Functionalization of Diazomethyl Aromatic Compounds onto Single Wall Carbon Nanotubes: A DFT Study

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A B S T R A C T

Density functional theory calculation (DFT) was carried out to study the functionalization of diazomethyl aromatic compounds, i.e., diazomethyl benzene, diazomethyl naphthalene, diazomethyl anthracene and diazomethyl pyrene onto (5,5) single-walled carbon nanotube (SWCNT) in both the perpendicular and parallel directions of the tube axis. All of computed binding energies are found to be negative value implying exothermic reaction. Functionalization in the perpendicular direction shows higher binding strength than that of the parallel direction. In addition, all of functionalizations can improve conductivity and solubility properties of SWCNT.

1. Introduction

The discovery of multi wall carbon nanotube (MWCNT) and single wall carbon nanotube (SWCNT) by Iijima produced a new branch in nanoscale (Iijima, 1991) (Iijima & Ichihashi, 1993). The specific geometrical structures and the excellent properties of carbon nanotubes (CNTs) have a wide range of potential applications owing to their structural, mechanical and electronic properties (Dresselhaus *et al.*, 1996; Meyyappan, 2005; Gogotsi, 2006). However, there are some features that are in limited use in many applications. For instances, the CNTs are

poor solubility in water or common solvents (Geckeler & Premkumar, 2011). So the functionalizations of CNTs have attracted to solve this problem. Experimental and theoretical studies indicated that the CNTs are able to be chemically or physically functionalized by the other atoms or molecules for the improvement of their properties (Popov & Lambin, 2006; Stafiej & Pyrzynska, 2007; Girão *et al.*, 2010; Zanolli, *et al.*, 2011). The chemical functionalized CNTs for improvement their solubility are also reported (Tasis *et al.*, 2003; Zhao *et al.*, 2004; Kim *et al.*, 2005; Vaisman *et al.*, 2006; Davis *et al.*, 2009).

In 1995, Smith III and his team successful synthesized the methyl functionalized fullerenes (C_{60} and C_{70}) via the cycloaddition of diazomethane followed by thermal extrusion of nitrogen gas to form the methanofullerene products (Smith *et al.*). After that the formations of methanofullerenes by addition of diazo compounds to benzene and fullerenes were theoretically studied and reported (Wallenborn *et al.*, 1998). In principle, the SWCNT wall, a multiply π-bonded system, should be amenable to these reactions with diazo compounds. In spite of many successful experiments on the soluble modification of CNTs, effects of functional groups on the geometrical and electronically structures of CNTs are not yet clearly understood due to the absence of a reliable theoretical model. In addition, the density functional theory (DFT) computations have been reported to be the high potential tool to study the structural, electronic and solubility properties of chemical systems (Tabtimsai *et al.*, 2012; Chasvised *et al.*, 2011; Malumgone *et al.*, 2011). In the present work, functionalizations of armchair (5,5) single-walled carbon nanotubes with diazomethyl aromatic compounds, i.e., diazomethyl benzene, diazomethyl naphthalene, diazomethyl anthracene and diazomethyl pyrene, were studied by using the DFT method.

2. Computational Details

Seven-layered armchair (5,5) SWCNTs were selected for this study. All of the atoms at both ends of the SWCNTs were terminated with hydrogen atoms. Functionalizations were applied on both C-C bonds at the perpendicular (type I) and parallel (type II) directions of tube axes as shown in Figure 1. After functionalizations of SWCNTs with diazomethyl benzene, diazomethyl naphthalene, diazomethyl anthracene and diazomethyl pyrene, the symbols for type I functionalizations, MB/SWCNT-I, MN/SWCNT-I, MA/SWCNT-I and MP/SWCNT-I, respectively, and for type II functionalizations, MB/SWCNT-II, MN/SWCNT-II, MA/SWCNT-II, MP/SWCNT-II respectively, were used. The optimizations of molecular structures of SWCNT and functionalized SWCNTs (fSWCNTs) were carried out using

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B3LYP–DFT method. All DFT calculations have been performed using the Becke's three–parameter exchange functional with the Lee–Yang–Parr correlation functional (B3LYP) and the 6–31G(d,p) basis set was used (Lee *et al*., 1988; Becke, 1993). After the optimizations, solubilities and the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) energies have been computed and compared. The binding energies (E_b) were calculated using the following equation:

$$E_b = (E(f\text{SWCNT}) + E(N_2)) - (E(\text{SWCNT}) + E(\text{Diazo})). \tag{1}$$

Where $E(f\text{SWCNT})$ is the total energy of the functionalized SWCNTs, $E(N_2)$ is the total energy of N_2 molecule, $E(\text{SWCNT})$ is total energy of the pristine SWCNT and $E(\text{Diazo})$ is the total energy of the diazomethyl aromatic compounds.

For the solubility in water of functionalized SWCNTs, the solvent effect using the conductor-like polarizable continuum model (CPCM) with UAKS cavity model was carried out (Barone *et al.*, 1998; Cossi & Barone, 1998). All calculations were performed with the GAUSSIAN 03 program (Frisch *et al.*, 2008). The molecular graphics of all related species were generated with the MOLEKEL 4.3 program (Flükiger *et al.*, 2000).
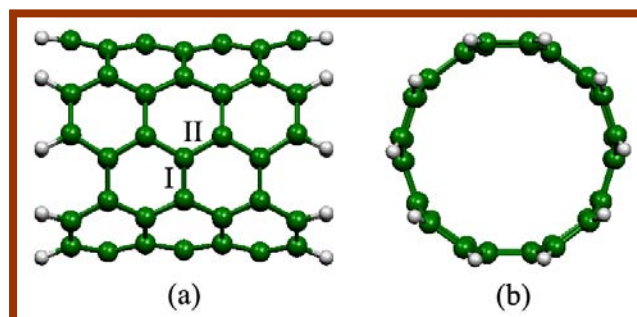

Figure 1: The B3LYP/6-31G(d,p)-optimized geometries of the SWCNT (a) side view and (b) front view. C atoms are in green and H atoms are in white.

3. Results and discussion

The geometries of pristine SWCNT, diazomethyl aromatic compounds and their functionalized SWCNTs computed by full optimization without any constrains using the B3LYP/6–31G(d,p) theoretical level were obtained. Figure 1 displays the optimized structures of pristine SWCNT, Figure 2 displays the optimized structures of all diazomethyl aromatic compounds and Figure 3 displays the optimized structures of all functionalized SWCNTs. From these figures, it is clearly seen the distortion on the tube walls (in both type I and type II sites) of SWCNTs, due to the side wall functionalizations. These indicate that the functional

groups can form covalent bond with the side wall of SWCNTs. Functionalizations of SWCNT also induced type I bond length changes from 1.41 to ca 2.12 Å, and type II bond length changes from 1.43 to ca 1.57 Å. Then it should be noted here that after functionalization, the C-C bonds of SWCNT change from sp^2 to sp^3 hybridization.
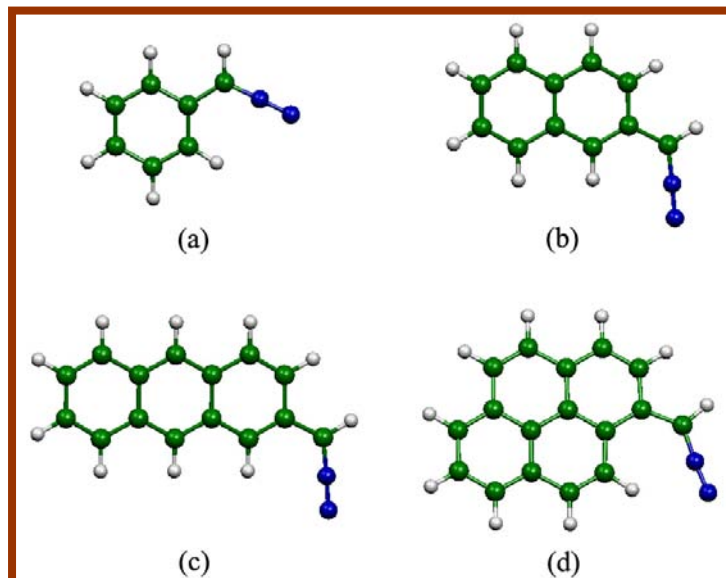

Figure 2: The B3LYP/6-31G(d,p)-optimized geometries of diazomethyl aromatic compounds (a) diazomethyl benzene, (b) diazomethyl naphthalene, (c) diazomethyl anthracene and (d) diazomethyl pyrene. C atoms are in green, N atoms are in blue and H atoms are in white.
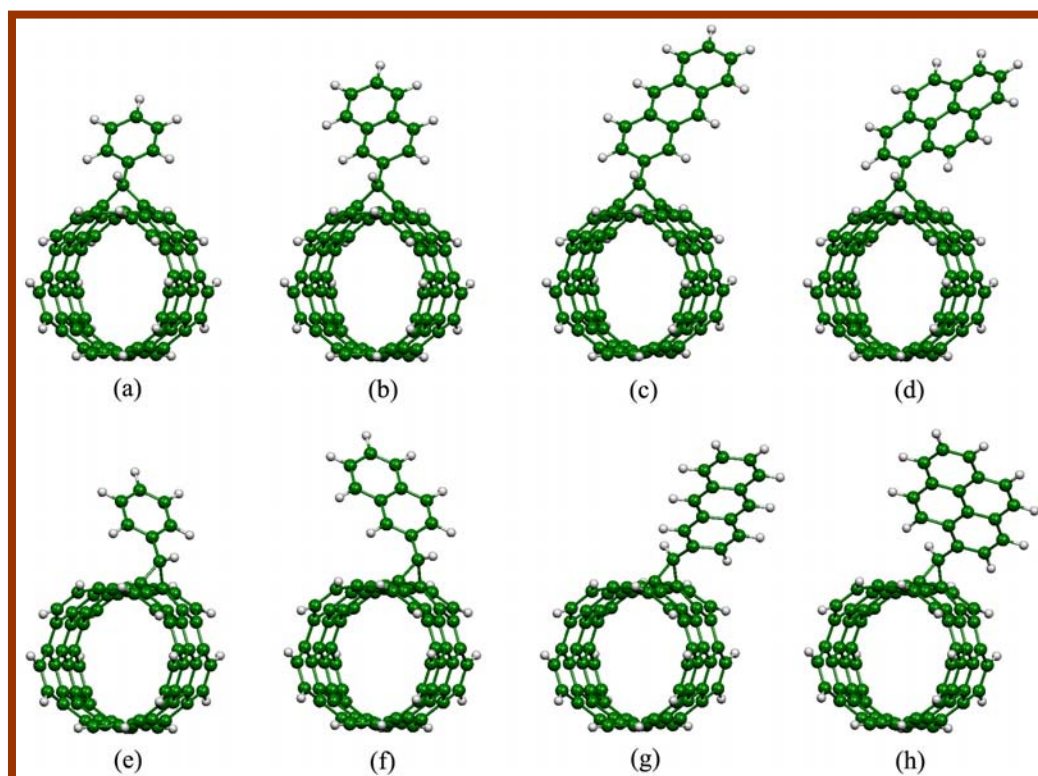

Figure 3: The B3LYP/6-31G(d,p)-optimized geometries of functionalized SWCNTs, (a) MB/ SWCNT-I, (b) MN/SWCNT-I, (c) MA/SWCNT-I, (d) MP/SWCNT-I, (e) MB/SWCNT-II, (f) MN/SWCNT-II, (g) MA/SWCNT-II, (h) MP/SWCNT-II.

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Table 1 displays the quantum molecular descriptors of all optimized structures of pristine SWCNT and functionalized SWCNTs. The results point out that the HOMO-LUMO energy gap (E_{gap}) of pristine SWCNT is 2.205 eV, then after functionalizations, the E_{gap} of functionalized SWCNTs decrease, compared with the pristine SWCNT. In addition, the HOMO-LUMO gaps of functionalized SWCNTs in type II site are more decreasing than those in type I site. These indicate that the conductivity of pristine SWCNT improves due to the functionalizations with diazomethyl aromatic compounds.

Table 1: Molecular descriptions for functionalized SWCNTs.

Complexes	E_{HOMO} [a]	E_{LUMO} [a]	E_{gap} [a,b]	η [a,c]	μ [a,d]	χ [a,e]
SWCNT	-4.509	-2.305	2.205	1.102	-3.407	3.407
MB/SWCNT-I	-4.421	-2.375	2.046	1.023	-3.398	3.398
MN/SWCNT-I	-4.428	-2.383	2.045	1.022	-3.405	3.405
MA/SWCNT-I	-4.431	-2.388	2.043	1.021	-3.410	3.410
MP/SWCNT-I	-4.437	-2.390	2.048	1.024	-3.414	3.414
MB/SWCNT-II	-4.351	-2.410	1.941	0.970	-3.381	3.381
MN/SWCNT-II	-4.356	-2.400	1.956	0.978	-3.378	3.378
MA/SWCNT-II	-4.356	-2.428	1.928	0.964	-3.392	3.392
MP/SWCNT-II	-4.351	-2.430	1.921	0.960	-3.390	3.390

[a] In eV. [b] $E_{\mathrm{gap}} = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$. [c] Chemical hardness, $\eta = E_{\mathrm{gap}}/2$.
[d] Chemical potential, $\mu = (E_{\mathrm{LUMO}} + E_{\mathrm{HOMO}})/2$.
[e] The Mulliken electronagativity, $\chi = -(E_{\mathrm{LUMO}} + E_{\mathrm{HOMO}})/2$.

The binding energies in gas phase (E_{b}) and Gibbs free energies of solvation (ΔG_{solv}) for pristine and functionalized SWCNTs in water are listed in Table 2. All of the computed binding energies are in negative value; implying that all of the functionalizations are favorable thermodynamically. In addition, the functionalization of SWCNT in type I site show the higher binding strength than those of type II site. That means it is being easier to attach the methyl aryl groups to C-C bond of SWCNT in the perpendicular direction than those of the parallel direction of tube axes.

The Gibbs free energies of solvation provide a measurement of the solubility of a substance in solvent. Negative values of the Gibbs free energies of solvation from thermodynamic consideration display that the solvation processes are spontaneous. Table 2 shows that all of functionalized SWCNTs have a negative Gibbs free energy of solvation which implies that the solvation processes of functionalized SWCNTs are spontaneous. The functionalized SWCNTs in type II site are more soluble in water than those of type I site. Moreover, the Gibbs free energy of solvation for pristine SWCNT in water is found to be   –19.05 kcal/mol. After functionalizations, Gibbs free energies of solvation are in the range of 21.42 – 25.19 kcal/mol,

that mean the solubility of SWCNT is clearly improved by functionalization with methyl aryl groups. Besides, increasing size of methyl aryl groups slightly improves in the solubility of SWCNTs. This behavior is in good agreement with the previously experimental report in which carboxylic acid-functionalized SWNTs prepared via the reaction of an amino acid, $NH_2(CH_2)_nCO_2H$, the solubility in water is improved or controlled by the length of the hydrocarbon side chain (i.e., n) (Zeng *et al.*, 2005).

Table 2: Binding energies in gas phase (E_b) and Gibbs free energies of solvation in water (ΔG_{solv}) for functionalized SWCNTs.

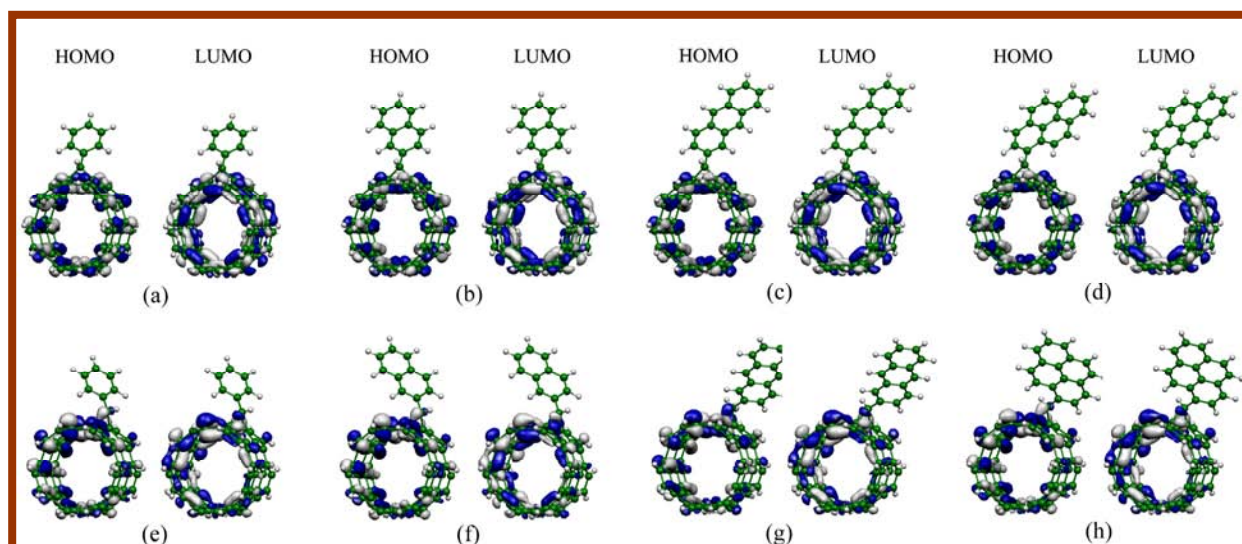| Complexes	E_b [a]	ΔG_{solv} [a]
SWCNT	-	-19.05
MB/SWCNT-I	-31.75	-21.42
MN/SWCNT-I	-31.71	-23.15
MA/SWCNT-I	-31.64	-24.79
MP/SWCNT-I	-32.34	-24.86
MB/SWCNT-II	-4.03	-21.61
MN/SWCNT-II	-4.18	-23.30
MA/SWCNT-II	-2.95	-25.19
MP/SWCNT-II	-6.59	-25.05

[a] In kcal/mol.

Figure 4: The calculated HOMO (left), LUMO (right) orbitals of functionalized SWCNTs, (a) MB/SWCNT-I, (b) MN/SWCNT-I, (c) MA/SWCNT-I, (d) MP/SWCNT-I, (e) MB/ SWCNT-II, (f) MN/SWCNT-II, (g) MA/SWCNT-II, (h) MP/SWCNT-II.

Figure 4 shows the HOMO and LUMO orbitals for pristine SWCNT and functionalized SWCNTs. From Figure 4, the HOMO and LUMO orbitals are mainly localized around the tubes without the distribution on the functional groups. In order to investigate effect of

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chemical functionalization of methyl benzene, methyl naphthalene, methyl anthracene and methyl pyrene groups onto the SWCNT to the electronic structure and electronic density of states (DOSs) of SWCNTs with and without funtionalized groups are plotted and displayed in Figure 5. These figures show that the DOS peaks of pristine SWCNT and functionalized are all symmetries. Nevertheless, Calculated DOS plots show that the band structure of the pristine SWCNT is changed upon the functionalization with the methyl aryl groups in which the DOSs near Fermi level of functionalized SWCNTs are narrower than that of pristine SWCNT. The decreasing of band gaps of adsorption structures were confirmed by the energy different between HOMO and LUMO energies (Table 1).
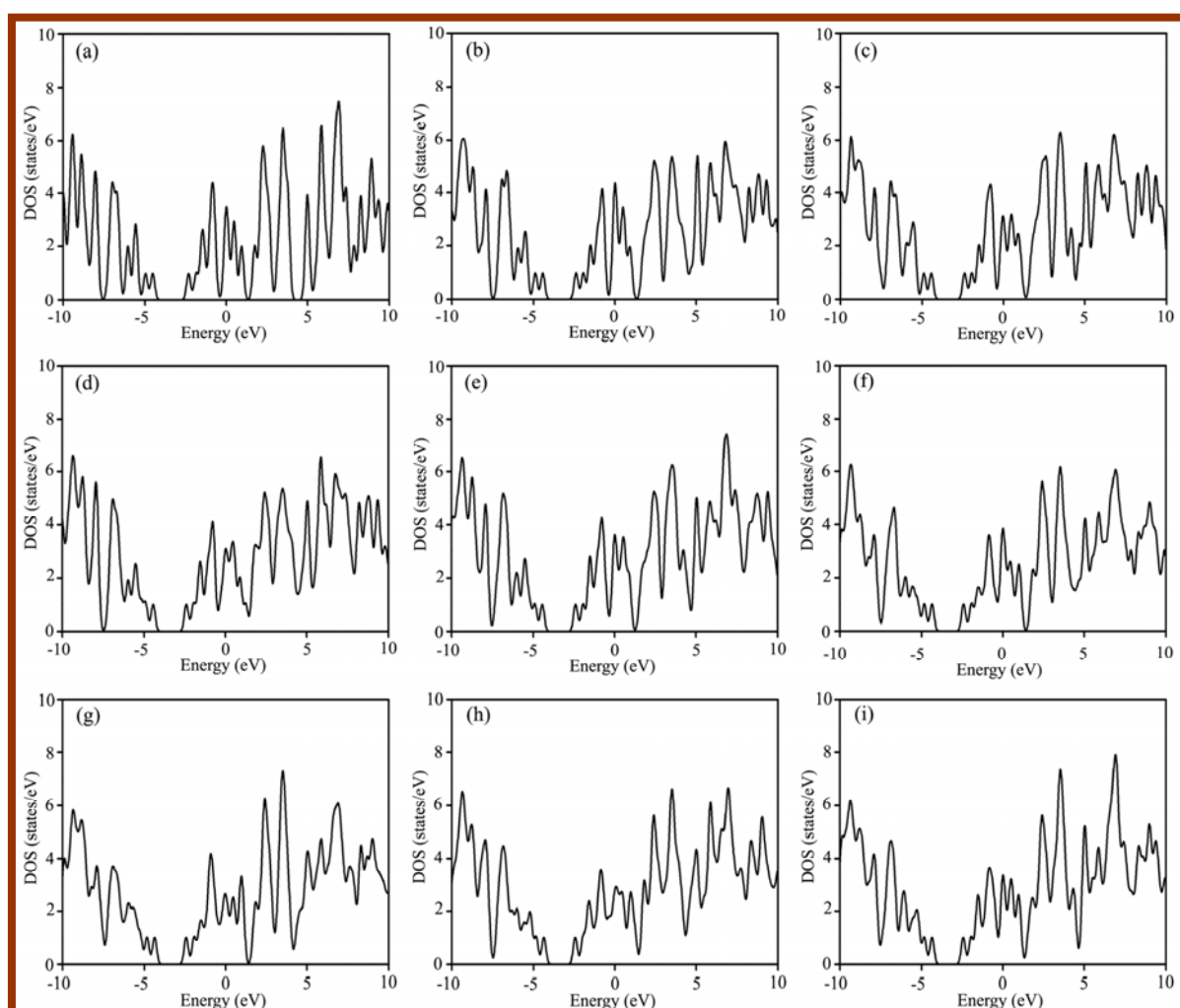

Figure 5: The DOS plots of (a) SWCNT, (b) MB/SWCNT-I, (c) MN/SWCNT-I, (d) MA/SWCNT-I, (e) MP/SWCNT-I, (f) MB/SWCNT-II, (g) MN/SWCNT-II, (h) MA/SWCNT-II, (i) MP/SWCNT-II.

4. Conclusion

The functionalizations of diazomethyl aromatic compounds (diazomethyl benzene,

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diazomethyl naphthalene, diazomethyl anthracene and diazomethyl pyrene) onto (5,5) single-walled carbon nanotube (SWCNT) were investigated using the B3LYP/6-31G(d,p) computation. The computed results indicated that binding energies of functionalizations are in negative value, implying that functionalizations are thermodynamically stable and exothermic reaction. The results also show that conductivity and solvation ability in water of SWCNT are improved by functionaliztions with diazomethyl aromatic compounds.

5. Acknowledgements

6. References

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