



Original Research Article

A quantum assessment of the interaction between $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, $\text{NSi}_{11}\text{C}_{12}$ and $\text{NSi}_{12}\text{C}_{11}$ nanocages with Glycine amino acid: A DFT, TD-DFT and AIM study

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ABSTRACT

The motivation of this study is to investigate the interaction of $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocages with Glycine amino acid (Gly). The density functional theory (DFT) and time-dependent density functional theory (TD-DFT) at the cam-B3LYP/6-31G (p, d) level of theory by using Gaussian 09 software are utilized for this aim. The calculated results illuminate that the interaction of Gly with $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocages is exothermic, and favorable in thermodynamic view. The adsorption of Gly from oxygen site (C=O) with $\text{NSi}_{11}\text{C}_{12}$ and $\text{BSi}_{12}\text{C}_{11}$ nanocage is more favorable than other complexes. The natural bonding orbital (NBO) results depicted that the electron charge transfer occur from Gly molecule toward SiC nanocage. The atom in molecule (AIM) and reduced density gradient (RDG) results confirm that the bonding between Gly and SiC nanocage is partially covalent or electrostatic type. The gap energy and global hardness of all studied complexes are lower than pure state, so the conductivity and reactivity of these complexes are more. The results of this study demonstrate that the Gly strong interact with $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocages and the electrical structures of Gly alter significantly from pure state. These results can be considered in biological systems to investigate the effect of SiC nanocage in drug carriers and also provide information about the interaction of this nanocage with proteins in the body.

Keywords: $\text{Si}_{12}\text{C}_{12}$ nanocage, B and N doped, Glycine amino acid, DFT, AIM

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Introduction

One of the important and most abundant proteins in the body of humans and animals is the Glycine amino acid (Gly). It is used as a precursor of various important low molecular weights, such as glutathione, glyphosine, porphyrins, imiprothrin, eglinazine, heme, purines, and creatine [1]. Gly has immunomodulatory, cytoprotective, anti-inflammatory, and anti-oxidant roles in both the central nervous system and peripheral tissues. It is used as an intermediate compound to produce medicines and thiamphenicol [2–4]. After the discovery of carbon nanoparticles, great attention focused on other nanoparticles and nanocages such as silicon carbide due to thermal stability, high conductivity, high hardness, gas sensing, hydrogen storage, electronic devices, and other adsorption properties [5–8]. Sun and coworkers [9] synthesized the SiC nanotubes successfully via a reaction of Si oxide with carbon nanotubes with the ratio of 1:1 Si to C atom. The theoretical study indicated that the aromaticity and stability of SiC nanotubes are lower than carbon nanotubes, and the electrical properties of SiC nanotubes are independent of their chirality, lengths, and tubular diameter [10–11]. Reports of various research on the pristine and doped silicon carbide nanotube with various elements and compounds (such as Fe, Ga, O₂, Fe, Co, Ni, and dichlorocarbon) demonstrated that SiC nanoparticles have valuable potential for special applications in the manufacture of electronic devices as a sensor and absorber of various compounds [12–18]. The interaction of SiC nanotube with NH₃BH₃ [19] CO [20–21], HCN [22], H₂ [23–25], O₂ [26], CO₂ [27], formic acid [28], NH₃ [29], CH₄ [30], formamide [31], phenol [32] are scrutinized by density functional theory. The structural results of SiC nanoparticles demonstrate that the electrical and magnetic properties of nanotube change significantly with different compounds, and this nanotube is a favorable candidate for preparing adsorbent, catalyst, and sensitive sensor [33–34]. Another structure of silicon carbide is the Si₁₂C₁₂ nanocage, which has recently attracted a lot of research and its electronic structure has been studied in the interaction of different compounds. Zhao et al. [35] and Duan et al. [36] reported the structural, electrical, stabilities, and optical properties of Si₁₂C₁₂ nanocage, their results show that Si₁₂C₁₂ nanocage is more stable and reactive. Solimannejad et al. [37–38] by using the DFT methods investigated the nonlinear optical (NLO) response of Si₁₂C₁₂ nanocage decorated with alkali metals (M= Li, Na, and K), and sensing performance of Cu-decorated Si₁₂C₁₂ nanocage towards toxic cyanogen gas. They found that nonlinear optical properties of SiC nanocage increase with decorating with alkali metals and Cu atoms. In the other work, Solimannejad et al [39] studied the hydrazine trapping

ability of $\text{Si}_{12}\text{C}_{12}$ nanocage, the calculated results confirmed that the adsorption of a monomer of hydrazine on the $\text{Si}_{12}\text{C}_{12}$ nanocage was more appropriate than the corresponding dimers, and this nanocage was a good candidate for removal of hydrazine molecule from environmental systems. Jouypazadeh et al. [40–41] studied the interaction of Tabun and sulfur mustard chemical warfare agent with various nanocages such as C_{24} , $\text{Si}_{12}\text{C}_{12}$, $\text{Al}_{12}\text{N}_{12}$, $\text{Al}_{12}\text{P}_{12}$, $\text{Be}_{12}\text{O}_{12}$, $\text{B}_{12}\text{N}_{12}$, and $\text{Mg}_{12}\text{O}_{12}$. The results revealed that the C_{24} , $\text{Be}_{12}\text{O}_{12}$, $\text{Al}_{12}\text{P}_{12}$, and $\text{B}_{12}\text{N}_{12}$ nanocages have a good potential for adsorbing Tabun and sulfur mustard. Following our previous study on the interaction of ammonia molecule, nitrate ion, Cd ion, and H_2S gas with boron nitride and HCN molecule with beryllium oxide nanotube BeONTs [42–44], in this work, We decided to investigate the interaction of the $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocages with Glycine amino acid at cam-B3LYP/6-31G (p, d) level of density functional theory. The results of this study can be used to understand the effects of these nanocages on protein of biological systems, and designing above nanocages for making sensor or carrier of drug.

Details of the Computational method

In this study, the Glycine amino acid (Gly) from O=C site (a label), O–C site (b label) and N–C site (c label) adsorb on the surface Si and C sites of $\text{Si}_{12}\text{C}_{12}$ (A, B models), $\text{BSi}_{11}\text{C}_{12}$ (C model), $\text{NSi}_{11}\text{C}_{12}$ (D model), $\text{BSi}_{12}\text{C}_{11}$ (E model), $\text{NSi}_{12}\text{C}_{11}$ (F model) nanocages (see Fig. 1). All considered complexes are optimized at the cam-B3LYP/6-31G (p, d) level of theory [45] by Gaussian 09 software [46]. The Maximum force and displacement in this study are 0.00042 Ha, 0.00015 Ha/Bohr. The global charge and multiplicity of all studied complexes are 0 and 1 respectively. In all optimized structures, no imaginary frequency is observed, so all complexes are stable. The adsorption energy (E_{ads}) and thermodynamic parameters (ΔH and ΔG), deformation energy of nanocage ($E_{\text{def-Nano}}$), Gly ($E_{\text{def-Gly}}$), and interaction energy (E_{int}) are calculated for all studied complexes by Eqs. 1–4.

$$E_{ads} = E_{Gly@SiC\ nano} - E_{SiC\ nano} - E_{Gly} \quad (1)$$

$$E_{def\ A} = E_A - E_{A\ in\ complex} \quad A: SiC\ nano, Gly \quad (2)$$

$$E_{int} = E_{Gly@SiC\ nano} - E_{SiC\ nano\ in\ complex} - E_{Gly\ in\ complex} \quad (3)$$

$$\Delta Q = Q_{Gly@SiC\ nano} - Q_{SiC\ nano} - Q_{Gly} \quad Q: H, G \quad (4)$$

Here the $E_{Gly@SiC\ nano}$, $E_{SiC\ nano}$ and E_{Gly} are the total potential electronic energy of Gly@SiC nanocage complex, SiC nanocage and Gly. The $E_{SiC\ nano\ in\ complex}$ and $E_{Gly\ in\ complex}$ are the single point energy of SiC nanocage and Gly in Gly@SiC nanocage complex.

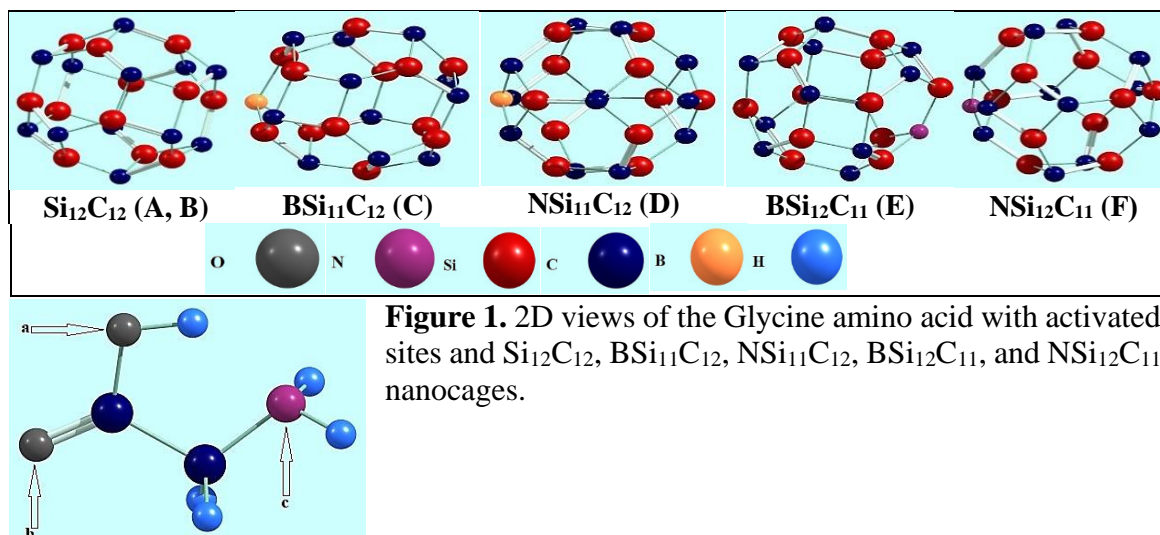


Figure 1. 2D views of the Glycine amino acid with activated sites and $Si_{12}C_{12}$, $BSi_{11}C_{12}$, $NSi_{11}C_{12}$, $BSi_{12}C_{11}$, and $NSi_{12}C_{11}$ nanocages.

For examining the electrical properties of interaction of Gly with pristine and B&N atoms doped $Si_{12}C_{12}$ nanocages, the HOMO (the highest occupied molecular orbital) and LUMO (the lowest unoccupied molecular orbital) energies, gap energy (E_{gap}), chemical potential (μ) and global hardness (η), and charge transfer parameters (ΔN) [41–44] of the A–a to F–c adsorption systems are calculated by using Eqs 5–8 and results are given in Table 2.

$$E_{gap} = E_{LUMO} - E_{HOMO} \quad (5)$$

$$\mu = (E_{HOMO} + E_{LUMO}) / 2 \quad (6)$$

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

$$\Delta N = -\frac{\mu}{\eta} \quad (8)$$

To investigate the nature of bonding between Gly and SiC nanocage complexes and the probability of finding an electron pair, the atom in molecule (AIM) topological parameters, reduced density

gradient (RDG) plots, and localized orbital locator (LOL) and the natural bond orbital (NBO) parameters [46–47] are computed for all A-a to F-c models using Multiwfn. 3.4 software [48]. The PCM (polarizable continuum) method is applied to investigate the effects of solvent on the interaction of Gly with SiC nanocages complexes [49].

Results and discussion

Geometrical and structural properties

The optimized configurations of A-a to F-c models are shown in Fig. 2. Based on the optimized structures at all models except D-c, E-c and F-c models the Gly is strongly adsorbed on the surface of the nanocage. In the D-c, E-c, and F-c models due to the repulsion effect, the Gly molecule localizes far from nanocage and interaction between Gly with nanocage is weak. The geometrical parameters such as bond length and bond angle of Si₁₂C₁₂ nanocage and distance between Gly and nanocage are calculated and results are presented in Figs. S1 and S2. Inspection of results indicates that the bond length Si-C in the pristine models is 1.83 Å and with doping B and N despite the Si and C position of nanocage the Si-B, C-B, Si-N and C-N bond lengths around adsorption position are 1.94, 1.61, 1.83, and 1.48 Å respectively, and is in agreement with other reports [36–41]. The bond distance between Gly and nanocage in the A-a to F-c models (except D-c, E-c, and F-c models) is in the range 1.56 to 1.99 Å. In the D-c, E-c and F-c models due to repulsion interaction the bond distance between nanocage and Gly increase significantly from 1.83 Å to 3.37, 3.79, and 3.87 Å respectively. The bond distance between Gly....SiC nanocage in the D-b, E-b, and F-a models is 1.56 Å and is lower than other models, so the adsorption of Gly on the surface of nanocage in these states is stronger than in other models.

The E_{ads} , E_{def} , and E_{int} for all studied complexes are calculated by Eqs. 1–3 and the results are listed in Table 1. According to the results of Table 1, it can be seen that the amount of adsorption energy for all studied complexes is negative and the adsorption process is exothermic and thermodynamically favorable. The highest and lowest absolute values of E_{ads} are related to D-a (–34.45 kcal/mol) and E-c (–1.39 kcal/mol) complexes, respectively. In the **a** direction of the drug, the E_{ads} of the A-a, B-a, C-a, D-a, E-a and F-a complexes decrease in order: D-a (–34.45 kcal/mol) > A-a (–29.46 Kcal/mol) > B-a (–26.85 kcal/mol) > F-a (–19.71 kcal/mol) > E-a (–17.09 kcal/mol) > C-a (–7.59 kcal/mol).

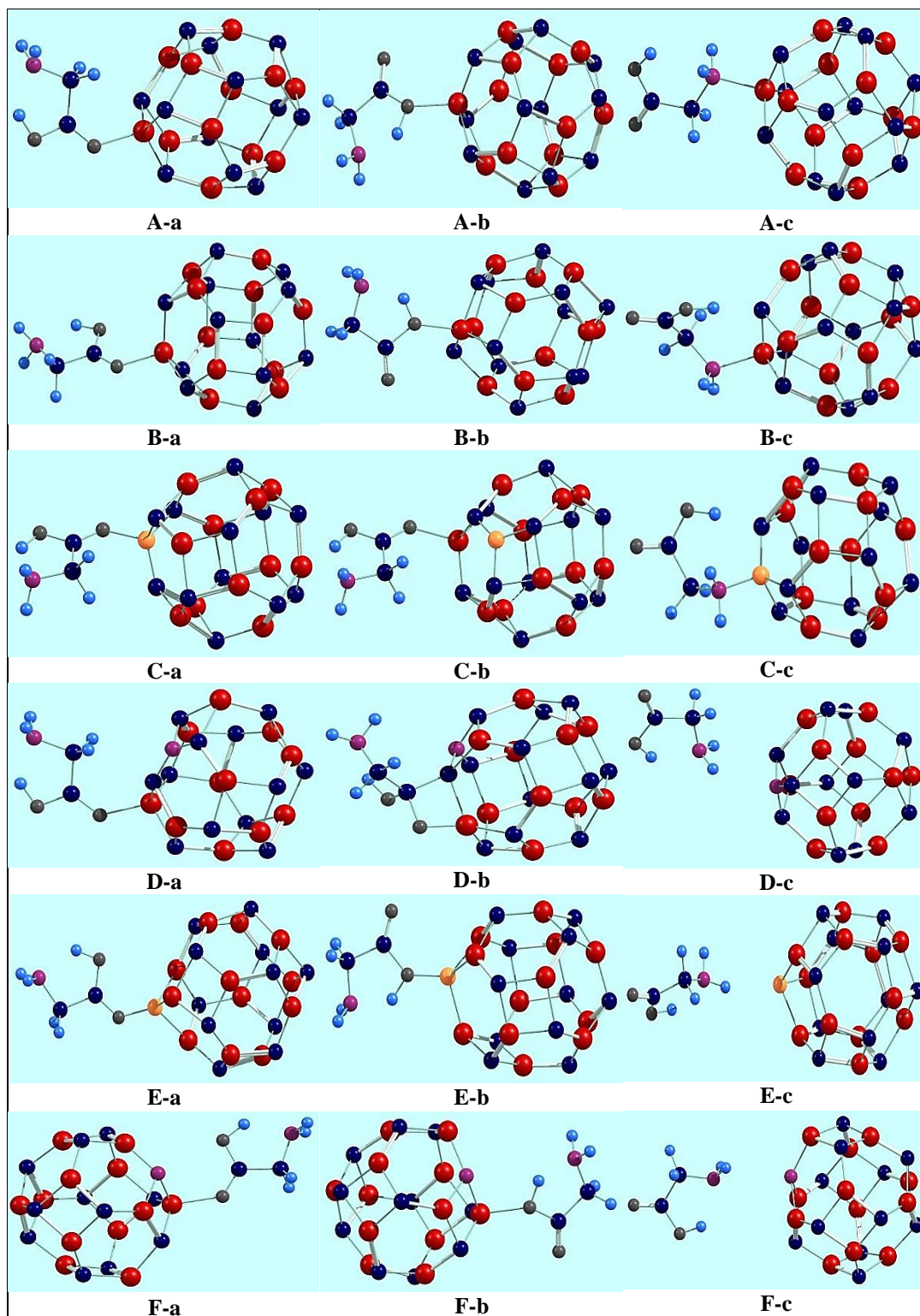


Figure 2. 2D views of Gly adsorption on the surface of $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocage (A-a to F-C models).

Table 1 Adsorption energy (E_{ads}), deformation energy of Gly ($E_{\text{def}}(\text{GLY})$), nanocage ($E_{\text{def}}(\text{nano})$), interaction energy E_{int} (Kcal/mol), thermodynamic parameters (ΔH and ΔG (Kcal/mol) Gly@Si₁₂C₁₂ complex for A-a to F-c models.

	$E_{\text{def.Nano}}$	$E_{\text{def. Gly}}$	E_{int}	E_{ads}	ΔH	ΔG	$\Delta\rho(\text{NBO})$
A-a	-4.03	-2.77	-33.66	-29.46	-28.57	-54.03	0.23
A-b	-7.47	-3.84	-23.60	-17.04	-16.34	-43.75	0.18
A-c	-2.72	-7.70	-32.39	-22.27	-20.18	-47.81	0.21
B-a	-4.03	-2.77	-33.26	-26.85	-25.43	-51.92	0.22
B-b	-2.51	-3.66	-23.15	-16.66	-16.01	-43.92	0.18
B-c	-3.74	-12.50	-49.88	-33.64	-32.17	-57.67	0.17
C-a	-14.53	-2.91	-25.04	-7.59	-5.95	-6.48	0.31
C-b	-3.64	-4.40	-40.25	-32.19	-30.16	-17.53	0.21
C-c	-15.49	-11.93	-46.40	-18.97	-17.08	-3.61	0.24
D-a	-10.08	-2.71	-38.95	-34.45	-35.58	-22.93	0.21
D-b	-3.76	-3.98	-28.50	-8.57	-53.65	-38.84	0.18
D-c	-10.95	-11.05	-19.24	-1.55	-2.29	-6.83	0.20
E-a	-10.03	-10.01	-15.44	-17.09	-35.58	-22.93	0.22
E-b	-10.49	-3.21	-30.80	-5.98	-53.65	-38.84	0.50
E-c	-8.91	-4.87	-19.77	-1.39	-2.29	-6.83	0.05
F-a	-13.48	-2.88	-34.09	-19.71	-15.99	-4.36	0.31
F-b	-3.49	-5.16	-29.16	-20.5	-5.74	-5.14	0.31
F-c	-0.03	-0.09	-1.88	-1.76	-0.28	-5.72	0.07

These results indicate that with doping N atom despite Si atom of nanocage (NSi₁₁C₁₂) the interaction and adsorption of Gly from carbonyl (C=O) site on the surface of nanocage is stronger than other complexes. While with doping B atom despite Si atom of nanocage (BSi₁₁C₁₂) the interaction and adsorption of Gly is weaker than other complexes.

The E_{def} (deformation energy) is the amount of energy need to deform of the structure of the material in the complex than in the free state. If the amount of E_{def} of the substance is large, it shows that the structure of the substance changes more due to combining with another substance. The results of Table 1 indicate that the E_{def} values of nanocage and Gly in all studied complexes are negative and the deformation process is spontaneous. The highest E_{def} value for SiC nanocage structure has occurred in C-a (-14.53 kcal/mol) and F-a (-13.48 kcal/mol) complex, while the lowest E_{def} value has appeared in the F-c (-0.03 kcal/mol) model. These results confirm that Si₁₂C₁₂ nanocages in the C-a and F-a models are more affected by the interaction of Gly and its structure changes. The absolute value of E_{def} in all studied complexes change in order C-a (-14.53 kcal/mol) > F-a (-13.48 kcal/mol) > D-a (-10.08 kcal/mol) > E-a (-10.03 kcal/mol) > A-a=B-a (-4.03 kcal/mol). The lowest change in the structure of the nanocage takes place in pristine Si₁₂C₁₂ nanocage, whereas the highest deformation of nanocage is observed in the C-a (B doped despite the Si atom of nanocage). The absolute values E_{def} of Gly in the B-c (-12.50 kcal/mol) and C-c (-11.93 kcal/mol) models are more than other complexes. In the B-c and C-c models, the structure

of Gly is deformed significantly from its original state due to interaction with the nanocage. The interaction energy (E_{int}) values for all studied complexes are negative, so the interaction of Gly with nanocage in these models is thermodynamically favorable. Most of the interaction energy is observed in D-a (-34.45 kcal/mol) and B-c (-49.88 kcal/mol) models. The E_{int} values of Gly&SiC nanocage complexes in a site of Gly decrease in order: D-a (-38.95 kcal/mol) > F-a (-34.09 kcal/mol) > A-a (-33.66 kcal/mol) > B-a (-33.26 kcal/mol) > C-a (-25.04 kcal/mol) > E-a (-15.44 kcal/mol). A comparison of results confirms that the NSi₁₁C₁₂ nanocage (D-a model) strongly interact with Gly and it may be noticeable in the biological system. The ΔH , and ΔG values of all studied complexes are negative and the adsorption processes are exothermic, spontaneous, and favorable. The change process of thermodynamic parameters is the same with absorption energy and interaction energy.

For understanding the solvent (water) effects on the interaction of Gly with nanocage, the $\Delta\Delta G_{(w)}$ values for all studied complexes are computed by equation $\Delta\Delta G_{(w)} = \Delta G_{(\text{Gly}\&\text{nanocage})} - \Delta G_{(\text{Gly})} - \Delta G_{(\text{nanocage})}$, using PCM model [51]. In this equation the $\Delta G_{(\text{Gly}\&\text{nanocage})}$, $\Delta G_{(\text{Gly})}$, and $\Delta G_{(\text{nanocage})}$ are solvation Gibbs free energy of Gly&nanocage, Gly, and nanocage in the presence of water solvent. While the $\Delta\Delta G_{(w)}$ is Gibbs free energy of formation Gly&nanocage complex from SiC nanocage and Gly. Based on calculated results of Table S1, the $\Delta G_{(w)}$ values of Gly, nanocage and Gly&nanocage complex in the A-a, B-a, C-a, D-a, E-a, and F-a studied complexes are negative and solvation process is spontaneous. The $\Delta\Delta G_{(w)}$ values for above complexes are positive and process is thermodynamically unspontaneous, and interaction of Gly with SiC nanocage in the presence of water is unfavorable.

QTAIM

QTAIM (quantum theory of atoms in molecules) is an important method for explaining the molecular structure and type of bonding between two compounds by electron density [47–48]. By applying the QTAIM method, the total electron density (ρ), electron density Laplacian ($\nabla^2\rho$), total electronic energy (H_r), and ellipticity (ϵ) factor for A-a to F-a studied complexes are computed and results are listed in Table 2.

Table 2. The QTAIM parameters of the A-a to F-a complexes.

	A-a	B-a	C-a	D-a	E-a	F-a
$\nabla^2\rho$	0.3374	0.2931	0.3541	0.3521	0.6416	0.3128
ρ	-0.0738	-0.0694	-0.0649	-0.0754	-0.0119	-0.0714
$H(r)$	-0.0170	-0.0169	-0.0543	-0.0172	-0.0594	-0.0170
ϵ	0.0430	0.0716	0.0002	0.0388	0.1180	0.0906

Based on the calculated results of QTAIM (Table 2) the sign of $\nabla^2\rho$ and H_r for A-a to F-a complexes in the bond critical point (BCP) are positive and negative respectively, so the type of bonding between Gly and nanocage is a partially covalent or van der Waals. The absolute value of ρ for the D-a complex is more than other complexes and so the interaction of Gly with $\text{NSi}_{11}\text{C}_{12}$ nanocage (D-a model) is strong, this result is in agreement with E_{ads} and ΔH . The ϵ values of A-a to F-a are <0.1 , so the bonding Gly and nanocage is σ type.

LOL plots

The localized orbital locator (LOL) plots for A-a, B-a, C-a, D-a, E-a, and F-a complexes are displayed in Fig. 3. In the LOL topological plots, the red, yellow, and blue colors illustrate the highest, low, and lowest density electron localized, respectively.

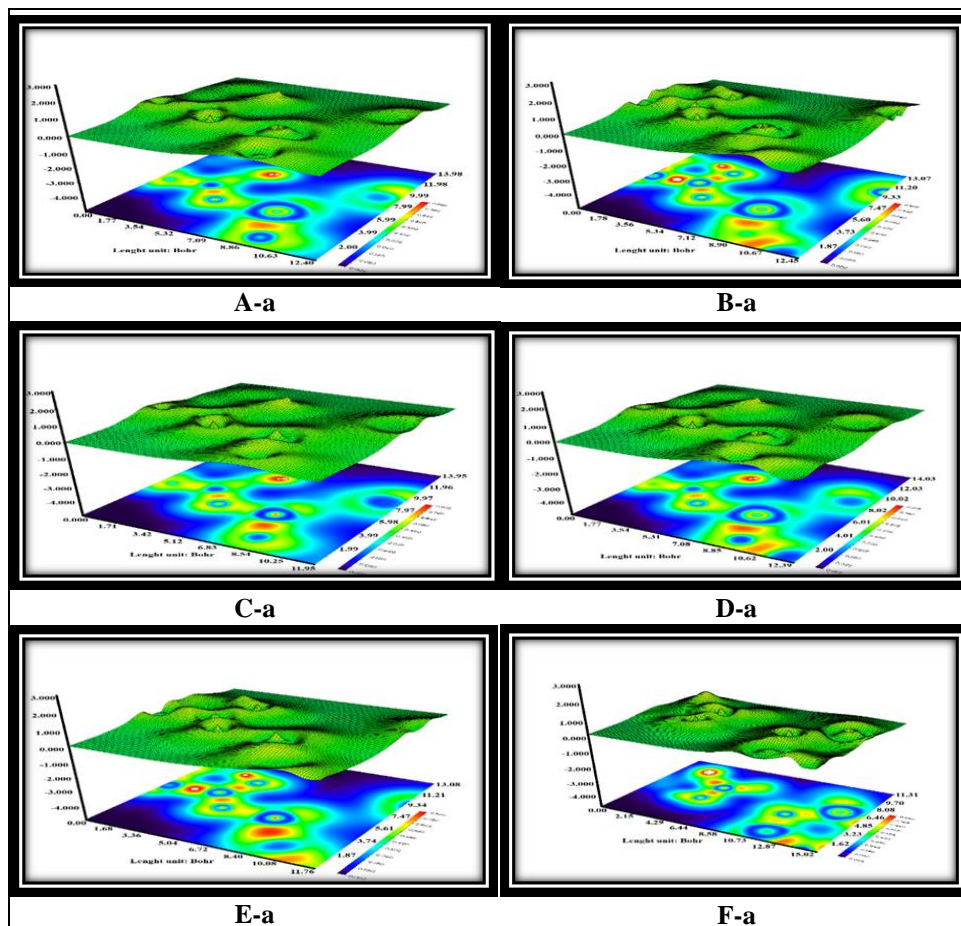


Figure 3. Topological structures of LOL of Gly interaction with $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocage (A-a to F-a models).

A close inspection of LOL plots shows that the localized electron density between the Gly and SiC nanocage is low, which confirms that the interaction between the two above compounds is non-covalent or electrostatic type.

RDG plots

To examine the nature of the non-covalent bond [52], the RDG (reduced density gradient) scatter is calculated according to Eq. 9, and the scatter plots for A-a to F-a complexes are shown in Fig. 4.

$$RDG(r) = \frac{1}{2(3\pi^2)^{1/3}} \frac{|\nabla\rho(r)|}{\rho(r)^{4/3}} \quad (9)$$

In the RDG scatter plots, the $\text{sign}(\lambda_2)\rho(r) < 0$, $\text{sign}(\lambda_2)\rho(r) > 0$, and $\text{sign}(\lambda_2)\rho(r) = 0$ indicate that the interaction between two compounds is electrostatic or hydrogen bond, repulsion, and van der Waals type respectively. A close inspection of RDG results confirms that the more RDG density localizes in the $\text{sign}(\lambda_2)\rho(r) < 0$, and $\text{sign}(\lambda_2)\rho(r) = 0$ regions. These results prove that the nature of the bond between Gly and SiC nanocage is electrostatic and van der Waals type.

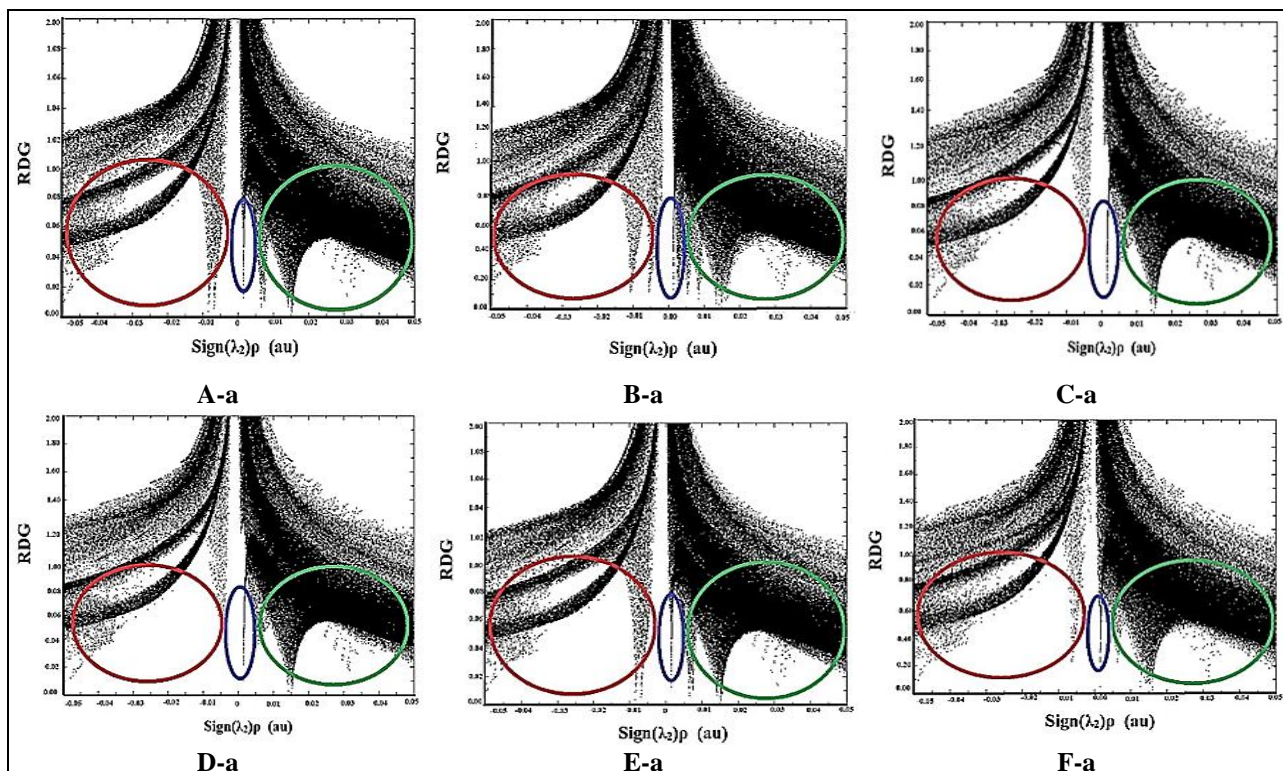


Figure 4. RDG scatter plots of Gly interaction with $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocages (A-a to F-a models).

UV-visible spectrum

Using the time-dependent density function method, it is possible to determine the states of electron transfer at the excited states and to extract the ultraviolet or visible spectrum of a compound. These spectra can also be used to identify compounds and trace them in biological systems [53–55]. The excited states and UV-visible spectra for studied complexes at 30 states are computed by cam-B3LYP/6-31G (d, p) level of DFT theory, and results are tabulated in Table 3 and are shown in Fig. 5.

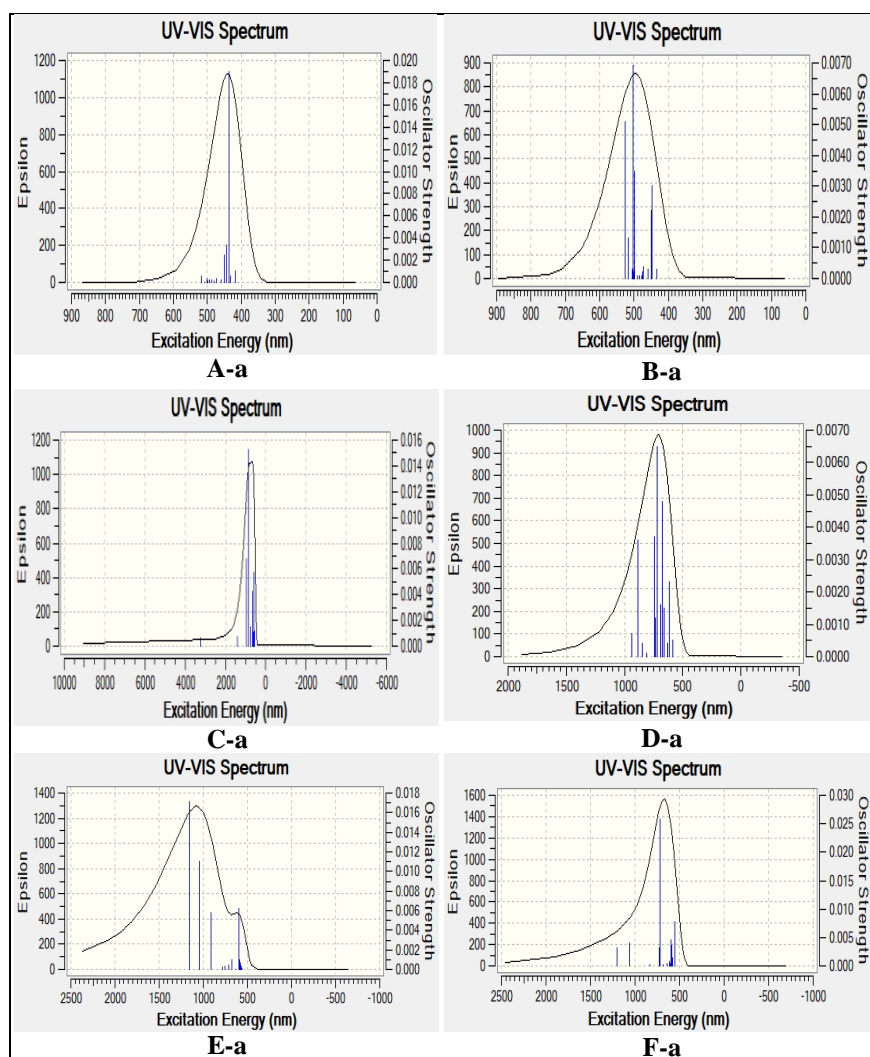


Figure 5. UV-visible plots of Gly adsorption on the surface of $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocage (A-a to F-a models).

Based on the results, it can be seen that the λ_{\max} of all studied complexes are in the range of 400 to 1162 nm. This wavelength locates in the visible region of spectroscopy. It is interested that with doping B and N atoms instead of carbon and silicon atoms of nanocage as well as Gly adsorption, the λ_{\max} increases significantly from original values, which can be used to track Gly associated with nanocage. Inspection of λ_{\max} results indicates that the most λ_{\max} (1162.19 nm) is observed for the E-a complex, which is related to the excited state $S_0 \rightarrow S_1$ with $(0.96(H \rightarrow L) + 0.04(H-1 \rightarrow L))$ with oscillator strength 0.017. The λ_{\max} of studied complexes decrease in order: E-a>C-a>D-a>F-a>B-a>A-a. This result confirms that doping of the B atom despite Si and C atoms of nanocage increase the λ_{\max} from 525.32 to 1162.19 nm ($BSi_{12}C_{11}$) and from 443.07 to 960.76 nm ($BSi_{11}C_{12}$). Therefore, the interaction of Gly with $BSi_{12}C_{11}$ and $BSi_{11}C_{12}$ nanocages can change the spectral properties of the system and this issue can be interesting in tracking the interaction.

Table 3 The UV-visible parameters for the excited state of the system for A-a to F-a models.

	Excited states	λ_{\max} / (nm)	E/ (eV)	Configuration composite	<i>f</i>
A-a	$S_0 \rightarrow S_{12}$	443.07	2.798	$0.72(H-1 \rightarrow L+5)+0.08(H \rightarrow L+4)$	0.003
B-a	$S_0 \rightarrow S_1$	525.32	2.360	$-0.02(H-1 \rightarrow L) - 0.02(H-1 \rightarrow L+2)+0.5(H \rightarrow L) + 0.02(H \rightarrow L+1)$	0.005
C-a	$S_0 \rightarrow S_3$	960.76	1.290	$0.03(H-3 \rightarrow L)+1.8(H-2 \rightarrow L)$	0.007
D-a	$S_0 \rightarrow S_1$	940.15	1.318	$0.03(H-1 \rightarrow L) + 1.28(H \rightarrow L) + 0.02(H \rightarrow L+1) + 0.5(H \rightarrow L)$	0.001
E-a	$S_0 \rightarrow S_1$	1162.19	1.067	$0.96(H \rightarrow L)+0.04(H-1 \rightarrow L)$	0.017
F-a	$S_0 \rightarrow S_5$	717.40	1.728	$0.28(H \rightarrow L+2)+0.72(H-2 \rightarrow L)$	0.026

HOMO and LUMO

In this section, to further investigate the electronic structure of the interaction of Gly with $Si_{12}C_{12}$, $BSi_{12}C_{11}$, $BSi_{11}C_{12}$, $NSi_{12}C_{11}$ and $NSi_{11}C_{12}$ nanocages, the HOMO and LUMO orbitals of all studied complexes are computed and the results are shown in Fig. 6. A close inspection of the HOMO and LUMO orbitals structures of Fig. 6 displays that the density of HOMO orbitals is localized on the SiC nanocage surface, so this surface is favorable for interaction with the electrophilic compound. While the density of LUMO orbitals is localized on the Gly molecule, so this surface is suitable for interaction with nucleophilic compounds. It is noteworthy that with the replacement of carbon and silicon atoms of nanocage with boron and nitrogen atoms the electron spin of orbitals is divided into two alpha and beta. In these models, it is observed that the most density of HOMO and LUMO orbitals is localized around the adsorption sites.

The most density of LUMO orbital in the B-a, E-a(α), and F-a(β) is localized on the Gly surface and this region is suitable for interacting with nucleophile compounds. By using the energy of HOMO and LUMO, the E_{gap} , η , μ , and ΔN for studied complexes are computed by Eqs. 5-8 and the results are listed in Tables 4 and S2. From Table 4 it is seen that the amount of E_{gap} and η are in the range of 1.16 to 3.16 eV and 0.58 to 2.45 eV respectively. With doping of B and N atoms and adsorbing of Gly the E_{gap} and η values of $\text{Si}_{12}\text{C}_{12}$ nanocage are significantly reduced from pristine $\text{Si}_{12}\text{C}_{12}$ nanocage, as a result the conductivity Gly&SiC nanocage according to $\sigma \propto e^{-E_g/2KT}$ equation [56] increases, which indicates that the B and N doped $\text{Si}_{12}\text{C}_{12}$ nanocage are more reactive and conductive than pristine model and it can be a suitable sensor for the detection of glycine in the chemical and biochemical system.

Table 4 The quantum parameters $\text{Si}_{12}\text{C}_{12}/\text{Gly}$ complex for A-a to F-a models

	A-a	B-a	C-a- α	C-a- β	D-a- α	D-a- β	E-a- α	E-a- β	F-a- α	F-a- β
E_{HOMO} (eV)	-5.36	-5.13	-5.10	-4.98	-4.66	-4.97	-4.09	-4.92	-4.02	-4.93
E_{LUMO} (eV)	-2.20	-2.15	-2.32	-3.81	-2.58	-2.70	-2.32	-2.48	-2.45	-2.45
E_{gap}	3.16	2.97	2.78	1.16	2.08	2.27	1.77	2.44	1.57	2.48
η /eV	1.58	1.49	1.39	0.58	1.04	1.13	0.88	1.22	2.45	1.24
μ /eV	-3.78	-3.64	-3.71	-4.39	-2.62	-3.83	-3.21	-3.70	-3.23	-3.69
ΔN	2.38	2.44	2.67	7.54	2.51	3.38	3.62	3.03	4.14	2.97

The negative values of chemical potential indicate that the formation of the Gly&SiC nanocage complex is stable. The maximum charge transfer (ΔN) values of Gly&SiC nanocage complexes are positive and in the range of 2.38 to 7.41, as a result, the electron charge transfer occur from Gly toward SiC nanocage, so the surface of the nanocage has a negative charge and may be interaction with electrophile compound.

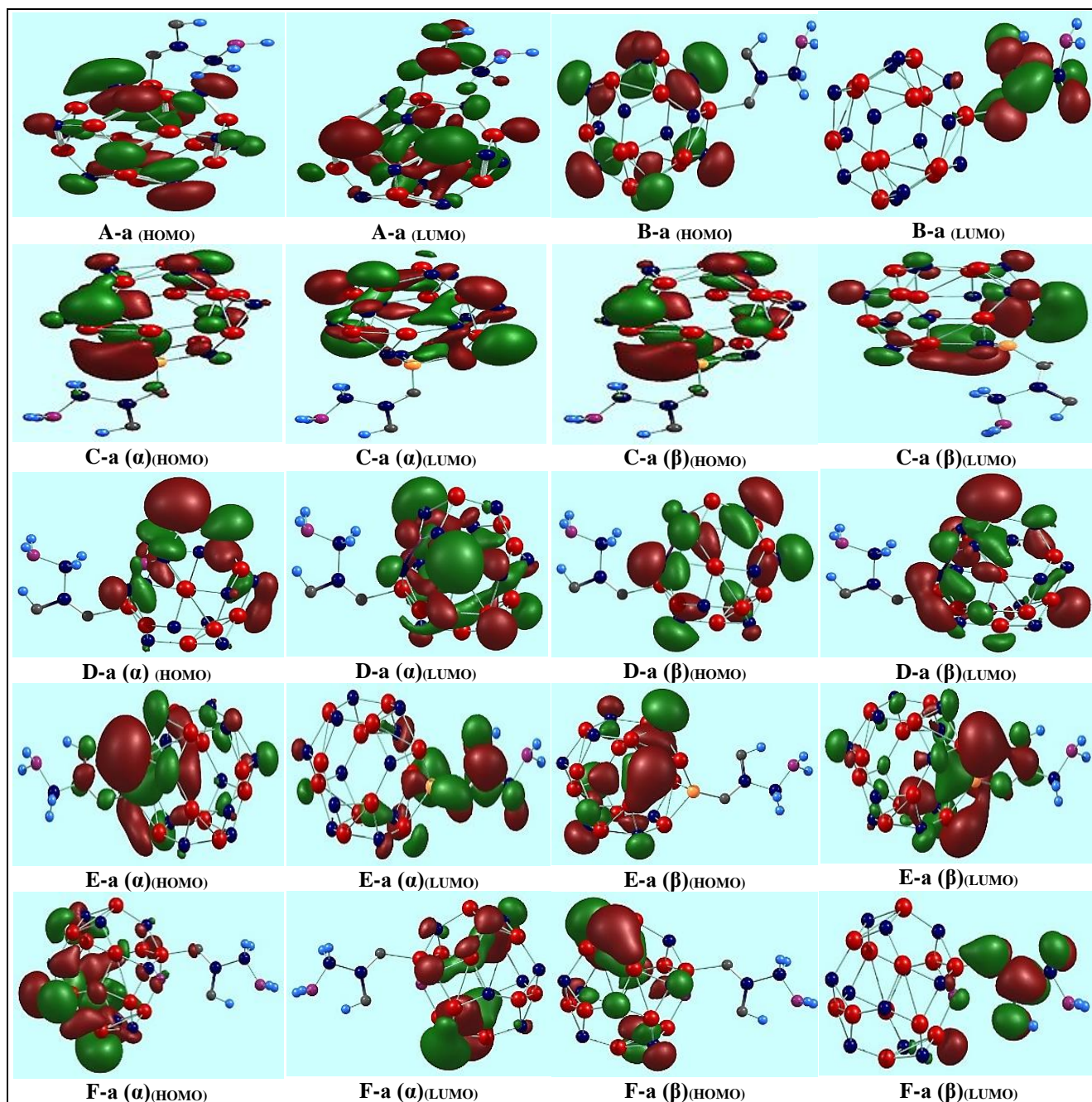


Figure 6. HOMO and LUMO orbital structures of Gly adsorption on the surface of $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocage (A-a to F-a models)

Using Gauss Sum 3.01 software [57], the density of state (DOS) diagrams for studied complexes are determined and the results are displayed in Fig. 7. Inspection of DOS diagrams (see Fig. 7) with doping of B and N atoms the HOMO and LUMO electron spin is separated into α and β , so the number of DOS states increases.

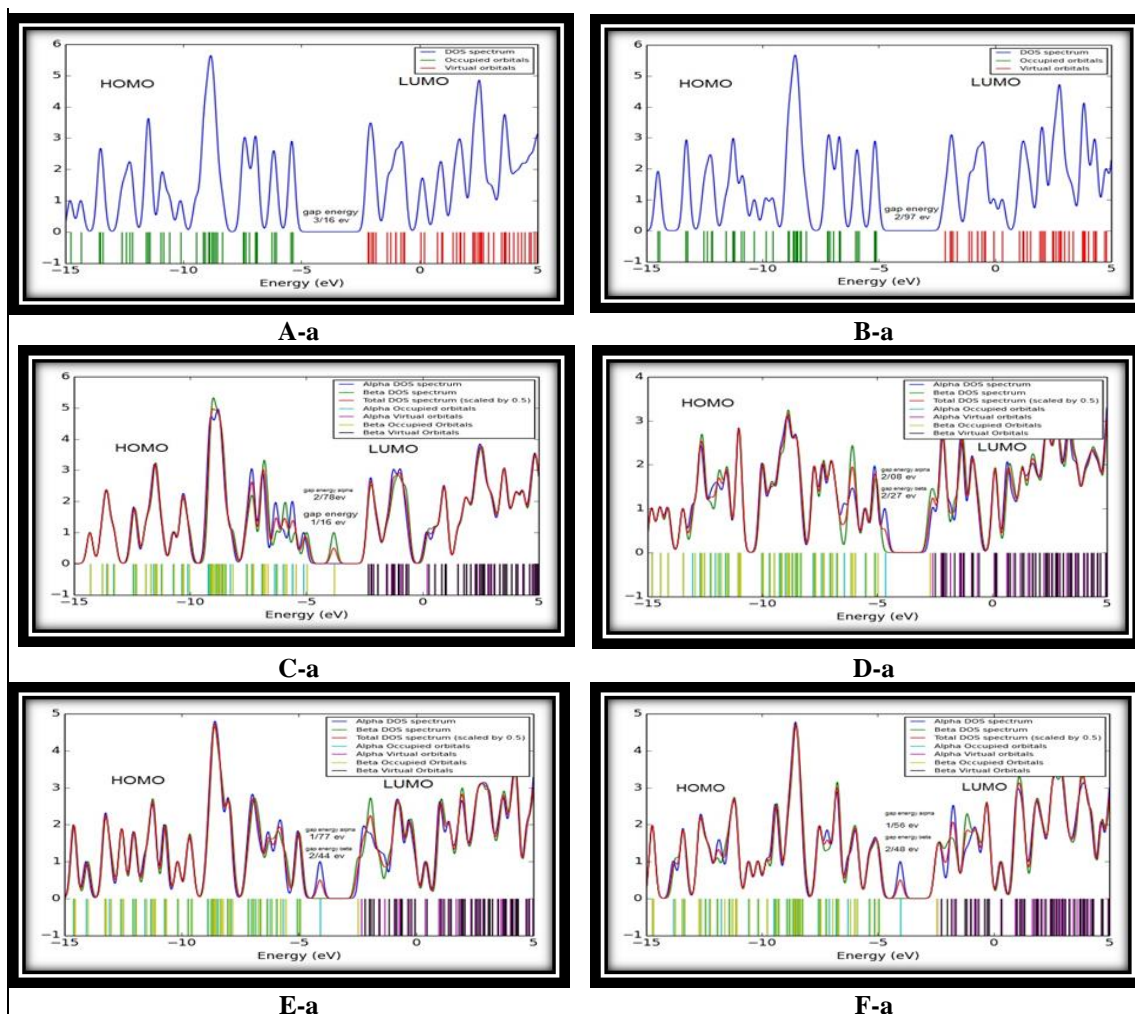


Figure 7. DOS plots of Gly adsorption on the surface of $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocage (A-a to F-a models)

The number of electron transitions between the HOMO and LUMO region increase, and as a result the optical behavior of the material increase. In these cases, with the appearance of a few small peaks in the gap region, the E_{gap} decreases significantly from the pristine state, which increases the conductivity of the nanocage. These results suggest that the electrical properties of Gly alter significantly in the presence of pristine and B&N atoms doped SiC nanocage, and this property can be significant in biological matters.

NBO analysis

The donor and acceptor electrical properties of Gly and $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ nanocage are investigated by using the natural bonding orbital (NBO). By using

NBO analysis the stabilization energy $E^{(2)}$ [58–59] of the bonding and antibonding orbitals are computed by Eq. 10.

$$E^{(2)} = q_i \frac{F_{ij}^2}{\varepsilon_j - \varepsilon_i} \quad (10)$$

The F_{ij} , q_i , and $\varepsilon_j - \varepsilon_i$ are the off-diagonal, orbital occupancy, and difference orbital energies, respectively. The computation results are tabulated in Table S3 and S4. From Table S3, it is observed that with doping B and N atoms despite Si and C atoms of $\text{Si}_{12}\text{C}_{12}$ nanocage the electrons density between Si-C bonding of nanocage decrease from a pure state, so the polarizability and stability of SiC nanocage decrease significantly from pristine models. On the other hand, maximum values of $E^{(2)}$ between donor and acceptor orbital in the A-a model occur in $\sigma\text{Si}_5\text{-C}_{10} \rightarrow \sigma^*\text{Si}_1\text{-C}_{13}$ (9.98 kcal/mol), in B-a model occur in $\sigma\text{Si}_1\text{-C}_{18} \rightarrow \sigma^*\text{Si}_1\text{-C}_{13}$ (10.11 kcal/mol), in C-a model occur in $\sigma\text{C}_{17}\text{-B}_{34} \rightarrow \sigma^*\text{Si}_{11}\text{-C}_{12}$ (2.89 kcal/mol), in D-a model occur in $\pi\text{C}_{15}\text{-N}_{34} \rightarrow \sigma^*\text{Si}_3\text{-C}_{13}$ (6.55 kcal/mol), in E-a model occur $\sigma\text{Si}_5\text{-B}_{34} \rightarrow \sigma^*\text{Si}_1\text{-C}_{13}$ (3.97 kcal/mol), and in F-a model occur in $\sigma\text{Si}_8\text{-N}_{34} \rightarrow n^*\text{Si}_{33}$ (3.28 kcal/mol). On the other hand, the results of NBO charge density indicate that the $\rho_{(\text{NBO})}$ around the Gly molecule is positive, and it indicates that the Gly has a donor electron effect, and electron charge transfer has taken place from the Gly molecule toward the nanocage.

Conclusions

In this work, the interaction of Glycine amino acid with $\text{Si}_{12}\text{C}_{12}$, $\text{BSi}_{11}\text{C}_{12}$, $\text{NSi}_{11}\text{C}_{12}$, $\text{BSi}_{12}\text{C}_{11}$, and $\text{NSi}_{12}\text{C}_{11}$ is investigated at the density functional theory. The geometrical results demonstrate that the bond length between Gly....SiC nanocage in the D-b, E-b, and F-a complexes is 1.56 Å and is lower than other complexes, so the interaction of Gly with SiC nanocage in these complexes is stronger than in other complexes. The negative values of E_{ads} , ΔH , and ΔG for all complexes reveal that the formation of the Gly&SiC nanocage complex is exothermic and spontaneous. The absolute values E_{ads} of studied complexes in a site decrease in order: D-a (–34.45 kcal/mol) > A-a (–29.46 kcal/mol) > B-a (–26.85 kcal/mol) > F-a (–19.71 kcal/mol) > E-a (–17.09 kcal/mol) > C-a (–34.45 kcal/mol). The $\Delta\Delta G_{(\text{w})}$ of the formation of Gly&SiC nanocage complexes in the water media are positive and unspontaneous in the thermodynamic approach. The AIM, LOL, and RDG results demonstrate that bonding between Gly and SiC nanocage is partially covalent or van der Waals type. The E_{gap} and η values of the pristine, and B&N doped $\text{Si}_{12}\text{C}_{12}$ nanocage with adsorbing of

Gly and reduce significantly from the pure state, therefore the conductivity and reactivity of the complexes are more than pure state. The results of this study confirm that the pristine, and B&N doped Si₁₂C₁₂ nanocage with Gly have a strong interaction in the biological system, and can affect and change the electrical properties of Glycine amino acid, which can be important in using these nanocages as a carrier, or sensor of the desired drugs.

Supplementary data

Figs. S1- S2 and Tables S1- S3 are given in supplementary data.

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References

- [1] Y. Yang, J. Wang, G. Wu, W. Wang, Z. Wu, Z. Dai, *Amino. Acid.* 45, 463 (2013).
- [2] R. Rezaei, W.W. Wang, Z.L. Wu, et al., *J. Anim. Sci. Biotech.*, 4, 7 (2013).
- [3] J. M. Phang, W. Liu, *C. Epigenetics.*, 8(3), 231 (2013).
- [4] J. J. Wang, Z. L. Wu, D. F. Li, et al. *Antioxid. Redox. Sig.*, 17, 282 (2012).
- [5] G. Xi, Y. He, C. Wang, *Chem. Eur. J.*, 16, 5184 (2010).
- [6] R. Wu, M. Yang, Y. Lu, Y. Feng, Z. Huang, Q. Wu, *J. Phys Chem. C.*, 112,15985 (2008).
- [7] W. Zhang, F. Zhang, Z. Zhang, S. Lu, Y. Yang, *Sci. Chin. Phys. Mech. Astronomy.*, 53, 1582 (2010).
- [8] F. Molani, S. Jalili, J. Schofield, *Monash. Chem.*, 146, 883 (2015).
- [9] X.-H. Sun, C.-P. Li, W.-K. Wong, N.-B. Wong, C.-S. Lee, S.-T. Lee, and B.-T. Teo, *J. Am. Chem. Soc.*, 124, 14464 (2002).
- [10] A. Wu, Q. Song, L. Yang, and Q. Hao, *Comput. Theo. Chem.*, 977, 92 (2011).
- [11] A. Ahmadi Peyghan, M. T. Baei, S. Hashemian, P. Torabi, *First Principles J. Clust. Sci.*, 24, 591 (2013).
- [12] M. T. Baei, .A. Ahmadi Peyghan, M. Moghimi, S. Hashemian, *J. Clust. Sci.* 23, 1119 (2012).
- [13] G.-X. Chen, D.-D. Wang, X. Yang, H.-X. Chen, J.-M. Zhang, *J. Super Cond. Nov. Magen.*, 28, 2605 (2015).
- [14] J.-M. Zhang, L.-Y. Chen, S.-F. Wang, and K.-W. Xu, *Eur. Phys. J. B.*, 73,555 (2010).
- [15] B. Xiao, H. Hu, J.-X. Zhao, Y. Ding, *Physica. E.*, 56, 377 (2014).
- [16] R. Ansari, M. Mirnezhad, M. Hosseinzadeh, *J. Mol. Model.*, 21, 51 (2015).
- [17] B. Zheng, J. E. Lowther, *Nanoscale.* 2, 1733 (2010).
- [18] I. K. Petrushenko, K. B. Petrushenko, *Monash. Chem.*, 146, 1603 (2015).
- [19] M. D. Esrafil, V. Mokhtar Teymurian, R. Nurazar, *Surf. Sci.*, 632, 118 (2015).
- [20] J. Jia, S.-p. Ju, D.-n. Shi, K.-f. Lin, *J. Nanopart. Res.*, 15, 1977 (2013).

- [21] R. Q. Wu, M. Yang, Y. H. Lu, Y. P. Feng, Z. G. Huang, Q. Y. Wu, *J. Phys. Chem. C.*, 112, 15985 (2008).
- [22] R. J. Baierle, R. H. Miwa, *Phys. Rev. B.*, 76, 205410 (2007).
- [23] T. Z. Meng, C. Y. Wang, S. Y. Wang, *Chem. Phys. Lett.*, 437, 224 (2007).
- [24] A. Gali, *Phys. Rev. B.*, 75, 085416 (2007).
- [25] S. Taheri, M. Shadman, A. Soltanabadi, Z. Ahadi, *Int. Nano. Lett.*, 4, 81 (2014).
- [26] A. Szabo, A. Gali, *Phys. Rev. B.*, 80, 075425 (2009).
- [27] J. X. Zhao, Y. H. Ding, *J. Chem. Theory. Com.* 5, 1099 (2009).
- [28] Y. Chen, H. Wang, J. Zhao, X. Wang, Q. Cai, Y. Ding, X. Wang, *J. Nanopart. Res.*, 14, 675 (2012).
- [29] M. D. Esrafil, R. Nurazar, *Struct. Chem.*, 26, 799 (2015).
- [30] Z. Mahdavi, M. Haghbayan, *App. Sur. Sci.*, 263, 553 (2012).
- [31] M. D. Esrafil, M. Ghanbari, R. Nurazar, P. Nematollahi, *J. Mol. Model.*, 21, 89 (2015).
- [32] J. Zhao, B. Gao, Q. Cai, X. Wang, X. Wang, *Theor. Chem. Acc.*, 129, 85 (2011).
- [33] M. Zhao, Y. Xia, L. Mei, *J. Comput. Theo. Nano sci.*, 9, 1999 (2012).
- [34] X. F. Duan, L.W. Burggraf, *J. Chem. Phys.*, 142, 034303 (2015).
- [35] M. Solimannejad, R. Rahimi, S. Kamalinahad, *J. Inorg. Oregano met. Ploy. Mater.* 27, 1234 (2017).
- [36] M. Solimannejad, A. K. Anjiraki, S. Kamalinahad, *Mater. Res. Expr.*, 4, 045011 (2017).
- [37] R. Rahimi, M. Solimannejad, *Str. Chem.*, 31, 133 (2020).
- [38] H. Jouypazadeh, H. Farrokhpour, *J. Mole. Stru.*, 1164, 227 (2018).
- [39] P. Fallahi, H. Jouypazadeh, H. Farrokhpour, *J. Mole. Liq.*, 260, 138 (2018).
- [40] M. Rakhshi, M. Mohsennia, H. Rasa, M. Rezaei Sameti, *Vacuum.*, 155, 465 (2018).
- [41] M. Rezaei-Sameti, P. Zarei, *Adsorption.* 24, 757 (2018).
- [42] M. Rezaei-Sameti, H. J. Behbahani, *Phys. Chem. Res.*, 6 (1), 31 (2018).
- [43] M. Rezaei-Sameti, B. Amirian, *Asian. J. Nanosci. Mater.* 1(4), 262 (2018).
- [44] M. Rezaei-Sameti, F. Zanganeh, *J. Sulfur. Chem.*, 38(4), 384 (2017).
- [45] T. Yanai, D. P. Tew, N. C. Handy, *Chem. Phys. Lett.* 393, 51 (2004).
- [46] M. J. Frisch, et al., *GAUSSIAN 09*, Revision D.01, (2009).
- [47] R. Bader, *Atoms in Molecule: A Quantum Theory*, USA, (1994).
- [48] M. Doust Mohammadi, H.Y. Abdullah, *J. Comp. Biophy. Chem.* 20, 765 (2021)
- [49] H. Jacobsen, *Can. J. Chem.*, 86, 695(2008).
- [50] T. Lu, F. Chen, *J. Comput. Chem.*, 33(5), 580 (2012).
- [51] R. Cammi, *J. Chem. Phys.*, 131(16), 164104 (2009).
- [52] E. R. Jonson, S. Keinan, P. Mori-Sanchez, J. Contreras-Garc, A. J. Cohen, W. Yang, *J. Am. Chem. Soc.*, 132, 6498 (2010).
- [53] M. Cossi, V. Barone, *J. Chem. Phys.*, 115, 4708 (2001).
- [54] Y. T. Sun, P. Y. Huang, C. H. Lin, K. R. Lee, M. T. Lee, *Bio. J.*, 5, 515 (2015).
- [55] M. Rezaei-Sameti, Z. Iraj Borojeni, *J. Biomol. Stru. Dynamics*, 41, 5882(2023).

- [56] J. L. de Assis, P. V. P. Grobas, A. M. Signoretti, M.A.C. Fernandes, B. F. Miranda, R. H. F. Silva, M. Valverde, P. A. Einicker-Lamas, D. Beule, *Bio. J.*, 110, 489 (2016).
- [57] S. Li, *Light-Emitting Devices, Semiconductor Physical Electronics*, second ed., Springer, Berlin (2006).
- [58] L. J. Na, C. Z. Rang, Y. S. Fang, *J. Zhejiang, Univ. Sci.*, 6, 584 (2005).
- [59] G. Keresztury, S. Holly, J. Varga, G. Besenyei, A. V. Wang, J. R. Durig, *Spec. Chim. Acta.*, 49, 2007 (1993).

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