Boron nitride nanoclusters as a sensor for Cyclosarin nerve agent: DFT and thermodynamics studies

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Abstract

To find a chemical sensor for detection of Cyclosarin (GF) nerve agent, we studied its interaction with $B_{24}N_{24}$, $AlB_{23}N_{24}$, $B_{16}N_{16}$ and $AlB_{15}N_{16}$ nanoclusters by means of density functional theory calculations. All calculations were investigated with the M06 method and 6-311G(d,p) basis set. It was demonstrated that the interaction of GF with $AlB_{23}N_{24}$ and $AlB_{15}N_{16}$ is more stable than that of the $B_{24}N_{24}$ and $B_{16}N_{16}$. Thermodynamic parameters indicated that the $AlB_{23}N_{24}$ and $AlB_{15}N_{16}$ interactions with the GF are exothermic and spontaneous. Despite both $AlB_{23}N_{24}$ and $AlB_{15}N_{16}$ demonstrated strong adsorption, the electronic properties calculation indicated that $AlB_{15}N_{16}$ is sensitive to the nerve agent adsorption. Our results predicted $AlB_{15}N_{16}$ has good potential as a sensor for the detection of GF.

Keywords Cyclosarin · BN nanoclusters · DFT · Adsorption · Sensor

1 Introduction

Detection of nerve agents is an important chemical process for our safety and health [1]. Also, their identification is important for military and civilian defense resources [2]. Cyclosarin (GF) is a highly toxic organophosphate that belongs to the member of nerve used in the Gulf War (GW) operations [3, 4]. Various methods introduced for nerve agent detection including chromatography [5], mass spectroscopy [6], photoluminescent [7] and fluorescent sensors [8]. By the advent of nanotechnology, nanostructures have attracted an extensive attention as gas sensors because their surface/volume ratio is much higher than that of the conventional micro sensors which makes the large adsorption area available for adsorption process [9–18]. Boron nitride (BN) nanostructures have been introduced as a capable tool for the adsorption of compounds due to their high amount of bonding energy [19, 20]. Unlike the carbon nanostructures, the BN nanostructures are wide bandgap semiconductors, offer greater applications in electronic

devices and sensors [21, 22]. Recently fullerene-like nanostructures of BN nanostructures have attracted considerable attention [23–27].

Oku et al. [28, 29] have synthesized $B_{16}N_{16}$ and $B_{24}N_{24}$ nanoclusters, detected by laser desorption time-of flight mass spectrometry. Seifert et al. [30] indicated that the $B_{16}N_{16}$ with 4 and 6 membered B-N rings is excellent stable BN nanoclusters and Wu and Jiao [31] indicated that $B_{24}N_{24}$ nanocluster with isolated 4, 6 and 8-membered B-N rings are more stable than other structures of $B_{24}N_{24}$. Various applications and properties of $B_{16}N_{16}$ and $B_{24}N_{24}$ nanoclusters have been widely studied [32–35]. For example, Shakerzadeh et al. have shown the adsorption of phosgene over the $B_{12}N_{12}$ and $B_{16}N_{16}$ nanoclusters using density functional theory (DFT) calculations. They reported that the $AlB_{11}N_{12}$ and $AlB_{15}N_{16}$ nanoclusters could be promising sensor for phosgene detection [36]. The structure and electronic properties of $B_{24}N_{24}$ nanocluster functionalized with formaldehyde molecule was studied by Rostami et al. [37] using DFT calculations. They found $B_{24}N_{24}$ is suitable

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for formaldehyde detection. Soltani et al. have shown the adsorption of 5-AVA drug over the $B_{12}N_{12}$ and $B_{16}N_{16}$ nanoclusters using DFT calculations. They reported that the nanoclusters could be suitable for 5-AVA drug delivery [38]. Computational methods significantly help the experimentalist to understand different compounds behavior [39].

In this research, the interaction of GF with the $B_{16}N_{16}$ and $B_{24}N_{24}$ nanoclusters were surveyed by using theoretical calculations. Moreover, we doped Al atom instead of B atom in the $B_{16}N_{16}$ and $B_{24}N_{24}$ ($AlB_{15}N_{16}$ and $AlB_{23}N_{24}$) to find the suitable gas sensor of GF nerve agent (Fig. 1). The obtained results may provide a new insight to the gas sensor nanotechnology.

2 Computational method

Adsorption of GF onto the $B_{24}N_{24}$, $AlB_{23}N_{24}$, $B_{16}N_{16}$ and $AlB_{15}N_{16}$ surfaces was investigated using density functional theory (Figs. 1, 2, 3, 4, 5 and 6). All calculations were carried out using GAMESS program package [40]

with the M06 method and 6-311G(d,p) basis set. The previous reports were indicated that M06 method is appropriate for predict electronic and structural properties [41, 42] and 6-311G(d,p) basis set has been known suitable for nanostructure systems [43, 44]. The adsorption energies (E_{ad}) were calculated with the following equations:

$$E_{ad} = E(GF/B_{24}N_{24}) - E(B_{24}N_{24}) - E(GF) + E_{BSSE} \quad (1)$$

$$E_{ad} = E(GF/AlB_{23}N_{24}) - E(AlB_{23}N_{24}) - E(GF) + E_{BSSE} \quad (2)$$

$$E_{ad} = E(GF/B_{16}N_{16}) - E(B_{16}N_{16}) - E(GF) + E_{BSSE} \quad (3)$$

$$E_{ad} = E(GF/AlB_{15}N_{16}) - E(AlB_{15}N_{16}) - E(GF) + E_{BSSE} \quad (4)$$

where $E(GF/B_{24}N_{24})$, $E(GF/AlB_{23}N_{24})$, $E(GF/B_{16}N_{16})$ and $E(GF/AlB_{15}N_{16})$ are the total energies of the $B_{24}N_{24}$, $AlB_{23}N_{24}$, $B_{16}N_{16}$ and $AlB_{15}N_{16}$ interacted with GF, $E(GF)$, $E(B_{24}N_{24})$, $E(AlB_{23}N_{24})$, $E(B_{16}N_{16})$ and $E(AlB_{15}N_{16})$ are the total energy of the lone GF, $B_{24}N_{24}$, $AlB_{23}N_{24}$, $B_{16}N_{16}$ and $AlB_{15}N_{16}$, respectively. E_{BSSE} is the basis set superposition error

Fig. 1 Optimized configurations, the FMO (HOMO and LUMO) and MEP plots of the GF, $B_{24}N_{24}$ and $AlB_{23}N_{24}$. (The color scheme for MEP surface is red-electron rich or partially negative charge; blue-

electron deficient or partially positive charge; light blue-slightly electron deficient region; yellow-slightly electron rich region, respectively)

(BSSE) corrected for all adsorption energy [45]. The thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) ($T=298.15$ K and $P=1$ atm) were investigated with the M06 method and 6-311G(d,p) basis set. Furthermore, frontier molecular orbitals (FMO), molecular electrostatic potential (MEP), natural bond orbital (NBO), and density of states (DOS) analysis were computed [38].

3 Result and discussion

The optimized structure, FMO and MEP plots for GF were provided in Fig. 1. As shown in MEP plot, the negative charges (red color) are mainly localized over the carbonyl oxygen (O head), F atom (F head) and etheric oxygen (O head), which can be interacted with electrophile sites of nanocluster. The calculated $P=O$, $P-O$ and $P-F$ bond lengths were calculated 1.46, 1.59 and 1.59 Å, respectively. The FMO plot for GF is located on all atoms in the HOMO and LUMO regions.

3.1 The adsorption of GF on the $B_{24}N_{24}$ and $AlB_{23}N_{24}$

The most stable configuration of $B_{24}N_{24}$ and $AlB_{23}N_{24}$ nanoclusters was shown in Fig. 1. The calculated B–N bond length between 6–8, 6–4 and 4–8 membered rings are 1.42, 1.49 and 1.47 Å, respectively, and is completely in agreement with the previous reports [37, 46]. The calculated Al–N bond length in $AlB_{23}N_{24}$ for 6–8, 6–4 and 4–8 membered rings are 1.77, 1.83 and 1.80 Å, respectively. The MEP plots of the $B_{24}N_{24}$ and $AlB_{23}N_{24}$ indicated the electrostatic potential in the Al atom of $AlB_{23}N_{24}$ is significantly more positive (blue color) compared to the B and N atoms which makes it the most electrophilic site for GF molecule.

The reactivity of GF with nanoclusters has been studied in the various adsorption sites (Fig. 2). The adsorption energies of GF with the $B_{24}N_{24}$ in state A, B and C were calculated to be -9.60 and -5.57 and -5.51 kcal mol $^{-1}$, respectively (Table 1). Nejati et al. indicated the interaction of GF with BN nanosheet with weak adsorption energies of -0.32 kcal mol $^{-1}$ at the B3LYP-D method and 6-31G* basis set [47]. Equilibrium distances between GF and nanocluster in state A, B and C were obtained to be 1.62, 2.67 and 2.43 Å, respectively. These results were

Fig. 2 Optimized configurations for the GF/ $B_{24}N_{24}$ (state A, B and C) and GF/ $AlB_{23}N_{24}$ (state D, E and F) at the M06 method

Table 1 Calculated adsorption energy ($E_{ad}/\text{kcal mol}^{-1}$), basis set superposition error ($E_{BSSE}/\text{kcal mol}^{-1}$), bond distance between GF and nanocluster ($D/\text{\AA}$), HOMO energies (HOMO/eV), LUMO energies (LUMO/eV), energy gap (E_g/eV), change of E_g after adsorp-tion ($\% \Delta E_g/\%$), enthalpy ($\Delta H/\text{kcal mol}^{-1}$), Gibbs free energy ($\Delta G/\text{kcal mol}^{-1}$) and entropy ($\Delta S/\text{kcal K}^{-1} \text{mol}^{-1}$) in the $B_{24}N_{24}$ and $AlB_{23}N_{24}$ nanoclusters

Name	E_{ad}	E_{BSSE}	D	HOMO	LUMO	E_g	$\% \Delta E_g$	ΔH	ΔG	ΔS
$B_{24}N_{24}$	–	–	–	–8.10	–1.05	7.04	–	–	–	–
State A	–9.60	4.07	1.62	–7.21	–0.49	6.72	–4.62	–12.35	0.70	–0.044
State B	–5.57	2.22	2.67	–8.20	–1.22	6.98	–0.86	–6.32	5.30	–0.039
State C	–5.51	2.93	2.43	–7.95	–0.91	7.04	–0.09	–7.54	5.60	–0.044
$AlB_{23}N_{24}$	–	–	–	–7.91	–2.36	5.55	–	–	–	–
State D	–50.63	4.02	1.83	–7.07	–0.62	6.45	16.30	–52.88	–42.54	–0.035
State E	–23.14	4.61	1.88	–7.57	–0.98	6.60	18.93	–27.75	–12.25	–0.052
State F	–30.61	3.89	1.98	–7.37	–0.94	6.44	16.05	–33.62	–18.88	–0.049

shown the interaction of state A (carbonyl oxygen) is stronger than that of state B (F atom) and C (etheric oxygen) since adsorption energies were indicated in state B is more negative than that of state B and C. The adsorption energy of GF/ $AlB_{23}N_{24}$ was calculated –50.63, –23.14 and –30.61 kcal mol^{-1} with equilibrium distances 1.83, 1.88 and 1.98 $\text{\AA}$ in state D, E and F, respectively. These results indicated that GF adsorption on the $AlB_{23}N_{24}$ is stronger than that on the pure one. NBO charge transfers in state D, E and F were calculated 0.183, 0.151 and 0.160 e, respectively. Positive values of charge transfers are indicated charge transfer from GF to the nanoclusters.

Furthermore, the thermodynamic parameters (Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS)) were calculated and listed in Table 1. The ΔH values for GF/ $B_{24}N_{24}$ in state A, B and C were calculated –12.35, –6.32 and –7.54 kcal mol^{-1} , respectively, and in GF/ $AlB_{23}N_{24}$ complexes were obtained –52.88, –27.75 and –33.62 kcal mol^{-1} in state D, E and F, respectively. The negative values of ΔH indicated that the reactions are exothermic. The ΔG values were calculated 0.70, 5.30, 5.60, –42.54, –12.25 and –18.89 kcal mol^{-1} in state A, B, C, D, E and F, respectively. Therefore, $B_{24}N_{24}$ interaction is non-spontaneous while $AlB_{23}N_{24}$ interaction is spontaneous.

The calculated ΔG values are less negative compared to the ΔH values, indicating an entropy reduction. The calculated negative values of ΔS confirm this matter. These results were indicated the interaction of the $AlB_{23}N_{24}$ is more suitable compared to the $B_{24}N_{24}$ nanocluster. The MEP plot of GF/ $AlB_{23}N_{24}$ in Fig. 3, shows significant change after adsorption in the electrostatic potential. These results reinforce the fact that GF gets chemically adsorbed on the $AlB_{23}N_{24}$.

Some of the electronic properties like HOMO, LUMO and E_g were reported in Table 1. The E_g is decreased from 7.04 eV in $B_{24}N_{24}$ to 5.55 eV in $AlB_{23}N_{24}$. Salari investigated E_g of $B_{24}N_{24}$ 7.11 eV at the M06/6-31G* level of theory [48]. The HOMO and LUMO values in the $B_{24}N_{24}$ and $AlB_{23}N_{24}$ nanoclusters were shifted to higher energy after adsorption (except GF/ $B_{24}N_{24}$ in state B). These results indicated that the adsorption of GF on the $B_{24}N_{24}$ and $AlB_{23}N_{24}$ nanoclusters destabilizes the HOMO and LUMO levels. In GF/ $B_{24}N_{24}$ complexes the E_g values were revealed that no significant change compared with pure $B_{24}N_{24}$ (–4.62%, –0.86% and –0.09% in state A, B and C, respectively) but in GF/ $AlB_{23}N_{24}$, E_g values were increased from 5.55 eV in pure $AlB_{23}N_{24}$ to 6.45, 6.60 and 6.44 eV in state D, E and F, respectively. The DOS plot of the pure $AlB_{23}N_{24}$ and

Fig. 3 MEP plot for GF/ $AlB_{23}N_{24}$ in state D and the DOS plot for pure $AlB_{23}N_{24}$ and GF/ $B_{23}N_{24}$ in state D

GF/ $\text{AlB}_{23}\text{N}_{24}$ in state D indicated this change (Fig. 3). The change of E_g will exponentially increase the sensitivity and electrical conductivity of the nanostructure [49–51]. Therefore, it is clear that the GF/ $\text{AlB}_{23}\text{N}_{24}$ is more sensitive rather than $\text{B}_{24}\text{N}_{24}$. change of E_g indicated that the $\text{AlB}_{23}\text{N}_{24}$ can detect the GF.

3.2 The adsorption of GF on the $\text{B}_{16}\text{N}_{16}$ and $\text{AlB}_{15}\text{N}_{16}$

Furthermore, we examined adsorption of GF molecule on the $\text{B}_{16}\text{N}_{16}$ and $\text{AlB}_{15}\text{N}_{16}$ nanoclusters. The optimized structures, MEP and FMO plots of $\text{B}_{16}\text{N}_{16}$ and $\text{AlB}_{15}\text{N}_{16}$ are shown in Fig. 4. The B–N bond lengths of $\text{B}_{16}\text{N}_{16}$ in 6–6

and 6–4 membered rings were calculated 1.45 and 1.47 Å, respectively and Al–N bond lengths for $\text{AlB}_{15}\text{N}_{16}$ were calculated 1.80 and 1.81 Å in 6–6 and 6–4 membered rings, respectively.

After adsorption of GF on the $\text{B}_{16}\text{N}_{16}$, adsorption energies were calculated –14.30, –1.46 and –16.52 kcal mol^{–1} in state G, H and I, respectively (Table 2). When GF is located from its etheric oxygen (state I) on the $\text{B}_{16}\text{N}_{16}$ nanocluster, it reoriented and attached from carbonyl oxygen to the $\text{B}_{16}\text{N}_{16}$ (Fig. 5). Equilibrium distances in state G, H and I were calculated 1.59, 2.53 and 1.57 Å, respectively. The adsorption energies of $\text{AlB}_{15}\text{N}_{16}$ complexes were obtained –54.84, –28.28 and –35.22 kcal mol^{–1} in state

Fig. 4 Optimized configurations, the FMO (HOMO and LUMO) and MEP plots of the $\text{B}_{16}\text{N}_{16}$ and $\text{AlB}_{15}\text{N}_{16}$

Table 2 Calculated adsorption energy (E_{ad} /kcal mol^{–1}), basis set superposition error (E_{BSSE} /kcal mol^{–1}), bond distance between GF and nanocluster (D/Å), HOMO energies (HOMO/eV), LUMO energies (LUMO/eV), energy gap (E_g /eV), change of E_g after adsorption

(% ΔE_g /%), enthalpy (ΔH /kcal mol^{–1}), Gibbs free energy (ΔG /kcal mol^{–1}) and entropy (ΔS /kcal K^{–1} mol^{–1}) in the $\text{B}_{16}\text{N}_{16}$ and $\text{AlB}_{15}\text{N}_{16}$ nanoclusters

Name	E_{ad}	E_{BSSE}	D	HOMO	LUMO	E_g	% ΔE_g	ΔH	ΔG	ΔS
$\text{B}_{16}\text{N}_{16}$	–	–	–	–8.06	–1.25	6.82	–3.15	–	–	–
State G	–14.30	3.98	1.59	–6.95	–0.35	6.60	–0.59	–17.86	–3.94	–0.047
State H	–1.46	1.53	2.53	–7.83	–1.05	6.77	–2.71	–2.19	9.80	–0.040
State I	–16.52	4.75	1.57	–7.12	–0.49	6.63	–	–19.76	–6.12	–0.046
$\text{AlB}_{15}\text{N}_{16}$	–	–	–	–7.65	–3.06	4.59	–	–	–	–
State J	–54.84	4.20	1.82	–6.63	–0.71	5.92	29.00	–57.53	–45.79	–0.039
State K	–28.28	4.85	1.86	–7.25	–1.15	6.09	32.71	–32.06	–20.22	–0.040
State L	–35.22	4.42	1.93	–7.00	–0.58	6.42	39.95	–38.80	–24.64	–0.047

Fig. 5 Optimized configurations for the GF/B₁₆N₁₆ (state G, H and I) and GF/AIB₁₅N₁₆ (state J, K and L) at the M06 method

Fig. 6 MEP plot for GF/AIB₁₅N₁₆ in state J and the DOS plot for pure AIB₁₅N₁₆ and GF/B₁₅N₁₆ in state J

J, K and L, respectively. These results were indicated the interaction of the AIB₁₅N₁₆ nanocluster is stronger than that of the B₂₄N₂₄, AIB₂₃N₂₄ and B₁₆N₁₆ nanoclusters. NBO charge transfer were calculated 0.190, 0.157 and 0.176 e and equilibrium distances were investigated 1.82, 1.86 and 1.93 Å in state J, K and L, respectively.

The ΔH (ΔG) values of GF/B₁₆N₁₆ and GF/AIB₁₅N₁₆ were calculated -17.86 (-3.94), -2.19 (9.80), -19.76 (-6.12), -57.53 (-45.79), -32.06 (-20.22) and -38.80 (-24.63) kcal mol⁻¹ in state G, H, I, J, K and L, respectively. The negative values of ΔH and ΔG indicated the reactions are exothermic and spontaneous. Upon adsorption of GF on

AlB₁₅N₁₆ in state J, their MEP changes significantly. These results confirm the fact that GF gets chemically adsorbed on the AlB₁₅N₁₆.

The HOMO, LUMO and E_g values for B₁₆N₁₆ and AlB₁₅N₁₆ at the M06 method were shown in Table 2. The HOMO values for the B₁₆N₁₆ and AlB₁₅N₁₆ were -8.06 and -7.65 eV while the LUMO values were -1.25 and -3.06 eV, respectively. The E_g is decreased from 6.82 eV in B₁₆N₁₆ to 4.59 eV in AlB₁₅N₁₆. Soltani et al. calculated E_g of B₁₆N₁₆ 6.37 eV at the B3LYP method [52] and Shakerzadeh et al. investigated E_g of B₁₆N₁₆ and AlB₁₅N₁₆ 6.17 and 3.97 eV at the M06-2X method [36]. The HOMO and LUMO values after adsorption process were increased to higher energy and destabilizes the HOMO and LUMO levels. E_g values after adsorption in GF/B₁₆N₁₆ reveal that no significant change compared with pure B₁₆N₁₆ and indication of B₁₆N₁₆ nanocluster cannot detect the GF. The E_g values are increased from 4.59 eV in AlB₁₅N₁₆ to 5.92 , 6.09 and 6.42 eV in state J, K and L, respectively. Compared to the B₂₄N₂₄, AlB₂₃N₂₄ and B₁₆N₁₆, the E_g represent more sensitivity in AlB₁₅N₁₆ (29.00% in state J, 32.71% in state K and 39.95% in state L). The DOS plot of AlB₁₅N₁₆ and GF/B₁₅N₁₆ in state J in Fig. 6 confirm this increase. The change of E_g was indicated the AlB₁₅N₁₆ nanocluster can detect the GF nerve agent.

4 Conclusions

In this study, the adsorption of the GF nerve agent on the B₂₄N₂₄, AlB₂₃N₂₄, B₁₆N₁₆ and AlB₁₅N₁₆ was investigated using DFT calculations. The doped atom (AlB₂₃N₂₄ and AlB₁₅N₁₆) nanoclusters facilitate the interaction of the GF compared to the pure B₂₄N₂₄ and B₁₆N₁₆ nanoclusters. Thermodynamic calculations were indicated adsorption of GF on the AlB₂₃N₂₄ and AlB₁₅N₁₆ in all states are exothermic and spontaneous. The results of E_g and DOS plots were shown that the AlB₁₅N₁₆ has greater sensitivity to the GF than the B₂₄N₂₄, AlB₂₃N₂₄ and B₁₆N₁₆. Therefore, the AlB₁₅N₁₆ may be used in GA sensor devices.

Compliance with ethical standards

Conflict of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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