



## Study of $B_{12}N_{12}$ and $AlB_{11}N_{12}$ fullerene as $H_2S$ absorbent and sensor by computational method

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### Abstract

The absorption of the  $H_2S$  on the small boron nitride fullerene ( $B_{12}N_{12}$ ) and its Al-inserted analog was theoretically analyzed by density functional theory. The structural stability was based on the minimum energy and non-complex vibrational frequencies. Different sites and orientations of  $H_2S$ , using the monomer unit, were considered. Compared with the weak physisorption on the pristine  $B_{12}N_{12}$ , the  $H_2S$  molecule presents strong physisorption on both Al-inserted fullerene, as indicated by the calculated geometrical structures and electronic properties for these systems. It is suggested that the Al-inserted  $B_{12}N_{12}$  presents high sensitivity to  $H_2S$ . Based on calculated results, the Al-inserted  $B_{12}N_{12}$  is expected to be a potential novel sensor for detecting the presence of  $H_2S$ .

**Keywords:** Hydrogen Sulfide, Boron Nitride Fullerene,  $B_{12}N_{12}$ , Al-inserted, Density Functional Theory Calculations

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## 1. Introduction

Hydrogen sulphide ( $H_2S$ ) is a colourless and extremely flammable toxic gas at a high concentration [1-3]. It is produced in small amounts along with the biogas from the fermentation of organic materials [4, 5], and is regarded as both an environmental and industrial pollutant.

Boron nitride (BN) nanostructures such as nanotubes [6], nanocapsules [7], and fullerenes have received much attention as promising materials for the electronic industry because of their unique structures and properties [8].

For the past few years, many studies have been made on the atomic arrangement and electronic structures of carbon fullerenes and nanotubes [9-16], because they have provided a band gap energy that is dependent on the helical structure and diameter [11, 13, 15, and 16]. BN has hollow cage structure similar to fullerenes [17-19], nanotubes [6, 16, 20-24] and nanocapsules [25], and is expected to show various properties such as chemical stability, semiconductor and heat resistance. These materials are expected to be useful as electronic devices, high heat-resistance semiconductors and insulator lubricants.

The boron nitride cages and nanotubes have been extensively investigated due to their high temperature stability, low dielectric constant, large thermal conductivity, ultra-violet light emission and oxidation resistance [6, 19, 26, and 27]. Because of the polar nature of B-N bonds, BN nanostructures are expected to have higher reactivity than their carbon analogs. Moreover, due to the significant charge separation between the boron and nitrogen atoms, the boron atom (electron deficient) and nitrogen atom (electron rich) can be viewed as Lewis acid and base, respectively. Therefore, BN nanostructures can be considered as a nano-metal catalyst with Lewis acid-base pairs.

In this work,  $B_{12}N_{12}$  was analyzed and its Al-inserted derivatives were selected as an absorber for  $H_2S$  Sensor. Electronic Energy, Dipole Moment differences, Electronic Chemical Potential and Energy Gap are calculated and results were reported.

## 2. Computational details

All calculations have been performed using Gaussian03 software package [28]. Full geometry optimizations are accomplished by means of Becke- three parameter density functional with Lee- Yang-Parr correlation functional (B3LYP)[29,30] with the 6-31G(d) basis sets[31]. The GaussView program was used for visual inspection of the normal modes and to propose an initial geometry of the investigated molecules. Using the ground state optimized geometry at the respective levels of theory; the vibrational frequencies were calculated to characterize the nature of the structures under study and to evaluate the vibrational spectra. This work has investigated their structural, electronic and spectroscopic properties on the singlet ground state. As a stability criterion of different configurations, Interaction energy  $E_{int}$  for each system was calculated using the following equation [32].

$$E_{int}=E_{tot}-(E_{fullerene} + E_{H_2S})$$

where  $E_{tot}$  is the total energy of the fullerene- $H_2S$  system derived from the optimization calculation, and  $E_{fullerene}$  and  $E_{H_2S}$  are the electronic energy of fullerene and  $H_2S$  atoms respectively.

### 3. Results and discussion

The interaction of  $H_2S$  molecule with  $B_{12}N_{12}$  and Al-inserted  $B_{12}N_{12}$  fullerenes was investigated from four directions, forming four structures as shown in Fig. 1. All four structures were optimized and two structures were obtained. The optimized structures were obtained for Al-inserted fullerene and two-component systems too. Fig. 2 depicts optimized two optimized structures.

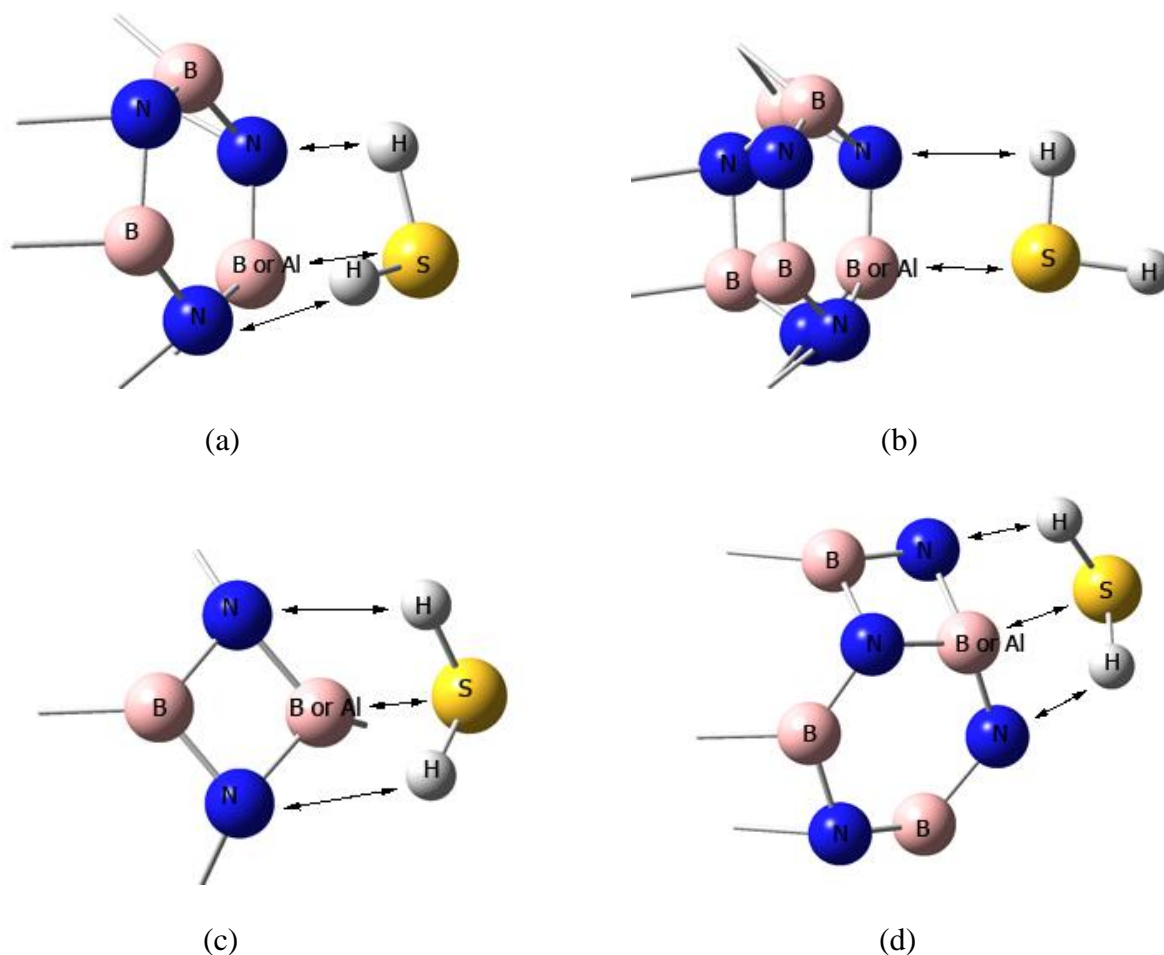


Fig. 1. Initial structures for fullerene- $H_2S$  systems, in a, b, c and d structures  $H_2S$  lies on the hexagon, between two hexagon, on the tetragon and between a tetragon and a hexagon of fullerene respectively (Double arrows show the interactive atoms).

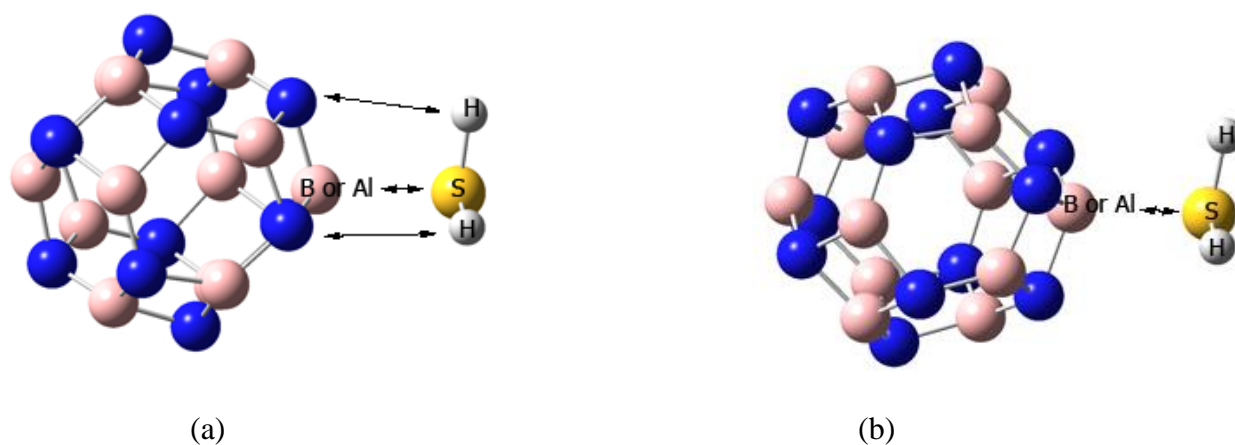


Fig. 2. Optimized structures for two component systems; in (a) system  $H_2S$  was placed on the tetragon and in (b) system between a tetragon and a hexagon of fullerene.

Table 1 demonstrates  $E_e$  (electronic energy), DM (dipole moment) and  $E_{int}$  (interaction energy) of structures.  $E_{int}$ . Results show structure b, Al-inserted fullerene, is the most stable system. Interaction energy of two-component systems shows the interaction between  $H_2S$  and fullerenes is physical type but in Al-inserted systems the interaction energy is more than pristine fullerene. On the basis of interaction energy Al-inserted fullerene is better absorbent for  $H_2S$  than pristine fullerene. We observed direct relationship between dipole moment and interaction energy. The relationship concludes that the more negative of interaction energy, the more its dipole moments.

In table 2, HOMO and LUMO energies and their corresponding parameters were compared. The energy gap in  $B_{12}N_{12}-H_2S$  did not have significant difference with that of fullerene. Therefore,  $H_2S$  absorption on this fullerene does not create significant change on conductivity and this fullerene is not an appropriate  $H_2S$  sensor. The energy gap in  $AlB_{11}N_{12}$  fullerene compared to pristine fullerene has decrease by more than 2.5 eV and remarkable increasing in energy gap was observed after adding  $H_2S$ . This increase is observed a little more in structure (a) than in structure (b). Consequently,  $AlB_{11}N_{12}$  could be an appropriate  $H_2S$  sensor.

Table1. Electronic Energy, Dipole Moments and Interaction Energies for systems

System	$E_e$ (kcal/mol)	DM (Debye)	$E_{int}$ (kcal/mol)
$H_2S$	-250599.0544	1.8022	
$B_{12}N_{12}$	-599740.3277	0.0038	
$B_{12}N_{12}H_2S$ (a)	-850344.3729	4.6896	-4.9909
$B_{12}N_{12}H_2S$ (b)	-850344.9214	5.1132	-5.5394
$AlB_{11}N_{12}$	-736270.9203	3.9418	
$AlB_{11}N_{12}H_2S$ (a)	-986893.6242	9.3179	-23.65
$AlB_{11}N_{12}H_2S$ (b)	-986894.0495	9.674	-24.075

Table2. Bonds length, energy gap, HOMO and LUMO energies

System	$E_{HOMO}$ (eV)	$E_{LUMO}$ (eV)	$E_g$ (eV)	Atoms	Displacement (Å)
$B_{12}N_{12}$	-1.5627002	-7.6275884	6.0648882		
$B_{12}N_{12}H_2S$ (a)	-7.1490608	-1.0893444	6.0597164	S...B	2.3557
$B_{12}N_{12}H_2S$ (b)	-7.13164	-1.0496032	6.0820368	S...B	2.27921
$AlB_{11}N_{12}$	-7.1972402	-3.7980066	3.3992336		
$AlB_{11}N_{12}H_2S$ (a)	-6.726062	-1.93262	4.793442	S...Al	2.53446
$AlB_{11}N_{12}H_2S$ (b)	-6.711091	-1.9669172	4.7441738	S...Al	2.52114

We investigated the bonds length in systems. The results show that in  $B_{12}N_{12}-H_2S$ , B...S distance in structure (a) is a little more than that of structure (b). This implies weaker interaction of sulphur and boron atoms in this structure.

In inserted fullerene structure, considering the size of inserted atom, the distance between atoms and bond length will increase. In  $\text{AlB}_{12}\text{N}_{12}$  fullerene, S...Al distance is more in (a) system which indicates weaker interaction in this structure.

Based on the thermodynamic information extracted from the Freq calculations as represented in table 3, it is concluded that for  $\text{B}_{12}\text{N}_{12}\text{---H}_2\text{S}$  system, the changes in thermal energy and enthalpy are negative. This implies that both interactions are exothermic. Considering reduction in the number of species in the adsorption process, the change in  $\Delta S$  has proved to be negative for two systems. It is observed  $\Delta S$  is more negative for (a) system which represents more reduction in entropy for this interaction. The change in Gibbs free energy was observed to be positive for pristine fullerene and  $\text{H}_2\text{S}$  which indicates  $\text{B}_{12}\text{N}_{12}\text{---H}_2\text{S}$  system will not spontaneously proceed towards thermodynamic equilibrium.

The change in Thermal energy and enthalpy in  $\text{AlB}_{11}\text{N}_{12}\text{---H}_2\text{S}$  are more negative than pristine fullerene. This indicates that this interaction is more exothermic and that the (a) system is a little more exothermic compared to the (b) system. Also, Gibbs free energy variations for both states are negative which suggest that  $\text{B}_{12}\text{N}_{12}\text{---H}_2\text{S}$  system will spontaneously proceed towards thermodynamic equilibrium and the  $\Delta G$  for (b) system is more negative for (a) system.

Table 3. Thermodynamic parameters for systems.

System	$\Delta H$ (kcal/mol)	$\Delta G$ (kcal/mol)	$\Delta S$ (cal/molK)
$\text{B}_{12}\text{N}_{12}\text{H}_2\text{S}$ (a)	-4.058103936	6.695526365	-36.069
$\text{B}_{12}\text{N}_{12}\text{H}_2\text{S}$ (b)	-4.005393139	5.811365479	-32.926
$\text{AlB}_{11}\text{N}_{12}\text{H}_2\text{S}$ (a)	-22.35439843	-11.89381506	-35.087
$\text{AlB}_{11}\text{N}_{12}\text{H}_2\text{S}$ (b)	-22.13728014	-13.19338724	-29.998

#### 4. Conclusion:

Our DFT calculations to study adsorption of  $\text{H}_2\text{S}$  molecules on the surface of boron nitride fullerene and Al-inserted analog exhibit that a single  $\text{H}_2\text{S}$  molecule gets physisorbed on the  $\text{B}_{12}\text{N}_{12}$  surface through an exothermic process. In case of  $\text{AlB}_{11}\text{N}_{12}$ , the interaction with the surface is physisorption with high interaction energy and the band gap is significantly increased. Physisorption of  $\text{H}_2\text{S}$  reduced the conductivity of the fullerene that can be implemented as  $\text{H}_2\text{S}$  gas sensor. The interaction between adsorbate and the surface is subjected to detailed electronic analysis such as NBO analysis and structural properties. The results based on thermodynamic parameters show that the interaction of  $\text{H}_2\text{S}$  and fullerene is not spontaneous for  $\text{B}_{12}\text{N}_{12}$  but is spontaneous for  $\text{AlB}_{11}\text{N}_{12}$ . The current results provide not only insightful information about the adsorption behavior of  $\text{H}_2\text{S}$  molecule at various orientations but also indicate potential applications of  $\text{B}_{12}\text{N}_{12}$  and  $\text{AlB}_{11}\text{N}_{12}$  as gas sensor and the Al-inserted fullerene show more favorite properties.

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