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Adsorption of proline amino acid on the surface of fullerene (C_{20}) and boron nitride cage ($B_{12}N_{12}$): A comprehensive DFT study

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Abstract

In this study, the performance of fullerene (C_{20}) and boron nitride cage ($B_{12}N_{12}$) as a sensing material for the detection of proline was evaluated by density functional theory. For this purpose, the structures of proline, C_{20}, $B_{12}N_{12}$ and the derived products from the proline adsorption on the surface of the nanostructures were geometrically optimized. Then, IR and Frontier molecular orbital calculations were performed on them. The obtained adsorption energies, enthalpy changes (ΔH_{ad}) and Gibbs free energy variations (ΔG_{ad}) demonstrate that proline adsorption on the surface of the boron nitride cage is exothermic, spontaneous and experimentally feasible. The proline interaction with C_{20} is endothermic, non-spontaneous and experimentally impossible. The effect of temperature on the adsorption process was also checked out and the results reveal that 298 K is the best temperature for the adsorption procedure. The calculated specific heat capacity values show that boron nitride cage can be utilized as a sensing material in the construction of thermal biosensors for proline determination. The calculated molecular orbital parameters indicate that $B_{12}N_{12}$ could be used as a neutral ion carrier and also an electroactive sensing material in the development of potentiometric and conductometric biosensors. All of the calculations were implemented by density functional theory method and B3LYP/6-31G(d) basis set.

Keywords: Proline; fullerene (C_{20}); boron nitride cage ($B_{12}N_{12}$); adsorption and density functional theory.

Introduction

Proline amino acid is an important nutrition, which is essential for the construction of proteins in the entire living organism. The chemical formula of this biological compound is $C_5H_9NO_2$ (Figure 1(a)) and it has various functions in plants and animals [1]. In plants, proline acts as an osmotic regulator and can mitigate the salt and drought stress impacts substantially. But in animals and humans, this amino acid plays the role of an energy reservoir that regulates the cellular reduction potential [2]. In addition, proline has strong antioxidant

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properties and can decline the inner acidity of the cells and conserve large molecules such as DNA, RNA and proteins [3]. The next matter that shows the importance of proline is that this amino acid converts to hydroxyl proline in our body, and hydroxyl proline is one of the main ingredients of collagen. And due to the fact that sufficient amount of collagen is necessary for the health and proper functions of skin, tendons, bones, cartilages and teeth, it seems determination of proline is of a great importance in the medical and nutritional fields [4].

Several analytical methods, including high-performance liquid chromatography (HPLC), fluorescence, electrochemiluminescence and UV-Visible spectrophotometry have been designed for proline determination [5]. Nevertheless, these techniques have numerous disadvantages which make them undesirable for routine analysis [6]. As the main downsides of the mentioned methods it can be referred to needing expensive and complex instruments that are not affordable for many laboratories, sample pre-treatment procedures before the analysis step which leads to the destruction of specimen matrix and also prolonging the analysis process, requiring sophisticated operators and poor selectivity [7]. Fortunately, thermal and electrochemical biosensors are appropriate alternatives for the cited techniques because they are portable, selective, applicable in colored and opaque samples without requiring any sample preparation steps, economical, time-saving and straightforward. Owing to the fact that finding a unique sensing material which has a strong interaction with the desired analyte is the key step in designing a novel biosensor. In this sense, theoretical studies can be so helpful in estimating the interaction of the desired analyte with various sensing materials and choosing the most sensitive one to be used in the construction of new sensors [8].

Boron nitride cage ($B_{12}N_{12}$) whose structure is given in (Figure 1(b)), has outstanding features like high-temperature stability, negligible dielectric constant, great thermal conductivity, large energy gap, oxidation resistance and structural stability [9-11]. Moreover, these characteristics make it an ideal candidate for the detection of various compounds so that the adsorption of HCN, OCN^-, amphetamine and N_2O on the surface of boron nitride has been evaluated [12,13]. Besides, Fullerene (C_{20}) is the smallest member of the fullerene family with a dodecahedral cage structure (Figure 1(c)) [14]. This nanostructure consists of only pentagonal rings and has extreme curvature. C_{20} has a high surface/area ratio and this trait has attracted a huge attention to this molecule because of its adsorption usages [15,16]. And the adsorption of NO_2, He, Ne, Ar and Kr on the surface of C_{20} has been investigated so far [17,18]. In this regard, it was decided to investigate the proline adsorption on the surface of fullerene and boron nitride cage for the first time by density functional theory in this study.

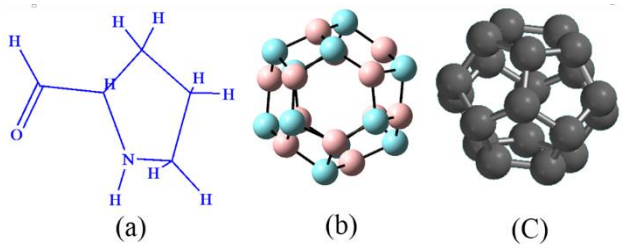

Figure 1. The structure of proline (a) The structure of boron nitride cage (b) Fullerene C_{20} cage structure (c)

Computational methods

The structures of proline, C_{20}, $B_{12}N_{12}$ and the derived products that are created from the adsorption of proline on the surface of the evaluated nano-adsorbents at two different configurations were optimized geometrically. Afterward, IR and Frontier molecular orbital calculations were implemented on them in the temperature range of 298-398 K at 10˚ intervals. All of the computations were performed in the aqueous phase and atmospheric pressure by density functional theory method and B3LYP/6-31G (d) basis set. This basis set was selected because it produced results which were in great agreement with the experimental data in our previous works [19-24]. All of the calculations were done by Spartan software. The studied reaction was as follows:

Proline + adsorbent→ proline-adsorbent (1)

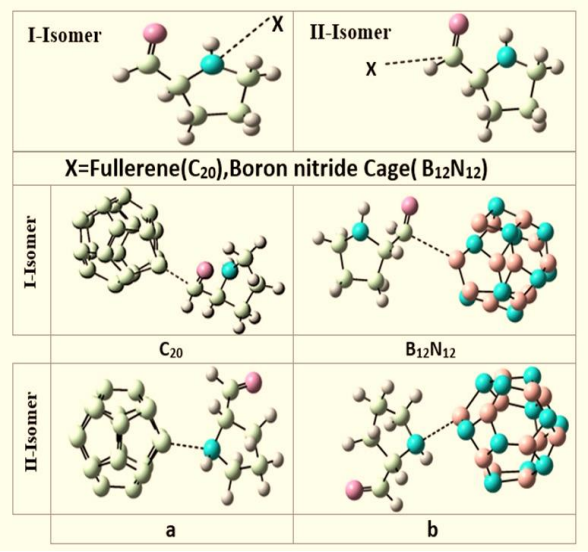

Figure 2. The structures of proline derivatives with C_{20} and $B_{12}N_{12}$ at two different configurations

Results and discussions

Adsorption energy values

In this study, proline amino acid was placed near the adsorbent from two different orientations in order to find the most stable configuration. As it is obvious from Figure 2, in one situation the carbon atom of the proline's carbonyl functional group is close to the surface of the nanostructure and the $B_{12}N_{12}$-I-Isomer and C_{20}-I-Isomer abbreviated names considered for the proline derivatives with boron nitride cage and fullerene in this position

respectively. But in the other condition, proline was inserted near the adsorbent from its nitrogen atom and the proline derived products with boron nitride cage and fullerene in this configuration were remarked by $B_{12}N_{12}$-II-Isomer and C_{20}-II-Isomer abbreviations consecutively. The adsorption energy for the investigated process was calculated by Equation 2. In this equation, E stands for the obtained total electronic energy of each material in the adsorption process which was computed in the geometrical optimization step. As it can be witnessed from Table 1, the adsorption energy values of proline- boron nitride cage derivatives are negative, whereas this parameter is positive for proline-C_{20} derived products. Therefore, the proline adsorption on the surface of $B_{12}N_{12}$ is experimentally feasible and proline adsorption on the fullerene surface is experimentally impossible. By a closer look at the table, it will be realized that proline has better and stronger interaction with boron nitride cage from its carbonyl group because the adsorption energy of $B_{12}N_{12}$-I-Isomer is more negative than the adsorption energy of $B_{12}N_{12}$-II-Isomer. The achieved bond lengths have also confirmed this result because the CO-B bond length is 1.491 (Å) which is shorter than the N-B bond length (1.773 (Å)).

$$E_{ad}=E_{\text{proline-adsorbent}} - (E_{\text{proline}} + E_{\text{adsorbent}}) \quad (2)$$

Table 1. The values of adsorption energy and the bond lengths between proline and the adsorbents

Derived complexes	The total electronic energy of proline (KJ/mol)	The total electronic energy of adsorbents (KJ/mol)	The total electronic energy of the derived products (KJ/mol)	E_{ad} (KJ/mol)	CO-C (Å)	CO-B (Å)	N-C (Å)	N-B (Å)
$B_{12}N_{12}$-I- Isomer	-839736.488	-2320716.537	-3160569.629	-116.604		1.491		
$B_{12}N_{12}$-II-Isomer	-839736.488	-2320716.537	-3160516.150	-63.125				1.773
C_{20}-I-Isomer	-839736.488	-1961763.993	-2800410.244	1090.238	3.918			
C_{20}-II-Isomer	-839736.488	-1961763.993	-2801174.284	326.197			1.843	

Thermodynamic parameters

The adsorption enthalpy changes (ΔH_{ad}), and Gibbs free energy variations (ΔG_{ad}) were calculated *via* Equations 3 and 4 respectively. In Equation 3, H represents the sum of the thermal enthalpy and total energy and in the Equation 4, G stands for the sum of the thermal Gibbs free energy and total.

$$\Delta H_{ad}= H_{\text{proline-adsorbent}} - (H_{\text{proline}} + H_{\text{adsorbent}}) \quad (3)$$

$$\Delta G_{ad}= G_{\text{proline-adsorbent}} - (G_{\text{proline}} + G_{\text{adsorbent}}) \quad (4)$$

The obtained adsorption enthalpy changes and Gibbs free energy alterations are presented in Table 2. As it can be perceived from the results, the proline adsorption on the surface of the boron nitride cage is exothermic and spontaneous in all derivatives. But on the other hand, the adsorption of this amino acid on the fullerene surface is endothermic and non-spontaneous at both configurations. The effect of temperature on the thermodynamic factors was also investigated. As it is obvious from the presented data, increasing of temperature does not have a remarkable effect on the values of enthalpy changes and Gibbs free energy alterations. Hence, it seems the ambient temperature is the best one for the proline adsorption process.

Table 2. Adsorption enthalpy changes values and Gibbs free energy changes values for the proline adsorption in the temperature range of 298-398 K

ΔH_{ad} (KJ/mol)[a], ΔG_{ad} (KJ/mol)[b]				
Temperature	**$B_{12}N_{12}$-I-Isomer**	**$B_{12}N_{12}$-II-Isomer**	**C_{20}-I-Isomer**	**C_{20}-II-Isomer**
298	-856.562[a]	-809.657	1016.489	175.653
	-805.447[b]	-759.647	1092.471	226.604
308	-853.650[a]	-806.728	1016.343	176.463
	-810.994[b]	-765.159	1095.000	225.260
318	-850.646[a]	-803.758	1016.200	177.299
	-816.610[b]	-770.805	1097.569	223.896
328	-847.582[a]	-800.706	1016.061	178.139
	-822.280[b]	-776.511	1100.180	222.491
338	-844.453[a]	-797.593	1015.925	178.997
	-828.019[b]	-782.284	1102.799	221.054
348	-841.271[a]	-794.404	1015.791	179.882
	-833.837[b]	-788.151	1105.425	219.632
358	-838.006[a]	-791.151	1015.659	180.795
	-839.742[b]	-794.124	1108.054	218.232
368	-834.676[a]	-787.811	1015.527	181.717
	-845.750[b]	-800.180	1110.538	216.794
378	-831.271[a]	-784.387	1015.396	182.655
	-851.851[b]	-806.218	1113.023	215.323
388	-827.783[a]	-780.878	1015.266	183.620
	-857.997[b]	-812.284	1115.510	213.845
398	-824.220[a]	-777.318	1015.135	184.629
	-864.191[b]	-818.443	1117.997	212.427

In thermal sensors, a sharp variation should be observed in the thermal conductivity of the utilized sensing material during its interaction with the desired analyte. And owing to the fact that according to Equation 6, the specific heat capacity has a direct relationship with the thermal conductance, investigating the alterations of C_V in the adsorption process can be so helpful for estimating the capability of the evaluated adsorbent as a thermal sensing material. In the Equation 5, n, $< v >$, λ, C_V and N are particles per unit, mean particle speed, mean free path, molecular specific heat capacity and Avogadro's number respectively [25]. As it can be witnessed in Table 3, the specific heat capacity of proline is 88.159 (J/mol. K). At the ambient temperature, which has a considerable discrepancy with the C_V values of fullerene and boron nitride cage. In addition, after the absorption of proline on the surface of nanostructures, this parameter has incremented significantly. Hence, the thermal conductivity has increased noticeably after the binding of proline to the evaluated nano-adsorbents. In this regard, $B_{12}N_{12}$ could be used in the thermal detection of proline because of its strong interaction with the amino acid and also the sharp carried out changes in the thermal conductivity during the adsorption procedure. The influence of temperature on this parameter was also checked out. The findings reveal that by increasing of temperature the C_V will be incremented linearly.

$$K = \frac{n<v>\lambda\, Cv}{3N} \qquad (5)$$

Table 3. The calculated specific heat capacity values for the proline adsorption in the temperature range of 298-398 K

	C_V (J/mol. K)						
Temperature	**Proline**	**C_{20}**	**$B_{12}N_{12}$**	**$B_{12}N_{12}$-I-Isomer**	**$B_{12}N_{12}$-II-Isomer**	**C_{20}-I-Isomer**	**C_{20}-II-Isomer**
298	88.159	152.495	210.052	310.638	313.327	228.201	233.679
308	90.767	158.426	216.784	320.006	322.682	237.051	242.901
318	93.431	164.361	223.392	329.293	331.961	245.897	252.144
328	96.144	170.287	229.876	338.495	341.158	254.725	261.391
338	98.901	176.193	236.236	347.609	350.268	263.521	270.625
348	101.696	182.066	242.472	356.629	359.287	272.272	279.832
358	104.524	187.897	248.586	365.551	368.209	280.966	288.998
368	107.379	193.676	254.579	374.373	377.031	289.594	298.109
378	110.254	199.397	260.451	383.089	385.747	298.144	307.154
388	113.146	205.050	266.204	391.698	394.356	306.608	316.121
398	116.048	210.631	271.840	400.194	402.852	314.978	325.002

Frontier molecular orbital analysis

In chemistry, HOMO and LUMO are the highest occupied molecular orbital and the lowest unoccupied molecular orbital consecutively. The energy difference between them is known as bandgap (HLG). HLG, which was calculated by Equation 6, has an obvious relationship with the electrical conductivity of a compound. In this regard, this parameter is an admissible standard for inspecting the performance of the evaluated nano-adsorbents in the proline determination by conductometric analytical methods. The provided data in Table 4, clearly demonstrates that boron nitride cage could be an excellent electroactive sensing material for proline detection. Because the HLG value of proline is 15.97 (eV) which has a perceptible discrepancy with the HLG value of the boron nitride cage and after the adsorption of amino acid this variable declines in 6.256 and 5.9 (eV) at $B_{12}N_{12}$-I-Isomer and $B_{12}N_{12}$-II-Isomer derivatives respectively. In other words, the electrical conductivity has ameliorated substantially by the junction of proline on the surface boron nitride cage at both configurations. And due to the fact that conductometric sensors and titrations are based on the severe variations in the conductance of a system or reaction. Therefore, it looks boron nitride cage can be used in the conductometric determination of proline.

$$HLG=E_{LUMO} - E_{HOMO} \quad (6)$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (7)$$

$$\mu = (E_{LUMO} + E_{HOMO})/2 \quad (8)$$

$$\omega = \mu^2/2\eta \quad (9)$$

$$\Delta N_{max}=- \mu/ \eta \quad (10)$$

Chemical hardness (η) was the next investigated parameter. This variable was calculated *via* Equation 7. Chemical hardness has a clear relationship with the softness of a compound. By a more precise glance at Table 4, it will be perceived that the chemical hardness of proline has

declined after its junction to the surface of the studied nanostructures at both configurations. Hence, proline derivatives with boron nitride cage and fullerene are more chemically smoother than pure proline. And given the fact that soft materials are able to vary their electron density more comfortably so, electron transmissions which are essential for the implementation of chemical reactions can be done in them more easily. In this regard, smooth compounds are more reactive than the hard ones. Therefore, the reactivity of proline has improved since its adsorption on the nano-adsorbents.

Table 4. Calculated E_H and E_L, band gap (HLG), chemical hardness (η) , electrophilicity index (ω), the maximum amount of electronic charge index (ΔN_{max}) and dipole moment for the proline adsorption process

	E_H (eV)	E_L (eV)	HLG(eV)	η(eV)	μ(eV)	ω (eV)	ΔN_{max} (eV)
Proline	-8.12	-7.85	15.97	7.98	-0.14	0	0.02
C_{20}	-4.350	2.840	7.190	3.595	-0.755	0.079	0.210
C_{20}-I-Isomer	-10.390	-3.590	6.800	3.400	-6.990	7.185	2.056
C_{20}-II-Isomer	-4.530	3.210	7.740	3.870	-0.660	0.056	0.171
$B_{12}N_{12}$	-5.760	1.240	7.000	3.500	-2.260	0.730	0.646
$B_{12}N_{12}$-I-Isomer	-5.830	0.426	6.256	3.128	-2.702	1.167	0.864
$B_{12}N_{12}$-II-Isomer	-5.340	0.560	5.900	2.950	-2.390	0.968	0.810

Electrophilicity (ω) and maximum electronic charge index (ΔN_{max}) are two parameters which demonstrate the propensity of a molecule towards electron. Equations 9 and 10 were used respectively in order to calculate ω and ΔN_{max}. When two molecules take part in a reaction, one of them acts as a nucleophile while the other one behaves as an electrophile. And a great positive value of electrophilicity and maximum transferred charge indicates the compound tends to absorb the electron. On the other hand, a low amount of ω and ΔN_{max} implies that the studied molecule has a low tendency towards electron and it tends to lose the electron. As it can be seen from the table, the electrophilicity value of proline is zero, which means it acts as a nucleophile. However, the electrophilicity of boron nitride cage is 0.730 which has a meaningful gap with the proline's one. Indeed, proline is a Lewis base and $B_{12}N_{12}$ is a Lewis acid and they can undergo complexation reaction. Therefore, the boron nitride cage can be utilized as a neutral ion carrier in the construction of the potentiometric proline selective electrode for determination of this amino acid. But it seems this matter is not applied for fullerene because its electrophilicity and the maximum transferred charge are too close to the proline's ones. The next point that can be understood is that proline derivatives with both nano-adsorbents are more electrophile than pure amino acid.

Conclusion

Proline determination is of a great importance in medical and nutritional fields. In this regard, the performance of fullerene (C_{20}) and boron nitride cage ($B_{12}N_{12}$) as a sensing material in the thermal and electrochemical biosensors was investigated by density functional theory. The obtained results exhibit that proline adsorption on the surface of the boron nitride cage is exothermic, spontaneous, non-equilibrium and experimentally feasible. However, the adsorption of proline on the fullerene surface is endothermic, non-spontaneous, equilibrium, and experimentally

impossible. The calculated band gap, electrophilicity and specific heat capacity parameters show that boron nitride cage can act as an excellent electroactive and thermal sensing material in the construction of proline potentiometric, conductometric and thermal sensors. In this regard, the experimental use of this nanostructure in the detection of proline is recommended to be evaluated by the experts of this field.

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