Computational and Theoretical Chemistry 1115 (2017) 323–329

Contents lists available at ScienceDirect

Computational and Theoretical Chemistry

journal homepage: www.elsevier.com/locate/comptc

The interaction of propargylamine-based sulfonamide with pristine, Al and Si doped boron nitride nanotubes: A theoretical study

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ARTICLE INFO

Article history:
Received 23 June 2017
Received in revised form 12 July 2017
Accepted 13 July 2017
Available online 14 July 2017

Keywords:
Sensor
Boron nitride (BN) nanotube
Sulfonamide-based drugs
Density functional theory
Adsorption
Electronic properties

ABSTRACT

Interactions of a bioactive propargylamine-based sulfonamide with the pristine, Al, and Si doped boron nitride nanotubes (BNNT) were studied using density functional theory calculations. The relative reactivity of the studied nanotubes toward the sulfonamide-based compound was as: Al-doped ≫ Si-doped > pristine BNNTs. It was found that there is a weak interaction between the sulfonamide and the pristine BNNT with adsorption energy of about −3.1 kcal/mol; therefore for this complex any change in the electronic properties is not expected. The sulfonamide adsorbed preferably on the Al and Si dopants from an oxygen atom of —SO_2 group with adsorption energies of about −28.8 and −14.9 kcal/mol, respectively. Despite the highest reactivity of the Al-doped BNNT, its electronic properties were not sensitive to the sulfonamide. The results showed that after adsorption of the sulfonamide on the Si-doped BNNT, the electrical conductivity of BNNT significantly increases. Therefore, the Si-doped BNNT can be a potential candidate for detection of sulfonamide-based drugs. It was predicted that this sensor benefits a short recovery time of about 72 ms.

1. Introduction

Sulfonamide-based drugs are synthesized in large quantities, and largely used in medical treatment [1–5]. Sulfonamide residues and metabolites which are found in agricultural run-off and civic waste water, have a great potential to enter groundwater or surface water [6]. Today the removal of sulfonamides by current water treatment technologies is incomplete [7]. Thus, selective detection and decontamination of sulfonamides and their derivatives in waste are of great interest. Recently, Bukhardt has used carbon nanotubes (CNTs) as an effective adsorbent for detection and removal of two sulfonamide derivatives from aqueous solution [7]. The CNTs have a great potential for different applications, including adsorption and removal of organic pollutants from water supplies [8–11]. The CNTs tend to adsorb various hydrophobic organic compounds from waste because of its high surface hydrophobicity and large surface area.

In some cases, chirality and tubular diameter are shown on restrictions for CNTs applications. Numerous investigations have been focused on these nanotubes which their electronic properties are independent of chirality and diameter. Nanotubes consisting groups III and V elements are introduced as potential replacement of CNTs. The popular example is boron nitride nanotubes (BNNTs) which were computationally modeled and proposed in 1994 [12,13] and then, were synthesized. Several theoretical and experimental works have been devoted to different structures and electronic properties of BNNTs [14–18]. These nanotubes are known as polar compounds because of the partial negative and positive charges of nitrogen and boron atoms, respectively. This polarity cause more reactivity of the BNNTs toward different molecules compared to the CNTs. Also, BNNTs profit from high thermal conductivity, superb resistance against oxidation, and heat resistance which make them one of the most adapted materials for using in high-temperature, oxidative, hazardous environment [19,20].

Previously, it has been indicated that BNNTs can be used as adsorbents for removal and base of sensors detection of different toxic gas molecules [21–24]. In this work, we study the adsorption a propargylamine-based sulfonamide molecule [25] on BNNT and its Al and Si doped forms using density function theory (DFT) method. Also, capability of BNNT and its Al and Si doped structures as sensors for detection of the sulfonamide molecules is investigated.

2. Computational details

All calculations were performed by the B3LYP functional with an empirical dispersion term (B3LYP-D) using 6-31G* basis set as

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http://dx.doi.org/10.1016/j.comptc.2017.07.009
2210-271X/

executed in the GAMESS program [26]. The self-consistent field (SCF) convergence criterion was set at 10^{-8}. The maximum displacement, that is, the maximum structural change of one coordinate as well as the average change over all structural parameters thresholds are set at 1.8×10^{-4} and 1.2×10^{-4}, respectively. Also, for the optimization, the maximum remaining force on an atom in the system as well as the average root mean square (RMS) force on all atoms thresholds are set at about 4.5×10^{-4} and 3.0×10^{-4}, respectively. GaussSum code was applied to draw density of states (DOS) plots [27]. The adsorption energy (E_{ad}) of sulfonamide-based molecule on the BNNT was calculated using the following Eq. (1):

$$E_{ad} = E\,(\text{sulfonamide/Tube}) - E\,(\text{Tube}) - E\,(\text{sulfonamide}) + E_{BSSE} \quad (1)$$

where E (sulfonamide/Tube) is the total electronic energy of sulfonamide adsorbed on the pristine or Al, and Si doped BNNT surface and E (Tube) and E (sulfonamide) are the total electronic energies of the BNNT and a sulfonamide molecule, respectively. The E_{BSSE} is the basis set superposition error (BSSE) energy corrected for the all interaction energies, using counterpoise method [28].

3. Results and discussion

3.1. Pristine BNNT

A *zigzag* BNNT was modeled which is consists of 54 B, and 54 N atoms as shown in Fig. 1. The length and diameter of the optimized pristine BNNT were calculated to be about 20.4 and 4.8 Å, respectively. Two kinds of B—N bonds can be recognized: one in parallel with the tube axis with the bond length of 1.46 Å, and another in diagonal to the tube axis with the bond length of 1.48 Å. The results are in good agreement with those reported previously [29]. The natural bond orbitals (NBO) charge analysis shows a charge transfer of about 0.32 *e* from the B atom to its adjacent N atoms through the sidewall, demonstrating partially ionic character of the B-N bonds. The energies of HOMO and LUMO levels of the pristine BNNT are about −6.33 and −2.34 eV, respectively i.e. an E_g of 3.99 eV.

The synthesized sulfonamide molecule has three nucleophile oxygen atoms including —OCH_3 (**1**), —SO_2 (**2**), and —COC— (**3**) (Fig. 1). These oxygen atoms are more accessible compared to the N atoms with the least steric effect for attack to the B atoms of the BNNT. However, the sulfonamide adsorption by its all O heads on the B atoms was considered with any constrain.

The results of structure optimization show that the sulfonamide weakly interacts with the BNNT surface. The most stable structure is shown in Fig. 2. The compound escapes from the tube surface upon the optimization process. The calculated adsorption energy for the most stable structure is about −3.1 kcal/mol. The results of the NBO charge analysis show a charge transfer of about 0.05 *e* from the compound to the BNNT.

Our main goal is investigation of the sensitivity of the HOMO-LUMO gap (E_g) of the BNNT to the bioactive sulfonamide-based compound. It has been frequently shown that the E_g is connected to the electrical conductivity (σ) based on the following equation, and can be used as an appropriate index for a sensor response to a chemical [30].

$$\sigma = AT^{3/2} \exp\left(-\frac{E_g}{2kT}\right) \quad (2)$$

where *k* is the Boltzmann's constant, and *A* (electrons/m^3 $K^{3/2}$) is a constant. It has been reported that there is a worthy agreement between the results of this approach, and those obtained experimentally [30–32]. As it is indicated in Table 1, the electronic

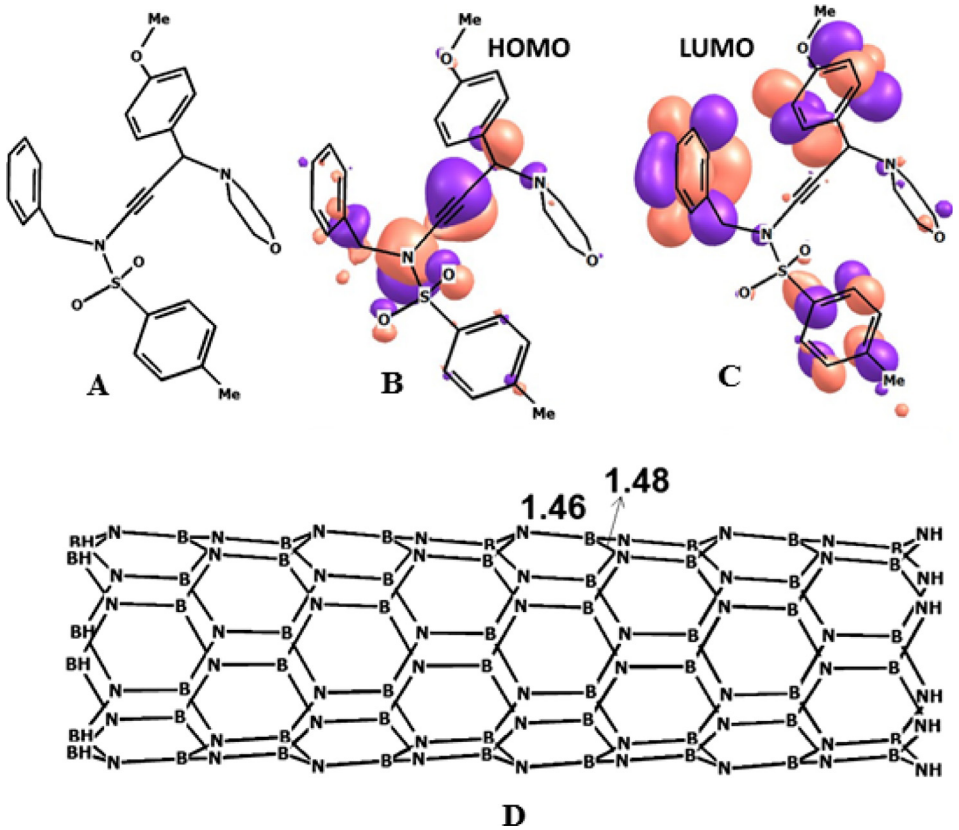

Fig. 1. The structure of sulfonamide (A) and BNNT (D), as well as the HOMO (B) and LUMO (C) orbitals of the sulfonamide molecule. The distances are in Å.