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Theoretical Study of stereoelectronic effects of Boron Nitride Nanotubes in interaction with 7-hydroxy phenothiyazine 3-one sulphure dye by electron density functional theory

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ABSTRACT: In this study interaction of phenothiazine sulfur dye with (5, 5) armchair open-end boron nitride nanotubes (BNNTs) in interaction (with a length of 7 Å) was investigated. The impacts of the estereoelectronic effect associated with donor-acceptor electron delocalizations, dipole-dipole interactions and total steric exchange energies on the structural and electronic properties and reactivity of semiconductors of (5, 5) armchair open-end boron nitride nanotube (BNNT) in interaction with 7-hydroxy phenothiyazine 3-one sulphure dye was studied based on the Density Functional Theory (DFT) calculations by using the B3LYP/6-31G* level of theory in gas phase and water solution. Delocalization of charge density between the bonding or lone pair and antibonding orbitals calculated by NBO (natural bond orbital) analysis. These methods are used as a tool to determine structural characterization BNNTs during the adsorption reactions in the gas phase. In order to investigate of conductivity and electronic properties of (5, 5) open-end boron nitride nanotube (BNNT) in the reaction with 7-hydroxy phenothiyazine 3-one sulphure dye, the thermodynamic functions, the total electronic energy, dipole moment, orbital energies, charge density, density of state (DOS), LUMO-HOMO energy bond gaps, Adsorption energies (E_{Ad}) were calculated. The calculated LUMO-HOMO energy bond gap show that charge density transfer occurs within the molecules and the semi-conductivity of BNNTs could be justified.

Keywords: *Adsorption; BNNTs; Dye removal; Density Functional Theory (DFT); Natural Bond Orbital (NBO)*

INTRODUCTION

The prediction of the carbon nanotubes (CNTs) by (Injima, 1991), which can be metallic or semiconductor in character, depending on their chirality and their diameter; CNTs have recently revealed as materials of different properties and various applications in gas storage, sensors and in environment applications. In 1994 (Rubio, *et al.*, 1994) theoretically suggested the existence of the boron nitride nanotubes (BNNTs), which were synthesized, by (Chopra, *et al.*, 1995). BNNTs possess excellent mechanical properties, high thermal conductivity, chemical stability; unique properties including tensile strength, stiffness and deformation are the features of BNNTs, and resistance to the oxidation, among other properties. Boron nitride nanotube (BNNT) has unique properties of semiconductor behaviour. BNNT

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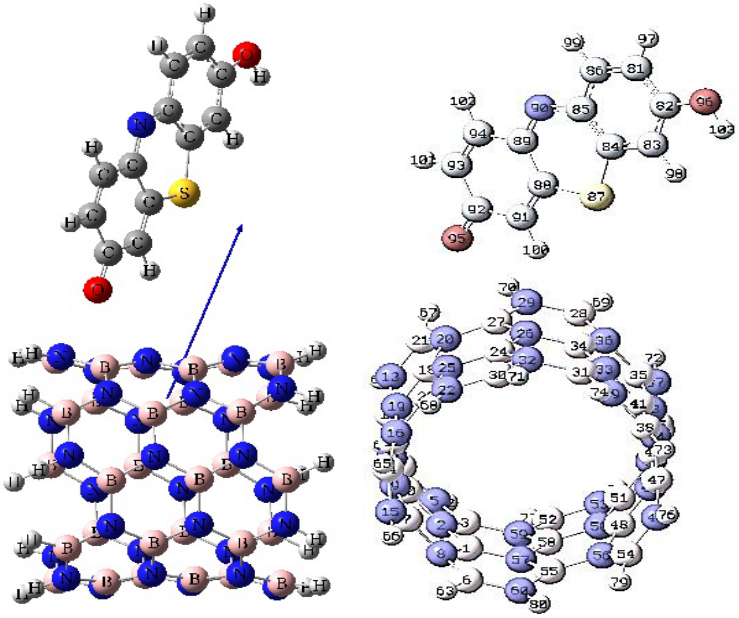

Dipole Moment = 6.356 Debye
Point Group = C1
E(RB3LYP) = -3468.19457756 a.u.

Fig. 1. The optimized structure of sulfur dye-BNNT

has a smaller band gap of a material that is interesting for applications in nanoscale devices. Previously adsorption of different molecules toward nanostructures has been studied (Kaur, *et al.*, 2015, Azarakhshi, *et al.*, 2011, Azarakhshi, *et al.*, 2012, Masnabadi, *et al.*, 2013, Politzer, *et al.*, 2005, Peralta-Inga, *et al.*, 2003, Peyghan, *et al.*, 2013, Beheshtian, *et al.*, 2013, Baei, *et al.*, 2013, Farmanzadeh & Ghazanfary, 2014, Peyghan, *et al.*, 2013, Soltania, *et al.*, 2012). There is sufficient published experimental information about the dye removal from textile wastewater but there is no quantitative theoretical published data about the electronic properties and reactivity of boron nitride nanotube (BNNT) in interaction with sulfur dye. In this study, (5, 5) armchair BNNT have been carried out to adsorption of 7-hydroxy phenothiazine 3-one dye as environmental pollution by DFT method. Also, the stabilization energies (E_2) associated with electronic delocalization and their influences on the structural properties of sulfur dye-BNNT were quantitatively investigated by the NBO (Natural Bond Orbital) analysis (Glendening, *et al.*, 2004). The resonance energies (LP→ σ* or π*) are proportional to $S^2/\Delta E$ where S is the orbital overlap and ΔE is the energy differences between the donor and acceptor (LP and σ* or π*) orbitals (Dionne and St-Jacques, 1987).

COMPUTATIONAL DETAILS

The structures of (5, 5) armchair BNNT (B30N30H20) nanotube and sulfur dye molecules was optimized at the B3LYP/6-31G* level of theory by using Gaussian quantum chemical package (Frisch, *et al.*, 2009). The B3LYP is commonly used functional in the study of different nanostructures method (Seminario and Politzer, 1995). The vibrational frequencies have been calculated at the same level of theory, which enable us to confirm real minima. The sulfur dye molecule has been sat in different sites to be close to the BNNT (Figs. 1, 2). The Adsorption energies (E_{Ad}) of 7-hydroxy phenothiazine 3-one dye on the BNNT are determined through the following equation (1):

$$\Delta E_{adsorption} = E(\text{sulfur dye} - \text{BNNT}) - [E(\text{sulfur dye}) + E(\text{BNNT})] \quad (1)$$

Where E(sulfur dye-BNNT) is the total energy of the BNNTs interacting with sulfur dye, E(sulfur dye) and E(BNNT) are total energies of the pure BNNT and sulfur dye respectively. NBO analysis was then per-

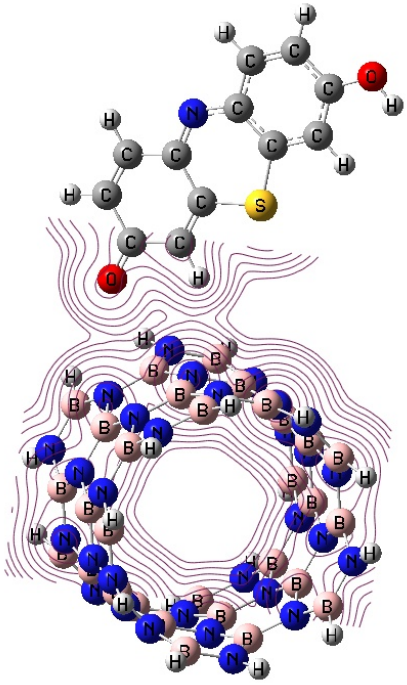

Fig. 2. Contour lines represent the range of atoms involved in electron resonance in the adsorption reaction of a dye molecule on (5, 5) BNNT

formed using the B3LYP/6-31G* level for the adsorption interaction of 7-hydroxy phenothiazine 3-one dye on the BNNT by the NBO (Natural Bond Orbital) analysis 5.G program (Glendening, *et al.*, 2004).

RESULTS AND DISCUSSION

Thermodynamic functional analyses on the fully optimized geometries were calculated. The free Gibbs energy (ΔG) and enthalpy (ΔH) values are negative and entropy (ΔS) values are positive, that suggesting thermodynamic favourability for attachment of sulfur dye on (5, 5) BNNT in both gas and solvent phases. Figure 1 shows the optimized structure of sulfur dye-BNNT, in order to obtain the most stable adsorption mode; sulfur dye set at the different positions of (5, 5) BNNT and the structural energies was calculated. The data shows that the adsorption energy value for optimized structure of sulfur dye- BNNT at 25ºC and Pressure= 1atm in gas and solvent phases is equal to -2176326.779 kcal/mol and -2176328.745 kcal/mol respectively. Chloroform was used as a solvent with the best adsorption energy value. The adsorption energies (E_{Ad}) of 7-hydroxy phenothiazine 3-one dye on the surfaces of BNNT for the optimized structure of sulfur dye-BNNT was calculated in gas phase (-3.117 kcal/mol) and solvent phase (-3.623 kcal/mol) and results showed that the physical adsorption reaction was occurred (Table 1).

Also, the HOMO/ LUMO energy gap (Eg) for sulfur dye-BNNT (Eg= 2.925 eV) was calculated (Fig. 3). Earlier studies indicated the usefulness of calculations of (NBO analysis) for the investigation structural properties and reactivity of boron nitride nanotubes (BNNTs). Herein, NBO analysis was performed at the B3LYP/6-31G* level of Density Functional Theory (DFT) on the optimized models. The results of HOMO and LUMO molecular orbitals justify the non-bonded interactions and electron transfer from sulfur dye to BNNT and inverse from BNNT to sulfur dye. So that the shape related to molecular orbitals shows the HOMO and LUMO orbitals spread on sulfur dye. The results of stabilization energies (E_2) calculations associated with electron delocalization confirm the shape of HOMO and LUMO orbitals. The bonding-antibonding orbital interactions and also the stabilization energies (E_2) associated with electron delocalization and their influences on the structural properties of sulfur dye and BNNT were quantitatively investigated by the NBO approach based on B3LYP/6-31G*

Table 1. The calculated Electronic Energy and Adsorption Energy (Ead) in (kcal/mol) for sulfur dye-BNNT in both gas and solvent phases

Sulfur dye- BNNT	Sulfur dye	BNNT	Adsorption Energy (kcal/mol)
Electronic Energy (kcal/mol) in gas phase			-3.117
-2176326.779	-668205.447	-1508118.215	
Electronic Energy (kcal/mol) in solvent phase (chloroform)			-3.623
-2176328.745	-668206.906	-1508118.215	

Table 2. Calculated resonance energies associated with electron delocalization (donor-acceptor interactions), orbital overlap (off-diagonal elements) (a.u.) and orbital energies (a.u.) for sulfur dye-BNNT

Sulfur dye -BNNT	E_2	ΔE	F_{ij}
from (BNT) to (sulfur dye)			
π N20 - B27 → σ* C92 - O95	0.05	0.84	0.006
LP (1) N26 → σ* C91 - H100	0.44	0.70	0.018
π* N20 - B27 → σ* C92 - O95	0.06	0.49	0.013
π*B24 - N32 → σ* C91 - H100	0.10	0.42	0.015
Σ	0.65		
from (sulfur dye) to (BNT)			
σ C92 - O95 → π* N20 - B27	0.14	1.12	0.012
π C92 - O95 → π* N20 - B27	0.07	0.45	0.005
π C92 - O95 → σ* B27 - N29	0.10	0.86	0.008
LP (1) O95 → σ* N20 - B27	0.57	1.15	0.023
LP (1) O95 → π* N20 - B27	2.19	0.76	0.038
LP (1) O95 → σ* B27 - N29	0.23	1.17	0.015
LP (2) O95 → σ* N20 - B27	0.37	0.73	0.015
LP (2) O95 → π* N20 - B27	3.54	0.34	0.032
LP (2) O95 → σ* N26 - B27	0.18	0.74	0.010
LP (2) O95 → σ* B27 - N29	0.24	0.76	0.012
π C88 - C91 → π* B24 - N32	0.08	0.05	0.004
π C92 - O95 → π* N20 - B27	0.07	0.08	0.004
Σ	7.78		

level of theory. The NBO analysis showed that the most stabilization energies associated with electron delocalization related to LP (1) O95 → π* N20-B27 and LP (2) O95 → π* N20-B27 for sulfur dye- BNNT compound. So the stabilization energies related to electron delocalization are explained the electronic behaviour of sulfur dye and BNNT during the adsorption reaction (Table 2). The NBO result shows the partial charges on the whole of atoms. The stability and reactivity of a molecule relates to energy bond gaps, which means the molecule with least HOMO-LUMO energy gap is more stable because of high electron delocalization between HOMO & LUMO orbitals (Fig. 3). Moreover, the decrease of the bonding orbital occupancies and the increase of the anti-bonding orbital occupancies in the BNNTs cause to electron distribution in these compounds. The energy bond gaps show that charge density transfer occurs during the reaction.

CONCLUSIONS

The adsorption of sulfur dyes on the surface of (5, 5) armchair BNNT has been studied by using DFT method. Bases on the results, the BNNTs are effective adsorbents for the dye removal from textile wastewater. Therefore, the investigation of Electronic Behaviour of sulfur dye- BNNT can provide valuable information about its structural properties and reactivity of BNNTs in interaction with sulfur dyes. The results show it is clearly possible to apply armchair BNNTs as a semiconductor, at the presence of sulfur dyes and therefore can potentially be used for sulfur dyes adsorbent.

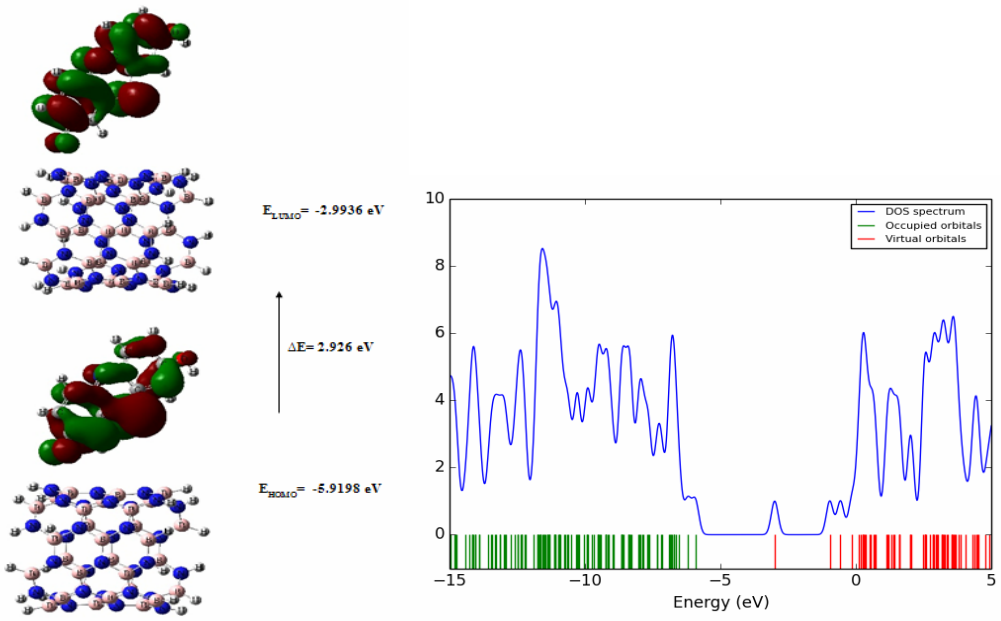

Fig. 3. LUMO and HOMO molecular orbitals of sulfur dye- BNNT and DOS spectrum

REFERENCES

Iijima, S., (1991). Helical Microtubules of Graphitic Carbon. Nature, 354: 56-58.

Rubio, A., Corkill, J.L., Cohen, M.L., (1994). Theory of graphitic boron nitride nanotubes. Physical Review B, 49: 5081-5084.

Chopra, N.G., Luyken, R.J., Cherrey, K., Crespi, V.H., Cohen, M.L., Louie, S.G., (1995). Boron nitride nanotubes. Science, 269: 966–967.

Kaur, J., Singla, P., Goe, N., (2015). Adsorption of oxazole and isoxazole on BNNT surface: A DFT study. Appl. Surf. Sci., 328: 632-640.

Azarakhshi, F., Nori-Shargh, D., Attar, H., Masnabadi, N., Yahyaei, H., Mousavi N. and Boggs, E., (2011). Conformational behaviours of 2-substituted cyclohexanones: A complete basis set, hybrid-DFT study and NBO interpretation. Mol. Simul., 37(14): 1207-1220.

Azarakhshi, F., Nori-Shargh, H., Masnabadi, N., Yahyaei, H., Mousavi N., (2012) Conformational Behaviors of 2-Substituted Cyclohexanone Oximes: An AB Initio, Hybrid Dft Study, and NBO Interpretation. Sulfur Silicon Relat. Elem., 187: 276-293.

Masnabadi, N., Taghva Manesh, A., Azarakhshi, F., (2013). Ab Initio Calculations of the Conformational Preferences of 1,3-Oxathiane S-Oxide and its Analogs Containing S and SE Atoms Evidence for Stereoelectronic Interactions Associated with the Anomeric Effects. Sulfur Silicon Relat. Elem., 188: 1053-1063.

Politzer, P., Lane, P., Murray, J.S., Concha, M.C., (2005). Comparative analysis of surface electrostatic potentials of carbon, boron/nitrogen and carbon/boron/nitrogen model nanotubes, J. Mol. Mod. 11: 1-7.

Peralta-Inga, Z., Lane, P., Murray, J.S., Boyd, S., Grice, M.E., O'Connor, C.J., Politzer, P., (2003). Characterization of surface electrostatic potentials of some (5,5) and (n,1) car-bon and boron/nitrogen model nanotubes, Nano Lett., 3: 21-28.

Peyghan, A.A., Noei, M., Yourdkhani, S., (2013). Al-doped graphene-like BN nanosheet as a sensor for para-nitrophenol: DFT study. Superlattices Microstruct. 59: 115–122.

Beheshtian, J., Peyghan, A.A., Tabar, M.B., Bagheri, Z., (2013). DFT study on the functionalization of BN nanotubes with sulfamide. Appl. Surf. Sci., 266: 182–187.

Baei, M.T., Payghan, A.A., Bagheri, Z., (2013). Covalent functionalization of AlN nanotubes with acetylene. Physica E, 47: 147–151.

Farmanzadeh, D. & Ghazanfary, S., (2014). Interaction of vitamins A, B1, C, B3 and D with zigzag and armchair boron nitride nanotubes: a DFT study. C. R. Chim., 17: 985–993.

Peyghan, A.A., Soltani, A., Pahlevani, A.A., Kanani, Y., Khajeh, S., (2013). A first-principles study of the adsorption behaviour of CO on Al- and Ga-doped single-walled BN nanotubes. Appl. Surf. Sci., 270: 25–32.

Soltania, A., Ahmadianb, N., Amirazamic, A., Masoodia, A., Lemeskic, E.T., Moradi, A.V., (2012). Theoretical investigation of OCN-adsorption onto boron nitride nano-tubes. Appl. Surf. Sci., 261: 262–267.

Glendening, E.D., Badenhoop, J.K., Reed, A.E., Carpenter, J.E., Bohmann, J.A., Morales, C.M., Weinhold, F., (2004). Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, NBO Version 5.G.

Dionne P. & St-Jacques, M., (1987), Mechanism of the gauche conformational effect in 3-halogenated 1,5-benzodioxepins. J. Am. Chem. Soc., 109: 2616-2632.

Frisch, M.J., Truks, G.W., Schlegel, H.B., Scuseria, G.E. , Robb, M.A., Cheeseman, J.R., Scalmani, G., Barone, V., Mennucci, B., Petersson, G.A., Nakatsuji, H., Caricato, M., Li, X., Hratchian, H.P., Izmaylov, A.F., Bloino, J., Zheng, G., Sonnenberg, J.L., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Montgomery, J.A., Jr., Peralta, J.E., Ogliaro, F., Bearpark, M., Heyd, J.J., Brothers, E., Kudin, K.N., Staroverov, V.N., Keith, T., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A., Burant, J.C., Iyengar, S.S., Tomasi, J., Cossi, M., Rega, N., Millam, J.M., Klene, M., Knox, J.E., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi,

R., Pomelli, C., Ochterski, J.W., R.L., Martin, K. Morokuma, V.G. Zakrzewski,G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B.Foresman, J.V. Ortiz, J. Cioslowski, and D.J. Fox, Gaussian, Inc., Revision D.01,Wallingford CT, 2009.

Seminario, J.M. & Politzer, P., (Eds(., (1995). Modern Density Function Theory, a Tool for Chemistry, 53. Elsevier, Amsterdam.

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