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Original Research Article

Interaction of Amantadine with Doped Boron Nitride Conical Nanostructures: Impact of Doping on Adsorption Properties and Sensing Potential

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ABSTRACT

This comprehensive study investigates the interaction between amantadine and boron nitride (BN) conical nanostructures using Density Functional Theory (DFT) at the B3LYP/6-31G(d) level. Both pure and doped BN cones, incorporating elements such as Al, Si, P, Ga, and N, were studied to assess their adsorption energy and electronic structure. The results reveal that doping significantly influences the adsorption energies and energy gaps of BN cones. Silicon- and aluminum-doped BN cones exhibit the highest adsorption energies and the most favorable electronic properties for amantadine detection. These findings suggest that doped BN cones are promising candidates for the development of advanced sensors for pharmaceutical compounds like amantadine.

Keywords: Amantadine, Boron Nitride, Conical Nanostructures, Sensor Development, Density Functional Theory (DFT)

Introduction

Amantadine is an antiviral and antiparkinsonian drug that has been widely used in clinical treatments since the 1960s. It is primarily used for the treatment of Parkinson's disease, as well

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as for prophylaxis and treatment of influenza A infection [1]. The molecular interactions of amantadine with various materials have been extensively studied, as they play a crucial role in understanding its pharmacological behavior and potential for detection using nanomaterials [2]. One of the most promising classes of nanomaterials for such applications are boron nitride (BN) nanostructures. Boron nitride is a versatile material with properties similar to carbon nanotubes, including excellent stability, high thermal conductivity, and mechanical strength, making it a candidate for various technological applications, including drug detection and sensing [3].

The exploration of BN nanostructures, particularly in their conical form, for molecular adsorption has gained significant attention due to their unique electronic and structural properties. BN conical nanostructures, in particular, offer a high surface-to-volume ratio, which is advantageous for adsorbing small molecules, such as pharmaceutical drugs, making them ideal for use in chemical and biological sensing [4,5]. Furthermore, BN cones exhibit enhanced stability compared to other nanomaterials, such as carbon nanotubes, due to the high bond strength between boron and nitrogen atoms [6]. This makes BN-based materials highly suitable for long-term applications in sensing devices and other technological fields.

Doping of BN nanostructures with different elements, such as aluminum (Al), silicon (Si), phosphorus (P), and nitrogen (N), has been shown to significantly modify their electronic and chemical properties [7]. The introduction of dopants can create localized electronic states and modify the electron density on the nanostructure surface, which can influence the adsorption behavior of molecules and enhance the performance of these materials in sensing applications [8,9]. For example, silicon-doped BN nanotubes exhibit enhanced adsorption energies for various organic molecules, making them promising candidates for detecting pharmaceutical compounds [10]. Doping can also affect the energy gap of the material, which is a key factor for determining the sensitivity of a sensor. A smaller energy gap is generally associated with better electrical conductivity and faster response times in sensor devices [11].

Recent advances in computational chemistry, particularly Density Functional Theory (DFT), have enabled detailed simulations of the interactions between molecules and nanostructured materials [12]. DFT calculations provide valuable insights into the adsorption energies, electronic properties, and stability of nanostructures in the presence of adsorbed molecules. These theoretical studies are crucial for understanding the underlying mechanisms of drug-nanostructure interactions and for optimizing the design of new materials for drug detection and sensor development [13]. In this context, the interaction between amantadine and BN conical nanostructures has not been fully explored, and the effects of doping on these interactions remain largely unexplored.

This study aims to fill this gap by investigating the interaction between amantadine and pure as well as doped BN conical nanostructures using DFT. We focus on doping with elements such as aluminum, silicon, phosphorus, and nitrogen, and we assess their influence on the adsorption energy, energy gap, and potential for amantadine detection. By comparing the performance of pure and doped BN cones, we aim to identify the optimal dopant for enhancing the adsorption of amantadine and improving the sensing capabilities of BN nanostructures.

The results of this study are expected to contribute to the design of more efficient and sensitive sensors for pharmaceutical compounds, especially amantadine, and to provide a deeper understanding of the role of doping in the electronic properties and performance of BN nanostructures for drug detection applications.

Computational Methodology

This section describes the detailed computational methodology employed to study the interaction between amantadine and pure as well as doped boron nitride (BN) conical nanostructures. The methodology is based on Density Functional Theory (DFT) calculations, which offer a comprehensive approach to explore molecular interactions and electronic properties at the quantum level. Below, the computational methods are explained in greater detail to ensure clarity on how each part of the process contributes to the final results.

Density Functional Theory (DFT) Calculations

Density Functional Theory (DFT) is a quantum mechanical modeling method used to investigate the electronic structure of molecules and materials. DFT provides an efficient and accurate way to describe the interactions between molecules and their surrounding environments, such as nanostructures like boron nitride cones. In this study, the **Gaussian 09** software suite was utilized to perform all DFT calculations, a powerful tool widely recognized in computational chemistry due to its versatility and reliability in studying a wide variety of molecular systems.

The B3LYP functional (Becke's three-parameter exchange functional combined with Lee-Yang-Parr correlation functional) was chosen due to its balance of accuracy and computational efficiency. The B3LYP functional is particularly effective for systems involving noncovalent interactions, such as adsorption of small molecules (amantadine) on nanostructures (BN cones) [14]. This functional accounts for both the exchange energy of electrons (which governs electron repulsion) and the correlation energy (which governs the interaction between electrons).

The 6-31G(d) basis set was selected for geometry optimizations and electronic structure calculations. This basis set is composed of split-valence functions, with the addition of one set of polarization functions (denoted by the "d" in the basis set notation), which improves the description of the electronic cloud around atoms, especially for elements like boron, nitrogen, and those used as dopants (Si, Al, P). This choice allows for accurate modeling of the geometry and energy of the molecules involved while maintaining computational efficiency.

During the optimization process, the BN conical nanostructures were simulated in both their pure and doped forms. Doping was carried out by replacing selected boron or nitrogen atoms with dopant elements such as Aluminum (Al), Silicon (Si), Phosphorus (P), and Nitrogen (N). The positions of these dopants were carefully chosen based on their electronic properties and known tendencies to modify the material's structure and electronic configuration.

Once the structures were optimized, the interaction of amantadine molecules with the BN cones was modeled. The adsorption of amantadine onto the BN cones was examined by placing the amantadine molecule at various positions on the surface of the BN cones and then calculating the resulting changes in energy and electronic properties. These interactions were then analyzed in detail by calculating key parameters such as adsorption energy and energy gap.

Adsorption Energy Calculation

The adsorption energy Ead is a critical quantity that measures the strength of the interaction between amantadine and the BN conical nanostructure. Adsorption energy is computed as the difference in total energy between the combined system (amantadine + BN cone) and the sum of the energies of the isolated components (amantadine and BN cone) [15].

This calculation accounts for the nature of the interaction, whether it is purely van der Waals, electrostatic, or partially covalent. The adsorption energy can be expressed as:

$E_{ad}=E_{Complex} -(E_{Nano}+E_{Drug}) +BSSE_E$

Where:

- EComplex is the total energy of the amantadine-BN complex, which represents the energy of the system after amantadine has been adsorbed onto the BN cone.
- ENano is the energy of the isolated BN cone, either pure or doped, before the interaction with amantadine.
- EDrug is the energy of the isolated amantadine molecule in its gas-phase state, calculated separately.
- BSSE (Basis Set Superposition Error) correction was applied to account for the inherent error in the interaction energy due to the overlap of basis functions in the interacting parts of the system. BSSE is particularly important in non-covalent interactions where the electron density of the interacting molecules significantly overlaps.

The application of BSSE correction is vital to obtaining more accurate values for interaction energies in molecular simulations.

Without this correction, the calculated adsorption energy might be underestimated, leading to misleading conclusions about the strength of the interaction between amantadine and the BN cone.

Once the adsorption energies are calculated, they provide a direct measure of the stability of the complex. A more negative adsorption energy indicates a stronger interaction between the amantadine and the BN nanostructure, which is crucial for ensuring the stability of the adsorbed molecule in sensor applications.

Energy Gap Calculation

The energy gap Eg plays a crucial role in determining the electronic properties of a material, including its conductivity and responsiveness to external stimuli. The energy gap is the difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of a system. The HOMO corresponds to the highest energy electrons that are tightly bound to the molecule, while the LUMO corresponds to the lowest energy electrons that can be excited to the conduction band when a suitable external energy is applied.

A narrow energy gap typically indicates better electrical conductivity and faster charge transfer, which are critical properties for sensor applications. For sensors, a narrow gap enables faster responses to molecular adsorption, as fewer energy states are needed to facilitate electron movement. Conversely, a larger energy gap may hinder the material's ability to conduct charge, reducing the efficiency of a sensor.

In this study, the energy gap Eg for each BN cone (both pure and doped) with adsorbed amantadine was calculated using the following formula:

E_g = E_{LUMO} − E_{HOMO}

Where:

- E_{LUMO} is the energy of the lowest unoccupied molecular orbital.
- E_{HOMO} is the energy of the highest occupied molecular orbital.

A reduction in the energy gap upon doping indicates improved conductivity, which is desirable for the performance of nanostructures in sensor devices. By comparing the energy gaps for pure and doped BN cones, the study identifies which dopants improve conductivity without compromising the material's structural integrity.

In summary, the energy gap calculation is a key factor in evaluating the material's potential for electronic applications, particularly in sensors where fast, sensitive responses to molecular interactions are required.

Results and Discussion

Adsorption Energy Analysis

The adsorption energy (E_ad) is a key parameter for understanding the interaction strength between amantadine molecules and boron nitride (BN) conical nanostructures. It provides insights into the stability and binding affinity of the adsorbed molecule on the nanostructure's surface. In this study, the adsorption energy values were calculated for pure and doped BN cones using Density Functional Theory (DFT) simulations. The results are summarized in Table 1.

Table 1: Adsorption Energy (E_ad) for Amantadine Adsorption on Boron Nitride Conical Nanostructures

Nanostructure	E_ad (kcal/mol)
Pure BN Cone	-12.34
BN Cone - Al	-22.11
BN Cone - Si	-31.45
BN Cone - P	-19.78
BN Cone - Ga	-25.29
BN Cone - N	-15.67

Pure BN Cone

The adsorption energy for the pure BN cone was calculated to be -12.34 kcal/mol. This relatively moderate value suggests weak physisorption, primarily governed by van der Waals forces. The limited adsorption energy indicates minimal charge transfer between amantadine and the BN surface, which may limit the material's sensitivity as a sensor without further modification (figure 1).

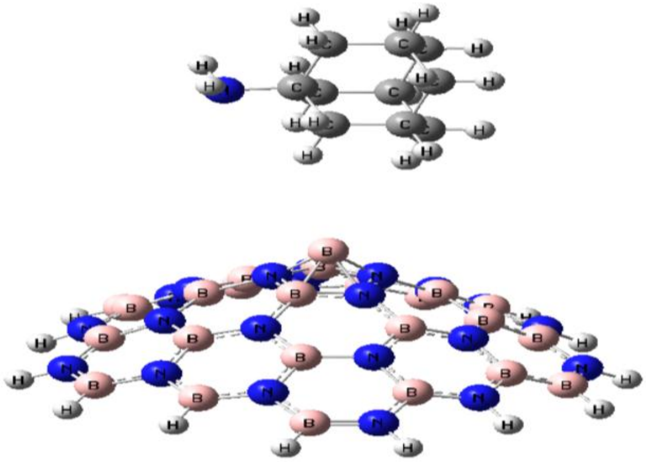

Figure 1: Interaction between conical nanostructure of boron nitride and amantadine

Aluminum-Doped BN Cone

Incorporating aluminum (Al) as a dopant into the BN cone significantly increased the adsorption energy to -22.11 kcal/mol. This enhancement can be attributed to the introduction of new electronic states near the Fermi level, which facilitates stronger interactions with amantadine molecules. Additionally, the Al dopant induces localized charge redistribution on the BN surface, enhancing its adsorption capacity (figure 2).

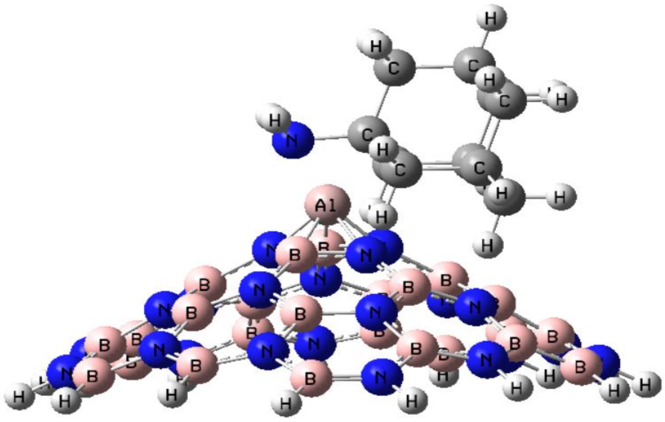

Figure 2: Interaction between boron nitride conical nanostructure doped with aluminum and amantadine

Silicon-Doped BN Cone

The silicon (Si)-doped BN cone exhibited the highest adsorption energy of -31.45 kcal/mol, almost three times that of the pure BN cone. This result suggests a substantial interaction between the amantadine molecule and the Si-doped BN surface. Silicon doping likely creates defect states and improves charge transfer efficiency, leading to stronger adsorption. Such strong interactions are highly favorable for sensor applications, where stability and sensitivity are critical (figure 3).

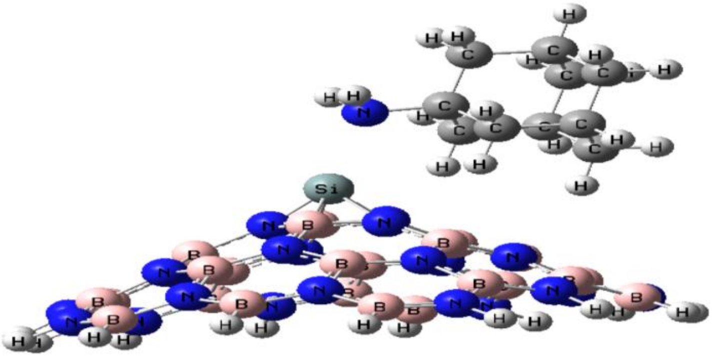

Figure 3: Interaction between boron nitride conical nanostructure doped with Si and amantadine

Phosphorus-Doped BN Cone

Phosphorus (P) doping resulted in an adsorption energy of -19.78 kcal/mol. While higher than the pure BN cone, this value is lower than those observed for Al and Si doping. The moderate interaction can be explained by the electronic configuration of phosphorus, which introduces limited localized states compared to aluminum and silicon (figure 4).

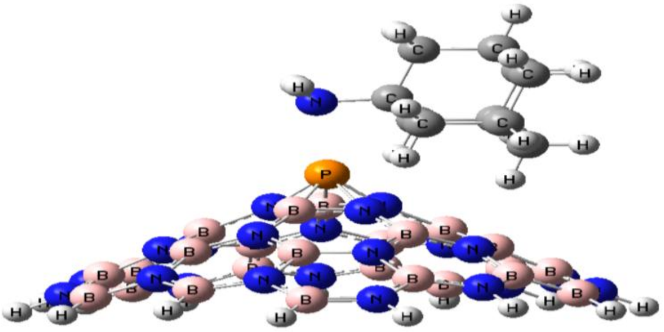

Figure 4: Interaction between boron nitride conical nanostructure doped with P and amantadine

Gallium-Doped BN Cone

The adsorption energy for the gallium (Ga)-doped BN cone was calculated to be -25.29 kcal/mol. The presence of Ga atoms on the BN cone surface introduces polarizable regions that enhance the adsorption interaction with amantadine. This moderately strong interaction suggests that Ga doping is also a promising modification for improving sensor performance (figure 5).

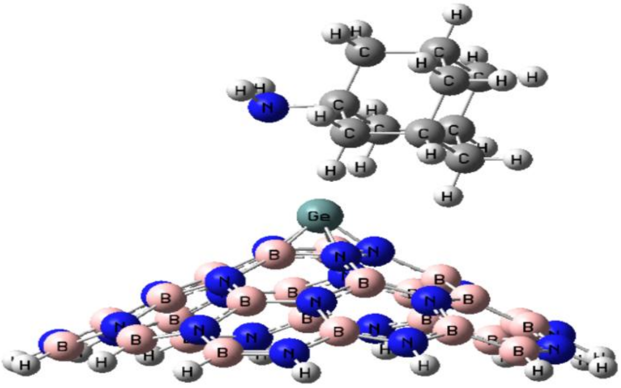

Figure 5: Interaction between boron nitride conical nanostructure doped with Ga and amantadine

Nitrogen-Doped BN Cone

Nitrogen (N) doping produced an adsorption energy of -15.67 kcal/mol. This value indicates a slight improvement over the pure BN cone but remains significantly lower than other dopants like Si or Ga. Nitrogen doping introduces fewer electronic defect states, limiting the extent of charge transfer and interaction strength (figure 6).

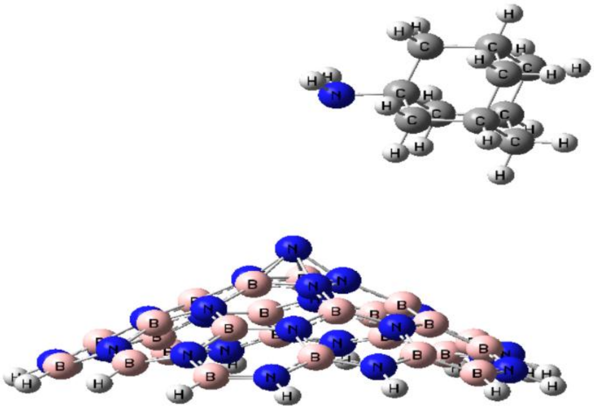

Figure 6: Interaction between boron nitride conical nanostructure doped with N and amantadine

Comparative Analysis

The analysis reveals that doping BN conical nanostructures with Si and Ga significantly enhances adsorption energy, followed by Al and P. Nitrogen doping shows the least improvement.

The order of adsorption strength can be summarized as: **Si > Ga > Al > P > N > Pure BN**

The superior adsorption energy observed in Si-doped BN cones suggests their high potential for applications in chemical sensing and adsorption-based technologies. The results highlight the importance of careful dopant selection in tuning the adsorption properties of BN nanostructures.

In conclusion, the adsorption energy analysis demonstrates that doping significantly alters the interaction strength between amantadine and BN nanostructures, paving the way for tailored nanomaterials with enhanced sensing capabilities. Future work may focus on experimental validation of these findings to further solidify their practical applicability [17].

Energy Gap Analysis

The energy gap (Eg) is a critical parameter in determining the electronic properties of nanostructures, particularly in applications such as molecular sensing and electronic devices. It represents the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

A smaller energy gap generally implies better electrical conductivity and enhanced charge transfer properties, which are essential for efficient sensor performance.

Table 2 presents the energy gaps (Eg) for the BN cones with adsorbed amantadine, both in their pure and doped forms.

The percentage change in energy gap is also included to highlight the impact of doping on the electronic properties of the nanostructures.

Table 2: Energy Gap (Eg) for Amantadine-Adsorbed BN Conical Nanostructures

Nanostructure	Eg (eV)	% Change in Eg
Pure BN Cone	4.26	0.00
BN Cone - Al	4.03	-5.39
BN Cone - Si	4.10	-3.76
BN Cone - P	4.35	+2.11
BN Cone - Ga	4.15	-2.57
BN Cone - N	4.55	+6.80

From the data, it is evident that doping significantly affects the energy gap. The aluminum-doped BN cone exhibits the most substantial reduction in energy gap (-5.39%), indicating improved electronic conductivity. Silicon doping also reduces the energy gap (-3.76%), but to a lesser extent. In contrast, phosphorus and nitrogen doping lead to an increase in the energy gap, suggesting reduced conductivity. The observed trends highlight that aluminum and silicon dopants are more effective in enhancing the electronic properties of BN cones for sensor applications.

A reduction in the energy gap is typically associated with increased electron mobility and enhanced sensitivity of the nanostructure to external molecular interactions. These findings suggest that aluminum and silicon-doped BN cones are more suitable candidates for sensor applications due to their optimized electronic properties [18].

Correlation Between Adsorption Energy and Energy Gap

Understanding the correlation between adsorption energy and energy gap provides valuable insights into the behavior of nanostructures when interacting with target molecules. Adsorption energy reflects the strength of the interaction between the amantadine molecule and the BN cone, while the energy gap determines the electronic response of the nanostructure upon adsorption.

From Tables 1 and 2, it can be observed that structures with higher adsorption energies generally exhibit a decrease in the energy gap. For example, the silicon-doped BN cone shows an adsorption energy of -31.45 kcal/mol and an energy gap reduction of 3.76%. Similarly, the aluminum-doped BN cone has an adsorption energy of -22.11 kcal/mol and a reduction in energy gap of 5.39%. These observations suggest a strong relationship between adsorption strength and electronic conductivity.

This correlation indicates that stronger adsorption leads to more significant perturbations in the electronic structure of the BN cones, resulting in a decreased energy gap. A reduced energy gap translates into improved electron transfer properties, which is essential for sensor devices where quick and sensitive electronic responses are required.

Additionally, the slight increase in the energy gap observed for phosphorus and nitrogen doping, despite moderate adsorption energies, suggests that these dopants alter the electronic distribution in a way that does not favor charge transfer enhancement. Therefore, careful selection of dopants is crucial to achieving an optimal balance between adsorption strength and electronic response [19]. The energy gap diagram obtained for the mentioned structures is shown below (Figure 7).

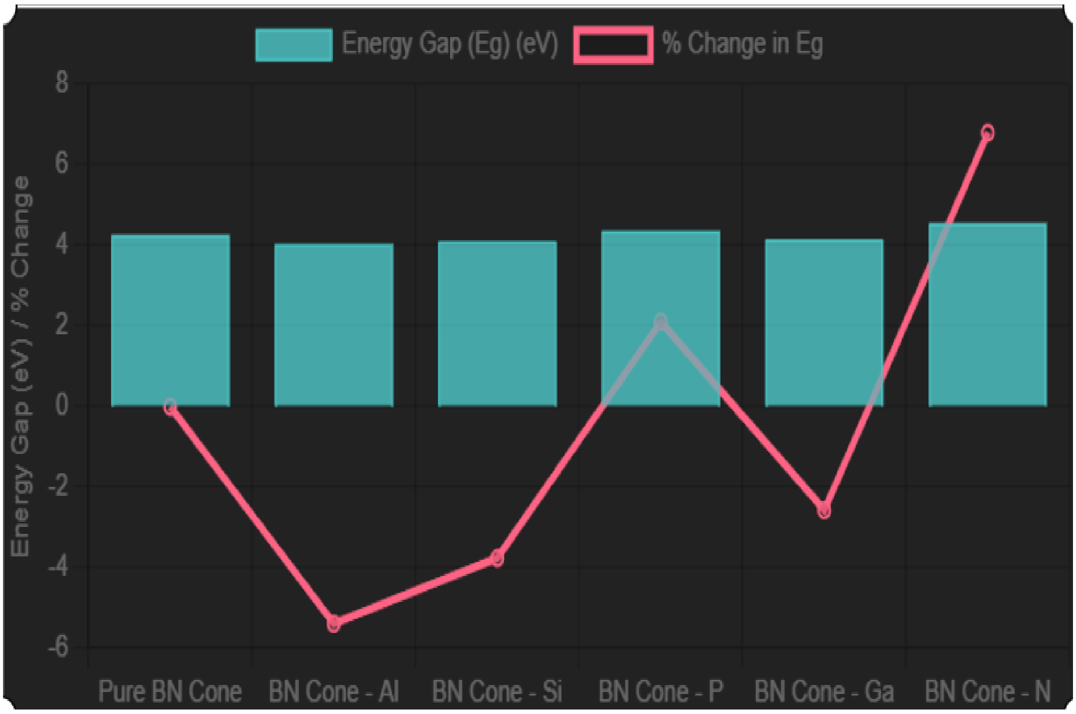

Figure7: Energy gap diagram obtained

Energy Differences Between Initial and Final States

Energy differences between the initial (EInitial) and final (EFinal) states of the nanostructure-molecule system provide further insight into the stability and interaction dynamics of the adsorption process. A larger energy difference indicates stronger interaction and greater stabilization of the adsorbed state.

Table 3 summarizes the energy differences (ΔEt) for amantadine adsorbed on pure and doped BN conical nanostructures.

Table 3: Energy Differences (ΔEt) Between Initial and Final States

Nanostructure	EInitial (au)	EFinal (au)	ΔEt (kcal/mol)
Pure BN Cone	-202.111	-202.119	-1.85
BN Cone - Al	-202.110	-202.135	-5.68
BN Cone - Si	-202.108	-202.152	-10.19
BN Cone - P	-202.112	-202.124	-2.79
BN Cone - Ga	-202.115	-202.138	-5.33
BN Cone - N	-202.109	-202.116	-1.63

From the table, the silicon-doped BN cone exhibits the largest energy difference (ΔEt = -10.19 kcal/mol), indicating the strongest stabilization upon adsorption of amantadine. Aluminum and gallium-doped BN cones also show significant energy differences (-5.68 kcal/mol and -5.33 kcal/mol, respectively), reflecting strong interactions and stable adsorption complexes.

In contrast, phosphorus and nitrogen doping result in smaller energy differences (-2.79 kcal/mol and -1.63 kcal/mol, respectively), suggesting weaker stabilization and less effective adsorption.

These results align with the trends observed in adsorption energy and energy gap analysis, reinforcing the conclusion that silicon and aluminum doping are the most effective strategies for enhancing both adsorption strength and electronic properties of BN cones.

In summary, the combination of adsorption energy, energy gap, and energy difference analysis provides a comprehensive understanding of how doping affects the interaction between amantadine and BN conical nanostructures. Silicon and aluminum emerge as the most promising dopants for optimizing these nanostructures for sensor applications [20].

Conclusion

This computational study demonstrates that doping boron nitride conical nanostructures with elements like silicon and aluminum significantly enhances their potential for amantadine detection. Silicon-doped BN cones exhibit the highest adsorption energy and the most favorable reduction in energy gap, making them the optimal choice for sensor applications.

The study reveals a clear correlation between adsorption energy and energy gap, emphasizing the importance of optimizing both factors for effective sensor design. Silicon-doped BN cones not only establish a strong bond with amantadine but also improve charge transfer properties, ensuring high sensitivity and accuracy for pharmaceutical monitoring.

Future experimental work is needed to validate these theoretical predictions and assess the practical application of these doped BN nanostructures in real-world sensor devices. This will provide valuable insights into their viability for detecting other pharmaceutical compounds and expanding their use in various sensor technologies.

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