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DENSITY FUNCTIONAL THEORY INVESTIGATION OF DOUBLE SILICON DECORATED FULLERENES AND SINGLE WALLED CARBON NANOTUBES FOR THE DETECTION AND ADSORPTION OF IBUPROFEN

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ABSTRACT

A widely used and prescribed drug Ibuprofen (IBP) is known its anti-inflammatory, and antipyretic effects. Fullerenes and carbon nanotubes appear as the novel elements of drug delivery and sensor application particularly when they are doped with some impurity atoms. In this work double silicon decoration of fullerene C_{60} and single walled carbon nanotube (SWCNT) using with M06-2X and B3LYP functionals were examined to see the possible adsorption and sensor properties of the examined systems. HOMO─LUMO gap energies and natural bond orbital analyses (NBO) were also investigated in the scope of this work.

Keywords: Ibuprofen, Fullerene, Carbon nanotube, DFT,

1. INTRODUCTION

Fullerenes and carbon nanotubes are widely incorporated in sensor applications since they have very remarkable physical and chemical properties [1-3]. Due to their versatile physical and chemical properties they were included in the search for electrochemical bio-optical sensor applications [4, 5]. Dealing with fullerene and carbon nanotube molecular systems bring about the problem of solubility which can be considered as a main obstacle for the applications of these systems in sensor and drug delivery applications. It has been shown that the solubility problem can be overcome by substituting of hetero atoms [6].

Ibuprofen (IBP) is a very famous and widely prescribed drug known its anti-inflammatory, analgesic and antipyretic effects [7]. Further, Density Functional Theory (DFT) is a well-known and widely applied theoretical approach for the determination of structural and spectroscopic properties of many different types of molecules and molecular systems [8-12]. Therefore, especially starting with huge efforts requiring experimental applications, beforehand evaluation of molecular systems based on the theoretical approaches are very useful. In this work double silicon decorated fullerene C_{60} and single walled carbon nanotubes (SWCNT) were examined taking the advantage of density functional theory (DFT). Possible sensor applications and adsorption properties of double silicon decorated systems were investigated and each result obtained in the frame of this work was presented briefly.

2. COMPUTATIONAL METHODS

Geometric optimizations to a certain minimal energy configurations were carried out with M06-2X functional and 6-31G(d) basis set. The choice of M06-2X functional is based on the fact that it produces acceptable results for adsorption energies [13]. In the optimization procedure, first C_{60}, IBP and SWCNT were optimized. Using optimized structures two carbon atoms on the surfaces of C_{60} and SWCNT were

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replaced by two silicon atoms. Then, the resultant structures were re-optimized again. For each step vibrational frequency calculations were performed as well to see if any imaginary frequencies obtained at the end of the calculations. If any imaginary frequencies were seen at the end of the calculations by applying small iterations on the examined structures, the processes were repeated again. It is indeed a time consuming procedure but it is required to reach the true minima on the potential energy surface.

Based on the study conducted by Hadad et al. the active site of IBP was taken into account as carbonyl edge [14]. In order to create the molecular structures GaussView program was used [15]. Since the functional M06-2X produces overestimated gap energy results, the highest occupied and the lowest unoccupied molecular orbitals (HOMO-LUMO) energy difference, chemical hardness (η), electrophilicity index(ω), Wiberg bond index (WBI) and Fuzzy bond order (FBO) calculations were carried out with B3LYP/6-31G(d) level of theory. Multiwfn program was used to reach WBI and FBO parameters to examine the bond characteristics [16]. Gaussian program was used for the optimizations and the frequency calculations of all the structures investigated in this work [17].

3. RESULTS AND DISCUSSIONS

For the examination of electronic sensitivity of double silicon doped C_{60} and SWCNT to the examined IBP drug molecule, the widely accepted correlation between the gap energy (E_g) and the electronic conductivity (σ) was taken into account as following [18]:

$$\sigma \; \alpha \exp(-Eg/2kT)$$

The given equation implies that there is a direct correlation between σ and E_g values. Therefore, it seems possible to manipulate the conductivity of a given system by adjusting the gap energy values. The optimized energy of the Si_2C_{58}…IBP system (Fig. 1) after the basis set superposition error (BSSE) correction was found as -30.42 kcal/mol. This result implies that Si_2C_{58}…IBP system has a strong adsorption energy. The Si….O (C=O) distance was calculated as 1.86 Å for the present system (Fig. 1). E_g energy was calculated as 1.738 eV for Si_2C_{58}…IBP system and percent change from Si_2C_{58} to Si_2C_{58}…IBP was found as 6.26 %. Chemical hardness and electrophilic character of Si_2C_{58} system were reduced from 0.927 & 12.078 eV to 0.869 & 7.898 eV, respectively, upon interaction with IBP. WBI and FBO parameters for Si….C=O and Si….OH were calculated as 0.615 & 0.910 and 0.011 & 0.022, respectively. This fact indicates that the interaction between the cage Si_2C_{58} and IBP drug molecule mainly occurs at the carbonyl oxygen of IBP.

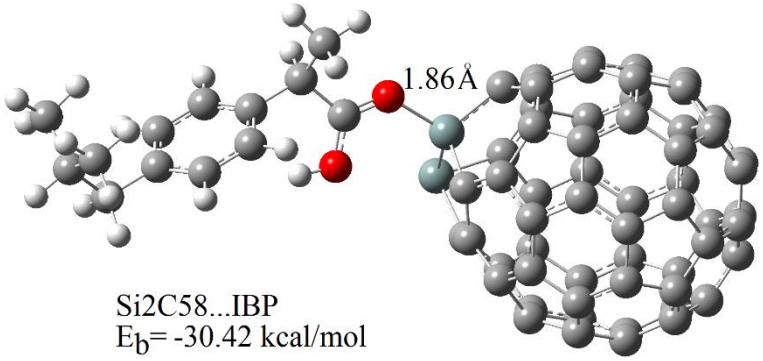

Figure 1. Optimized structure of Si_2C_{58}…IBP with M06-2X/6-31G(d).

Optimized energy for Si_2@SWCNT...IBP was calculated as -30.08 kcal/mol (Fig. 2). This value is slightly smaller than Si_2C_{58}…IBP system in magnitude. The Si….O (C=O) distance was found as 1.91 Å for Si_2@SWCNT...IBP system. E_g energy increased from 1.328 eV to 1.661 eV upon IBP interaction with Si_2@SWCNT. This increase in E_g energy makes the system less conductive addressing that Si_2@SWCNT is not a good choice for sensor application of IBP when compared to Si_2C_{58}. While the chemical hardness of Si_2@SWCNT system increased from 0.664 to 0.831 eV, the electrophilicity index decreased from 10.725 to 5.355 eV, respectively upon interaction with IBP. WBI and FBO parameters for Si….C=O and Si….OH connections for the Si_2@SWCNT system were found as 0.559 & 0.854 and 0.012 & 0.025, respectively. This fact again implies that the interaction between the cage Si_2@SWCNT and IBP drug molecule mainly takes place at the carbonyl oxygen of IBP as it happens for the Si_2C_{58} system.

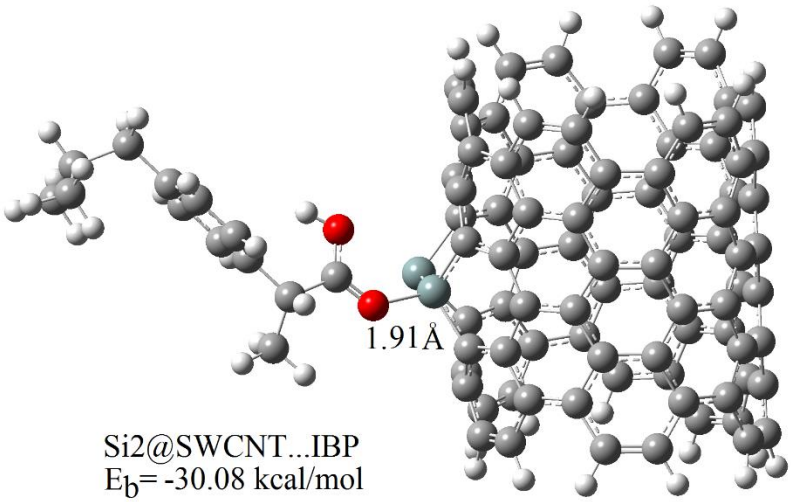

Figure 2. Optimized structure of Si_2@SWCNT…IBP with M06-2X/6-31G(d).

4. CONCLUSIONS

Based on the obtained the results, in summary, following conclusions can be drawn: the obtained binding energies for Si_2C_{58} and Si_2@SWCNT are comparable with the values of -30.42 and -30.08 kcal/mol, correspondingly. It is further seen that the interaction based on binding energy results slightly higher in magnitude with Si_2C_{58} system. Gap energy values showed different trends with Si_2C_{58} and Si_2@SWCNT systems. That is while gap energy decreased for Si_2C_{58}, it increased for Si_2@SWCNT upon interaction with IBP. This results implies that while Si_2C_{58} is a possible candidate for sensor application of IBP, Si_2@SWCNT is not. It was also observed that IBP interacts predominantly from its carbonyl edge for the related systems undertaken in this work

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