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Structural and Electronic Properties of SWGaPNT Drug Carrier

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Abstract The interaction of drug 5-fluorouracil with (4, 0) single wall Gallium-Phosphide nanotube (SWGaPNT) have been studied by using quantum mechanics. All of the calculations have been performed using a hybrid density functional method (DFT/B3LYP) and 6-31G* standard basis set. Quantum molecular descriptors and frontier orbital analysis in the drug nanotube systems were studied. (SWGaPNT) and it's applied as drug-delivery is also discussed. Results show that the SWGaPNT can act as a suitable drug delivery vehicle of 5-fluorouracil within biological systems.

Keywords Density functional theory (DFT), SWGaPNT, Drug-delivery, 5-fluorouracil (5FU)

1. Introduction

The emerging field of nanotechnology offers enormous potential to existing areas of biotechnology and medical technology innovations [1]. The major aim of nanomedicine is the design of material capable of delivery and targeting of pharmaceutical, therapeutic, and diagnostic agents [2]. Nanotechnology techniques are being used to fabricate and control nanobiomaterials structure and medical nanodevices investigating theproperties of matter at sizes below 100 nm [1]. Nanomedicine is the branch of nanotechnology and nanoscience that would allow the ability to cure disease from inside the body and at the cellular or molecular level; it is one of the most promising fields within the potential new technological advances in medicine [3]. There have been recent advances in the use of nanotechnology in detection, disease diagnosis, imaging, monitoring, therapeutics and drug-delivery systems in modern medicine [4]. Ever since the discovery of carbon nanotubes (CNTs) by Iijima [1] considerable efforts have been performed to investigate their electronic and structural properties in which the dependencies on tubular diameter and chirality have been recognized [5].

The physical and chemical properties of nanostructures such as nanotubes, nanowires, and Nanoclusters can be tuned by Varying their sizes, geometries, and chemical compositions. The knowledge of these variations plays important role while downscaling the size of Nanodevices [6].

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Many investigations centered on non-carbon-based nanotubes, which exhibit electronic properties different from the properties of their carbon relatives. Among them, from the groups three and five of the periodic table, which are the neighbors of C, boron nitride (BN), aluminum nitride (AlN), gallium nitride (GaN), indium nitride (InN), boron phosphide (BP), aluminum phosphide (AlP), gallium phosphide (GaP), and indium phosphide (InP) [7]. It's had stabilized tubular structures [8]. These nanotubes are inorganic analogs of CNTs and display physical properties suited to a broad variety of applications, and these nanotubes behave as semiconductors in every case. Also, the nanotubes are being considered as more appropriate materials than the CNTs [7]. Gallium phosphide (GaP) is a popular semiconductor with a wide band gap of 2.26 eV, GaP nanotubes are polycrystalline with zinc blende structure [9].

5-fluorouracil molecule (5-FU) is a fluorinated pyrimidine analogue chemotherapeutic agent using as solid cancer treatment like esophagus, stomach, intestines, carcinoma [10]. It has been used as an anti-cancer drug for 40 years. The structure of fluorouracil is observed in (Figure. 1). It is anti-metabolite drug and acts in several ways, but principally as synthesis inhibitor. These days there are ways to deliver a drug in the body without side effects [2]. In this study, a theoretical study, we reported types of drug delivery system such as GaP nanotube. The structural stabilities of GaP nanotubes (GaPNTs) are examined by performing density functional theory (DFT) calculations on the representative (4, 0) zigzag models (Figure 1). The atomic geometries are allowed to relax by optimization.

2. Computational Detail

All of the calculations were carried out using a personal computer has name Lenovo G50 which has processor Intel core (TM) i7-5560u CPU 2.4 GHZ 2.4 GHZ with 8-GB RAM at 37°C. The representative zigzag model of the single-walled GaPNT is considered within this work. The diameter and length of (4, 0) SWGaPNT are about 6.95 and 9.50 Å, respectively. SWGaPNTs consisting of 32 atoms (12 Gallium atoms, 12 Phosphorus atoms, and 8 hydrogen atoms). Hydrogen atoms are used to saturate the Ga and P atoms to avoid dangling effects at the two ends by keeping three covalent bonds for each Ga and P atoms of nanotubes [8] (Figure 1b). A nanotube is formed using a nanotube modeler package [11]. The selected drug (5-fluorouracil) were made using Gauss View. The structures (complexes of the single-walled nanotube with fluorouracil) are individually optimized employing DFT/ B3LYP exchange-functional and 6-31G* standard basis set by Gauss View and Gaussian 09 program package [12] (Figure 1).

The bond length (Å), total energy, band gap and HOMO/LUMO were investigated in the composites. The Binding energy (E_B) of SWGaPNT and complexes are obtained from equation (1) [13].

$$E_B = [(N\,E_{Ga} + M\,E_P) - E_{GaPNT}\,]/(N+M) \quad (1)$$

Where, E_{GaPNT} stands for the total energy considered for GaP single wall nanotube (SWNT), E_{Ga}, E_P energy of Ga and P atoms respectively. N and M are the number of gallium and phosphorous atoms present in the tube respectively.

The quantum molecular descriptors [14] for nanotubes were determined as follows:

Chemical potential (μ) which shows escape tendency of an electron from equilibrium is defined as follows:

$$\mu = -\,I + A/2 \quad (2)$$

$$\chi = -\mu \quad (3)$$

Where χ is Electronegativity.

The global hardness (η) shows the resistance of one chemical species against the change in its electronic structure (Equation (4)), and the softness is given as in equation (5):

$$\eta = I - A/2 \quad (4)$$

$$S = 1/2\eta \quad (5)$$

Electrophilicity index (Ω) was defined as follows:

$$\Omega = \mu^2/2\eta \quad (6)$$

The amount of charge transfer between the drug and the SWGaPNT, as calculated using the ΔN method:

$$\Delta N = \mu_B - \mu_A/2(\eta_A + \eta_B) \quad (7)$$

Where I (-EHOMO) is the ionization potential and EA (-ELUMO) the electron affinity of the molecule. μ_A, μ_B and η_A, η_B are the chemical potential and the chemical hardness of the systems A and B. A positive value of ΔN indicates that charge flows from nanotube to the drug and the drug act as an electron acceptor, while a negative value of ΔN indicates that charge flows from the drug to nanotube and the drug acts as an electron donor [14].

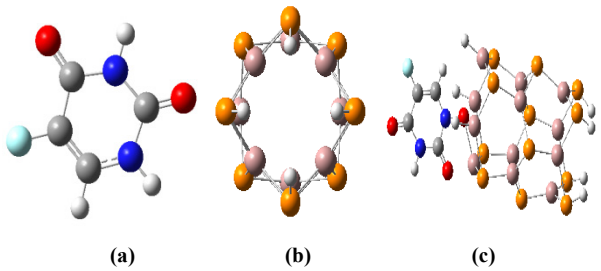


Figure 1. The structures of optimized molecular by B3LYP/6-31G* method **(a)** Fluorouracil, **(b)** Nanotube (4, 0), and **(c)** Complex

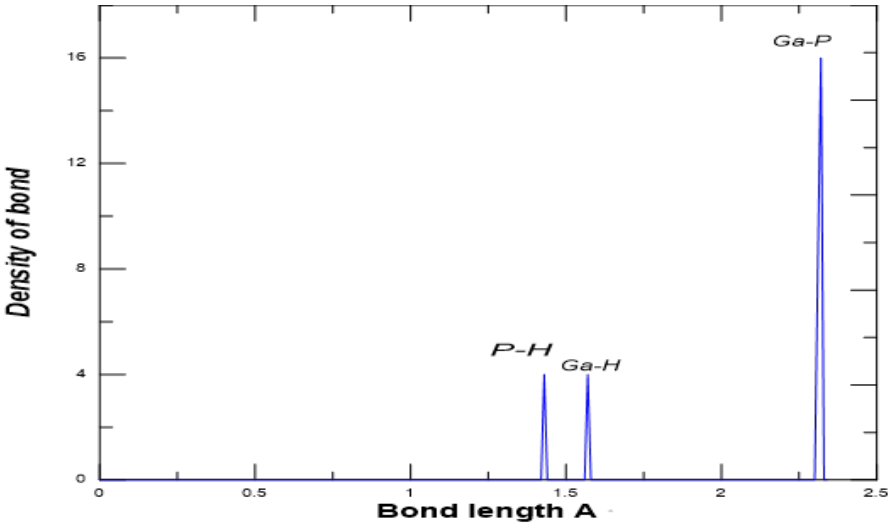
3. Results and Discussion

First of all, we discussed the structural and electronic properties of the zigzag (4, 0) SWGaP nanotube and SWGaPNT coupled to 5-fluorouracil (5-FU) molecule (see Figure 1). The optimized structure parameters of GaP nanotube and composite calculated by DFT-B3LYP levels with the 6-31G* basis.

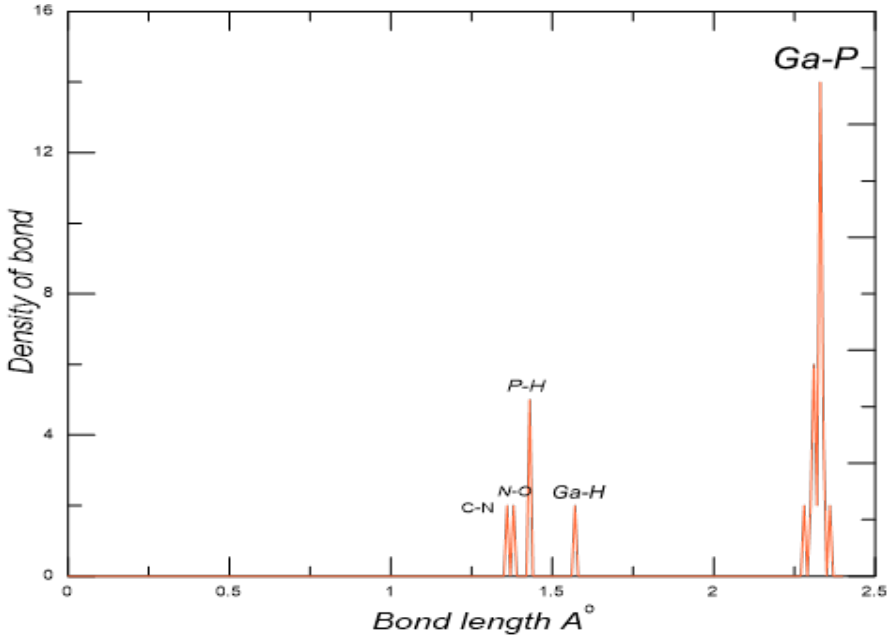
From Figure (2.a) the optimized structure of the pristine SWGaPNT has the Ga-P bond length 2.30 Å, the presented results in this work are in agreement approximately with previous studies provided by Anurag Srivastava et al [14]. It can be noticed that the bond length at about 1.42 Å and 1.56 Å for (P-H) and (Ga-H) bonds respectively, the presented results in this work are in agreement with previous studies provided by Maryam Mirzaei and Mahmoud Mirzae [5]. As seen in Figure (2b) that the averaged values for Ga–P bond lengths are 2.31 Å which is slightly longer than those in the pristine model for nanotube. The values for Ga–H and P–H bonds do not show notable changes. With an additional bond density equal to 1.36 Å and 1.39 Å for (C-N) and (N-O) bonds. While the tetrahedral angle of Ga-O-N is 108.28° which is represent couple angle of the drug with the GaP -nanotube.

Table 1. Structural and electronic properties of the GaP nanotube and complex configuration with the (5-FU) molecule

Property	5-FU	GaP Nanotube	Complex
E_{Total}/Mev	-0.013987	-0.739514	-0.755518
E_B/ev	6.453	4.367	5.130
E_{HOMO}/ev	-6.785	-6.445	-6.401
E_{LUMO}/ev	-1.379	-4.113	-3.840
Eg/ev	5.406	2.331	2.561
I/ev	6.785	6.445	6.401
EA/ev	1.379	4.113	3.840
η/ev	2.703	1.165	1.280
μ/ev	-4.082	-5.279	-5.121
χ/ ev	4.082	5.279	5.121
S/ev-1	0.184	0.428	0.390
Ω/ev	3.082	11.955	10.240
ΔN	-	-	-0.154



(a)



(b)

Figure 2. **(a)** Distribution of bond lengths (R) in Ga-P nanotube structure using B3LYP/6-31G of an image with acceptable resolution. **(b)** Influence of bond length on density of bond length (R) in Ga-P nanotube Structure using B3LYP/6-31G of an image with acceptable resolution

The quantum molecular descriptors for the (5-FU), (4, 0) SWGaPNT and (4, 0) GaPNT-5FU are summarized in Table 1. It is obvious the final total energy of the product is the collection of total energy of all small atoms which build the product nanotube. The nanotube with lowest total energy and highest binding energy has been considered as the most stable. It is well known that the frontier molecular orbitals (FMO), (the highest occupied molecular orbital (HOMO)) and (the lowest unoccupied molecular orbital (LUMO)). The values of HOMO and LUMO energy levels are negative, that shows neither adding nor removing electrons from GaP nanotube is energetically favorable. This reflects high stability and inertness of the GaP nanotube structure which is useful for drug carriers.

The three dimensions plots of the frontier orbitals HOMO, LUMO for GaPNT are shown in Figure (3). It can be seen that the majority of the molecular orbital density in the HOMO is highly localized at the one end of tube and a small amount is distributed on the other end of tube, the HOMO is distributed on the terminals phosphorus atoms, which is basically due to unequal charge distribution along the atoms.

Whereas the LUMO is highly localized inside one end of the tube and over the same the tube end that distributed on the gallium atoms and a small amount is distributed on the phosphorus atoms as shown in figure 3: (a) and (b). The energy of HOMO is often associated with the electron-donating ability of a molecule; high values of HOMO are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy and empty molecular orbital. Therefore, the energy of

LUMO indicates the ability of the molecule to accept electrons [15].

After conjugation of (5-FU) with GaPNT, the LUMO energy of molecules is lower than that of the original (5-FU) molecule, with decreasing energy gap. Thus electrons can be easily excited from the ground state. Figure (3.c and d), indicates the HOMO and LUMO of the complex (5-FU with GaPNT).In the 5-FU/GaPNT system, the HOMO plot indicates that the electron density is distributed throughout the P atoms of GaPNT with an energy value almost -6.401 ev while the LUMO plot indicates that the electron density is distributed toward the (5-FU) molecule with an energy value of -3.840 eV (see Table 1).

Global hardness (η) is an important property to measure the molecular stability and reactivity; a high global hardness signifies high stability of the system [16]. When the global hardness of drug has a low value this shows that drug exhibiting the highest reactivity. Also, the highest electron affinity, which means that it, can adopt electrons readily. In general, a small hardness means a high chemical activity and a low chemical stability. Results show that, hardness of the (4, 0) GaPNT-5FU (complex) are highest than the pristine (4, 0) GaPNT, therefore, the chemical activity for whole complex is decreased and the chemical stability relatively stable.

According to the data in table 1, η, I, and Eg related to the (5-FU) drug are higher than complex, showing the stability of the (5-FU) decreases in the complex and its reactivity increases. Also, in confirmation of the previous issue, it is observed that μ of the (5-FU) becomes more negative in the complex. Increased electrophilicity Ω due to increase in charge transfer from (5-FU) to (4, 0) GaPNT.

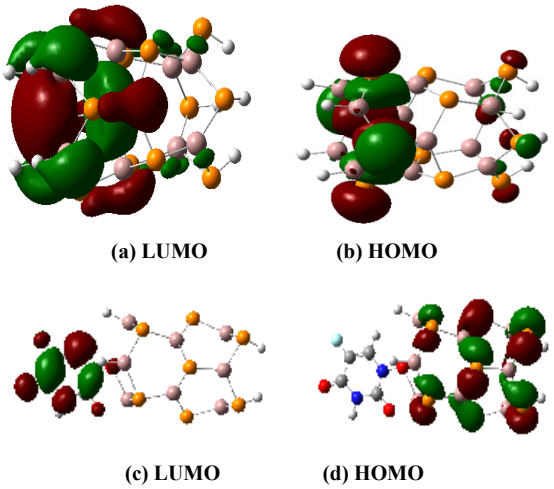


Figure 3. HOMO and LUMO level of. **(a)** LUMO of GaPNT. **(b)** HOMO of GaPNT and **(c)** LUMO of Complex, and **(d)** HOMO of complex

An important application of electronegativity is the prediction of polar nature of the resulting structure after conjugation with SWGaPNT and this is convinced with a lower hardness, a higher softness and much higher electrophilicity index I.P is small value; this small ionization may make the SWGaPNT useful for high energy particle detectors (cancer cells) or as catalysis for infections. Electronegativity value reflects the enable of SWGaPNT to be more reactive toward electron to accept and exchange reactions. The decreasing of hardness is the main feature as a sign for the band gap that goes to be rather soft and lowering the resistance of species to lose an electron. The amount of charge transfer between the (5-FU) and the (4, 0) SWGaPNT (ΔN) method, is given in table 1. A positive value of ΔN indicates that the (5-FU) act as an electron acceptor, while a negative value of ΔN indicates that the (5-FU) act as an electron donor. From the results ΔN value is negative, indicating that (4, 0) SWGaPNT act as electron acceptors.

4. Conclusions

Using density functional theory, the effects of the coupled of (5-FU) with single wall Gallium Phosphide nanotube (SWGaPNT) have been studied in details. The total energies for complex cause decreasing in energy and more stable structure. A small energy gap means small excitation energies of manifold of the excited states. The capability of a nanotube to accept precisely one electron from a donor is measured by its electron affinity (E_A). The strength of an accepter molecule is measured by its electron affinity (E_A) which the energy released when adding one electron to LUMO. An accepter must have a high E_A. FMO and structural analyses show that the low energy level of LUMO. Decrease in global hardness, energy gap, and ionization potential and also, increase in electron affinity and electrophilicity of the complexes shows a charge transfer from the (5-FU) molecule to the nanotube model.

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