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Fullerene (C_{20}) as a potential sensor for thermal and electrochemical detection of amitriptyline: A DFT study

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ABSTRACT

In this research, amitriptyline adsorption on the surface of fullerene C_{20} was studied by density functional theory computations. The calculated adsorption energies showed amitriptyline interaction with C_{20} is experimentally possible. The negative values of Gibbs free energy changes and great values of thermodynamic constants indicated the adsorption process is spontaneous. The negative values of adsorption enthalpy changes and the increase of specific heat capacity in the adsorption process revealed the interaction of amitriptyline with fullerene is exothermic and this nanostructure is an admissible sensing material for thermal detection of amitriptyline. The density of states (DOS) plots showed the bandgap of fullerene reduced from -32.13% from 7.145 (eV) to 4.849 (eV) when amitriptyline adsorbed on its surface. Therefore, C_{20} can be used as a sensor for electrochemical detection of amitriptyline. The influence of the temperature on the amitriptyline interaction with fullerene was also investigated and the results showed the adsorption process is more favorable in the lower temperatures.

1. Introduction

Amitriptyline (AMP, Figure 1a), is a tricyclic antidepressant medicine that is prescribed for the treatment of depression, eating disorders, neuropathic pains, migraine prevention, nocturnal enuresis, fibromyalgia, insomnia, irritable bowel syndrome, anxiety disorders and attention deficit hyperactivity disorder [1-3]. AMP is one of the best-selling antidepressants that induces its therapeutic effects by inhibiting the uptake of norepinephrine and serotonin [4-6]. However, in high doses, AMP can be highly toxic and its adverse effects are agitation, drowsiness, coma, seizures and tachycardia. In this respect, AMP determination is very important. To date, various analytical techniques such as high-performance liquid chromatography (HPLC), gas chromatography (GC), fluorimetry, capillary electrophoresis and UV-Visible spectrophotometry have been reported for the quantitation of AMP [7-9].

However, these methods are too expensive, time-consuming and tedious. Besides, large amounts of organic solvents are used in the mentioned methods. But, electrochemical and thermal sensors are prominent alternatives for the refereed analytical techniques because these types of sensors are rapid, simple, economic, portable, selective and sensitive devices that can determine the amount of the analyte with excellent accuracy and repeatability [10-14]. However, the first step in the development of a new electrochemical and thermal sensor is to find a recognition element that interacts with the analyte selectively and this interaction should lead to a considerable change in the electrochemical and thermal conductivity of the utilized recognition element which is used as a signal for determination of the analyte concentration [15-17].

On the other hand, fullerene (C_{20}, Figure 1b) is the smallest nanomaterial with a dodecahedral cage structure

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[18]. The structure of this fullerene is highly curved and it is composed of pentagonal rings. C_{20} has unique traits that make it an eminent sensing material like high conductance, great surface area/ volume ratio and excellent reactivity [19]. In this respect, the goal of this study is to evaluate the sensing performance of C_{20} for thermal and electrochemical detection of AMP by density functional theory simulations.

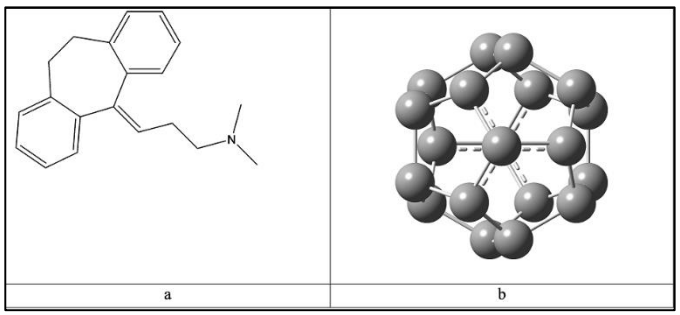

Figure 1. the chemical structure of AMP (a) and C_{20} (b)

2. Results and Discussion

In order to find the most stable configuration, the adsorption process was investigated at two different positions. As can be seen from the presented optimized structures of AMP-fullerene complexes at Figure 2, in A-Conformer, the nanostructure is inserted near the central three adjacent rings of AMP and in the B-Conformer, fullerene is placed near the amine group of AMP. The calculated total electronic energies in table 1, showed that A-Conformer is more energetically stable than B-Conformer. Besides, the computed adsorption energies indicated AMP interaction with the adsorbent is experimentally feasible and the adsorption process is more favorable at A-conformer. In order to obtain more information about the adsorption mechanism, the NBO computations were also carried out and the results are given at Table 1. As it is clear, at A-conformer the interaction nature is chemisorption because a monovalent 2 containing electron bond is formed between the medicine molecule and the adsorbent with $SP^{2.97}$ hybridization and -0.323 eV bond energy. But, in the case of B-Conformer the AMP interaction with fullerene is physisorption because no chemical bond was observed between the adsorbent and the adsorbate in this configuration [9-11].

The maximum (ν_{max}) and lowest vibrational frequencies (ν_{min}) of structures were also calculated by IR computations. As can be seen from Table 1, no negative frequency was observed for the studied structures. Therefore, all of the investigated structures are in a true local minimum [12].

The dipole moments of the structures were also computed. As the provided data at table 1 reveals clearly when AMP adsorbs on the surface of fullerene the dipole moment increases from 1.340 to 3.590 and 5.350 at A and B conformers respectively. Therefore, the solubility and bioavailability of AMP enhance significantly when it is adsorbed on the surface of fullerene [13].

Table 1. The structural and NBO parameters of AMP, C_{20} and their complexes

		Bond length (Å)	**Bond order**	**Occupancy**	**Hybridization**	**Bond energy (a.u)**
AMP	---	---	---	---	---	---
C_{20}	---	---	---	---	---	---
A-Conformer	C-C	1.780	1.000	1.989	$SP^{2.97}$	-0.323
B-Conformer	---	---	---	---	---	---
	Total electronic energy (a.u)	**Adsorption energy (kJ/mol)**	**ZPE (kJ/mol)**	**ν_{min} (cm^{-1})**	**ν_{max} (cm^{-1})**	**Dipole Moment (Debye)**
AMP	-815.233	---	1176.660	15.223	3753.799	1.340
C_{20}	-747.196	---	325.260	261.392	1690.640	0.000
A-Conformer	-1562.534	-274.948	1546.900	13.564	3753.717	3.590
B-Conformer	-1562.478	-127.920	1527.430	1.172	3753.944	5.350

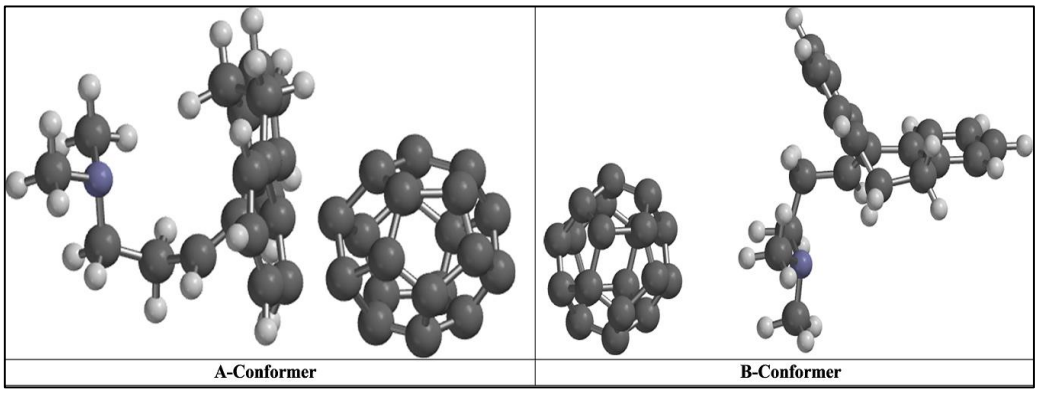

Figure 2. Optimized structures of AMP-C_{20} complexes

The thermodynamic parameters of AMP adsorption process were also calculated and the results are presented in Figure 3. As can be seen, the adsorption Gibbs free energy (ΔG_{ad}) is negative at both conformers which indicates the interaction process is spontaneous. The values thermodynamic equilibrium constants (K_{th}) are great for A-conformer that indicates the interaction is irreversible and non-equilibrium at this configuration but in the case of B-Conformer K_{th} values are near to zero which implies the adsorption process is reversible in this condition. The impact of temperature on both parameters was also checked out and the results demonstrates the interaction process is more favorable at lower temperatures [14].

The negative values of adsorption entropy changes (Δs_{ad}) showed the adsorption process is inappropriate in terms of entropy because of the aggreagtion of AMP-C_{20} complexes. The chaos has decreased when AMP adosrbs on the surface of fullerene [15].

The negative values of adsorption enthalpy changes (ΔH_{ad}) showed the interaction process is exothermic and the increasing of the specific heat capacity (C_V) values of fullerene indicated the thermal conductance of fullerene improved when AMP adsorbs on its surface. Hence, this nano-adsorbent is an appropriate sensing material for the construction of a novel thermal sensor for the measurment of AMP. In this type of sensors, the analyte (here AMP) takes part in a highly exothermic reaction with the recognition element (here C_{20}). Then, the changes in the temperature of the sensor microenvironment will be measured by a sensitive thermistor and it will be used as a signal for detection of the analyte [16].

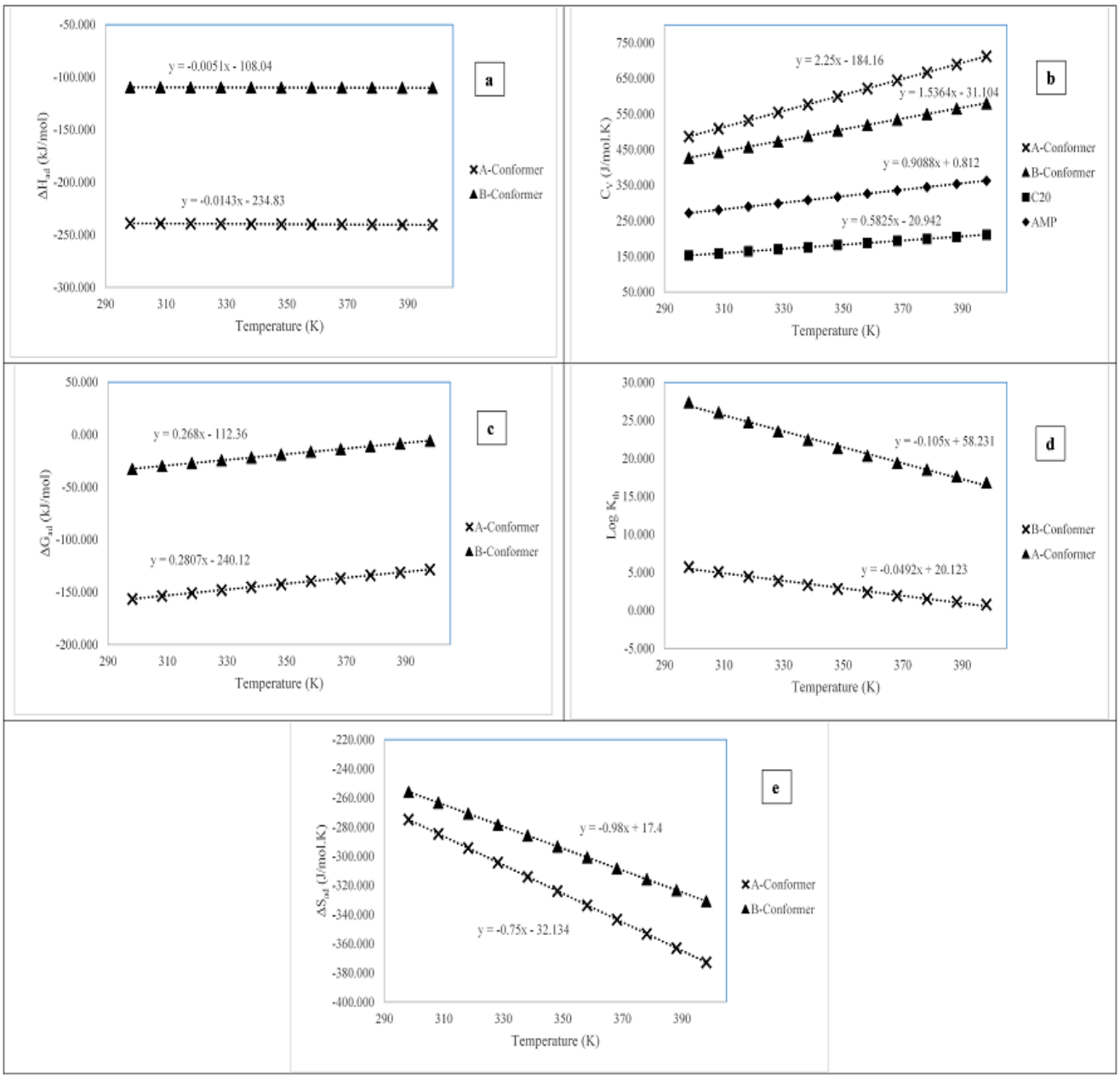

Figure 3. the values of ΔH_{ad} (a), C_V (b), ΔG_{ad} (c), the logatim of K_{th} (d) and ΔS_{ad} (e) as a function of temperature in the range of 298-398 K.

In order to evaluate the performance of fullerene as an electroactive sensing material towards AMP. The density of states (DOS) spectrums of AMP, nano-adsorbent and the complexes were also computed and the obtained results are presented in Figure 4. As can be seen, the bandgap of C_{20} is 7.145 (eV) but when AMP adsorbs on its surface, this parameter reduces sharply (-32.13% and 27.42%) to 4.849 and 5.186 (eV) at A and B conformers respectively. Bandgap has an inverse relationship with electrical conductivity. In other words, the compounds with low values of bandgap are more conductive than molecules with wide bandgaps. Therefore, it can be deduced that the electrical conductance of C_{20} enhances tangibly when AMP adsorbs on its surface and this nanostructure is a suitable sensing material for the fabrication of new electrochemical sensors for the detection of AMP [17-19].

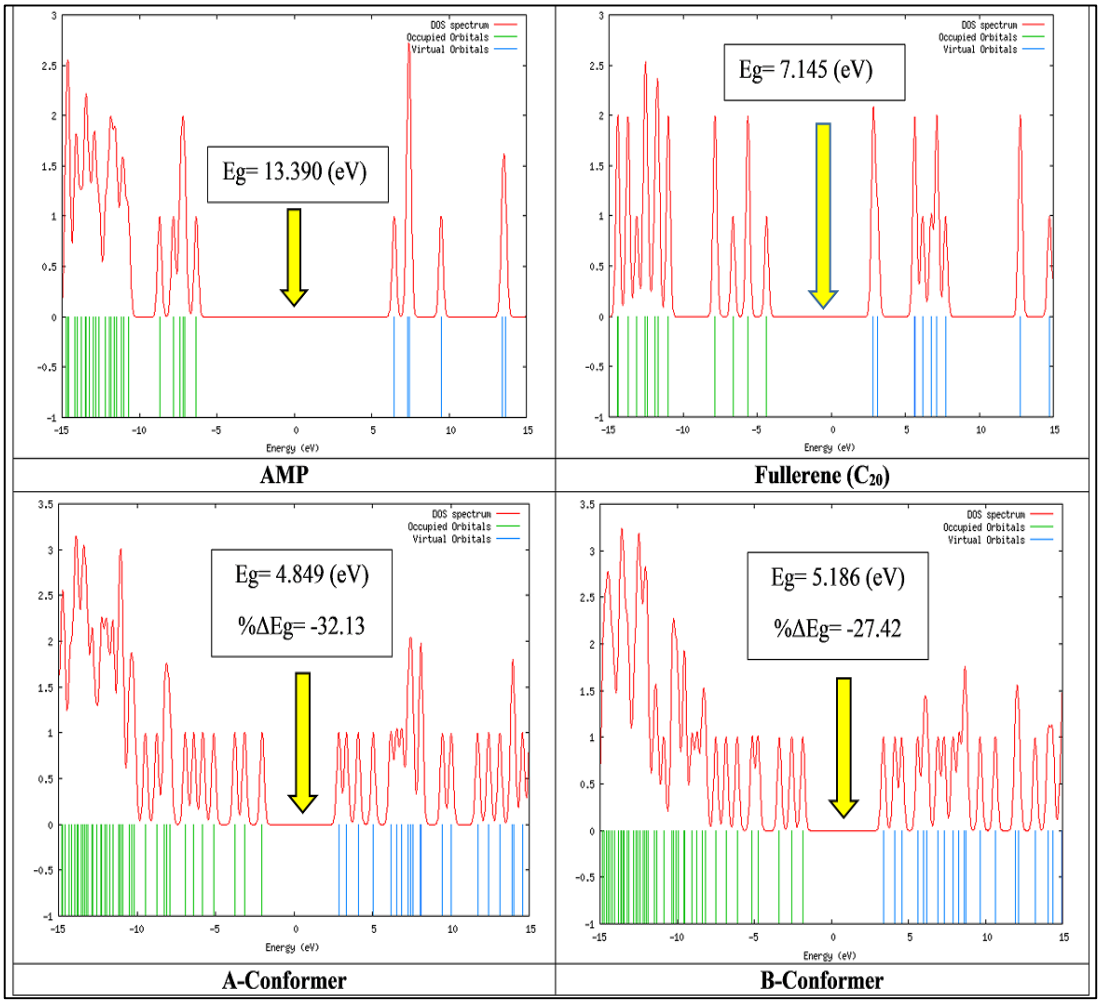

Figure 4. The DOS spectrums of AMP, C_{20} and their complexes

3. Computational Details

The structures of Fullerene, AMP and their complexes were designed by Nanotube modeler 1.3.0.3 and GuassView 6 softwares [20, 21]. At the first step, the designed structures were optimized geometrically. Then, IR, NBO and FMO computations were implemented on them. All of the computations were performed by Gaussian 16 software [22] by the density functional theory method in the B3LYP/6-31G (d) level of theory because in former studies about nanomaterials its results were in a good agreement with the experimental data. The density of states (DOS) spectrums was obtained by GuassSum 3.0 software [23]. All of the calculations were implemented in the aqueous medium and in the temperature range of 298-398 at 10˚ intervals.

The studied processes were as follows:

AMP + Fullerene ⟶ AMP-Fullerene (1)

The values of adsorption energy values (E_{ad}) and thermodynamic parameters including adsorption enthalpy changes (ΔH_{ad}), Gibbs free energy changes (ΔG_{ad}), entropy changes (ΔS_{ad}), and thermodynamic equilibrium constants (K_{th}) were calculated by Equations 2-6 respectively.

$$E_{ad} = \left(E_{(\text{AMP-Fullerene})} - \left(E_{(\text{AMP})} + E_{(\text{Fullerene})} + E_{(\text{BSSE})}\right)\right) \quad (2)$$

$$\Delta H_{ad} = \left(H_{(\text{AMP-Fullerene})} - \left(H_{(\text{AMP})} + H_{(\text{Fullerene})}\right)\right) \quad (3)$$

$$\Delta G_{ad} = \left(G_{(\text{AMP-Fullerene})} - \left(G_{(\text{AMP})} + G_{(\text{Fullerene})}\right)\right) \quad (4)$$

$$\Delta S_{ad} = \left(S_{(\text{AMP-Fullerene})} - \left(S_{(\text{AMP})} + S_{(\text{Fullerene})}\right)\right) \quad (5)$$

$$K_{th} = \exp\left(-\frac{\Delta G_{ad}}{RT}\right) \quad (6)$$

In the referred equations, E is the total electronic energy of each structure, E_{BSSE} denotes the basis set superposition correction energy, H stands for enthalpy of the evaluated materials. The G denotes Gibbs free energy, S is the thermal correction of entropy, R is the ideal gas constants, T denotes the temperature [9-11].

Frontier molecular orbital parameters including bandgap (E_g), and $\%\Delta E_g$ were calculated by equations 7-8 [32].

$$Eg = E_{LUMO} - E_{HOMO} \quad (7)$$

$$\%\Delta Eg = \left(\frac{Eg2-Eg1}{Eg1}\right) \times 100 \quad (8)$$

E_{LUMO} and E_{HOMO} in equation 6 are the energy of the lowest unoccupied molecular orbital and the energy of the highest occupied molecular orbital respectively. The E_{g1} and E_{g2} in Equation 7, are the bandgap of AMP-C_{20} complex and bandgap of C_{20} respectively [12-14].

4. Conclusion

AMP is a tricyclic antidepressant that is prescribed for the treatment of depression and anxiety disorders. This medicine has serious adverse side effects in high dosages and even can be lethal in the case of overdose. Therefore, AMP determination is very important. In this research, the performance of C_{20} as a novel sensing material for the construction of new thermal and electrochemical sensors to AMP measurement was evaluated by DFT computations. The values of adsorption energy and thermodynamic parameters showed AMP interaction with fullerene is exothermic, spontaneous and experimentally possible. The decrease of bandgap and increase of specific heat capacity of fullerene in the adsorption process showed this nanostructure is a suitable sensing material for the thermal and electrochemical detection of AMP.

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