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Research Paper

Computational studies on the Li-B12N12 as potential adsorbent for aniline from environment

Mozhgan Sabzehzari*

[a]Department of Chemistry, School of Basic Science, Jundi-Shapur University of Technology, Dezful, Iran

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Abstract

Aniline (C6H5NH2) is an important organic compound due to its wide applications in the manufacturing of dyestuffs, rubbers, pesticides, plastics and paints. Aniline is released throughout the environment by industrial wastewater and/or through degradation of some of the above mentioned compounds. Adsorption of aniline molecule on the surface of Li-encapsulated B12N12 nanocage is scrutinized using at Density functional theory (DFT) calculations to investigating its potential as chemical adsorbent. DFT calculations at the B3LYP /6-31G*level were performed in terms of energetic, geometric, and electronic properties. People had shown that piristin nanocages are weak absorbents. In order to improve the properties of the nanocage adsorbent, Li encapsulating process was investigated. The obtained results show that encapsulating process changes electrical properties of B12N12 dramatically. It was found that aniline is more likely adsorbed via its nitrogen atom on the Li-B12N12 surface. The adsorption energy of aniline on the nanocage in the most stable state is -45.06 kcal/mol and about 0.38|e| is transferred from the aniline molecule to the nanocage. It is expected that Li-encapsulated B12N12 acts as new potential nanosensor for toxic aniline molecules from environmental systems.

Keywords: Boron nitride nanocage, aniline, adsorbent, electronic structures.

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Introduction

A common problem in most industries is the disposal of large volumes of wastewater containing potentially toxic organic solutes Considering general safety and the environmental consequences of these solutes, their presence in wastewater requires treatment prior to disposal. Aniline is one of the most common pollutants found in effluents from the pharmaceutical, pesticide, dyestuff, petrochemicals and agrochemical industries. Aniline harmfully affects both public health and environmental quality. Aniline-containing wastewater has created a series limits on the release of aniline have been of serious environmental problems due to its high toxicity and environmental accumulation. Strict established. Traditionally, aniline-containing wastewater is treated with photodecomposition [1–3], electrolysis [4], adsorption oxidation [7,8], biodegradation [9] and other processes.

Generally adsorption technology has proved to be one of the most effective techniques in the separation and removal of a wide variety of organic pollutants from wastewater [10]. These techniques do not produce harmful byproducts, and the regeneration of both the adsorbent and pollutants is possible. One challenge faced by adsorption technologies is the discovery of new adsorbents that successfully remove organic pollutants, such as aniline, from aqueous solutions. After discovery of C60 in 1985[11], scientists paid attention to other fullerene-like materials such as (BN)n cages with n = 12, 24, 28 and 32 [12-15]. Among boron nitride nanocages, B12N12 is the

* Corresponding Author's e-mail: msabzehzari@jsu.ac.ir

most stable structure with The point group [12]. B12N12 nanocluster has been synthesized by Oku et al. in 2004 by using laser desorption time-of-flight mass spectrometry method [16,17]. Experimental results showed that the synthesized cage consists of 8 hexagon and 6 tetragonal B-N rings, with two distinct bonds between B and N atoms. One of the bonds is between two six membered rings (6-MR) and another one locates between one six membered and one four membered rings (4-MR) B12N12 has been attracted attention of many researchers due to notable physical and chemical properties such as oxidation resistance, wide band gap, large surface to volume ratio, low dielectric constant and high temperature stability [18,19] . Several quantum mechanical studies about adsorption of different molecular moieties on the exterior surface of B12N12 nanocage were reported recently [20-34].
In the current study, an attempt has been made to present Li-encapsulated B12N12 nanocge with its unique electronic properties as a promising sensor for detection of Aniline. Main focuses have been placed on adsorption energies and the changes of electronic properties of Li-encapsulated B12N12 in the presence of aniline. The advantage of the present work is introducing a nanostructure as a sensor for Aniline.

Computational Methods

All the calculations were performed using Gaussian 09 package. Geometry optimizations energy calculations and density of states (DOS) analysis were performed on the Li-B12N12 nanocage and Aniline/Li-B12N12 complexe using B3LYP functional with 6-31G(d) basis set. To study the adsorption systems, the van der Waals interactions are recommended to be considered, while B3LYP method does not consider it. We have shown that it is not important in this system, so B3LYP is a reliable method in the present study (see supporting information). Vibrational frequencies were also calculated at the same level of theory to confirm all the stationary points corresponding to the local minima on the potential energy surface. Adsorption energy (Ead) of the studied complexes is obtained in the usual way as

$$Ead = Ecomplex - (E_{Aniline} + E_{Li\text{-}B12N12}) + EBSSE \quad (1)$$

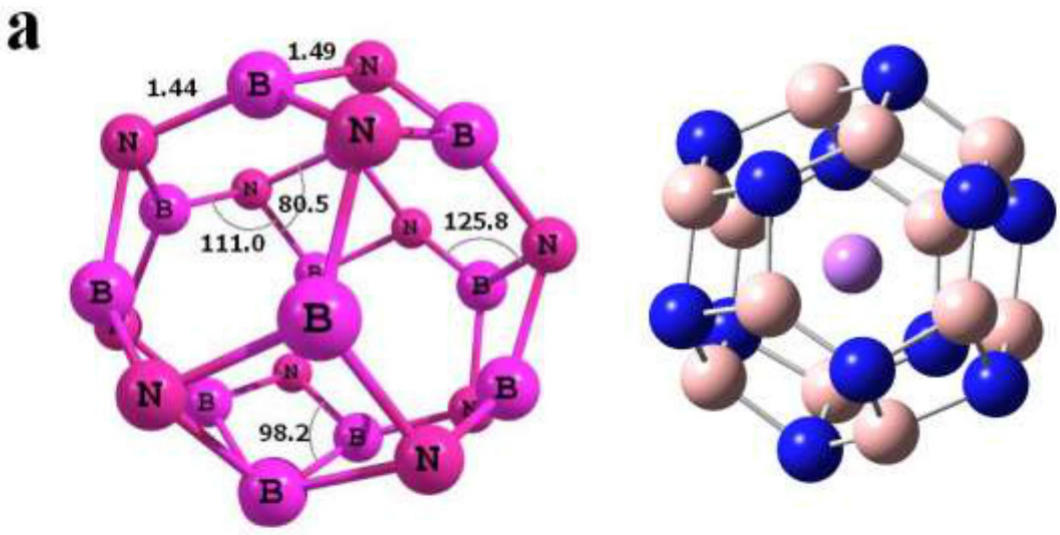
Where Ecomplex corresponds to the energy of Li-B12N12 in which Aniline has been adsorbed on the cage, $E_{Li\text{-}B12N12}$ is the energy of the isolated cage and $E_{Aniline}$ is the energy of a single Aniline molecule. EBSSE is the energy of the basis set superposition error calculated using the counterpoise method.
Negative or positive value for Ead is referred to exothermic or endothermic processes, respectively.
Natural bond orbitals (NBO) analysis was performed to obtain charge transfer between B12N12 nanocage and Aniline molecule. GaussSum program was also used to present density of states (DOS) pristine B12N12 and Li-B12N12 and the mentioned complexe.
Thermodynamic parameters of adsorption (ΔHad and ΔGad) are obtained from the following equations:

$$\Delta Had = Hcomplex - (HAniline + H_{Li\text{-}B12N12}) \quad (2)$$

$$\Delta Gad = \Delta Had - T\Delta Sad = \Delta Had - T(Scomplex - (S_{Aniline} + S_{Li\text{-}B12N12})) \quad (3)$$

RESULTS AND DISCUSSION

The structure of the optimized B12N12 nanocage is shown in Fig. 1a. It is formed from eight 6-membered (hexagon) rings and six 4-membered (tetragon) rings with Th symmetry so that the calculated electric dipole moment is zero.



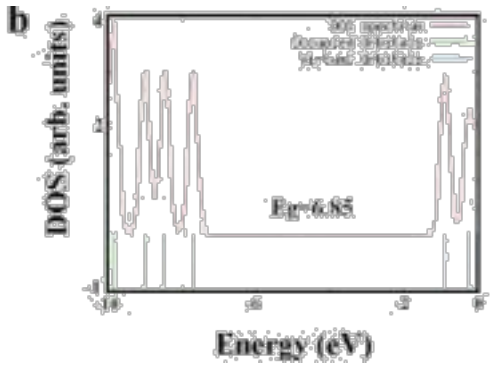


Fig 1: Structural parameters (a) and electronic density of states (DOS) (b) for the optimized structure of the pristine B12N12 nanocage and Li-encapsulated B12N12.

Two types of B–N bonds are identified in the B12N12 nanocage, one with a bond length of 1.44Å. which is shared between two hexagon rings, and the other with a length of 1.49Å 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 ionicity nature. The angles in the 4-membered and the 6-membered rings in B12N12 nanocage vary from 80.5° to 98.2° and from 111.0° to 125.8°, respectively. The placement of the lithium atom in the center of the boron nitride cage (Li-encapsulated B12N12) does not alter its symmetry. Also, the bond lengths and bond angles in the Li-encapsulated B12N12 do not change much compared to pristine B12N12.

In order to find the minimum adsorption configurations of single aniline adsorbed on the Li-B12N12 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 one local minima structure was obtained for the adsorption of aniline via the phenyl group and the nitrogen atom that are shown in Figs. 3.

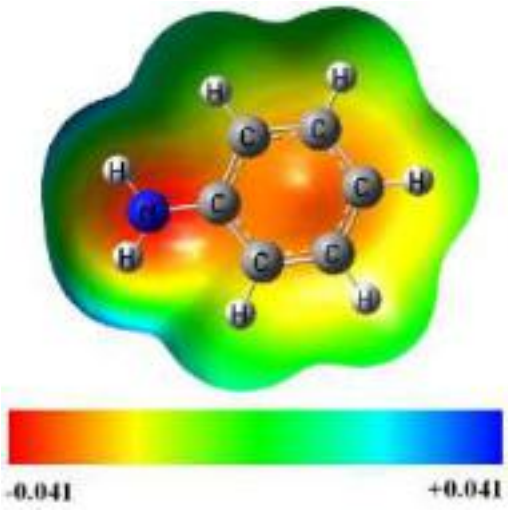


Fig 2: Molecular electrostatic potential surface of the aniline molecule. The surfaces are defined by the 0.0004 electrons/b3 contour of the electronic density. Color ranges, in a.u.

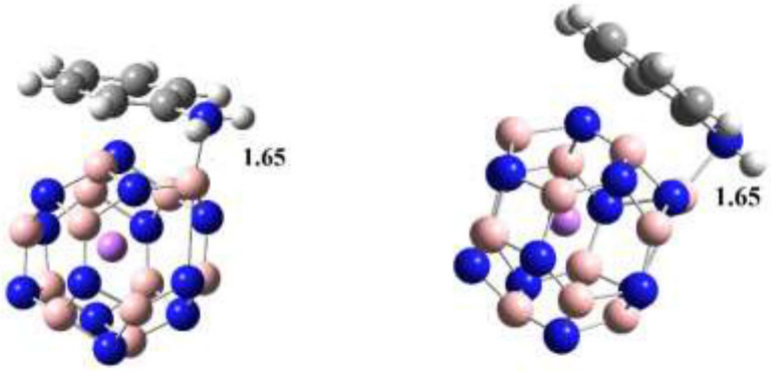


Fig 3: Stable configuration of Li-B12N12-Aniline. Distances are in Å.

Covalent functionalization is the other type of interaction between aniline and the Li-B12N12 nanocage, so that the N atom of the molecule is bonded to one B atom of the nanocage (Fig. 3). The Ead for the configuration is (-45.06 kcal/mol) with a rather significant NBO charge transfer of 0.38|e| from the aniline to the nanocage. Therefore, the B atoms of the nanocage are a thermodynamicallymore 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 this configuration is 1.65 Å. Also, the electric dipole moment has increased from 0.00 Debye in the pristine nanocage and Li-B12N12 nanocage to 8.35 Debye in this configuration. Small bond length of B…N, significant change in dipole moment, and more negative Ead for the applied this configuration 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 this configuration shows almost local structural deformation on both the aniline molecule and the Li encapsulated 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 Li- B12N12 increased from 1.44and 1.49Å to 1.52, 1.56 and 1.82 Å in this configuration for B–N bonds located in immediate neighborhood of the aniline molecule. All above indicates that aniline is strongly chemisorbed on Li-B12N12 and the nanocage can be a promising candidate for the adsorption of aniline from environmental systems.

Conclusions

Aniline is adsorbed on the Li encapsulated B12N12 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 Li-B12N12 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 Li-B12N12 in the most stable configuration was calculated to be -45.06 kcal/mol with a charge transfer of 0.38|e| from aniline to the nanocage. The calculations also indicated that attachment of the aniline on the surface of the Li-B12N12 nanocage induces changes in the electronic properties of the nanocage and its Eg is reduced after the adsorption process. The results showed that the Li-B12N12 nanocage can significantly attach aniline molecules and the Li-B12N12 nanocage can be an efficient potential adsorbent for adsorption of the aniline from environmental systems.

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