

B₁₂N₁₂ nanocage as a potential adsorbent for the removal of aniline from environmental systems

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Density functional theory (DFT) calculations at the B3LYP/6-31G* level were performed to investigate aniline adsorption on a B₁₂N₁₂ nanocage in terms of energetic, geometric, and electronic properties. It was found that aniline is more likely adsorbed *via* its nitrogen atom on the B₁₂N₁₂ surface. The adsorption energy of aniline on the nanocage in the most stable state is -24.95 kcal/mol and about 0.34|e| is transferred from the aniline molecule to the nanocage. The calculated density of states shows that the electronic properties of the B₁₂N₁₂ nanocage are changed after the aniline adsorption process. Fermi level is dramatically changed from -4.28 eV in the pristine nanocage to higher energies after the aniline adsorption, which decreases the work function of the nanocage. The results show that the B₁₂N₁₂ nanocage can be used for adsorption of toxic aniline molecules from environmental systems.

Keywords: boron nitride nanocage, aniline, adsorbent, electronic structures

INTRODUCTION

Aniline (C₆H₅NH₂) is an important organic compound due to its wide applications in the manufacturing of dyestuffs, rubbers, pesticides, plastics and paints [1]. Aniline is released throughout the environment by industrial wastewater and/or through degradation of some of the above mentioned compounds [2-3]. Much attention should be taken concerning the contamination of groundwater because aniline is a toxic and persistent pollutant that is very harmful not only to aquatic life but also to humans [4- 5]. Aniline is toxic by inhalation of the vapor, ingestion, or contact with the skin. Therefore, it is very important to remove aniline from wastewater or environment.

In recent years, there have been several studies on the removal of aniline from wastewater [6-7]. However, these methods cannot be currently widely applied due to high cost, long duration, etc. Therefore, further study of aniline adsorption is an important task. Among different methods, using nanostructures as adsorbents is an interesting approach because of their unique physical and chemical properties including high surface/volume ratio and very sensitive electronic properties. For example, the adsorption of simple molecules on nanostructures has a considerable potential for applications in surface modification [8], fuel cells

[9], gas sensors [10] and hydrogen storage [11]. Among nanostructures, boron nitrides (BN)_x are isoelectronic to the fullerenes and have attracted considerable attention due to their high-temperature stability, low dielectric constant, large thermal conductivity, wide-band gap, and oxidation resistance [12-14]. Seifert *et al.* [15] showed that B₁₂N₁₂, B₁₆N₁₆ and B₂₈N₂₈ are magic BN fullerenes and B₁₂N₁₂ appears to be more stable than the others. Oku *et al.* [16] have synthesized B₁₂N₁₂ nanocage by laser desorption time-of-flight mass spectrometry, showing that these clusters consist of eight hexagon rings and six tetragon rings. The aim of this research is to investigate theoretically the adsorption of aniline on a B₁₂N₁₂ nanocage based on the analysis of structure, energies, stability, and electronic properties using density functional theory (DFT) calculations.

COMPUTATIONAL METHODS

Spin-unrestricted B3LYP/6-31G* level of theory was used to describe the adsorption of aniline on surfaces of B₁₂N₁₂ nanocage, specifically the geometry optimizations, energy calculations, and density of states (DOS) analysis. B3LYP is the commonly used approach for investigations of different nanostructures [17-18].

This method was used to calculate the adsorption energy (E_{ad}) of aniline on the surface of B₁₂N₁₂ nanocage as follows:

$$E_{ad} = E_{\text{aniline/B}_{12}\text{N}_{12}} - [E_{\text{B}_{12}\text{N}_{12}} + E_{\text{aniline}}] \quad \text{Eq. (1)}$$

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where $E_{\text{aniline}/B_{12}N_{12}}$ is the total energy of the complex (adsorbed aniline molecule on the $B_{12}N_{12}$ surface), $E_{B_{12}N_{12}}$ and E_{aniline} are the total energies of the pristine $B_{12}N_{12}$ nanocage and the aniline molecule. Negative or positive value for E_{ad} is referred to exothermic or endothermic processes, respectively. The canonical assumption for a Fermi level is that in a molecule at 0 K it lies approximately in the middle of the energy gap (E_g). Also, the chemical potential of a molecule lies in the middle of the E_g . Therefore, the chemical potential of a free gas of electrons is equal to its Fermi level as traditionally defined. Herein, the Fermi level of the considered systems is at the middle of the E_g . All calculations were carried out using the GAMESS suite of programs [19].

RESULTS AND DISCUSSION

The structure of the optimized $B_{12}N_{12}$ nanocage is shown in Fig. 1a. It is formed from eight 6-membered (hexagon) rings and six 4-membered (tetragon) rings with T_h symmetry so that the calculated electric dipole moment is zero.

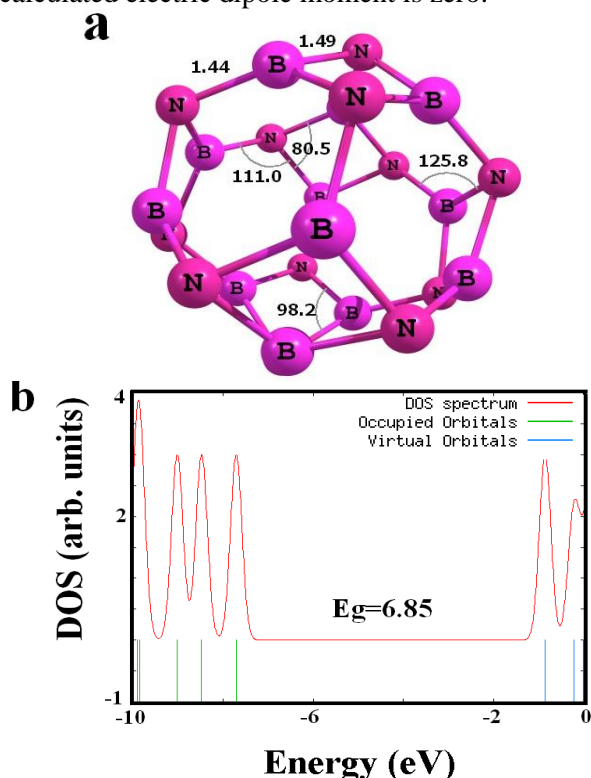


Fig. 1. Structural parameters (a) and electronic density of states (DOS) (b) for the optimized structure of the $B_{12}N_{12}$ nanocage.

Two types of B–N bonds are identified in the $B_{12}N_{12}$ nanocage, one with a bond length of 1.44 Å

which is shared between two hexagon rings, and the other with a length of 1.49 Å which is shared between a tetragon and a hexagon ring. The results are in good agreement with those obtained by Beheshtian *et al.* [20]. The natural bond orbital (NBO) population charge analysis showed a net charge transfer of 1.17 |e| from B to N atom in the nanocage, indicating an ionic nature. The angles in the 4-membered and the 6-membered rings in $B_{12}N_{12}$ nanocage vary from 80.5° to 98.2° and from 111.0° to 125.8°, respectively.

In order to find the minimum adsorption configurations of single aniline adsorbed on the $B_{12}N_{12}$ nanocage, various possible adsorption structures were considered. The molecular electrostatic potential (MEP) surfaces of single aniline are shown in Fig. 2. As can be seen, the partial negative charge on the N atom and phenyl group of aniline makes it reactive toward the Lewis acid sites of B atoms. Therefore, aniline can approach the walls of the nanocage *via* the N atom (amino group) and/or *via* the phenyl ring (π - π interaction). Finally, only two local minima structures were obtained for the adsorption of aniline *via* the phenyl group and three stable structures *via* the nitrogen atom that are shown in Figs. 3 and 4.

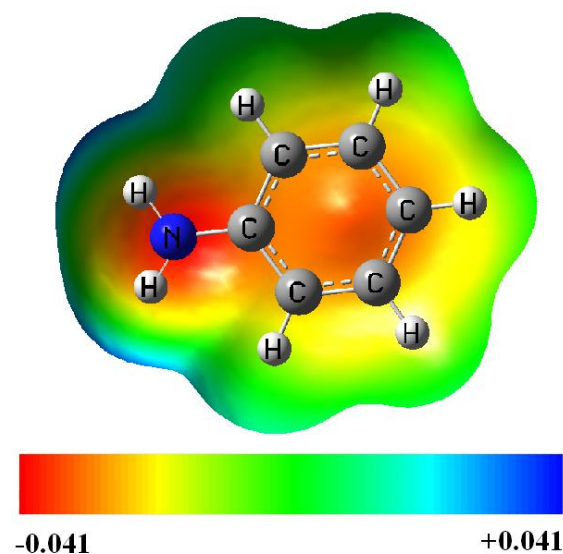


Fig. 2. Molecular electrostatic potential surface of the aniline molecule. The surfaces are defined by the 0.0004 electrons/b³ contour of the electronic density. Color ranges, in a.u.

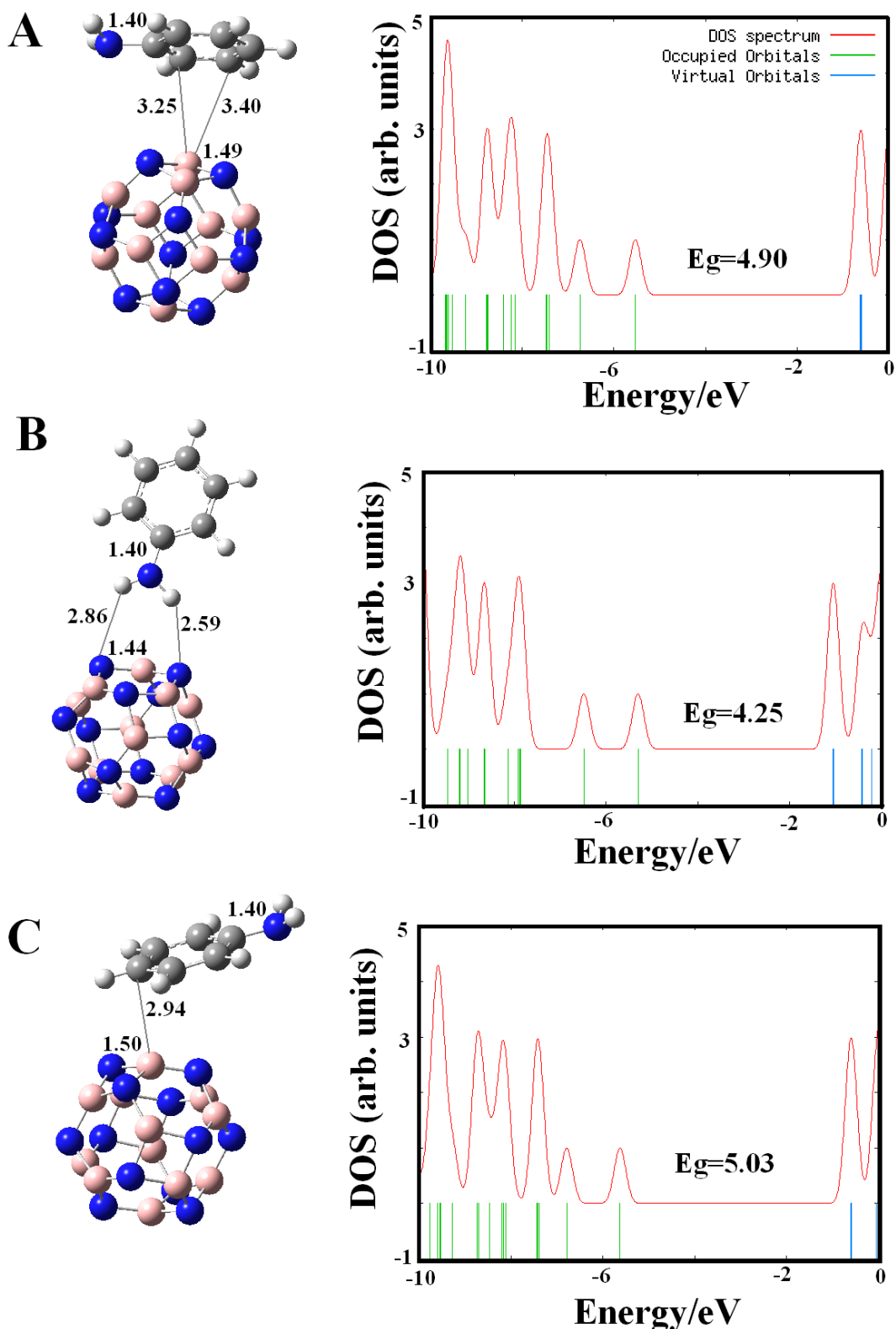


Fig. 3. Models for three different physisorption configurations and their density of states (DOS) plots. Distances are in Å.

As shown in Fig. 3, configuration A shows an interaction between the carbon atoms of aniline molecule (phenyl group) and the B atoms of a

tetragon ring of the nanocage so that the two C atoms of aniline are closer to one B atom of the nanocage with distances of 3.25 and 3.40Å. In this

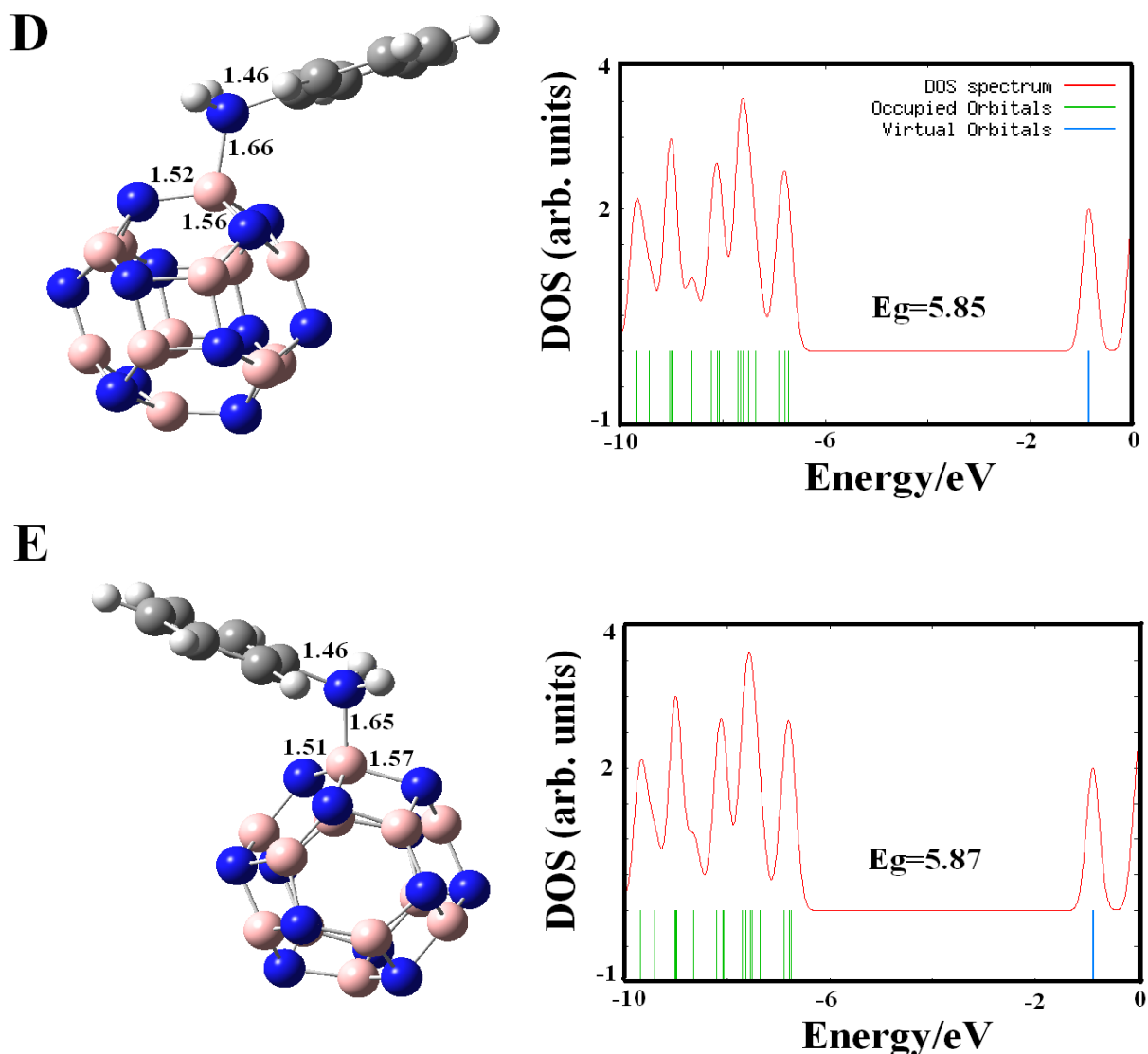


Fig.

4. Models for two different chemisorption configurations and their density of states (DOS) plots. Distances are in Å.

configuration, a net charge of 0.02 electrons is transferred from the aniline to the nanocage and E_{ad} is about -2.04 kcal/mol (Table 1). The above results indicate that this interaction is weak and should be considered as physisorption. Another aniline physisorption approach is shown in Fig. 2B in which the aniline molecule is located atop of a hexagon ring and its hydrogen atoms, so that the distances between the two H atoms of aniline and the two N atoms of the hexagon ring are 2.86 and 2.54 Å, respectively. This configuration has an E_{ad} of -2.23 kcal/mol and does not show charge transfer to take place between aniline and $B_{12}N_{12}$ nanocage. In Fig. 2, configuration C, the aniline molecule weakly interacts with the $B_{12}N_{12}$ nanocage through van der Waals forces and *via* the phenyl group. The smallest distance of the molecule to the nanocage is found to be 2.94 Å. Based on the natural bond orbital charges (NBO) analysis, a net charge of 0.04 electrons is transferred from aniline to the nanocage and its corresponding calculated E_{ad} value is -2.41 kcal/mol, indicating that the interaction is physisorption in nature. Moreover, the adsorption of aniline on the nanocage in the above complexes has no local structural deformation on both the aniline molecule and the nanocage. The small E_{ad} values and the large interaction distances in the above aniline/ $B_{12}N_{12}$ complexes indicated that aniline cannot be significantly adsorbed on the sites and undergoes weakly physical adsorption on the pristine nanocage.

Covalent functionalization is the other type of interaction between aniline and the $B_{12}N_{12}$ nanocage, so that the N atom of the molecule is bonded to one B atom of the nanocage (Fig. 4). The E_{ad} for the configuration D (-24.37 kcal/mol) is a little smaller than that of E (-24.95 kcal/mol) with a rather significant NBO charge transfer of $0.34|e|$ from the aniline to the nanocage. Therefore, the B atoms of the nanocage are a thermodynamically

more favorable site for the adsorption of aniline because the partial negative charge on the N atom of aniline makes it reactive toward the Lewis acid sites of the B atoms. The corresponding interaction distance between the B atom of the nanocage and the N atom of aniline for configurations **D** and **E** is 1.66 and 1.65 Å, respectively. Also, the electric dipole moment has increased from 0.00 Debye in the pristine nanocage to 8.35 and 8.38 Debye in the configurations **D** and **E**. Small bond length of B...N, significant change in dipole moment, and more negative E_{ad} for the applied configurations indicate that the aniline binds to the exposed B atom and can receive electrons from the lone pair orbital of nitrogen. In addition, the adsorption of aniline in these configurations shows almost local structural deformation on both the aniline molecule and the B₁₂N₁₂ nanocage. The C-N bond length of aniline increased from 1.40 Å in the isolated aniline to 1.46 Å in the adsorbed state. Also, the length of B–N bonds in the pristine B₁₂N₁₂ increased from 1.44 and 1.49 Å to 1.52 and 1.56 Å in configuration **D** and to 1.51 and 1.57 Å in configuration **E** for B–N bonds located in immediate neighborhood of the aniline molecule. All above indicates that aniline is strongly chemisorbed on B₁₂N₁₂ and the nanocage can be a promising candidate for the adsorption of aniline from environmental systems.

However, in order to investigate the effect of adsorption of the aniline molecule on the electronic properties of the B₁₂N₁₂ nanocage, the total densities of states (DOS) of aniline/B₁₂N₁₂ complexes were studied. As shown in Fig. 1b and Table 1, the calculated energy gap ($E_g = E_{LUMO} - E_{HOMO}$) of the B₁₂N₁₂ nanocage is 6.85 eV, indicating that the nanocage is an insulator. DOSs for different models of the aniline/B₁₂N₁₂ complex are shown in Figs. 2-4. In comparison to the DOS of the pristine B₁₂N₁₂ nanocage and the physisorption configurations **A**, **B**, **C**, it is found that their E_g values have changed in the range of

26.57-37.96 % after aniline adsorption. The results show that the electronic properties of the B₁₂N₁₂ nanocage are sensitive to aniline in the configurations. Also, the E_g values for the chemisorption configurations **D** and **E** have changed in the range of 14.31-15% after aniline adsorption, indicating that the changes in the electronic properties of the nanocage from physisorption to chemisorption are reduced. Also, the E_g value for all aniline/B₁₂N₁₂ complex models is reduced which might result in an electrical conductivity change of the nanocage according to the following equation [21]:

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right) \quad \text{Eq. (2)}$$

where σ is the electric conductivity of the complexes and k is the Boltzmann's constant. According to the above equation, smaller E_g at a particular temperature leads to a higher electric conductivity. Table 1 indicates that the Fermi level energy (E_{FL}) of the aniline/B₁₂N₁₂ complex models is increased. This increase in E_{FL} with aniline adsorption leads to a decrement in the work function which is important in field emission applications. The decrement in the work function shows that the field emission properties of the complexes are improved upon aniline adsorption. The values of the induced electric dipole moment (D_M) vector obtained from these calculations increased with aniline adsorption, thus increasing the reactivity of the nanocage.

In order to interpret the aniline interaction with the B₁₂N₁₂ nanocage, we drew plots of the HOMO and LUMO for the most stable structure (configuration **E**). As shown in Fig. 5, after aniline adsorption, the HOMO is more localized on the nanocage. Energy level of HOMO in this configuration is -6.75 eV, indicating that it has become less stable upon aniline adsorption due to

Table 1 Calculated adsorption energy (E_{ad} , kcal/mol), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g), and Fermi level energy (E_{FL}) of the systems in eV, sum of NBO charges on the adsorbed aniline (Q_T), and dipole moment (D_M) in Debye.

Structure	E_{ad}	E_{HOMO}	E_{LUMO}	E_g	$^a\Delta E_g(\%)$	$^bQ_T[e]$	E_{FL}	D_M
B ₁₂ N ₁₂	-	-7.71	-0.86	6.85	-	-	-4.28	0.00
A	-2.04	-5.53	-0.63	4.90	28.47	0.02	-3.08	2.72
B	-2.23	-5.30	-1.05	4.25	37.96	0.00	-3.18	2.35
C	-2.41	-5.63	-0.60	5.03	26.57	0.04	-3.12	3.52
D	-24.37	-6.72	-0.87	5.85	15.00	0.34	-3.76	8.38
E	-24.95	-6.75	-0.88	5.87	14.31	0.34	-3.82	8.40

^aChange in HOMO–LUMO gap of B₁₂N₁₂ nanocage after aniline adsorption

^b Q is defined as the total natural bond orbital charges on the aniline molecule and positive values mean charge transfer from the aniline molecule to the B₁₂N₁₂ nanocage

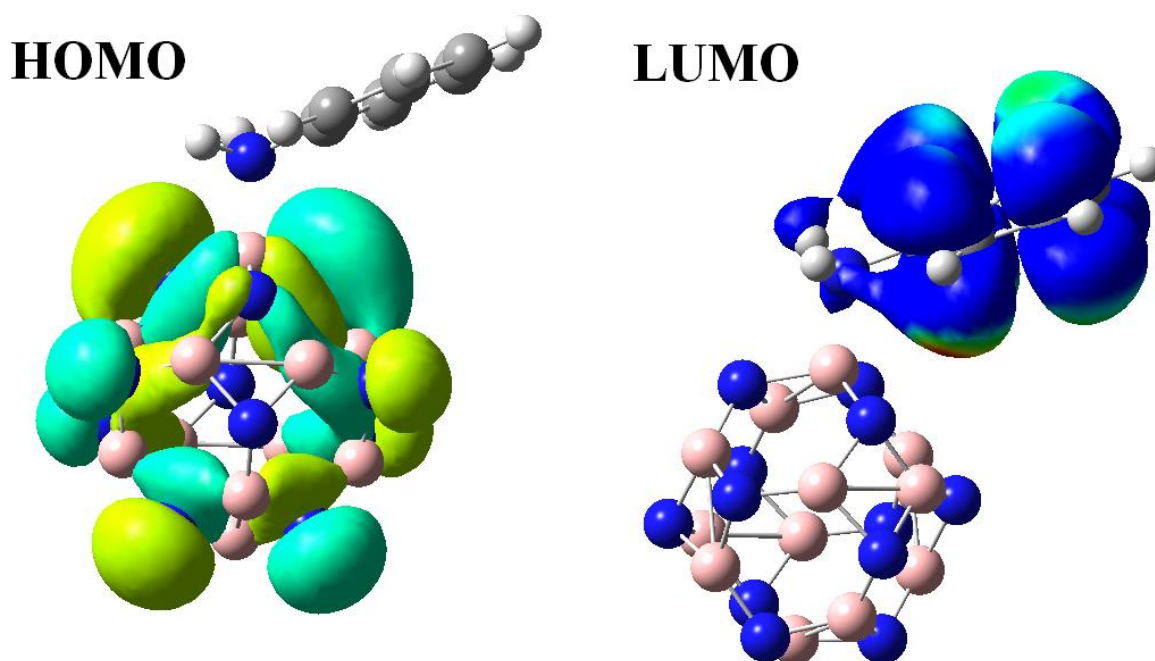


Fig. 5. HOMO and LUMO profiles of configuration E.

stronger charge transfer of aniline to the nanocage (energy level of HOMO of pristine $B_{12}N_{12}$ nanocage is -7.71 eV). On the other hand, LUMO for the configuration is localized on the aniline molecule, indicating that the LUMO has not contributed to the adsorption process. However, the study of the electronic properties of $B_{12}N_{12}$ shows that the aniline molecule is strongly chemisorbed on the $B_{12}N_{12}$ and the nanocage can be used for aniline adsorption in environmental systems.

CONCLUSIONS

Aniline is adsorbed on the $B_{12}N_{12}$ nanocage surface in molecular form through interaction of the amino group with surface active sites (B atoms). The mechanism of the intermolecular interaction between aniline and the $B_{12}N_{12}$ nanocage surface is mediated through donation of an electron lone pair from the amino group to the Lewis acid sites of the B atoms. Adsorption energy of aniline on $B_{12}N_{12}$ in the most stable configuration was calculated to be -24.95 kcal/mol with a charge transfer of $0.34|e|$ from aniline to the nanocage. The calculations also indicated that attachment of the aniline on the surface of the $B_{12}N_{12}$ nanocage induces changes in the electronic properties of the nanocage and its E_g is reduced after the adsorption process. With aniline adsorption the work function decreased which may facilitate the field electron emission from aniline to the $B_{12}N_{12}$ surface. The results showed that the

$B_{12}N_{12}$ nanocage can significantly attach aniline molecules and the pristine $B_{12}N_{12}$ nanocage can be an efficient potential adsorbent for adsorption of the aniline from environmental systems.

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B₁₂N₁₂-НАНОКЛЕТКА КАТО ПОТЕНЦИАЛЕН АДСОРБЕНТ ЗА ОТСТРАНЯВАНЕТО НА АНИЛИН В ОКОЛНАТА СРЕДА

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(Резюме)

Извършени са пресмятане на the B3LYP/6-31G* -ниво по теорията на функционалната теория на полето (DFT) за изследване на адсорбцията на анилин в наноклетка от B₁₂N₁₂ като енергетични, геометрични и електронни отнасяния. Намерено е, че анилинят се адсорбира чрез своя азотен атом в молекулата си на повърхността на B₁₂N₁₂. Адсорбционната енергия на анилина върху наноклетката в най-стабилното си състояние е -24.95 kcal/mol и около 0.34|e| е пренесената от молекулата на анилина към наноклетката. Пресметнатата енергия на състоянието показва, че електронните свойства на наноклетката B₁₂N₁₂ се променят при адсорбцията на анилин. Нивото на Fermi се променя драстично от -4.28 eV в началната наноклетка до високи енергии след адсорбцията на анилин, които намаляват работата в наноклетката. Резултатите показват, че наноклетката B₁₂N₁₂ може да се използва за адсорбция на анилинови молекули в системи от околната среда.