		Arylation	
	δR (C_1C_2)	δR (C_1O)	δR (C_1C_2)	δR (C_1–C(L))
6-31G*//6-31G*	1.644	1.470	1.668	1.563
3-21G//3-21G	−0.008	+0.045	−0.003	0.000
AM1	−0.034	+0.016	−0.071	−0.035
ONIOM (*Model*/A:B)[c]				
2C/6-31G*:UFF	+0.050	−0.038	−0.032	+0.005
2C/6-31G*:AM1	+0.045	−0.015	+0.029	+0.003
2C/6-31G*:3-21G	−0.027	−0.013	[c]	[c]
10C/6-31G*:UFF	+0.036	+0.014	+0.026	+0.004
10C/6-31G*:AM1	+0.079	−0.001	+0.109	0.000
10C/6-31G*:3-21G	−0.004	−0.006	−0.006	−0.001
16C/6-31G*:UFF	+0.059	−0.010	+0.041	−0.011
16C/6-31G*:AM1	+0.009	−0.006	−0.005	−0.002
16C/6-31G*:3-21G	−0.006	−0.005	−0.008	0.000
SLDB (L-*n*/B1+B2)				
2C/6-31G*+3-21G)	+0.001	−0.001	−0.001	−0.001
6C/6-31G*+3-21G	−0.006	−0.002	−0.007	0.001
10C/6-31G*+3-21G)	−0.009	0.000	−0.009	0.001
16C/6-31G*+3-21G)	−0.005	0.000	−0.007	0.000

[a] Bond lengths are overestimated (underestimated) by positive (negative) values compared to B3LYP/6-31G* distances.
[b] See footnotes of Table 1 for definition of different methods.
[c] Local minimum not found.

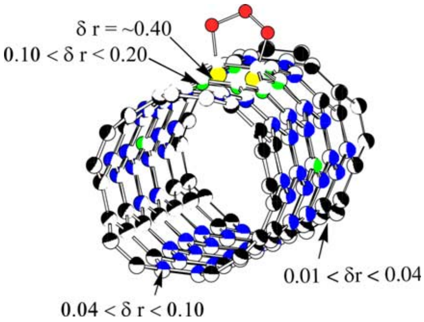


Fig. 2. Structural deformation of a C(5,5) SWCNT uopn ozonation. White and colored circles indicate the positions of the carbon atoms of the functionalized and pristine SWCNTs, respectively. Different colors depend on the displacement (δR Å) of the carbon atoms of the entire tube. Oxygens of O_3 are shown in red.

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