A Theoretical Study on Interaction between Nitrobenzene and Carbon Nanotube (A DFT approach)

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ABSTRACT

The Density Functional Theory (DFT) and the Natural Bond Orbital (NBO) calculations based method B3LYP/6-31G* were carried out to study the interaction of carbon nanotube (8,0) with nitrobenzene in two situations perpendicular and parallel. Formation energies of compounds, charges, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and the HOMO-LUMO band gap were calculated. The parallel direction is more stable than the perpendicular direction. The lower HOMO-LUMO gaps confirm this stability.

Keywords: NBO; DFT; HOMO- LUMO gap; Nanotube; Nitrobenzene

INTRODUCTION

Since their discovery, [1] carbon nanotubes have stimulated intense experimental and theoretical interest in their physics, chemistry, and materials science. Their unique structure and properties make them suitable for a variety of potential applications [2].Single-wall nanotubes _SWNTs_ are multifunctional materials that have potential for use as efficient gas storage elements and in battery devices, as sensors and electromechanical systems in nanoelectronics, and as biocompatible agents and sensors in medicine [3].

Interaction of SWNTs with chemical molecules is important. For example interaction of O_2, H_2 and NO_2 with SWNTs change transport properties of the SWNTs [4-10]. Organic aromatic molecules can have functionalize SWNTs through noncovalent [11, 12]. SWNTs functionalization with biological molecules such as proteins, DNA and nucleic acids that contain aromatic rings that make a good potential for drug development drug delivery systems and sensors[13]. Although these compounds have many advantages but it can create risks for human health. Nanoparticles that can penetrate the air or the food chain and can cause allergenic reactions [14-17].In benzene, carbon atoms have sp^2-hybrid and create a resonant bond shared by six carbon atoms. π orbitals are perpendicular to the molecular plane. Graphene, metallic and semi-conductor SWNTs have perpendicular π orbitals to the surface [18].Therefore SWNTs / molecule systems can be π....π interactions. The π....π interaction is relatively weak and includes Vander Waals forces. Benzene derivatives are produced by the substitution of one or more hydrogen atoms in the benzene ring with NO_2, NH_2, and so on. These derivatives have π systems in the benzene ring. We found that the interaction of compounds with closed shells

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is usually physisorption. Aromatic compounds interacting with SWNTs are of particular interest. Noncovalent sidewall SWNT functionalization with aromatic organic molecules [19, 20] has attracted increasing attention. Using SWNTs as sensors for some aromatics has also been demonstrated experimentally [19-23]. In addition, SWNT functionalization with biological molecules such as proteins, DNA, and nucleic acids, which contain repetitions of many aromatic rings, provides potential for developing drug delivery systems, molecule immobilization, and sensors [24]. Therefore, a fundamental theoretical and systematic understanding of SWNT interaction with benzene derivatives, which appear as building blocks in large organic and biological systems, is necessary.

In this work, the adsorption of a simple benzene derivative 'nitrobenzene' on a semiconducting SWNT (8, 0) is investigated using first-principles calculations based on the density functional theory 'DFT'.

The paper is organized as follows. In Sec. II, the method for the calculations is described. Section III gives the results from the calculations, which are discussed in Sec. IV.

COMPUTATIONAL METHOD

First of all a nanotube (8, 0) is formed by Nanotube Modeler Package [25]. Then this nanotube is optimized by Gaussian 03 software [26] by DFT/B3LYP method and 6-31G* basis set. Nitro benzene is optimized

by Gaussian 03 using B3LYP functional with the basis set 6-31G* [27] .Then the complexes between nanotube and nitrobenzene (in parallel and perpendicular directions) are formed and optimized by B3LYP/6-31G* method (Fig.2). Because the two Oxygen atoms have almost the same positions, one of them was studied. After optimization of complexes, the single point energies obtained by B3LYP/6-311++G** method. Delocalization of electron density between the filled (bond or lone pair) Lewis type NBOs and empty antibonding non-Lewis NBOs calculated by NBO (Natural Bond Orbital) analyzing by B3LYP/6-31G level [28].

RESULTS AND DISCUSSION

All of calculations were carried out by the GAUSSIAN 03 program package that five basis sets 3-21G, 6-31 G , 6-31 G (d) , 6-31 G (d,p) , 6-31+ G (d) were employed at the B3LYP type of DFT procedure .The results are shown in table 1.With increase basis set quality, energy becomes more negative. In all structures, more stable obtained in 6-31+ G (d) basis set. Energy is more favorable in 6-31+ G (d) basis set than 3-21G. The parallel complex respect with perpendicular complex has more favorite energy and more stable (table4).in parallel complex, $\pi...\pi$ interaction nitrobenzene ring and six-member ring of SWNT create the physisorption.
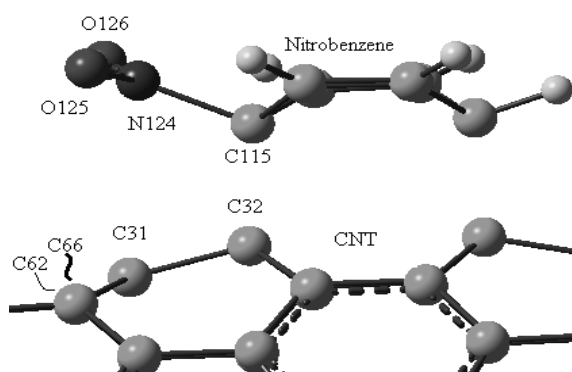

Fig. 1. The labeling of atoms in CNT-nitrobenzene (parallel).

Comparing the values calculated at the nitrobenzene and combination of CNT-nitrobenzene (parallel), we found that the N=O bond length increases by more than 0.005A°, the C-N bond length increases 0.068A° and in CNT nitrobenzene (parallel) compound .Moreover we can see such trend in CNT – nitrobenzene vs. CNT. In perpendicular complex oxygens of NO_2 in nitrobenzene are on c_{66}, c_{62} atoms of SWNT. Most changes in the length and angle is related to the parallel complex. In parallel complex nitrobenzene ring has an Interaction by two carbon atoms (c_{115}, c_{118}) with the six-member ring of SWNT (c_5, c_{32}). (Fig.1)

The NBO analysis results indicate that the charges for the carbon atoms are positive and Oxygen atoms are negative. The labeling of atoms in CNT-nitrobenzene (parallel) is given in Fig.1.The optimized geometrical parameters in gas phase are listed in Table 2.

The formation energy values, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the HOMO-LUMO band gap have been found as a measure of the structural stability properties. These descriptors for the complexes and each component listed in tables 4and 5. As can be observed the complexes between nitrobenzene and nanotube are less stable than the single agents. Also the parallel direction is more stable than the perpendicular direction. The lower HOMO-LUMO gaps confirm this stability.
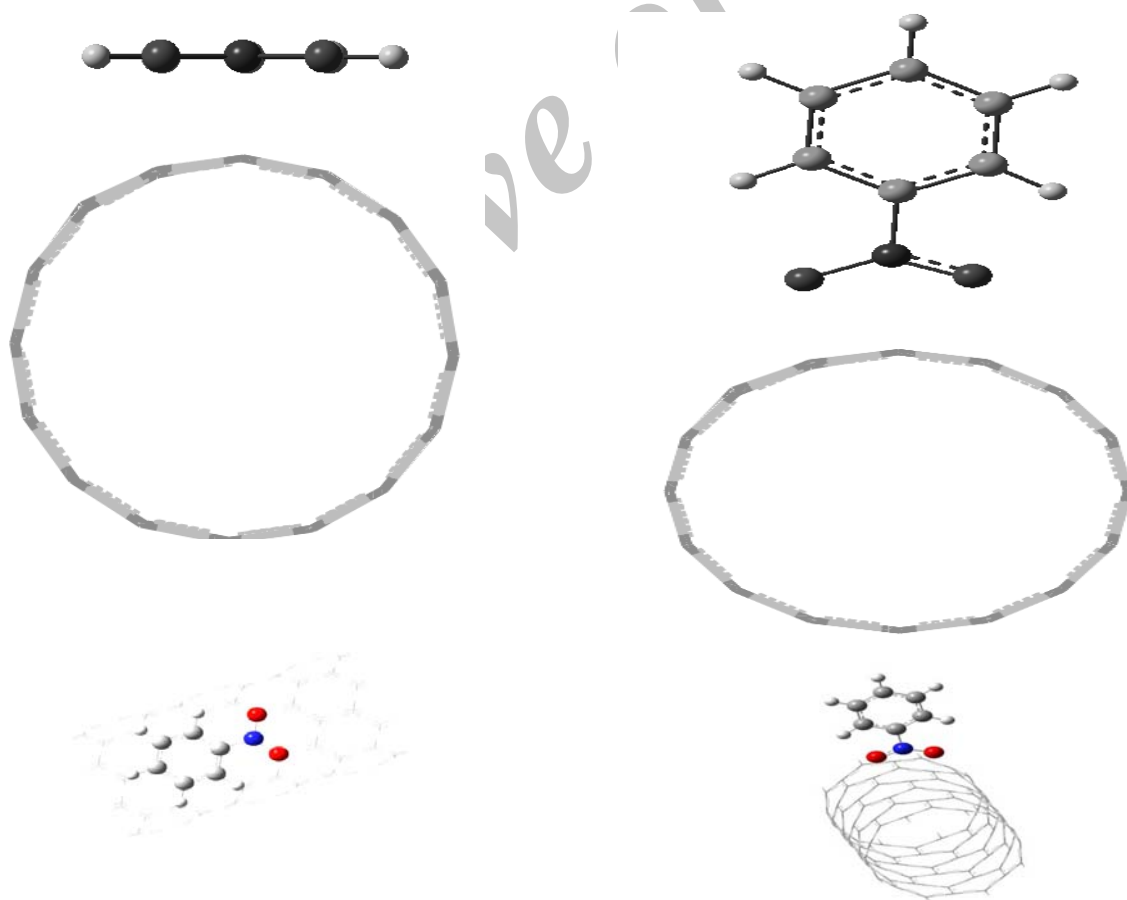

Fig. 2. Complexes between CNT (8,0) and nitrobenzene in parallel and perpendicular situations.

CONCLUSION

In this work, the stability of nitrobenzene with carbon nanotube (8,0) has been investigated. The data and discussion in the previous sections, lead us to the following major conclusions:

-The complex of nanotube and nitrobenzene is less stable than the single agents.

Although CNT – nitrobenzene in parallel situation is more stable than the perpendicular one.

- NBO analysis indicated the lower HOMO-LUMO gap in CNT-nitrobenzene in parallel situation. Therefore, this composite is more stable than the other one.

Table 1. Energy (kJ/mol) and Dipole moment (Debye) of CNT (8, 0) and nitrobenzene obtained in various basis set at B3LYP method

Basis set	Energy CNT	Dipole moment CNT	Energy Nitrobenzene	Dipole moment Nitrobenzene
3-21G	-2288804.203	0.0012	-272538.4851	4.4240
6-31G	-2301000.805	0.0001	-273982.513	5.1072
6-31G(d)	-2301558.307	0.0004	-274065.3595	4.5792
6-31G(d,p)	-2301573.591	0.0000	-274070.3359	4.5558
6-31+G(d)	-2301423.195	0.0000	-274077.5127	4.9824

Table 2. Optimized geometry of CNT-Nitro benzene complex in gas phase (Parallel)

Coordinate	Nitrobenzene Nitrobenzene length	order	SWNT (8 ,0) - nitrobenzene length	order
O_{125}-N_{124}	1.23066	1,1/2	1.22585	1,1/2
O_{126}-N_{124}	1.23066	1,1/2	1.22936	1,1/2
N_{124}-C_{115}	1.47300	1	1.54151	1
C_{115}-C_{114}	1.39339	1,1/2	1.53873	1
C_{114}-C_{113}	1.39305	1,1/2	1.31738	2
C_{113}-C_{118}	1.39735	1,1/2	1.53053	1
C_{118}-C_{117}	1.39735	1,1/2	1.53881	1
C_{117}-C_{116}	1.39305	1,1/2	1.31927	2
C_{116}-C_{115}	1.39339	1,1/2	1.53333	1

Table 3. DFT calculated based on the B3LYP/6-31G level

Species	Charge			Bond length	
	N	C	O	C-N	C-O
N_{124}-C_{31}	+0.518	0.017	-	2.712	-
O_{125}-C_{62}	-	0.006	-0.394	-	3.259
O_{126}-C_{66}	-	0.006	-0.394	-	3.259

Table 4. Obtained energies and dipole moment

Species	E (eV)	D(D)
CNT-Nitro benzene(perpendicular)	-4059.67	3.1658
CNT-Nitro benzene(Parallel)	-4059.82	3.1741
CNT (8,0)	-3647.44	4.3382
Nitrobenzene	-436.75	2.1710

Table 5. Obtained some descriptors by B3LYP/6-31G level

Descriptors/ kcalmol^{-1}	Nitrobenzene –CNT parallel	Nitrobenzene –CNT perpendicular
ΔE_f	663.20	667.16
$\Delta E_{HOMO-LUMO}$	0.04215	0.16184

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