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Adsorption of Celecoxib on $B_{12}N_{12}$ fullerene: Spectroscopic and DFT/TD-DFT study

Nafiseh Abdolahi [1], Mehrdad Aghaei [1], Alireza Soltani *, Zivar Azmoodeh, Hanzaleh Balakheyli, Fatemeh Heidari

Golestan Rheumatology Research Center, Golestan University of Medical Science, Gorgan, Iran

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ABSTRACT

In this study, we evaluated the effect of the Celecoxib (CXB) adsorption on the electronic and optical properties of $B_{12}N_{12}$ fullerene by using density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations with the M06-2X functional and the 6-311+G** basis set. The calculated adsorption energies of CXB with the $B_{12}N_{12}$ fullerene was evaluated at $T = 298.15$ K in the vacuum and solvent (water) environments with the M06-2X functional. UV absorption and IR spectra were calculated and studied in order to identify the most important changes happening as a consequence of interactions between CXB and $B_{12}N_{12}$ fullerene. The results revealed that the adsorption of the CXB molecule from its NH_2 head on the $B_{12}N_{12}$ is more favorable than those of the SO_2 and NH groups in the gas and solvent environments. It is anticipated that the applied $B_{12}N_{12}$ fullerene could be suitable as a biomedical carrier for the delivery of CXB drug.

1. Introduction

In recent years, $B_{12}N_{12}$ fullerene has been introduced a suitable for biomedical and biosensor applications because of their unique chemical, physical, and surface features [1, 2]. The $B_{12}N_{12}$ fullerene is one of the known stable sorts of small III–V fullerenes, a structure built from squares and hexagons, with the network of boron nitrogen bonds being energetically more significant than those built from pentagons and hexagons [3–5]. In comparison with the carbon materials, the BN materials have been shown to possess better biocompatibility and lower cytotoxicity [6–11]. In biomaterial areas, the BNNTs are very valuable because of their biological applications, including cell targeting [12, 13], drug delivery [14], sensing [15], etc. Especially, applications of the BNNTs and other BN materials for the biological studies are still unknown. The BN fullerenes ($B_{12}N_{12}$) are one of the most concerned nanomaterials based on the recent reports, with unique electrical, mechanical and surface properties for biomedical application.

Celecoxib or 4-[5-(4-Methylphenyl)-3-(trifluoromethyl) pyrazol-1-yl] benzene sulfonamide is a COX-2 selective nonsteroidal anti-inflammatory drug (NSAID) and it is presently endorsed by the Food and Drug Administration (FDA) to treat the pain and inflammation of osteoarthritis, and rheumatoid arthritis [16, 17]. To the best of our knowledge, the effects of nonsteroidal anti-inflammatory drug celecoxib loaded to $B_{12}N_{12}$ fullerene can improve the dispersion and solubility of this drug in water with a stable interaction. For example, Vessally and co-authors have shown that the aspirin-functionalized $B_{12}N_{12}$ and $B_{11}AlN_{12}$ fullerenes have strong binding energies in a gas environment in comparison with the protic (water) or aprotic (benzene) environments [18]. Weng and co-authors experimentally reported BN nanotubes are biocompatible and can effectively load anticancer drug doxorubicin [19]. Recently, we performed a DFT study on the covalent interaction of the $B_{12}N_{12}$ fullerene with 5-aminolevulinic acid in the gaseous and aqueous environments [20]. Gou and co-workers performed DFT calculations to investigate the noncovalent functionalization of the BN nanotubes with perylene derivative molecules [21]. Xie et al. experimentally found that the BN nanotubes can be functionalized with amino-based systems. Regarding the noncovalent functionalizations of the BN nanotubes by aromatic structures, polymers, and surfactants, π–π stacking interactions have attracted rising considerations because of their potential applications in the preparation of the novel biosensors, and as biofunctional systems, nanovectors for cell therapy, and in drug and gene delivery systems [22]. In a theoretical study, we represented that the $B_{12}N_{12}$ can be used as a drug delivery carrier for both the 5-fluorouracil (5-FU) drug and its tautomeric forms which results demonstrated that the drug molecule covalently bond from its nitrogen head to the surface of $B_{12}N_{12}$ fullerene, whereas the other forms indicate weak interactions due to noncovalent bonds between two species [23]. Herein, we are reporting on the adsorption of CXB from the N and O-sites of drug molecule on the surface of $B_{12}N_{12}$ fullerene in terms of energy, geometry, binding site, electronic properties, frontier molecular orbital, molecular electrostatic potential plot, spin density plot, and Mulliken charges analysis. Simulated IR and UV–visible spectra of the $B_{12}N_{12}$ and CXB-$B_{12}N_{12}$ systems (DFT level) were calculated and compared with the experimental

* Corresponding author.
E-mail address: alireza.soltani@goums.ac.ir (A. Soltani).
[1] Co-first authors: N.A. and M.A. contributed equally to this research.

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data. We hope the results indicated could provide better condition for the usage of BN fullerenes as drug vehicles.

2. Computational Methods

The optimized geometries of the $B_{12}N_{12}$ fullerene, CXB and their adsorbed complexes with different orientations have been fully relaxed and then studied by the means of hybrid density M06-2X functional and 6-311+G** basis set [24]. The hybrid M06-2X functional indicates a higher percentage of HF (Hartree-Fock) exchange (54%) and is suitable for applications in many nanoscale molecular systems. Additionally, this hybrid density M06-2X functional has been previously demonstrated to have a good reliability in computing molecular binding energies of aspirin and amphetamine upon the $B_{12}N_{12}$ fullerene [25–27]. Solvent effects are taken into account by using the PCM (polarizable continuum model) with water as a solvent that having a dielectric constant of 78.4 and helps to understand the properties of the $B_{12}N_{12}$ loaded with CXB and provide in depth knowledge on the effective mediation of therapeutics by fullerenes within the body [28]. In addition, molecular electrostatic potential (MEP), frontier molecular orbital (FMO), partial density of states (PDOS), and Mulliken population analysis (MPA) have also been performed to evaluate other important parameters of the studied interaction systems. All the calculations have been carried out by the DFT formalism implemented in Gaussian 09 quantum chemistry software package [29]. Basis set superposition error (BSSE) mostly originated due to the incompleteness of basis set in the calculations of week intermolecular interactions which has also been resolved in the present study by estimating the BSSE energy using counter poise correction method. The M06-2X functional and the 6-311+G** standard basis set have been used for the calculations of this work. Moreover, time-dependent density functional theory (TD-DFT) has also been performed by incorporating the M06-2X method with 6-311+G** standard basis set. All the calculations have been performed at $T = 298.15$ K. In addition, the M06-2X functional has also been discussed to obtain high precision in thermodynamic parameters and adsorption energy values. The binding energy (E_b) of CXB upon the pure BN fullerene is represented by:

$$E_b = E_{Fullerene-CXB} - (E_{Fullerene} + E_{CXB}) + E_{BSSE} \quad (1)$$

where $E_{Fullerene}$ is the total energy of the pure $B_{12}N_{12}$ fullerene. $E_{Fullerene-CXB}$ is the total energy of CXB adsorbed over the pure $B_{12}N_{12}$ and E_{CXB} represents the total energy of an isolated CXB molecule.

3. Results and Discussion

3.1. Geometric Parameters of CXB and the $B_{12}N_{12}$ Fullerene

The numbering of different atoms in CXB molecule and the $B_{12}N_{12}$ fullerene is displayed in Fig. 1. The relaxed structural parameters of CXB and the $B_{12}N_{12}$ fullerene are computed by the means of M06-2X functional with 6-311+G** basis set. The lengths of C_2-S_1, S_1-O_{25}, S_1-N_{24}, and N_8-N_{23} bonds for the CXB molecule are calculated to be 1.783, 1.468, 1.704, and 1.424 Å, respectively and our calculations show good agreement with the experimental and theoretical data [30,31]. The angles of O_{25}-S_1-O_{26}, C_2-S_1-N_{24}, C_5-N_8-N_{23}, N_8-C_9-C_{10}, and F_{22}-C_{19}-F_{21} bonds for the CXB molecule are 122.1, 103.5, 117.5, 125.5, and 108.2°, respectively. Vijayakumar et al. have shown that the bond angles of C4-N11-C15, C14-C13-C16, and N11-C15-C20 in the CXB molecule are 129.64, 127.97, and 124.78° by B3LYP/6-311G** level of theory [31]. The bond angles of C—N—C (110.7°), C—C—C (109.6°) and N—C—C (110.5°) in piperidine have been determined by electron diffraction technique [32]. The geometry of the $B_{12}N_{12}$ fullerene is built of six four-membered rings with the symmetry of T_h. There are two non-equivalent B—N bonds: B—N bond in the four-membered ring has a length of 1.483 Å, while the B—N bond between the four-membered rings has a length of 1.437 Å, calculated at the M06-2X method, which is similar to those obtained previously by other methods [33–36].

In this section, we evaluate the adsorption of CXB molecule on the outer surface of the $B_{12}N_{12}$ fullerene in three various orientations. Our calculations result represents that the CXB molecule most prefer strong junction through nitrogen in NH_2 group of the molecule on the B atom of the fullerene in comparison with -SO_2 and -NH groups in both gas and solvent (water) phases. When CXB molecule was attached to the $B_{12}N_{12}$ fullerene, and the length of B_8-N_{15} bond was raised from 1.483 Å to 1.557 (**X**), 1.566 (**Y**), and 1.581 Å (**Z**), which is in agreement with the theoretical value of 1.480 Å [37]. The large E_b values in the states **X** (−0.95 eV), **Y** (−1.31 eV), and **Z** (−1.03 eV) leads to growing dipole moment (**X**: 7.80 Debye, **Y**: 7.56 Debye, and **Z**: 10.89 Debye) in the system (see Table 1), suggesting that the interaction of $B_{12}N_{12}$ fullerene and CXB molecule (see states **Y** and **Z**) was relatively strong in the nature (covalent interaction). In comparison with our results, the adsorption energy of 5-aminolevulinic acid drug from its NH_2 head on the $B_{12}N_{12}$ fullerene is calculated to be −1.34 (B3LYP), −1.39 (PBE), and −1.42 eV (B3PW91), which is a result of the covalent interaction [20]. The charge transfer between CXB and the $B_{12}N_{12}$ fullerene was further investigated by calculating the MPA parameter, as it was found just 0.194 (**X**), 0.287 (**Y**), and 0.268 (**Z**) electrons have been transferred from the $B_{12}N_{12}$ fullerene to drug molecule, which was coincident with the strong interaction. The state **Y** was significantly more stable than other adsorption states such as **X** and **Z**. These results explain that a significant hybridization happens because of a strong covalent interaction between the drug molecule and the $B_{12}N_{12}$ fullerene. In order to study the thermodynamic parameters of the CXB adsorption on the $B_{12}N_{12}$ fullerene, the alterations of free Energies (ΔG_{298}) and enthalpies (ΔH_{298}) of the adsorption states at 298.14 K and 1 atm are calculated from the frequency calculations. It is found that the values of ΔG_{298} and ΔH_{298} for the states **Y** are −15.39 and −26.62 kcal/mol, while these values for the state **Z** are found to be −8.93 and −22.62 kcal/mol, respectively. This result reveals that the $B_{12}N_{12}$ has a strong interaction with the CXB drug in the state **Y** in comparison with the state **Z** and showed the adsorption process is exothermic and spontaneous at room temperature. Rad and Ayub reported the chemisorption of guanine from its carbonyl head on $Al_{12}N_{12}$ (−2.15 eV), $Al_{12}P_{12}$ (−1.64 eV), $B_{12}N_{12}$ (−1.33 eV), $B_{12}P_{12}$ (−0.97 eV) fullerenes, while adsorption of guanine with $B_{12}N_{12}$ and $B_{12}P_{12}$ fullerenes indicate higher

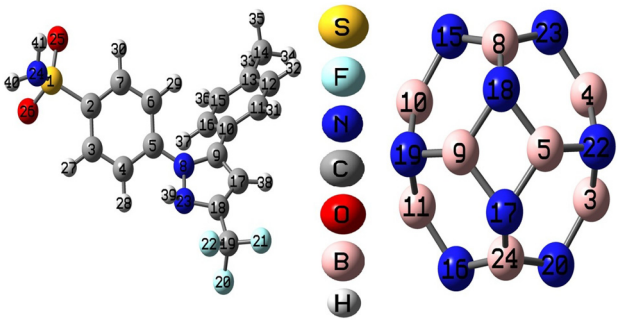

Fig. 1. Relaxed molecular structures of celecoxib and $B_{12}N_{12}$ fullerene.

Table 1
Calculated E_H (eV), E_L (eV), E_{HLG} (eV), and E_F (eV) for *CXB* adsorbed on the surface of $B_{12}N_{12}$ fullerene.

Property	E_b (eV)	E_H (eV)	E_L (eV)	E_{HLG} (eV)	ΔE_{HLG} (%)	E_F (eV)	DM (Debye)
CXB	–	−5.27	−0.51	4.76	–	−2.89	3.49
$B_{12}N_{12}$	–	−8.44	−1.24	7.20	–	−4.84	0.0
Model X	−0.95	−6.61	−1.24	5.37	25.42	−3.93	7.80
Model Y	−1.31	−5.31	−1.41	3.90	45.83	−3.36	7.56
Model Z	−1.037	−5.57	−1.13	4.44	38.33	−3.35	10.89