Theoretical study of interaction of 4-amino phenyl-azobenzene with (SWCNTs), A DFT method

F. Azarakhshi[*], *M. Arabsalmani, N. Tajdini, N. Farhadyar*

Department of Chemistry, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran

ABSTRACT: The electronic and structural properties of single wall carbon nanotubes (SWCNTs) interacted with 4-amino phenyl-azobenzene were theoretically investigated by using the hybrid DFT (hybrid-density functional theory) calculations. The amount of thermodynamic parameters of this reaction in the gas and aqueous phase suggesting thermodynamic favourability for adsorption of 4-amino phenyl-azobenzene on (5, 0) zigzag CNT in both phases. The binding energy (BE) for the optimized structure of azo dye-CNT was calculated -3.92 (kcal/mol) and results showed that the physical adsorption reaction was occurred. The bonding-antibonding orbital interactions on the structural properties and reactivity of azo dye and CNNT, HOMO-LUMO bond gap and the total density of states (DOS) were quantitatively investigated by the NBO approach based on B3LYP/6-311+G** level of theory.

Keywords: *Azo dye; Adsorption; Carbon nanotubes; DFT; Electronic effects; NBO*

INTRODUCTION

In the last decades, carbon-based materials have been widely studied. The discovery of carbon forms such as fullerenes, carbon nanotubes and graphene have brought a big interest because these materials exhibit remarkable properties to be applied in several technological areas (Jorio, *et al.*, 2008). They have unique electrical and mechanical properties such as exceptionally high thermal conductivity (Krishnan, *et al.*, 1998), high tensile strength (Hone, *et al.*, 2002), electronic nanodevices (Romo-Herrera, *et al.*, 2008), and electronic properties ranging from metallic to semiconducting (Durkop, *et al.*, 2004). In particular, carbon nanotubes are promising materials for several applications such as components in water filters (Brady-Estevez, *et*

al., 2008, Mauter and Elimelech, 2008), environmental sensors (Hierold, *et al.*, 2007), efficient gas storage elements and sensors in medicine (Dresselhaus, *et al.*, 2000). About one million tonne of different chromogens are synthesized annually worldwide of which approximately 10-15% remain in textile wastewaters after application. Azo dyes represent the largest class of dyes listed in general category of dyes (60-70% of all dyes) (Rezaee and Movahedian Attar, 2006, Lopes, *et al.*, 2004). Azo dyes contain at least one chromogenic factor of nitrojen-nitrojen double bond ($-N=N-$) called azo group with one or more aromatic groups (Daneshvar, *et al.*, 2008, Joshi, *et al.*, 2008). The presence of very small amounts of color in water is visible, seriously affecting the aesthetic quality and water clarity, and

(*) Corresponding Author - e-mail: fa_azarakhshi@yahoo.com

also the aquatic oxygen concentration and destroying aquatic environment. The researchers have found that during the decomposition process, some chromogens such as azo dyes produce aromatic amines which are potentially carcinogenic and mutagenic azo dyes are generally resistant under aerobic conditions, and despite being reduced easily under anaerobic conditions, their products are aromatic amines that are potentially carcinogen and mutagenic (Rezaee and Movahedian Attar, 2006, Daneshvar, *et al.*, 2008, Somasiri, *et al.*, 2008). In recent years, advanced oxidation technologies have been described as efficient methods to obtain high yields of oxidation of different types of organic compounds (Joshi, *et al.*, 2008, Tauber, *et al.*, 2008). Moreover, during the two past decades, photocatalitic decomposition of toxic chemicals that have caused severe environmental pollution has been widely studied. Colours make many problems and these are major sources of environmental pollution and should be treated before discharging to environment. Nanotubes are new adsorbents with extend application for adsorption of different compounds. In this study the single-walled carbon nanotubes as adsorbent to reactive 4-amino phenyl-azobenzene was theoretically investigated. The main aims of this work are to find the structural and electronic properties of (5, 0) zigzag single walled carbon nanotube (SWCNT) including structural parameters, dipole moments, and energy gaps (ELUMO–HOMO), and the quantum molecular descriptors by using DFT method.

COMPUTATIONAL DETAILS

In order to investigate of electronic and structural properties of (SWCNTs) interacted with Azo Dyes, first principle calculations of all the geometry optimizations, thermodynamic functions, natural bond orbital (NBO) for (5, 0) zigzag CNT interacted with 4-ami-

no phenyl-azobenzene molecule are performed using Gaussian 09 quantum package (Frisch, *et al.*, 2009) at the level of density functional theory (DFT) with B3LYP/6–31G* basis set (Seminario and Politzer, 1995). The 4-amino phenyl-azobenzene molecule was made in the different positions of the site to be close to the C30H10 nanotube and its adsorption has been calculated by using the Eqn (1). In addition, δBSSE is representing the basis set super position error.

$$E_{adsorption} = E_{(Dye-C30H10\ nanotube)} - (E_{Dye} + E_{C30H10\ nanotube}) + \delta BSSE \quad (1)$$

All structures were optimized without symmetric constraints. The optimized models are stable structures verified via frequency calculations with the absence of imaginary frequency. The Density of states (DOS) plots has been obtained using Gaussum software (O'Boyle, *et al.*, 2008). The effect of polar solvent on the property of functionalized CNT was investigated by using the method of Polarizable Continuum Model (PCM) (Tomasi, *et al.*, 1999). The stabilization energies associated with electronic delocalization, HOMO/ LUMO energy gap (Eg), frontier molecular orbitals (FMO) analyses were quantitatively investigated by the NBO analysis (Glendening, *et al.*, 2004).

RESULTS AND DISCUSSION

Thermodynamic parameters [ΔH, ΔG (in kcal/mol) and ΔS (in cal mol^{-1}K^{-1})] and relative energies ΔE^0 (E0= ZPE + Eel (in kcal/mol), for the energy minimum azo dye–CNT at 25 ºC and 1 atm pressure was calculated at the level B3lyp/6-31g*, all parameters are negative in gas and aqueous phase and the adsorption reaction is exothermic (Tables 1, 2). In order to obtain the most stable adsorption mode, the azo dye set in different positions of C30H10 nanotube. The data shows that the best torsional angle, bonding an-

Table 1. The thermodynamic parameters differences for azo dye–CNT in gas phase

Compounds	B3LYP/6-31G*				
	ΔG	ΔH	ΔS	ΔE_0	$\Delta E_{Thermal}$
Azo dye-CNT	-3.825	-2.257	-0.030	-2.945	-1.665

Table 2. The thermodynamic parameters differences for azo dye–CNT in aqueous phase

Compounds	B3LYP/6-31G*				
	ΔG	ΔH	ΔS	ΔE_0	$\Delta E_{Thermal}$
Azo dye-CNT	-4.475	-3.536	-0.039	-3.628	-2.943

$$\Delta H_{adsorption} = \Delta H_{(in\ gas\ phase)} - \Delta H_{(in\ aqueous)} = (-3.536) - (-2.257) = -1.279$$

gle and distance values for azo dye-CNT is equal to the $\varphi_{46-45-15-12}$= -90.0°, $\theta_{48-46-15}$= 60.0° and r_{15-46}= 3.515, r_{15-48}= 3.384 Å, respectively. The binding energy value for optimized structure of azo dye–CNT is equal to -3.922 kcal/mol and the physical adsorption was occurred.

Also, the HOMO/ LUMO energy gap (Eg) for pristine carbon nanotube (Eg= 0.916 eV) and azo dye (Eg= 3.547 eV) and the energy gap for azo dye-C30H10 nanotube (Eg= 0.988 eV) was calculated (Fig. 1). Considering HOMO-LUMO energy bond gap shows that a soft molecule has small HOMO-LUMO energy gap and a hard molecule has a large HOMO-LUMO energy gap. The stabilization orbital interactions should increase as the donor orbital energy increases and the acceptor orbital energy decreases. Moreover, the electron delocalization in the CNTs could be justified by variation of Orbital Occupancies.

The decrease of the bonding orbital occupancies and the increase of the anti-bonding orbital occupancies in the SWCNTs could be explained by the decrease of energy differences between donor and acceptor orbitals for the azo dye-CNT that cause to electron distribution.

For an N-electron system with a total energy (E) and total external potential $v(r)$, the global indexes (Zevallos and Toro-Labbe, 2003, Chattaraj and Poddar, 1999, Prystupa, et al., 1994, Pearson, et al., 1978) of the equilibrium state at (T) temperature are calculated as the following equations:

$$\chi = -\left(\frac{\partial E}{\partial N}\right)_{v(r),T} = -\mu \qquad (1)$$

Where μ is the chemical potential of the species and is defined as the negative value of the electronegativity. Similarly, the global hardness (η) is expressed in
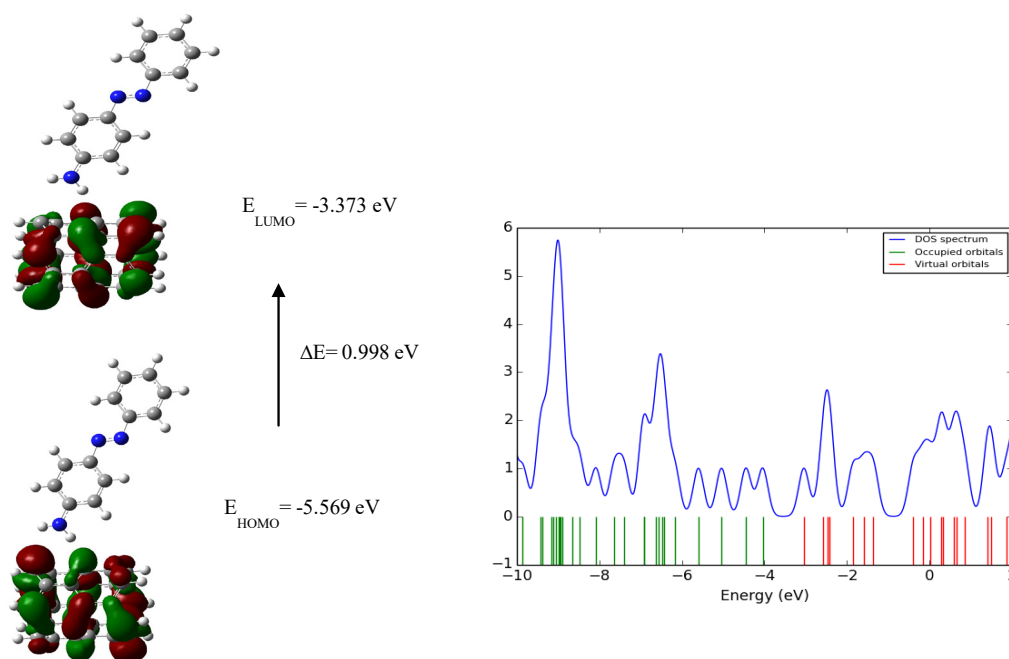

Fig. 1. LUMO and HOMO molecular orbitals of azo Dye –C30H10 nanotube and DOS spectrum

$E_{LUMO} = -3.373$ eV

$\Delta E= 0.998$ eV

$E_{HOMO} = -5.569$ eV

Table 3. Comparison of Dipole Moments (Debye), chemical hardness (in hartree), chemical softness (S) (in hartree^{-1}), electronic chemical potential (μ) (in hartree), the Muliken electronegativity (χ) (in hartree), electrophilicity index (w) (in hartree), the maximum amount of electronic charge index (ΔN_{max}) (in hartree), HOMO, LUMO energy gaps (in hartree) and Total Electronic Energy (in hartree) calculated for azo dye, C30H10 nanotube and azo dye-C30H10 nanotube by using B3LYP/6-31G*method.

Compounds	Dipole Moment	η	S	$\mu = -\chi$	w	ΔN_{MAX}	E_{HOMO}	E_{LUMO}	E_g	EI	EA
Azo dye	3.113	1.773	0.282	-3.592	3.638	-	-5.365	-1.818	3.547	5.365	1.818
CNT	0.000	0.458	1.092	-3.215	11.287	-	-3.673	-2.757	0.916	3.673	2.757
Azo dye-CNT	5.868	0.499	1.001	-3.542	12.564	7.098	-4.041	-3.042	0.998	4.041	3.042

terms of the second derivative of energy with respect to the external potential of $v(r)$ (Sen and Jorgensen, 1987, Pearson, 1997, Parr and Pearson, 1983, Parr and Zhou, 1993, Pearson, 1989):

$$\eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{v(r),T} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{v(r),T} \qquad (2)$$

The global softness (S) is the inverse of global hardness:

$$S = \left(\frac{\partial N}{\partial \mu}\right)_{v(r),T} \qquad (3)$$

In finite difference approach, chemical potential, global hardness and global softness (S) can be approximated as (Parr and Zhou, 1993):

$$\mu = \frac{(E_{HOMO} + E_{LUMO})}{2} = -\chi \qquad (4)$$

$$\eta = \frac{(E_{LUMO} + E_{HOMO})}{2} \qquad (5)$$

$$S = \frac{1}{2\eta} \qquad (6)$$

$$EI = -E_{HOMO} \qquad (7)$$

$$EA = -E_{LUMO} \qquad (8)$$

where I is the ionization potential and A is the electron affinity of the molecule. The Frontier orbital approach as proposed by Koopmans' theorem (Koopmans, 1933) for closed shell system is totally appropriate in explaining stability and chemical reactivity of the

molecules based on HOMO and LUMO orbitals. The energy corresponding to HOMO represents the ionization potential of the molecule and the LUMO corresponds to electron affinity value. The electrophilicity index is a measure of the electrophilic power of a molecule and the electrophilicity index as defined by Parr *et al.* (Parr, *et al.*, 1999) is given by the expression:

$$\Delta N_{max} = \frac{(\mu_A + \mu_B)}{2(\eta_A + \eta_B)} \qquad (9)$$

The fractional number of electrons transferred from one system (say A) to another system (say B) is denoted by ΔN (Lukovits, *et al.*, 2001) and has been calculated as follows:

$$w = \left(\frac{\mu^2}{2\eta}\right) \qquad (10)$$

where, μ_A, μ_B and η_A, η_B are the chemical potential and chemical hardness of the systems A and B, respectively. A positive value of ΔN indicates that charge flows from B to A and A acts as an electron acceptor, while a negative value of ΔN indicates that charge flows from A to B and A acts as an electron donor.

Considering the small HOMO−LUMO energy bond gap and the measure of chemical hardness means a soft compound and it is related to molecular property of conducting electrical current. The electronic chemical potential (μ), the global index includes electronegativity (χ), chemical hardness (η), softness (S), electrophilicity index (w), the maximum amount of electronic charge index (ΔN_{max}) and dipole moment were calculated for azo dye, C30H10 nanotube and azo dye-C30H10 nanotube by using DFT/B3LYP method are listed in Table 2.

CONCLUSIONS

Due to the small size, high surface area and unique regularity of the network, the reactivity of single-walled carbon nanotubes is very high. The investigation of adsorption behaviour of azo dye on CNT surfaces can provide valuable information about its reactivity, electronic and structural properties of carbon nitride nanotubes in interaction with azo dye. The obtained result shows that, the charge transfer occurs within the SWCNTs that give rise to the conductivity of carbon nanotubes and the (5.0) CNNT with (Eg= 0.998 eV) is effective adsorbent for the 4-hydroxy phenyl-azobenzene dye removal from environment.

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AUTHOR (S) BIOSKETCHES

Fatemeh Azarakhshi, Assistant Professor, Department of Chemistry, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran, *Email: fa_azarakhshi@yahoo.com*

Masoud Arabsalmani, M.Sc., Department of Chemistry, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran

Nilofar Tajdini, Assistant Professor, Department of Chemistry, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran

Nazanin Farhadyar, Associate Professor, Department of Chemistry, Varamin-Pishva Branch, Islamic Azad University, Varamin, Iran