



Original Research Article

TNT interaction with BN Nanocone: A comprehensive computational study

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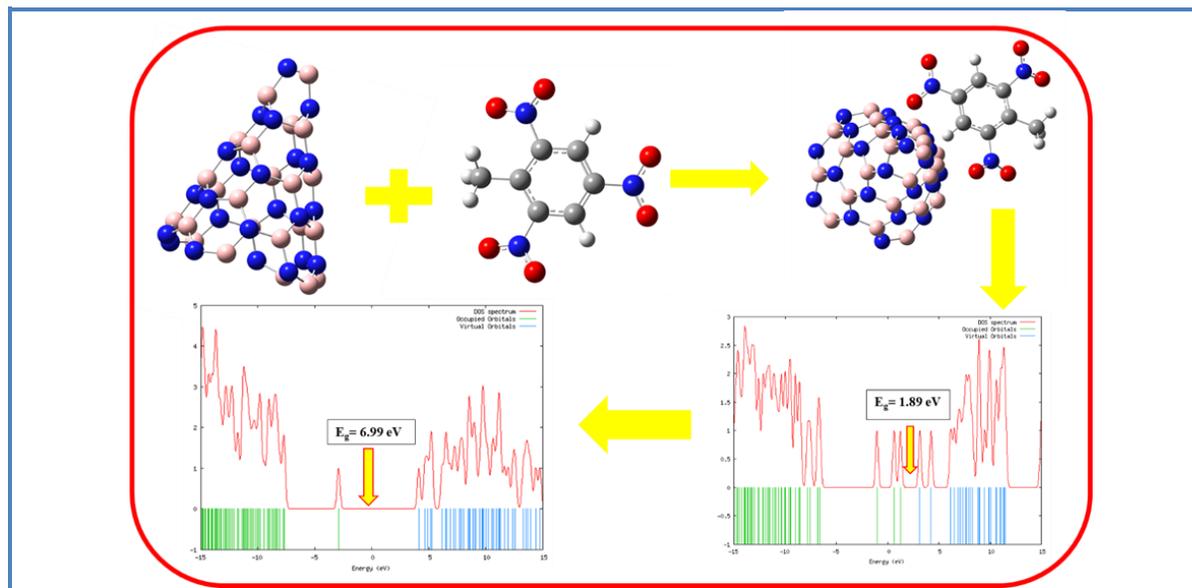
ABSTRACT

In this study, trinitrotoluene (TNT) adsorption on the surface of the boron nitride nanocone was investigated using the infra-red (IR), natural bond orbital (NBO), and frontier molecular orbital (FMO) computations. The calculated negative adsorption energies, Gibbs free energy changes (ΔG_{ad}) and great thermodynamic constants (K_{th}) showed that the TNT adsorption was spontaneous, irreversible, and experimentally possible. The effect of temperature on the thermodynamic parameters was also studied and the findings indicated that, at 298.15 K the TNT adsorption process had the highest efficiency. The values of the enthalpy changes (ΔH_{ad}) and specific heat capacity (C_v) revealed that, BN nanocone can reduce the heat sensitivity of the TNT and this nanostructure can be used for making new thermal sensors for detecting the TNT. The NBO results revealed that, TNT interaction with BN nanocone was a chemisorption as monovalent chemical bonds with SP^3 hybridization were formed between TNT and the adsorbent in all of the evaluated configurations. The computed DOS spectrums showed that, the BN nanocone was an ideal recognition element for developing novel TNT electrochemical sensors as the bandgap experienced a sharp increase in all of the studied configuration when TNT was adsorbed on the surface of the nanostructure. The frontiers molecular orbital parameters including the energies of HOMO and LUMO orbitals, electrophilicity, chemical hardness, chemical potential and maximum transferred charge was also evaluated and the results demonstrated that, the TNT reactivity and softness improved when it was adsorbed on the BN nanocone. All of the computations were conducted using the density functional theory method in the B3LYP/6-31 G(d) level of theory.

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Graphical Abstract

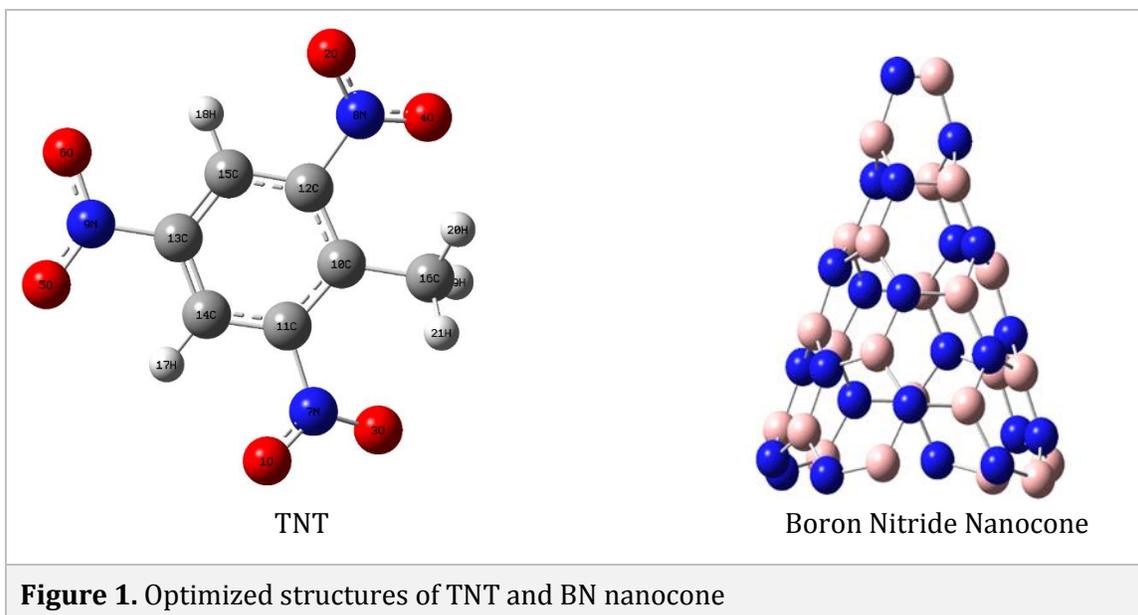


Introduction

TNT (Figure 1) detection and removal is very important as it has been widely used in the production of bombs, war weapons, photographic compounds and dyes and its discharge in the environment is a global concern [1-3]. This nitroaromatic explosive creates irreversible problems for human and other living organisms including the skin rashes and haemorrhages, arrhythmia, liver and renal malfunction, peripheral neuritis and aplastic anemia [4-6]. Moreover, previous studies showed that, the TNT is mutagenic and carcinogenic and the people who work in ammunition sites or live in places with high terroristic activities are more probable to be exposed to this toxic contaminant [7-9]. therefore, finding a novel adsorbent and sensor for TNT is of great importance. The next problem about nitroaromatic explosives is their high heat sensitivity which can lead to explosions at inappropriate times and unwanted economic damages and casualties. consequently, reducing the heat sensitivity of

explosives has become an attractive research field in the recent years [10-14].

On the other hand, boron nitride nanocone (Figure 1) has prominent features such as chemical oxidation inertness, mechanical toughness, excellent thermal and electrical conductivity, constant bandgap, good specific surface area and high biocompatibility that make it very suitable in some research areas like drug delivery, sensor, removal of contaminants and advanced materials [15-23]. In addition, in the recent decade, BN nanostructures gained a huge attention all over the world because of their lower toxicity and more environmental friendly behaviour than their carbon-based counterparts [24-28]. In this regard, the applicability of BN nanocone as an adsorbent for removal of TNT, a new recognition element for fabricating thermal and electrochemical sensor for detection of TNT and also the influence of this nanostructure on the heat sensitivity of this nitroaromatic explosive were evaluated by density functional theory computations in this study.



Results and Discussion

NBO and structural analysis

To find the most stable configuration, TNT interaction with BN nanocone was assessed at three different situations. As seen in [Figure 2](#), in A-Conformer, TNT was located at the open-end of the nanocone. In B-Conformer, TNT was inserted near the surface of the adsorbent towards its nitro (NO_2) functional group and in C-Conformer, the benzene ring of TNT is placed in parallel form towards the surface of BN nanocone. Both the initial and optimized structures are presented in [Figure 3](#). It seems in all of the studied situations some chemical bonds are formed between BN nanocone and the adsorbate because after geometrical optimization tangible deformations occurred in the structures of TNT and BN nanocone specially near the place of interaction [[20-22](#)].

For obtaining further information about the nature of interactions and also the mechanism of adsorption, adsorption energy and NBO parameters including occupancy, bond order, bondlengths, bond energy and hybridizations were calculated and the results are given in [Table 1](#). As it is obvious, adsorption process in

all of the investigated situations is experimentally possible because the computed adsorption energy values are -1152.828, -453.319 and -108.375 kJ/mol for A, B and C conformers respectively. The next matter can be deduced from the presented data at [Table 1](#) is that A-Conformer is the most stable configuration as it has the lowest total electronic energy and the most negative adsorption energy. In other words, formation of this conformer is more probable than other derived products [[26-28](#)]. The NBO results showed that, at A-Conformer, four covalent bonds with SP^3 hybridization are created between the oxygen atoms of TNT nitro functional groups and BN nanocone. However, in B and C conformers, only one covalent bond is formed between the adsorbate and the adsorbent. Therefore, the TNT interaction with BN nanocone is a chemisorption in all of the studied configurations and the interactions in A-Conformer is stronger than that of the other configurations. The NBO results are in an admissible accordance with the calculated adsorption energy values and also the tangible changes in the complexes structures after geometrical optimizations [[23-25](#)].

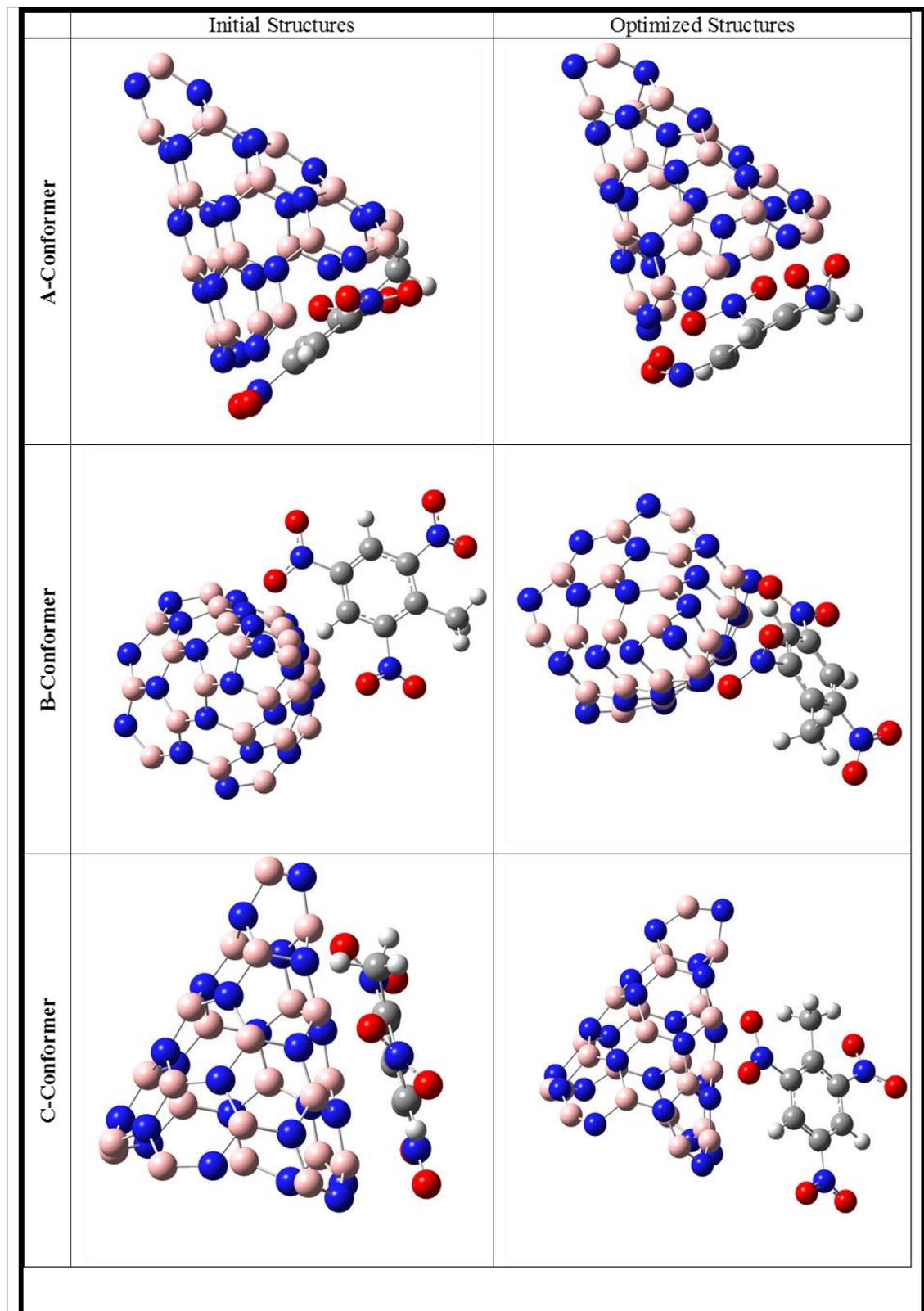


Figure 2. Initial and optimized structures of TNT complexes with BN Nanocone

Table 1. The calculated NBO and structural parameters for TNT, BN nanocone and their complexes

		Bond length (Å)	Bond order	Occupancy	Hybridization	Bond energy (a.u.)	Total electronic energy (a.u.)	Adsorption energy (kJ/mol)	The lowest frequency (cm ⁻¹)	Zero-point energy (kJ/mol)
TNT	---	---	---	---	---	---	-868.580	---	45.029	394.35
BN Nanocone	---	---	---	---	---	---	-1798.737	---	75.428	724.21
A-Conformer	O ₁ -N	1.48	1	1.96	Sp ^{2.99}	-0.740	-2667.756	-1152.828	106.651	1171.43
	O ₃ -B	2.01	1	1.98	Sp ^{2.98}	-0.650				
	O ₅ -N	1.76	1	1.95	Sp ^{2.96}	-0.540				
	O ₆ -N	1.89	1	1.99	Sp ^{2.96}	-0.410				
B-Conformer	O ₆ -N	1.94	1	1.99	Sp ^{2.93}	-0.665	-2667.490	-453.319	13.663	1125.41
C-Conformer	O ₄ -B	1.88	1	1.97	Sp ^{2.97}	-0.650	-2667.359	-108.375	8.731	1122.62

Thermodynamic parameters

The values of adsorption enthalpy changes (ΔH_{ad}) were calculated using the Equation 3, and the results are presented as a function of temperature (Figure 3). As can be seen, adsorption process in all of the configurations is exothermic and temperature does not have any tangible effect on this parameter. Therefore, BN

nanocone is an ideal sensing material for developing new thermal sensors to TNT detection. As, thermal sensors are based on a reaction between the desired analyte and a recognition element and this reaction should be highly exothermic or endothermic. Then, the temperature changes will be detected by a sensitive thermistor and this signal can be used for the determination of the analyte [26-28].

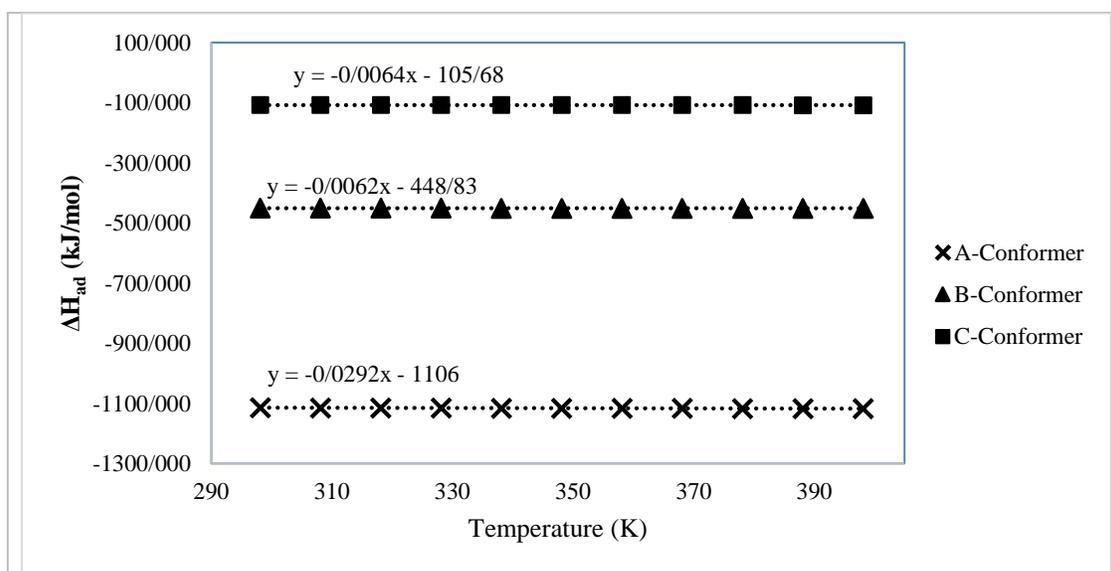


Figure 3. The calculated adsorption enthalpy changes values (ΔH_{ad}) in the temperature range of 298-398 K at 10° intervals

The values of Gibbs free energy changes (ΔG_{ad}) and thermodynamic equilibrium

constant (K_{th}) were calculated using the Equations 4 and 5, and then, the logarithm of K_{th}

and ΔG_{ad} were depicted as a function of temperature (Figures 4 and 5). As it is obvious, TNT interaction with BN nanocone is spontaneous and irreversible in all of the evaluated conformers. By enhancing of

temperature ΔG_{ad} values experienced a slight increase and K_{th} decreased sharply for all of the investigated conformers which indicates in the room temperature TNT adsorption is more favourable [24].

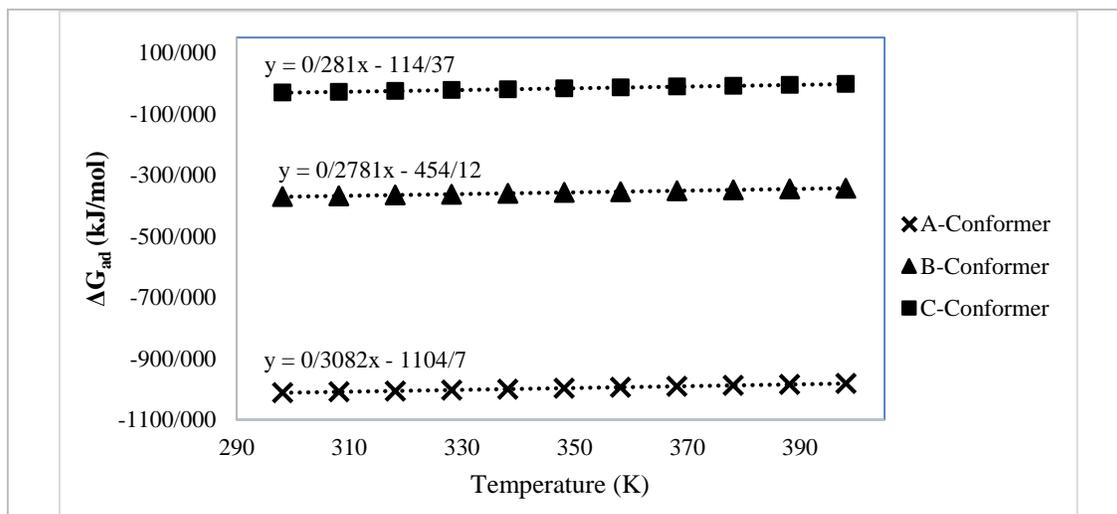


Figure 4. The calculated Gibbs free energy changes values (ΔG_{ad}) in the temperature range of 298-398 K at 10° intervals

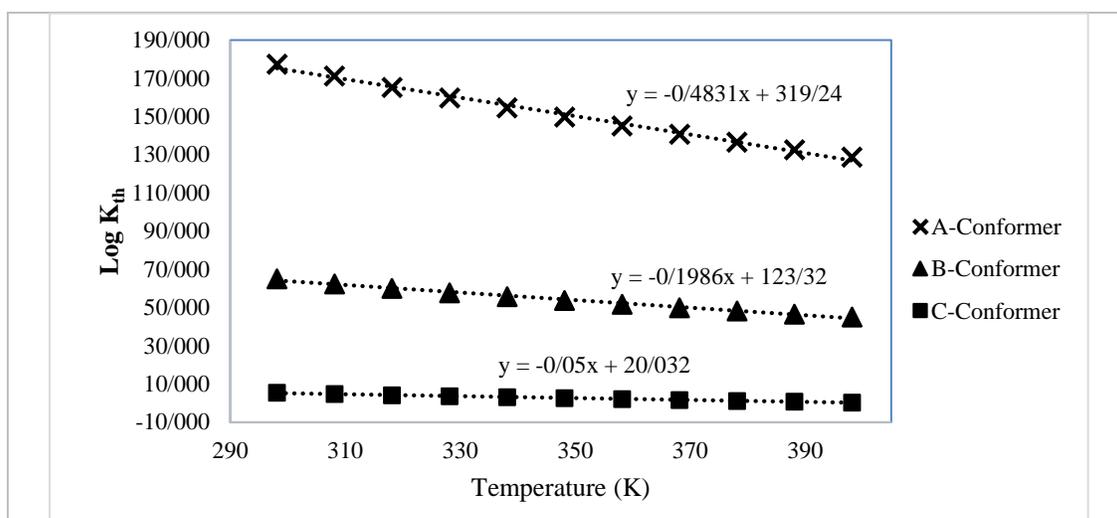


Figure 5. The logarithm of calculated thermodynamic equilibrium constant values ($\log K_{th}$) in the temperature range of 298-398 K at 10° intervals.

The values of adsorption entropy changes were also calculated using the Equation 6 and the results are presented in Figure 6. As can be observed, this parameter is negative for all of

the conformers which show TNT adsorption on the surface of BN nanocone because of the aggregation in TNT complexes with the nanostructures [28].

The calculated specific heat capacity values (C_v) for the TNT and its derived products with BN nanocone are provided in Figure 7. As it is clear, the C_v increased remarkably when TNT adsorbs on the surface of the nanostructure. C_v is described as the amount of heat which is needed for increasing the temperature of a

substance to 1 °C. Therefore, energetic molecules with higher C_v values will have lower heat sensitivity. So, it can be deduced that the heat sensitivity of the TNT complexes with BN nanocone are lower than the pure TNT without nanostructure [24].

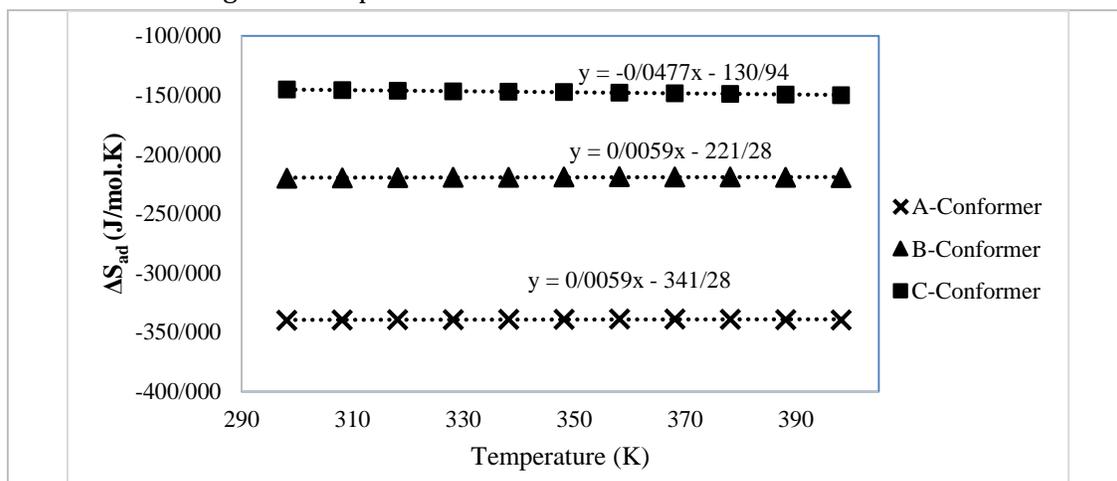


Figure 6. The calculated adsorption entropy changes values (ΔS_{ad}) in the temperature range of 298-398 K at 10° intervals

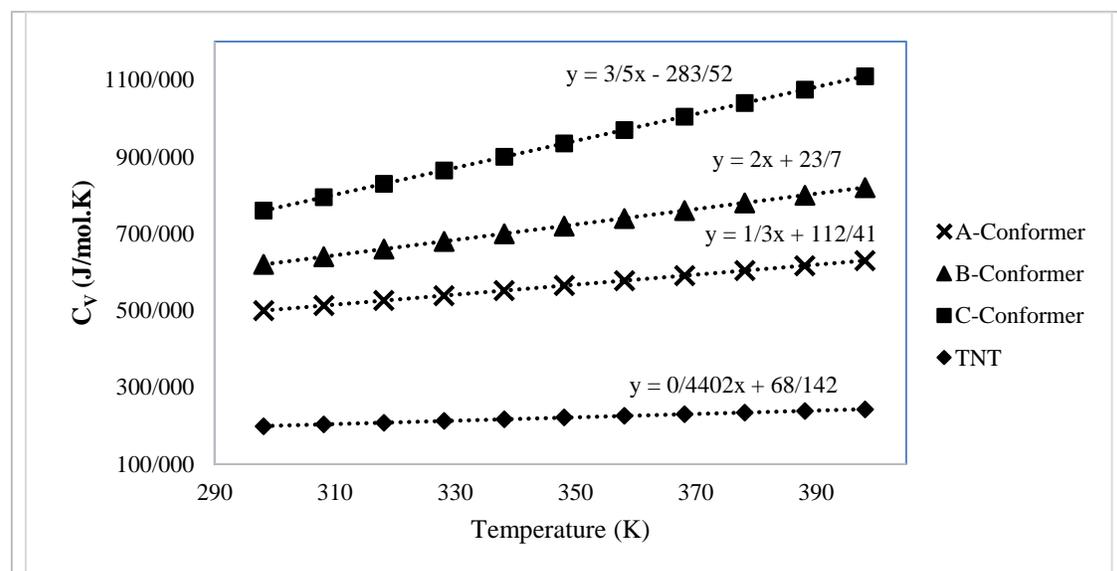


Figure 7. The calculated specific heat capacity values (C_v) in the temperature range of 298-398 K at 10° intervals

8. As can be seen, the bandgap of BN nanocone which is shown by E_g symbol is 1.89 eV which indicates this nanostructure is conductive and it has a good electrocatalytic activity; however, when the TNT adsorbs on the surface of the adsorbent E_g increases tangibly. Therefore, this sharp reduction in the electrical conductance can be used as a signal for TNT detection and BN nanocone is an ideal electroactive sensing material for construction of TNT electrochemical sensors [24]. Chemical hardness (η) and chemical potential (μ) were the next investigated parameters that were calculated using the Equation 8 and 9 and the results are reported in Table 2. These parameters are acceptable standards for estimating the reactivity of molecules. In fact, soft molecules with low chemical hardness and high chemical potential are more reactive than hard compounds because electron transmissions that are essential for implementation of chemical reactions can be done more conveniently in them [25]. The presented data in Table 2, reveals that chemical hardness and chemical potential experience a

remarkable decline and increase when TNT adsorbs on the surface of BN nanocone. Therefore, TNT complexes with BN nanocone are more reactive than the pure TNT [26-28].

Electrophilicity (ω) and maximum transferred charge capacity (ΔN_{\max}) of the studied structures were also calculated by Equations 10 and 11 and the results are tabulated in Table 2. Both parameters explain the tendency of molecules for absorbing electrons. As it is obvious, B-Conformer has more ω and ΔN_{\max} than pure TNT which indicates this derived product has more affinity towards electron. However, A and C conformers has lower tendency for absorbing electron due to their lower ω and ΔN_{\max} values in comparison to pure TNT without nanostructure [2].

The dipole moment of the studied structures was also investigated. As the provided data in Table 2, demonstrate clearly TNT complexes with BN nanocone have higher dipole moment values than the pure TNT. Therefore, TNT complexes with BN nanocone have better solubility in water than the pure TNT [10].

Table 2. The values of E_H , E_L , bandgap, chemical hardness, chemical potential, electrophilicity, maximum transferred charge capacity and dipole moment for TNT, BN Nanocone and their complexes

	E_H (eV)	E_L (eV)	E_g (eV)	η (eV)	μ (eV)	ω (eV)	ΔN_{\max} (eV)	Dipole moment (Deby)
TNT	-8.001	3.264	11.265	5.633	-2.368	0.498	0.420	1.110
BN nanocone	1.241	3.130	1.889	0.944	2.186	2.529	-2.314	6.340
A-Conformer	-2.905	4.081	6.987	3.493	0.588	0.049	-0.168	19.020
B-Conformer	-3.781	0.432	4.213	2.107	-1.675	0.666	0.795	29.500
C-Conformer	-4.424	1.401	5.825	2.912	-1.511	0.392	0.519	14.710

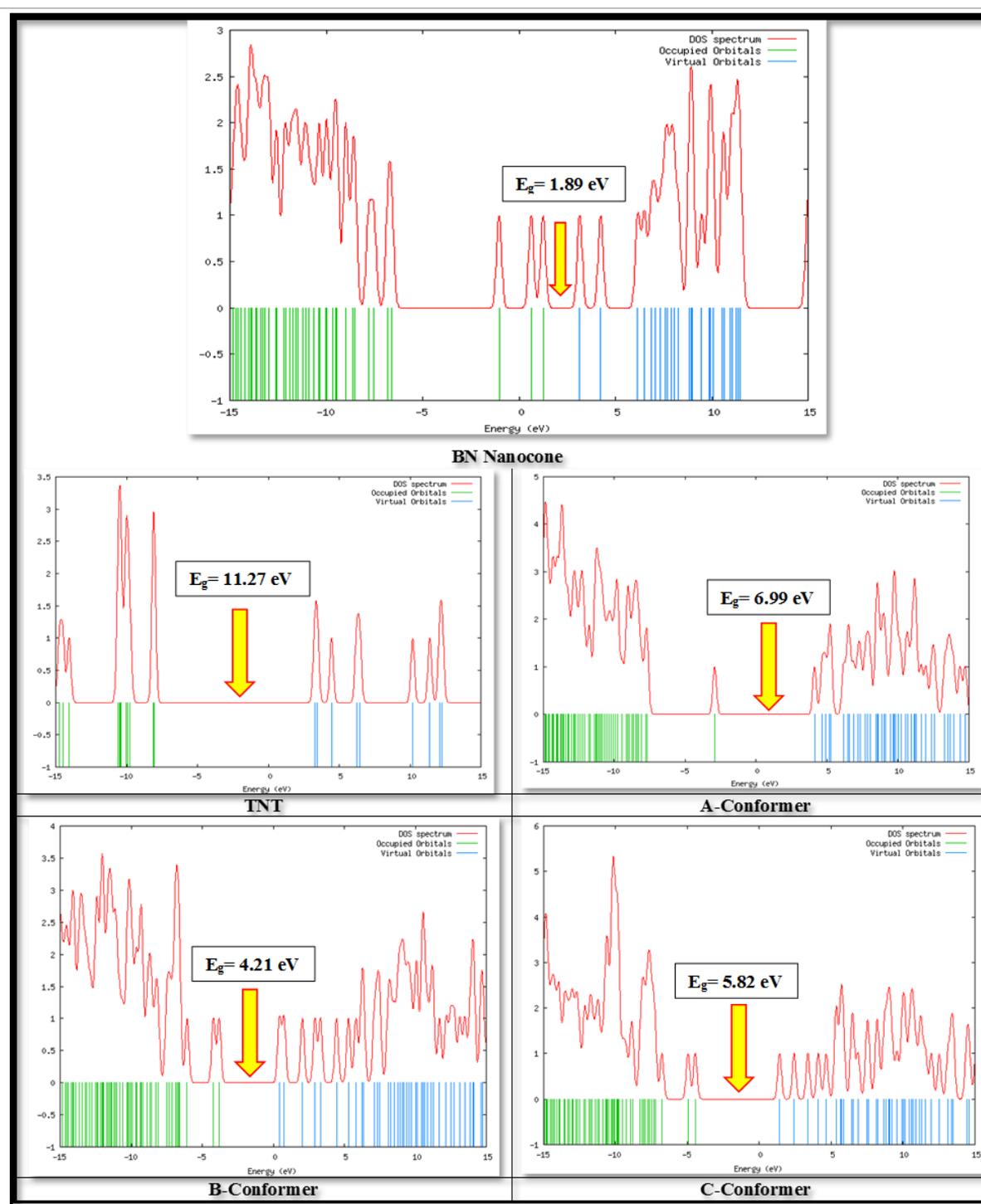


Figure 8. DOS spectra for TNT, BN Nanocone and their complexes

Conclusions

Removal, detection, and reducing the heat sensitivity of the TNT are very important. Also,

BN nanostructures have prominent features which make them suitable materials in sensor developments, removal of contaminants and

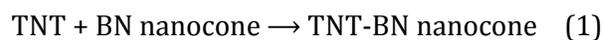
advanced materials. Therefore, TNT adsorption on the BN nanocone was evaluated in this research study by the DFT computations. The values of the adsorption energy, enthalpy changes, Gibbs free energy changes, and thermodynamic constants revealed that, the TNT interaction with the adsorbent is exothermic, spontaneous, irreversible, and experimentally feasible. The DOS spectrums showed that, the bandgap of the BN nanocone undergoes sharp changes which revealed the capability of this nanostructure for construction novel electrochemical sensors to TNT determination. The NBO results demonstrated strong chemical bonds are created between the TNT and the adsorbent and their interaction is a chemisorption in all of the conformers. In addition, the specific heat capacity values (C_v) proved the heat sensitivity of TNT decreased when it is adsorbed on the surface of BN nanocone. Some structural parameters such as electrophilicity, dipole moment, chemical hardness, and chemical potential were also discussed in details.

Computational methods

The structures of the BN nanocone, TNT and their derived products were designed by Nanotube modeler 1.3.0.3 and GuassView 6 softwares [29-30]. To find the most stable configuration, the adsorption process was evaluated at three different conformers. At first, all of the designed structures were optimized geometrically. Then, the IR, NBO and Frontier molecular orbital (FMO) computations were done on them [25]. All of the computations were performed by the Gaussian 16 software using the density functional theory method in the B3LYP/6-31G (d) level of theory [31]. This level of theory was selected because in former reports its results were in a good agreement with the experimental findings. GuassSum

software was employed for obtaining density of states (DOS) spectrums [32]. All of the computations were done in the aqueous phase in the temperature range of 298-398 at 10° intervals.

The studied processes were as follows:



Equations 2-6 were used for calculating adsorption energy values (E_{ad}) and thermodynamic parameters including adsorption enthalpy changes (ΔH_{ad}), Gibbs free energy changes (ΔG_{ad}) thermodynamic equilibrium constants (K_{th}) and entropy changes (ΔS_{ad}), respectively [22-24].

$$E_{ad} = (E_{(\text{TNT-BN nanocone})} - (E_{(\text{TNT})} + E_{(\text{BN nanocone})})) \quad (2)$$

$$\Delta H_{ad} = (H_{(\text{TNT-BN nanocone})} - (H_{(\text{TNT})} + H_{(\text{BN nanocone})})) \quad (3)$$

$$\Delta G_{ad} = (G_{(\text{TNT-BN nanocone})} - (G_{(\text{TNT})} + G_{(\text{BN nanocone})})) \quad (4)$$

$$K_{th} = \exp\left(-\frac{\Delta G_{ad}}{RT}\right) \quad (5)$$

$$\Delta S_{ad} = (S_{(\text{TNT-BN nanocone})} - (S_{(\text{TNT})} + S_{(\text{BN nanocone})})) \quad (6)$$

In the above mentioned equations, E denotes the total electronic energy of each structure, H stands for the sum of the thermal correction of enthalpy and total energy of the evaluated materials. The G is the sum of the thermal correction of Gibbs free energy and total energy for each of the studied structures. R is the ideal gas constants, T stands for the temperature and S is the thermal correction of entropy for each structure [24]. Frontier molecular orbital parameters including band gap (E_g), chemical hardness (η), chemical potential (μ), electrophilicity (ω) and the maximum

transferred charge (ΔN_{\max}) were calculated using the Equations 7-11 [25-27].

$$E_g = E_{LUMO} - E_{HOMO} \quad (7)$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (8)$$

$$\mu = (E_{LUMO} + E_{HOMO})/2 \quad (9)$$

$$\omega = \mu^2 / 2\eta \quad (10)$$

$$\Delta N_{\max} = -\mu/\eta \quad (11)$$

E_{LUMO} and E_{HOMO} in Equations 7 to 11 stand for the energy of the lowest unoccupied molecular orbital and the energy of the highest occupied molecular orbital respectively [28].

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Conflict of Interest

The author does not have any conflicts of interest to disclose.

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