Investigation of Adsorption Properties of Al$_{12}$N$_{12}$, SiAl$_{11}$N$_{12}$, and GaAl$_{11}$N$_{12}$ Nanoclusters for Sarin Detection: A Comparative DFT Study

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**Introduction**

Of the chemical warfare agents, the nerve agent is the most hazardous [1]. They influence fast on human health and lead to death [2, 3]. Sarin, as a dangerous nerve agent, is a potent acetylcholinesterase inhibitor [4]. Due to be odorless, tasteless, and colorless detection of sarin is very hard [5]. Thus, designing a reliable and facile technique for the sarin detection is highly essential.

For sarin detection, several techniques, such as chromatography [6], photo luminescent [7], mass spectroscopy [8], and fluorescent sensors [9] have been utilized. Nevertheless, these techniques need more energy and time and are expensive. Compared with these techniques, chemical sensors based on the nanostructures have been used widely due to their short response time, high selectivity, affordable, and comfortable applications [10-15]. Thus, nanoclusters have recently been considered as an alternative approach to the chemical sensors [16-21]. Among different kinds of nanoclusters, aluminum nitride (AlN) nanostructures were extensively used due to the wide bandgap, economic efficiency, and thermal stability [22-24].

The AlN nanostructures could be modified by loading noble metals and doping atomic impurities [25-29]. For example, Nayini et al. investigated the sensitivity and reactivity of pure and Si-, Ga-, and Ge-doped AlN nanoclusters with amphetamine drugs using density functional theory (DFT) calculations [26]. They indicated that Si-doped AlN is a potential nanocluster for the amphetamine detection. Thus, in this study, we investigated the adsorption and detection properties of sarin on the Al_{12}N_{12}, Si-doped AlN (SiAl_{11}N_{12}), and Ga-doped AlN (GaAl_{11}N_{12}) nanoclusters using the DFT calculations.

**Computational method**

The sarin interaction with the Al_{12}N_{12}, SiAl_{11}N_{12}, and GaAl_{11}N_{12} nanoclusters surfaces was calculated using the DFT calculations. The GAMESS program [30] and the M06 method with an and 6-311G (d, P) basis set were utilized for all investigations. Reports indicated that the M06 method is very reliable due to the excellent agreement with the experimental results. The previous reports have indicated that the M06 method is better than the other methods, such as B3LYP, MP2, B9W91, QCISD, and QCISD (T) [31, 32]. 6-311G (d, p) basis set has been known suitable for nanostructure systems [33, 34]. The adsorption energies (E_{ads}) of sarin onto the Al_{12}N_{12}, SiAl_{11}N_{12}, and GaAl_{11}N_{12} nanoclusters are as follow:

\[
E_{\text{ad}}=E(\text{sarin}/\text{Al}_{12}\text{N}_{12})-E(\text{Al}_{12}\text{N}_{12})-E(\text{sarin}) \quad (1)
\]

\[
E_{\text{ad}}=E(\text{sarin}/\text{SiAl}_{11}\text{N}_{12})-E(\text{SiAl}_{11}\text{N}_{12})-E(\text{sarin}) \quad (2)
\]

\[
E_{\text{ad}}=E(\text{sarin}/\text{GaAl}_{11}\text{N}_{12})-E(\text{GaAl}_{11}\text{N}_{12})-E(\text{sarin}) \quad (3)
\]

Where, E(sarin), E(Al_{12}N_{12}), and E(sarin/GaAl_{11}N_{12}) are the total energies of the sarin interacted Al_{12}N_{12}, SiAl_{11}N_{12}, and GaAl_{11}N_{12} nanoclusters, respectively. E(sarin), E(Al_{12}N_{12}), E(SiAl_{11}N_{12}), and E(GaAl_{11}N_{12}) are the total energy of pristine sarin, Al_{12}N_{12}, SiAl_{11}N_{12}, and GaAl_{11}N_{12}, respectively.

**Results and Discussion**

**Adsorption of sarin on Al_{12}N_{12}**

The molecular electrostatic potential (MEP) plot of sarin in Figure 1 indicated fluorine (F) and carbonyl oxygen atoms have a more negative charge (red color) and make it an electronnegative site for interaction with the electrophilic region. Figure 1 demonstrated the most stable structure of Al_{12}N_{12} with six-membered (6-R) and four-membered (4-R) rings. The bond lengths of the 6R-4R and 6R-6R mutual bonds of Al-N atoms were calculated at 1.84 and 1.78 Å, which is consistent with previous reports [35]. The MEP plot of Al_{12}N_{12} was shown that the Al and N atoms are electrophilic (blue color) and nucleophile (red color) regions, respectively. To investigate the adsorption properties of sarin with nanoclusters, various possible adsorption sites of sarin (F and carbonyl oxygen atoms) were considered for the interaction with Al_{12}N_{12} nanoclusters. After optimization, the adsorption energy and bound distance between the nanocluster and sarin from its carbonyl oxygen atom (state A) were calculated at -38.36 kcal.mol-1.
and 1.89 Å, which indicated an appropriate interaction. The sarin adsorption from its F atom was calculated in state B (Figure 2). Adsorption energies in state B were investigated at -20.62 kcal.mol\(^{-1}\), and equilibrium distances were 2.97 Å (Table 1). Therefore, these parameters demonstrated the adsorption of sarin from its carbonyl oxygen atom (state A) is stronger since the equilibrium distance between sarin and the Al\(_{12}N\(_{12}\) nanocluster was shorter and the adsorption energy was more negative. The AlN nanocluster dipole moment (DM) value increased after the adsorption of sarin from 0.00 Debye in pure Al\(_{12}N\(_{12}\) to 8.79 and 3.70 Debye, representing polar bonds between nanocluster and sarin.

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**Figure 1:** The optimized structures and MEP plot for the sarin and Al\(_{12}N\(_{12}\)

**Figure 2:** The optimized configurations for the Al\(_{12}N\(_{12}\) complexes in different states
Adsorption of sarin on the SiAl11N12 and GaAl11N12 nanoclusters

To investigate the doping effect on the adsorption process, Si and Ga atoms were doped into the Al12N12 nanocluster (Figure 3). The previous reports indicated Si and Ga atoms could be doped in the AlN nanoclusters [26]. The Si-O and Ga-O bond lengths in the 6R-4R and 6R-6R mutual bonds indicated a bond length of 1.84 and 1.78 Å, which is consistent with reports [36, 37].

After the sarin adsorption on the SiAl11N12, adsorption energies (equilibrium distances) were calculated at -25.95 (1.82 Å) and -3.71 kcal/mol (2.24 Å) in states C and D (Figure 4). The adsorption energies for GaAl11N12 in states E and F were investigated at -27.94 and -12.47 kcal/mol, respectively, and the equilibrium distances were calculated at about 2.02 and 2.25 Å. These values indicated similar to the Al12N12 adsorption of sarin from its carbonyl oxygen atom is stronger than the other states, and this orientation was the most stable state. The NBO charge transfers calculation indicated charge transfer from sarin to the nanoclusters. The DM values in Table 1 indicated that after the sarin adsorption on the SiAl11N12 and GaAl11N12, the values increase.

Table 1: The calculated adsorption energy (Ead), bond distance between sarin and nanoclusters (D), HOMO energy (E_HOMO), LUMO energy (E_LUMO), energy gap (E_g), electrical conductivity variation (%Δσ) after the sarin adsorption, and dipole moment (DM) in gas phase.

<table>
<thead>
<tr>
<th>Name</th>
<th>Ead (kcal mol⁻¹)</th>
<th>D (Å)</th>
<th>E_HOMO (eV)</th>
<th>E_LUMO (eV)</th>
<th>E_g (eV)</th>
<th>%Δσ</th>
<th>DM (Debye)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sarin</td>
<td>-</td>
<td>-</td>
<td>-8.61</td>
<td>0.88</td>
<td>9.49</td>
<td>-</td>
<td>3.03</td>
</tr>
<tr>
<td>Al12N12</td>
<td>-</td>
<td>-</td>
<td>-6.80</td>
<td>-2.23</td>
<td>4.57</td>
<td>-</td>
<td>0.00</td>
</tr>
<tr>
<td>A</td>
<td>-38.36</td>
<td>1.89</td>
<td>-6.13</td>
<td>-1.70</td>
<td>4.43</td>
<td>-3.04</td>
<td>8.79</td>
</tr>
<tr>
<td>B</td>
<td>-20.62</td>
<td>2.97</td>
<td>-6.51</td>
<td>-2.00</td>
<td>4.51</td>
<td>-1.31</td>
<td>3.70</td>
</tr>
<tr>
<td>SiAl11N12</td>
<td>-</td>
<td>-</td>
<td>-4.71</td>
<td>-2.22</td>
<td>2.49</td>
<td>-</td>
<td>1.61</td>
</tr>
<tr>
<td>C</td>
<td>-25.95</td>
<td>1.82</td>
<td>-2.93</td>
<td>-1.05</td>
<td>1.88</td>
<td>-24.64</td>
<td>12.81</td>
</tr>
<tr>
<td>D</td>
<td>-3.71</td>
<td>2.24</td>
<td>-3.34</td>
<td>-1.46</td>
<td>1.89</td>
<td>-24.1</td>
<td>7.06</td>
</tr>
<tr>
<td>GaAl11N12</td>
<td>-</td>
<td>-</td>
<td>-6.79</td>
<td>-2.34</td>
<td>4.46</td>
<td>-</td>
<td>0.67</td>
</tr>
<tr>
<td>E</td>
<td>-27.94</td>
<td>2.02</td>
<td>-6.22</td>
<td>-1.82</td>
<td>4.40</td>
<td>-1.16</td>
<td>7.49</td>
</tr>
<tr>
<td>F</td>
<td>-12.47</td>
<td>2.25</td>
<td>-6.53</td>
<td>-2.05</td>
<td>4.48</td>
<td>0.45</td>
<td>4.13</td>
</tr>
</tbody>
</table>

Electronic characteristics before and after interactions of nanoclusters

In Table 1, the electronic characteristics (HOMO, LUMO, and energy gap (E_g)) of pure and complexes of nanoclusters were provided. The HOMO and LUMO energies of Al12N12 were calculated at -6.80 and -2.23 eV. Thus, the E_g energy (LUMO-HOMO) will equal 4.57 eV. Hoseininezhad-Namin et al. calculated the HOMO, LUMO, and E_g values of Al12N12 at -8.54, -0.63, and 7.91 eV, respectively, at the wB97XD method and 6-311G (d, p) basis set [38]. After doping Si and Ga atoms, the HOMO and LUMO values were changed. Furthermore, E_g values after the doping process reduced -45.51% and -2.45% in the SiAl11N12 and GaAl11N12 nanoclusters, respectively. Based on the previous experimental studies, the change in the sensor’s signals is due to the electrical conductivity (σ) alteration after adsorption.

A shift in the electronic properties of AlN nanoclusters could change the electrical conductivity of these nanoclusters, as shown by the following equation with E_g:

\[ \sigma \propto \exp \left( \frac{-E_g}{2K_B T} \right) \]  

(4)

Where, T and K_B are the temperature and Boltzmann constant, respectively. According to Equation (4), when E_g decreases after adsorption of sarin, the electrical conductivity increases. This ratio of changes could be investigated by equation (5):

\[ \Delta \sigma = \left( \frac{\sigma - \sigma_0}{\sigma_0} \right) \]  

(5)
Figure 3: The optimized structures for the SiAl\textsubscript{11}N\textsubscript{12} and GaAl\textsubscript{11}N\textsubscript{12} nanostructures

Figure 4: The optimized configurations for the SiAl\textsubscript{11}N\textsubscript{12}, and GaAl\textsubscript{11}N\textsubscript{12} complexes in different states
Where, $\sigma_0$ and $\sigma$ are the electrical conductivity of pure nanoclusters and complexes, respectively. The $\%\Delta\sigma$ shows the signal strength, corroborating the sarin's existence. As indicated in Table 1, the $\%\Delta\sigma$ after the interaction of nanoclusters with sarin is -3.04%, -24.64%, and -1.16% for Al$_{12}$N$_{12}$, SiAl$_{11}$N$_{12}$, and GaAl$_{11}$N$_{12}$, respectively, in the most stable states. Thus, it is clear that SiAl$_{11}$N$_{12}$ has higher performance for sarin detection than Al$_{12}$N$_{12}$ and GaAl$_{11}$N$_{12}$. DOS and MEP plots of the SiAl$_{11}$N$_{12}$ complex are indicated in Figure 5. As displayed in Figure 5, after the sarin interaction with SiAl$_{11}$N$_{12}$, the DOS plots were changed in HOMO and LUMO energy levels and changed to the lower energies. Thus, the HOMO and LUMO energies stabilized after adsorption and altered the $E_g$ region. MEP plot of the SiAl$_{11}$N$_{12}$ complex in Figure 5 demonstrated the significant change in the electrostatic potential after the interaction. This Figure indicated that sarin is more positive (blue and green colors) after the adsorption processes. Therefore, these results demonstrated charge transfers from sarin to the SiAl$_{11}$N$_{12}$ nanoclusters, which confirm the charge transfer values.

Recovery time

The interaction strength is essential in developing sensors because a strong adsorption leads to the long-term desorption, and thereby increasing the recovery time. In experimental studies, sensor recovery time can be calculated through methods including heating or exposure to the UV light [39]. Thus, the recovery time could be investigated from the following equation:

$$\tau = \nu^{-1} \exp \left( \frac{E_d}{kT} \right)$$  

(6)

Where, $T$ is the temperature, $k$ is the Boltzmann’s constant, and $\nu$ indicates UV frequency. Therefore, the recovery time for Al$_{12}$N$_{12}$, SiAl$_{11}$N$_{12}$, and GaAl$_{11}$N$_{12}$ complexes will be about $12.37 \times 10^9$, 9.93, and 284.68 s at the UV frequency of $10^{18}$ s$^{-1}$ and 298 K, respectively. These values showed that Al$_{12}$N$_{12}$ and GaAl$_{11}$N$_{12}$ have a long recovery time and long-term desorption. Thus, it could not be used for sarin detection. On the other hand, SiAl$_{11}$N$_{12}$ demonstrated the short-term desorption suitable for sensor applications.

Conclusion

The interaction of sarin with the Al$_{12}$N$_{12}$, SiAl$_{11}$N$_{12}$, and GaAl$_{11}$N$_{12}$ nanoclusters was studied using DFT calculations to explore a new system for sarin detection. After optimization, adsorption energies were calculated at -38.36, -25.95, and -27.94 kcal mol$^{-1}$ for Al$_{12}$N$_{12}$, SiAl$_{11}$N$_{12}$, and GaAl$_{11}$N$_{12}$, respectively. The electrical properties calculations indicated the electrical conductivity changes after adsorption of sarin are -3.04%, -
24.64%, and -1.16% for Al$_{12}$N$_{12}$, SiAl$_{11}$N$_{12}$, and GaAl$_{11}$N$_{12}$, respectively. This variation can be considered as a signal of sarin detection. Thus, the SiAl$_{11}$N$_{12}$ nanocluster has a high sensitivity to the detection of sarin nerve agents. On the other hand, the recovery time calculation based on the transition theory confirmed that only the pristine SiAl$_{11}$N$_{12}$ showed a short recovery time of 9.93 s, demonstrating that sarin adsorption on that is reversible and more favorable. Therefore, it is concluded that the SiAl$_{11}$N$_{12}$ nanocluster can be used as a suitable sarin detector.

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Authors’ contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

We have no conflicts of interest to disclose.

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