Understanding the Interaction of glycine amino acid with graphene: An Alternative Theoretical Approach Based on Density Functional Theory

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ABSTRACT

The present work utilizes density functional theory (DFT) calculations to investigate the interaction of glycine amino acid with graphene. Quantum chemical calculations by DFT provide detailed geometrical parameters, electronic properties and the adsorption energies for the graphene and three different amino acid configurations on the graphene. DFT calculations confirmed the energetic stability of the optimized geometries and revealed that amino acid molecule adsorbed on the graphene through weak van der Waals (vdW) interaction, which means that the adsorption is physisorption process. The results of the theoretical investigations show that the adsorption of the amino acid molecule on the graphene surface results in a decrease the chemical potential (μ). Thus, the reactivity and electrical conductivity increase upon the adsorption process.

1. Introduction

In the past decade, various types of nanostructured materials have developed and employed for in treatment techniques [1-2]. Among different nanomaterials, Graphene is one of the most important nanostructures because of having a vast surface for bi-lateral adsorption in 2 dimensions and other unique properties like electron transport, high thermal conductivity, and high mechanical strength [3]. In addition to this, the ability of graphene to pass through biological membrane has motivated considerable studies where in its interactions with different biomolecules like amino acids [4] have been analyzed.

As amino acids play a vital role in the living organisms as building blocks of proteins and enzymes; elucidation of their nature of interactions with structurally analogous but widely graphene nanosheet is the focus of the current study [5].

In this work, quantum chemical calculations were employed in order to provide insightful information about the biomolecule (glycine (Gly)) adsorption on graphene nano-sheet (GNs). Since glycine is one of the 20 most common amino acids and easily extending the system to

proteins with its crucial biological roles such as structure maintenance, cell adhesion, and tissue remodeling [6]. Density functional theory (DFT) molecular simulation, as an extremely successful approach for the description of structural and electronic properties of standard bulk materials and complex materials such as biomolecules and interaction system, has been our choice to evaluate the electronic structure of the graphene/glycine composite system.

2. Computational methods

To study the adsorption behavior of glycine amino acid molecule, graphene (GNS) consisting of 54 carbon atoms has been chosen as the model where open ends are saturated by hydrogen atoms. All structure optimizations on the graphene and different GNs/Gly complexes are performed using density functional theory at ωB97XD functional [7] along with 6–31G** basis set as implemented in the Gaussian 09 program package [8]. The frequency calculations were performed to ensure the minima structure for all geometries and revealed that they are energetically minimum in structure. The zero-point

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vibration energy (ZPVE) correction was considered in the calculations of the adsorption energy (ΔE). The molecular orbital (MO) calculations such as the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are also performed on the studied complexes. The energy gap in the energy levels of a system is defined as $E_g = E_{LUMO} - E_{HOMO}$. Physical properties such as dipole moments ($\mu°$), chemical potential (μ), chemical hardness (η) [9] and electrophilicity (ω) [10] of these compounds have been systematically explored. These descriptors are able to measure the whole response of an electronic system to a chemical perturbation [11].

Roy and co-workers [12,13] proposed modified expression of stabilization energy, as well as its different components when the interaction happens between donors and acceptors with a comparable size. The interaction of amino acid molecule and the graphene on the basis of four reactivity descriptors such as the overall stabilization energy ($\Delta E_{SE(AB)}$) the individual energy change of acceptor ($\Delta E_{A(B)}$), the individual energy change of donor ($\Delta E_{B(A)}$) and charge transfer (ΔN) have been explained. These descriptors can be calculated by the methods described in references [14-17].

3. Results and discussion

It is well known that a glycine molecule has three active sites, the amino nitrogen (N), the hydroxyl oxygen (OH) and the carbonyl oxygen (O) sites. Therefore, it is expected for glycine to interact with the GNs via these three active sites. In order to examine the adsorption of a glycine on the GNs, three possible configurations, called (A), (B) and (C), were selected for a molecule approaching the center of a hexagon of carbon atoms: (A) denotes the hydroxyl oxygen (OH), (B) the carbonyl oxygen (O) and (C) the amino nitrogen (N) active sites. The orientation schemes employed in modeling glycine adsorption are shown in Figure 1. The adsorption energy for the GNs interaction with the glycine molecule in the gas phase and water solution was calculated and the obtained results were listed in Table 1. The calculated values of adsorption energy indicate that the glycine molecule can be physically adsorbed on the surface of the GNs and in all cases; the adsorption glycine on the surface was exothermic and favorable in the studied systems in both phases. The obtained results demonstrate that the most stable structure was configuration C with the most negative interaction energy -37.63 kJ/mol. The large adsorption energy of this configuration is accordance with the shortest intermolecular interaction distance between the GNs and Gly molecule. In this configuration, the H81 atom of Gly molecule prefers to attach to C24 of the graphene by the equilibrium distances of 2.80 Å and 2.83 Å in gas phase and water solution, respectively.

The listed results in Table 1 show a considerable increase in the dipole moment ($\mu°$) value of the

examined complexes in comparison with the GNs ($\mu°$ =0.00 debye). It is worth mentioning that the polarity of GNs was increased by the adsorption of Gly molecule onto the its surface (see Table 1). The increment in the polarity of the hybrid system is a highly desirable feature for drug delivery.

In order to investigate the degree of solubility of the studied complexes in water media, the solvation energy parameter has been calculated and the obtained results are tabulated in Table 1. Negative values of the solvation energy denote that the solvation is spontaneous and it signifies the solubility of the considered systems in aqueous environment.

A

B

C
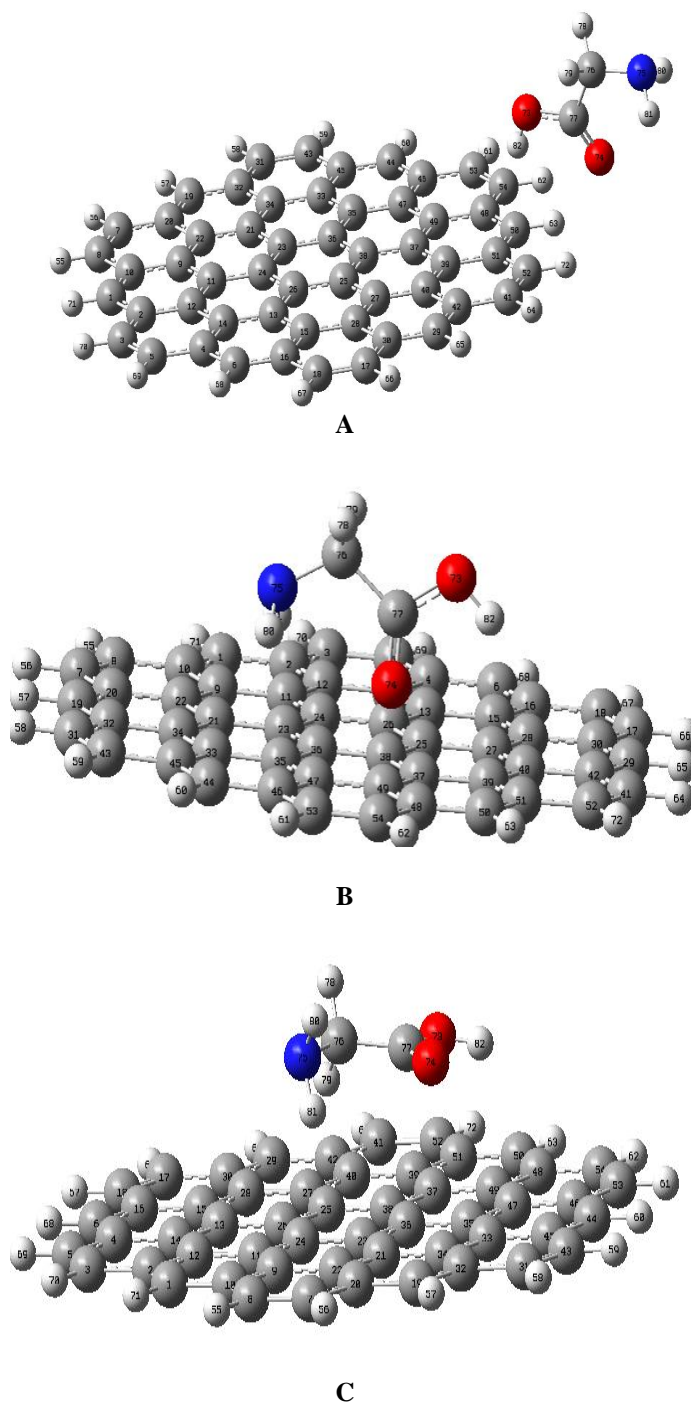
Figure 1. The possible different configurations of glycine amino acid molecule adsorption on the graphene

Table 1 Calculated adsorption (ΔE) and the solvation (ΔE_{sol}) energies (all in kJ mol^{-1}), dipole moment (μ°) (in Debye) and the interaction distances ($R_{GNs...Gly}$) (Å) at ωB97XD level in the gas phase (Values in parentheses refer to calculation in the water phase).

model	ΔE	$R_{GNs...Gly}$	μ°	ΔE_{sol}
A	-24.05 (-8.93)	C50...H82-O73 = 2.92 (C54...H82-O73 = 3.93)	1.01 (1.74)	- (-39.08)
B	-34.73 (-32.02)	C49...C77-O74 = 2.80 (C49...C77-O74 = 3.26)	1.37 (1.89)	- (-52.23)
C	-37.63 (-34.54)	C24...H81-N75 = 2.78 (C24...H81-N75 = 2.83)	2.00 (2.22)	- (-53.21)
Gly	-	-	1.31 (1.68)	- (-24.75)
GNs	-	-	0.00 (0.00)	- (-31.91)

In the present work the kinetic aspects of interaction between the GNs and the Gly molecule is examined using $\Delta E_{B(A)}$, whereas $\Delta E_{A(B)}$ and $\Delta E_{SE(AB)}$ are applied to understand the thermodynamic stability of the resultant adducts [18]. At first, we proposed that Gly molecule is donor (B) and the GNs is acceptor (A). The value of ΔN for GNs/Gly complex is positive (0.033), thus, the direction of electron flow is from the Gly molecule to GNs. The negative value of $\Delta E_{A(B)}$ (-0.004 eV) confirms that the GNs/Gly complex is more stable than the GNs and isolated amino acid molecule. Also, the positive value of $\Delta E_{B(A)}$ (0.004 eV) shows an energetically promising process i.e., the electrons have been transferred from Gly as a donor to GNs molecule as an acceptor. Moreover, the negative value of $\Delta E_{SE(AB)}$ (-0.0002 eV) shows the thermodynamic stability of the examined complexes.

Table 2 The values of the overall stabilization energy ($\Delta E_{SE(AB)}$), the individual energy change of acceptor ($\Delta E_{A(B)}$) and the individual energy change of donor ($\Delta E_{B(A)}$) (all in eV) and charge transfer (ΔN) within the reacting glycine molecule and the graphene.

	$\Delta E_{SE(AB)}$	$\Delta E_{A}(B)$	$\Delta E_{B(A)}$	ΔN
GAS	-0.0002	-0.004	0.004	0.033
PCM	-0.0004	-0.007	0.006	0.052

3.1. Electronic properties and the density of state analysis

To further probe the nature of the interaction between GNs and Gly molecule, the spatial distributions of HOMO and LUMO of the GNs, glycine and C complex were indicated in Figure 2. As it is illustrated in this figure, the HOMO of the Gly molecule is positioned on all of atoms, while LUMO is not located on N-H group; but, they cover the other parts of the amino acid molecule. Moreover, close inspection of of Figure 2 shows that the frontier orbital plots of the pristine GNs are distributed in the uniform states.

Also, it is found that in the most stable complex, HOMO is distributed on the Gly molecule, and LUMO is localized on the surface of GNs, displaying the electrons have been transferred from Gly molecule to GNs. The partial charge transfer between the HOMO of one unit and the LUMO of another is one of the most important terms for the interaction between two components [19].

The energy values of HOMO and LUMO of GNs and Gly molecule were used to calculate the $|HOMO_{(GNs)} - LUMO_{(Gly)}|$ and $|HOMO_{(Gly)} - LUMO_{(GNs)}|$ values. The value of $|HOMO_{(Gly)} - LUMO_{(GNs)}|$ (8.25 eV) is low in magnitude than the $|HOMO_{(GNs)} - LUMO_{(Gly)}|$ (8.82 eV) value which confirms that the electron density has been transferred from the HOMO of Gly to the LUMO of GNs that this result is in good agreement with the previous findings of this work.

Compounds	HOMO	LUMO
GNs		
Gly		
C		
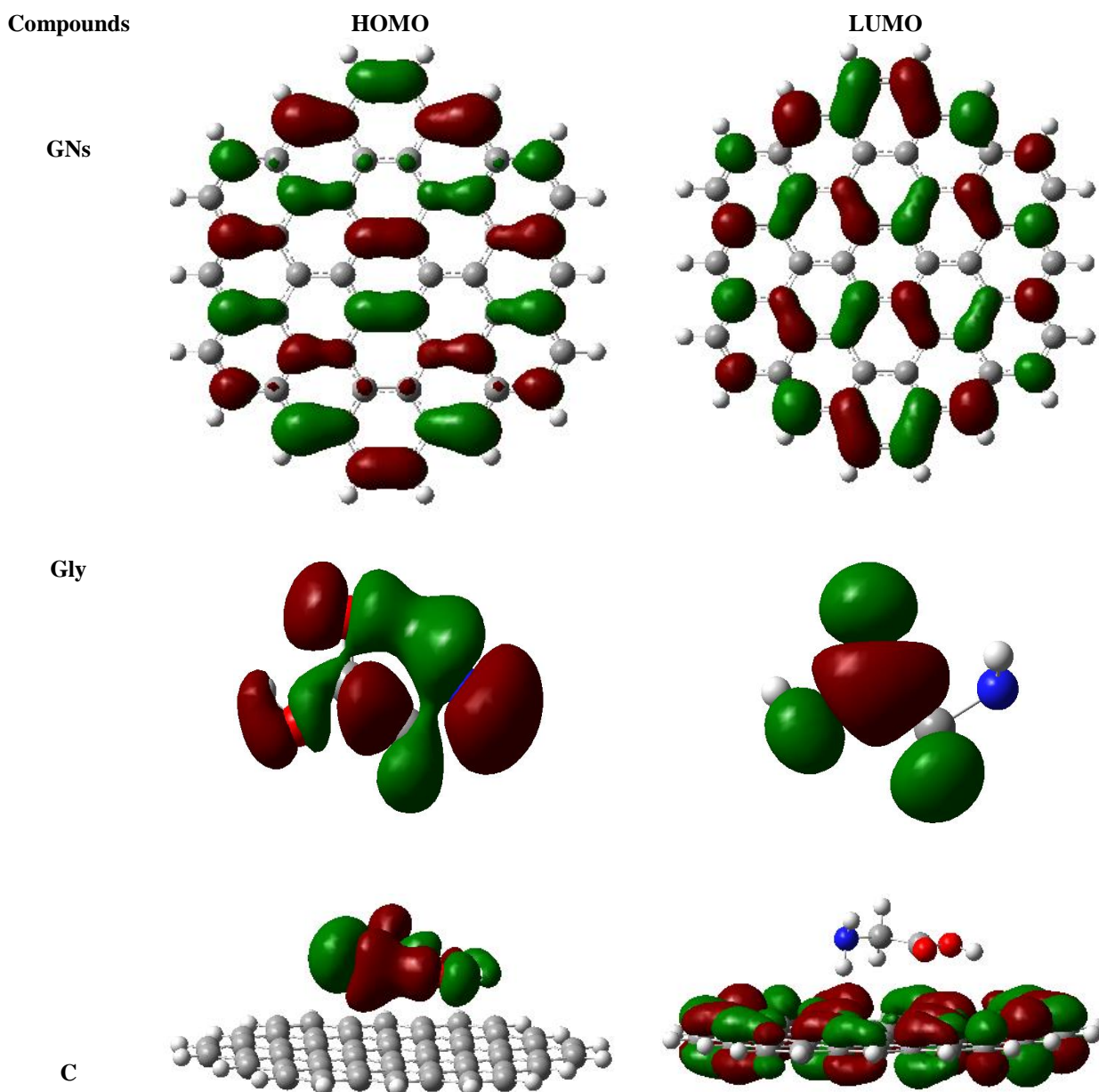
Figure 2. HOMO and LUMO distributions of GNs, Gly and C complex

To verify the impact of Gly adsorption on the electronic properties of the GNs, we have collected the electronic properties for the GNs/Gly complexes in Table 3. These results show that except for complex A, for other complexes the HOMO–LUMO gaps does not change appreciably after the adsorption of Gly.

Besides, considering the amount of chemical potential values of Table 3 confirms that electrons will flow from a particular occupied orbital in Gly molecule into a definite empty orbital in GNs. Indeed, the electron is transferred from higher chemical potential (Gly) to the lower electronic chemical potential (GNs), until the electronic chemical potentials become identical [20].

Based on the Pearson's maximum hardness principle (MHP) [21], it is found that the chemical hardness value of the GNs is smaller than that in the Gly molecule, indicating that this compound is softer than

the Gly molecule; therefore, the greatest polarizability there will be.

It is observed that when Gly molecule adsorbs on GNs, the electronic chemical potential values of the considered configurations are decreased and the electrophilicity values of these systems are increased, which means that the chemical stability of the complexes will be decreased and hence their chemical activity will be enhanced (see Table 3). As a result of theoretical calculations, the values of E_{HOMO}, E_{LUMO}, and energy gap of the studied configurations in solvent phase show less deviation with their obtained corresponding values in the gas phase (see Tables 3).

Close inspection of the obtained results shows that the HOMO and LUMO energy levels of the considered complexes are close to the HOMO and LUMO energies of the GNs at two phases (see Tables 3).

Table 3 The values of the highest occupied molecular orbital energies (E_{HOMO}) and the lowest unoccupied molecular orbital energies (E_{LUMO}), energy gap (E_g), the chemical potential (μ), global hardness (η), and electrophilicity index (ω) (all in eV) for glycine, the graphene, and different models at ωB97XD level in the gas phase (Values in parentheses refer to calculation in the water phase).

Property	Gly	GNs	A	B	C
E_{LUMO}	2.37 (2.39)	-0.77 (-0.97)	-0.88 (-0.95)	-0.83 (-0.99)	-0.81 (-0.99)
E_{HOMO}	-9.02 (-9.12)	-6.45 (-6.65)	-6.53 (-6.63)	-6.51 (-6.67)	-6.49 (-6.67)
E_g	11.39 (11.51)	5.68 (5.68)	5.66 (5.67)	5.68 (5.68)	5.68 (5.68)
μ	-3.33 (-3.36)	-3.61 (-3.81)	-3.71 (-3.79)	-3.67 (-3.83)	-3.65 (-3.83)
η	5.70 (5.76)	2.84 (2.84)	2.83 (2.84)	2.84 (2.84)	2.84 (2.84)
ω	0.04 (0.04)	0.08 (0.09)	0.09 (0.09)	0.09 (0.10)	0.09 (0.10)
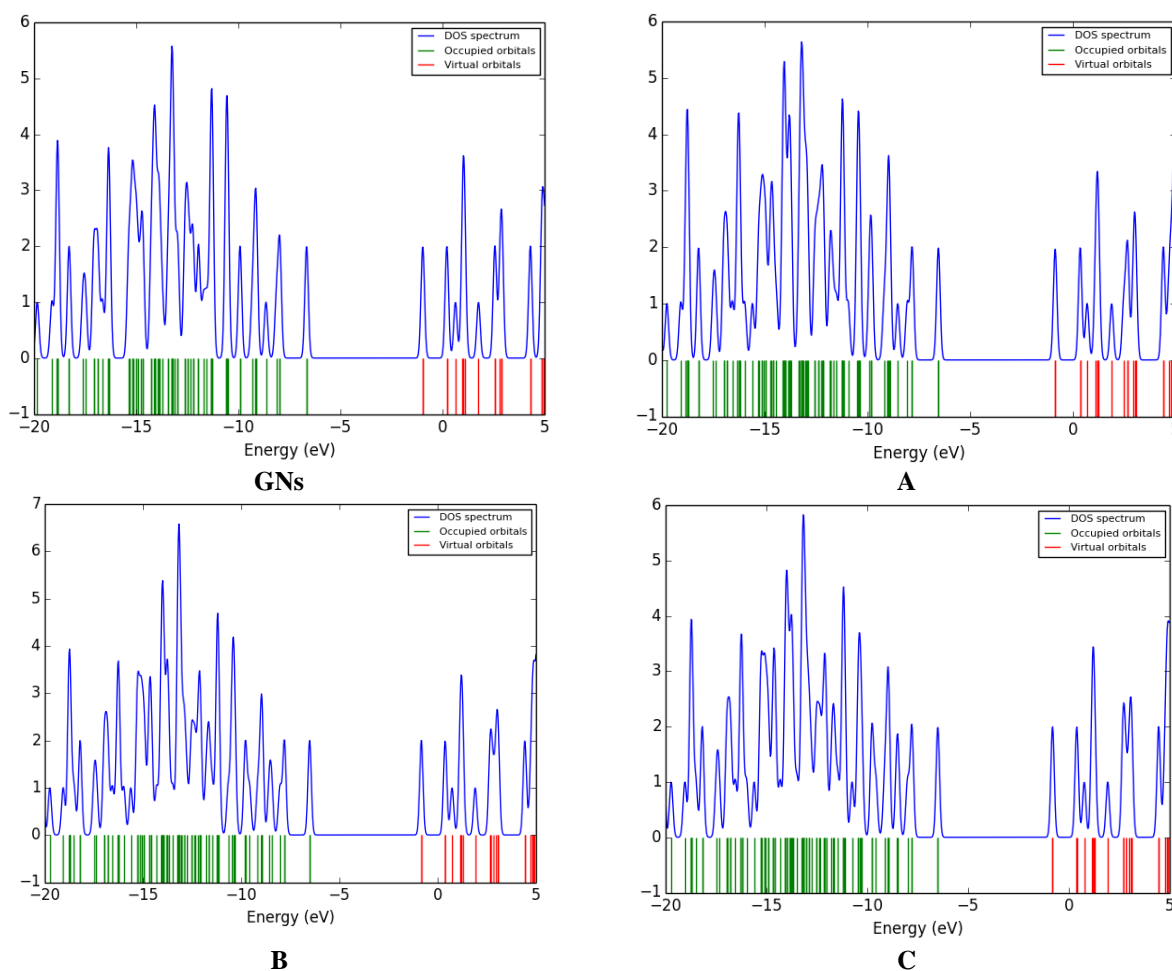
Figure 3. DOSs of pristine GNs and the A,B and C complexes

In addition, in order to study the effect of Gly adsorption on the electronic properties of the GNs, the total electronic density of states (DOS) have been measured and shown in Figure 3., the DOS plot of the configuration C has no distinct changes compared to that of the pristine nanosheet.

4. Conclusion

The density functional theory were applied to study the adsorption of glycine amino acid molecule on the graphene surface. DFT calculations were done to examine the details of the adsorption energy and structural properties between glycine molecule and

GNs surface. The adsorption energy values indicated that Gly adsorption onto the GNs surface was an exothermic process and energetically favorable. According to the obtained results, it is found that the amino nitrogen site of glycine are the best site for adsorption of the glycine molecule on the GNs surface. Our results also manifested that all GNs/Gly complexes have greater polarity and solubility as compared to isolated Gly molecule and GNs. Solvation energies displayed that the solubility of Gly increases in the presence of GNs.

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