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Theoretical Investigation of the Effect of (8,0) Single-walled Carbon Nanotubes on Acidity of Aliphatic Alcohols

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ONIOM calculation is carried out to estimate the acidity of five aliphatic alcohols before and after adsorbing on the tip of (8,0) single-walled carbon nanotube. The ONIOM method is performed using a combination of density functional theory and AM1 semiempirical method for alcohols and their corresponding conjugated bases. Deprotonation Gibbs free energies of alcohols are calculated and compared before and after adsorbing on the nanotube. Solute-solvent interactions are taken into account by employing the conductor polarized continuum model (CPCM). The results show that the acidity of alcohols change after adsorbing on the nanotubes and these alcohols have a little effect on (8,0) SWCNT.

Keywords: SWCNT, ONIOM, Aliphatic alcohol, CPCM, Acidity

INTRODUCTION

Carbon nanotubes (CNTs) have special structures with unique physical and chemical properties. So, they have many applications in several aspects like energy storing, electronic devices and chemical sensors [1-9]. Recent studies have shown that adsorption of atoms or molecules on single-walled carbon nanotubes could modify their physical properties [10,11]. Some of these molecules are NH_3, NO_2, O_2, N_2, CO, CO_2, CH_4, H_2 that were widely investigated to be adsorbed on SWCNTs and bundles [12-17]. Moreover, the behavior of organic molecules like cyanide and CH_3COOH adsorbed on external surface of single walled carbon nanotubes were studied by using density functional theory (DFT) calculations [18-21]. As well as adsorption on the side wall, some atoms or molecules can be substituted to the end of SWCNTs during mild oxidation. Such processes introduce some oxygen-containing functional groups at the tips of SWNTs [22-24]. For instance, DFT calculation was performed to study the adsorption of O_2 and H_2O on cap-ended and open ended SWCNTs [25]. Recently, AM1 semi-empirical method together with DFT calculations, were used for predicting structures and HOMO/LUMO energies of pristine and -OH, -COOH and -$CONH_2$ end-substituted SWCNTs [9,26]. In order to study the chemical reactions involving large molecular systems, computationally efficient methods, such as ONIOM [27,28] were found to be useful [15,29].

The Acidity value determines the amount of protonated and non-protonated forms of a molecule. The importance of the theoretically determination of acidity values has been discussed in a number of recent manuscripts [30-33]. Gas phase acidity of several carboxylate SWCNTs with different lengths and diameters were studied using the same level different basis set (SLDB) protocol for both zigzag and armchair tubes [34]. Deprotonation energies of the open ended molecular model of NT-COOHs indicate more acidic nature of zigzag-COOH than that of armchair-COOH.

One of the characteristic properties of alcohols is their low acidity. They have high pKa, from 14-16. In the present study, we aim to understand the effect of (8,0) SWCNT on the alcohols and to see if these useful materials can affect on acidity of alcohols and increase their acidity or not, as predicted in [34] for -COOH group.

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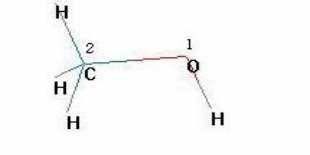
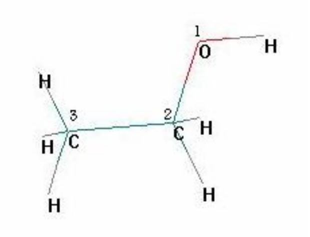
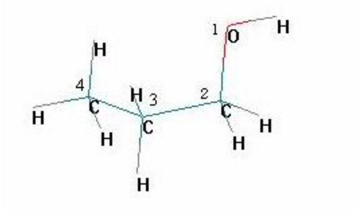
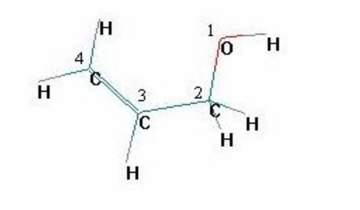
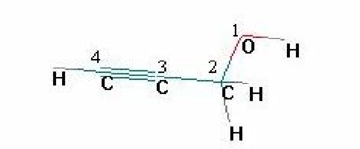
COMPUTATIONAL DETAILS

Investigations of large systems like nanotubes are computationally demanding and require the methods which are both accurate and feasible.

In this work, we have used ONIOM method for studying (8,0) SWCNT and its derivatives. The Nanotube length was considered to be 7.08 A°. These lengths of nanotubes were found to be sufficient for exohedral adsorption of alcohols on the nanotubes [20,21]. Aliphatic saturated and unsaturated normal alcohols were attached to the tip of (8,0) SWCNT and compared with each other (see Table 1 for the structure of these alcohols). The pK_a of theses alcohols are about 14-15. All the structures were fully optimized using a semiempirical AM1 method using the GAUSSIAN09 program [35]. The single point energy and frequency calculations were performed using ONIOM method. For this aim, the B3LYP/6-31+G** method was used for

Table 1. Investigated Aliphatic Alcohols with the Number of Atoms

No.	Structure	pK_a
1		15.54
2		15.90
3		16.10
4		15.52
5		13.55

alcoholic part of the molecule and AM1 method was used for (8,0) SWCNT. Previous studies predicted that deprotonation energy obtained using such technique is very close to higher level of calculations which was attributed to the cancellation of ZPEs and TEs of acids and their conjugated bases [34].

Frequency calculations were performed for calculating Gibbs free (ΔG) energies. Deprotonation energies were also calculated using the following reaction and Gibbs free energies of the molecules and their conjugated bases in

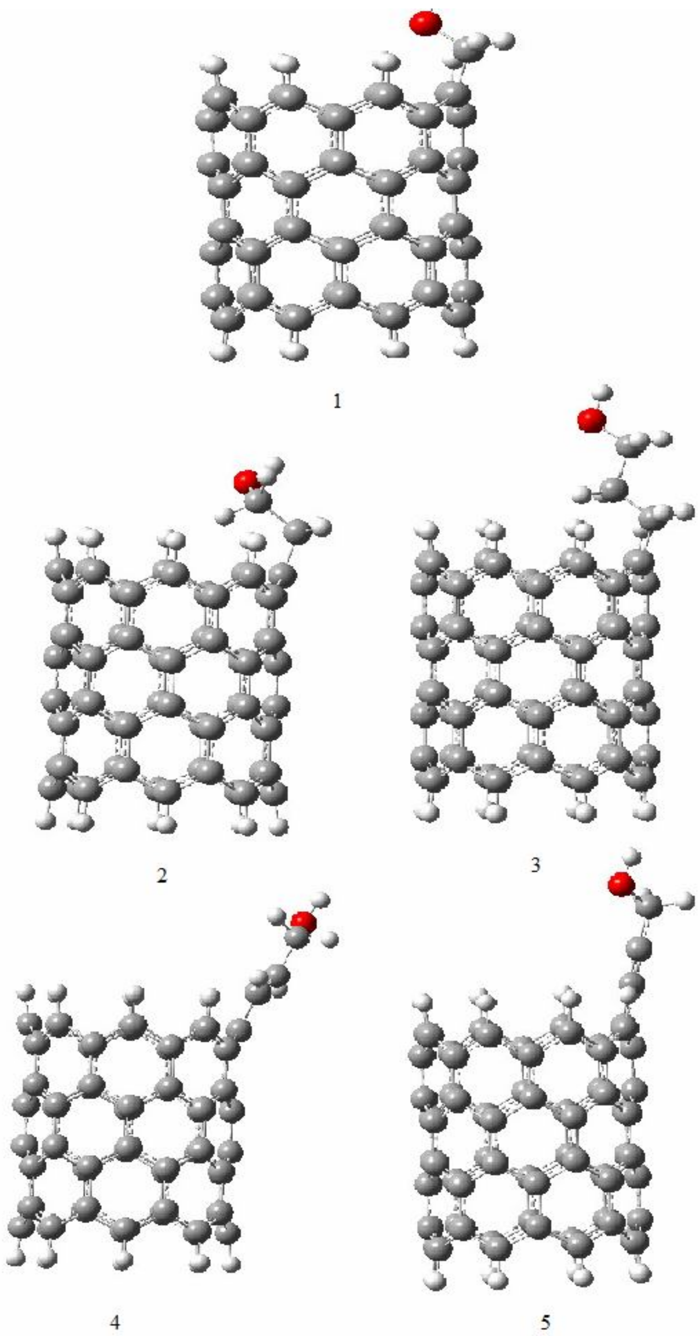


Fig. 1. Fully optimized structure of (8,0) SWCNT-R-OH.

solution phase.

$$\text{NT-R-OH} \rightarrow \text{NT-R-O}^- + \text{H}^+$$

For calculations in solution phase, solvation energies were determined by a self-consistent reaction field (SCRF) approach [36] and the conductor polarized continuum model (CPCM) [37] with Hartree-Fock (HF/6-31G*) approach [38]. CPCM model uses a series of over- lapping spheres to mimic the shape of the molecule.

RESULTS AND DISCUSSION

Fully optimized geometries of (8,0) SWCNT-R-OH are depicted in Fig. 1. In most structures the OH group pointed toward the nanotube after full optimization.

Table 2, shows some bond lengths and C-O-H angles of the alcohols compared to those adsorbed on the nanotube. These results show that the C-O bond lengths of alcohols reduce after adsorbing on the nanotube. The results also show, when the alcohols adsorbed on the nanotube, the C-O-H angle reduce from109°-106° or 107°, confirming that the molecule tends toward the inside of the nanotube. Anyway, the O-H bond length doesn’t change after adsorption to the nanotube. The NT-alcohol distances are placed at the last column of the table and are shorter in unsaturated alcohols. The results show that the distance between the alcohols and the nanotube is about 1.48 A° which reduces to 1.4 A° in unsaturated alcohols indicating their resonance with (8,0) SWCNT.

Table 3 shows the calculated gas phase and solvation energies of all the alcohols and their corresponding anions compared to those adsorbed on the nanotube. The results show that adsorbing the alcohols on the nanotube is associated with increasing the gas phase energies for the alcohols and their conjugated bases.

Carbon nanotubes are soluble in water and different organic solvents by covalent or non-covalent linkages [39,40]. In several instances, attaching the R-OH group to SWCNT made them more soluble. So, we explore the effect of polarized solvent (water) on alcohols and use it for calculating the acidity of alcohols. It was predicted that polarized solvent make NT more acidic [34]. The solvation energies of alcohols in Table 3 show that adsorbing on the nanotube reduces the solvation energies of alcohols. This reduction can be attributed to the higher cavity of NT-ROH molecules. Anyway, the conjugated bases of alcohols show lower solvation energies compared to NT-RO$^-$showing that the negative charge can be in resonance with the nanotube. The unsaturated NT-ROH show higher solvation energies compared to the saturated alcohols with the same number of atoms which can be due to their lower cavity and polarity.

Energies of the highest occupied and the lowest unoccupied molecular orbitals (HOMOs and LUMOs) and the energy gap of alcohols before and after adsorption on the nanotube are shown in Table 4. The band gap of alcohols are about 6-7 eV. After adsorbing on the nanotube, the band gap of the saturated alcohols becomes narrow about 1 eV, but the band gap of propanol increases about 2 eV. The band gap of methanol and ethanol does not change considerably.

To investigate the effect of alcohols on nanotubes we also investigated the band gap of pristine (8,0) SWCNT and SWCNT after ROH adsorption. The results presented in Table 5 show that the energy gap of pristine nanotube is about 1.86 eV and after adsorbing alcohols, the energy gap does not change considerably.

Deprotonation energies of NT-R-OH compared to R-OH in solution phase were calculated using the following equation:

$$\Delta G_{dp} = \Delta G_{aq,\ anion} - \Delta G_{aq,\ neutral} \qquad (1)$$

In Eq. (1), ΔG_{dp} is the deprotonation energy and $\Delta G_{aq,\ neutral}$ and $\Delta G_{aq,\ anion}$ are the energies of alcohols and their conjugated bases in solution phase respectively which are calculated using $\Delta G_{aq} = \Delta G_g - \Delta G_{solv}$. The results are presented in Table 6.

The calculated deporotonation energies are positive indicating that the alcohols are more stable than their conjugated bases. Comparing these results with those of NT-R-OH demonstrates that adsorbing the saturated alcohols on the nanotube increases the deprotonation energies. So, the acidity of these compounds reduces, while deprotonation energies of unsaturated alcohols reduce and their acidity increase after adsorption on the nanotube. These alcohols can have a resonance with the nanotube so their anionic forms become more stable. These results can

Table 2. Structural Results (Bond Lengths and Angles) of the Alcohols Compared to the Alcohols Adsorbed to the Nanotube

No.	Before adsorbing to the nanotube			After adsorbing to the nanotube			Nanotube alcohol distance
	C-O (A°)	O-H (A°)	<C-O-H	C-O (A°)	O-H (A°)	<C-O-H	NT-alcohol (A°)
1	1.43	0.96	109.47	1.42	0.96	106.24	1.49
2	1.43	0.96	109.47	1.41	0.96	107.62	1.48
3	1.43	0.96	109.47	1.42	0.96	106.68	1.48
4	1.43	0.96	109.49	1.42	0.96	106.46	1.43
5	1.43	0.96	109.49	1.42	0.96	105.60	1.40

Table 3. Calculated Gas Phase Energies and Solvation Energies of each Alcohols and their Corresponding Anion Compared to the Alcohols Adsorbed to the Nanotube

No.	Before adsorbing to the nanotube				After adsorbing to the nanotube			
	G_g (kJ)		G_{solv} (KJ)		G_g (kJ)		G_{solv} (kJ)	
	Alcohol	Anion	Alcohol	Anion	Alcohol	Anion	Alcohol	Anion
1	-72606.17	-72227.46	-4.184	-71.385	-71534.64	-70905.11	-17.046	-48.827
2	-97265.16	-96890.00	-3.934	-68.514	-96192.41	-95683.53	-29.665	-69.116
3	-121919.70	-121545.27	-3.973	-67.419	-120852.6	-120461.39	-36.267	-66.664
4	-121156.89	-120784.54	-4.477	-66.715	-120093.4	-119794.17	-18.235	-50.634
5	-120382.894	-120015.51	-5.100	-67.627	-119315.6	-119012.32	-23.641	-50.336

Table 4. Calculated HOMO-LUMO Energies and the Band Gap of Alcohols in eV

Before adsorption to the nanotube			After adsorption to the nanotube		
HOMO	LUMO	Gap	HOMO	LUMO	Gap
-7.651	-0.030749	7.6203	-7.6146	-0.03129	7.5833
-7.5675	-0.023402	7.5441	-7.5838	0.077552	7.6614
-7.561	-0.004082	7.5569	-7.1139	2.129291	9.2432
-7.0102	-0.280549	6.7296	-6.9819	-0.39810	6.5838
-7.6818	-0.324632	7.3571	-7.466	-0.53987	6.9261

Table 5. Calculated HOMO-LUMO Energies and the Band gap of Nanotubes in eV

	HOMO	LUMO	Gap
Pristine nanotube	-5.621	-3.7533	1.8672
1	-5.568	-3.6809	1.8868
2	-5.586	-3.6735	1.9121
3	-5.707	-3.5388	2.1685
4	-5.579	-3.732	1.8466
5	-5.643	-3.7353	1.9072

Table 6. Deprotonation Energies of Investigated Alcohols before and after Adsorption to the Nanotube in kJ

No.	Before adsorption	After adsorption
1	311.50701	597.7465
2	310.57686	469.4318
3	310.98323	360.8602
4	310.11137	266.8524
5	304.76418	276.5753

Table 7. Mulliken Charge Analysis of Alcohols before and after Adsorbing to the Nanotube

		Alcohols				Anions			
Atom No.		1	2	3	4	1	2	3	4
Alcohol No.									
Before adsorption	1	-0.514	-0.220			-0.805	-0.182		
	2	-0.52	-0.08	-0.433		-0.757	-0.402	-0.165	
	3	-0.52	-0.130	0.147	-0.495	-0.761	-0.41	0.297	-0.706
	4	-0.53	-0.21	0.049	-0.349	-0.771	-0.491	0.559	-0.657
	5	-0.48	-0.58	0.527	-0.329	-0.746	-0.917	1.027	-0.572
After adsorption	1	-0.518	-0.219			-0.465	-0.61		
	2	-0.52	-0.039	-0.489		-0.237	-0.14	-0.42	
	3	-0.54	0.07	-0.176	-0.316	-0.223	-0.209	-0.128	-0.497
	4	-0.52	-0.22	0.069	-0.352	-0.441	-0.491	0.121	-0.412
	5	-0.495	-0.57	0.63	-0.384	-0.309	-0.124	0.046	-0.063

be attributed to their charge density. Mulliken charge analyses of the investigated alcohols are presented in Table 7. The number of atoms is shown in Table 1. The Mulliken charge analysis of alcohols do not change considerably after adsorbing on the nanotube, except an increase in the negative charge of the carbon atoms attached to the nanotube. So, we have charge transfer from nanotubes to alcohols. Anyway, in anion form of alcohols, the negative charges of most atoms reduce after adsorption on the nanotube, showing the electron acceptor properties of nanotube. Comparing the charge analysis of alcohols and their conjugated bases show that NT pulls some electron density from the R-O^- group. This electron transfer is higher for unsaturated NT-R-O^- in comparison with their NT-R-OH structure. So, these alcohols become more acidic after adsorbing on the nanotube.

CONCLUSIONS

The ONIOM calculations were performed to investigate the acidity of five aliphatic alcohols before and after adsorbing on the tip of (8,0) SWCNT. The structural results show that the -OH group of alcohols tends toward the nanotube after full optimization. The energy results show that, HOMO-LUMO gaps of alcohols change a little after adsorption on the nanotube but the energy gap of nanotube does not change considerably. Based on deprotonation energies, saturated alcohols are more acidic before adsorbing on the nanotube. Anyway, unsaturated alcohols have lower deprotonation energies and their acidity increase after adsorption on the nanotube. This is described by their Mulliken charge analysis revealing that the (8,0) SWCNT pulls the electrons and stabilizes the anionic form of saturated alcohols more than their alcoholic forms.

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