



Original Research Article

Adsorption of Tetryl on the Surface of Carbon Nanocone: A Theoretical Investigation

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ABSTRACT

In this paper, the performance of carbon nanocone as an ideal adsorbent and sensing material for tetryl was investigated by density functional theory. For this aim, the structures of tetryl, carbon nanocone and their complexes were optimized geometrically. Afterwards, IR and FMO computations were done on them. The obtained thermodynamic parameters showed the interaction of carbon nanocone with tetryl is spontaneous, exothermic and experimentally possible. The Molecular orbital parameters like band gap, maximum transferred charge, electrophilicity, chemical potential and chemical hardness was also inspected and the results indicated that carbon nanocone can be used as an excellent sensing material for electrochemical detection of tetryl. The specific heat capacity values have also proved the heat sensitivity has abated after tetryl adsorption on carbon nanocone surface.

Keywords: Tetryl, Carbon Nanocone, Adsorption, Density Functional Theory, Explosives

Introduction

Tetryl which its chemical structure and IUPAC name is presented in figure 1, is a toxic nitroaromatic explosive. This energetic compound that is widely used in the construction of bombs, has negative effects on the health of humans and other living organisms like liver damage, nausea, allergenic dermatitis, anemia, blood damage, cataracts, discoloration of skin and hair, tingling sensation in the nose, skin rashes and irritation, severe headaches, nosebleeds, fatigue and weight loss. Therefore, its removal and determination is of critical significance [1-8]. On the other hand, carbon nanocone is an intermediate conical nanostructure between a graphene sheet and a carbon nanotube (Figure 2). This nanostructure could be synthesized by cutting 1-5 sectors of angle 60° from a graphene sheet connecting the originated edges by the cut, with 1-5 pentagons at the aspects. The mechanical stability and excellent electrocatalytic activity of carbon nanocone make it an appropriate adsorbent and recognition element for removal of various contaminants and developing new sensors [9-12]. The adsorption of proline amino acid, NO, H₂, HCl and NH₃ on the surface of carbon nanocone has also been studied. Hence, the aim of this investigation is evaluating the performance of carbon nanocone as an adsorbent and also as a sensor for removal and determination of tetryl by density functional theory [13-20].

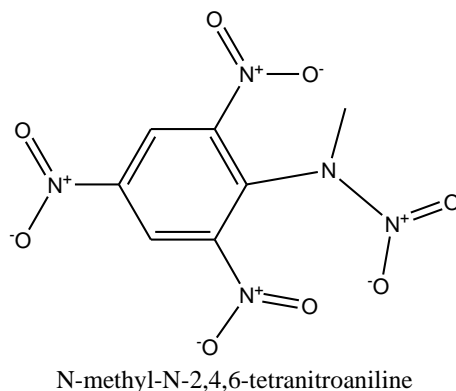


Figure 1. The chemical structure and IUPAC name of tetryl

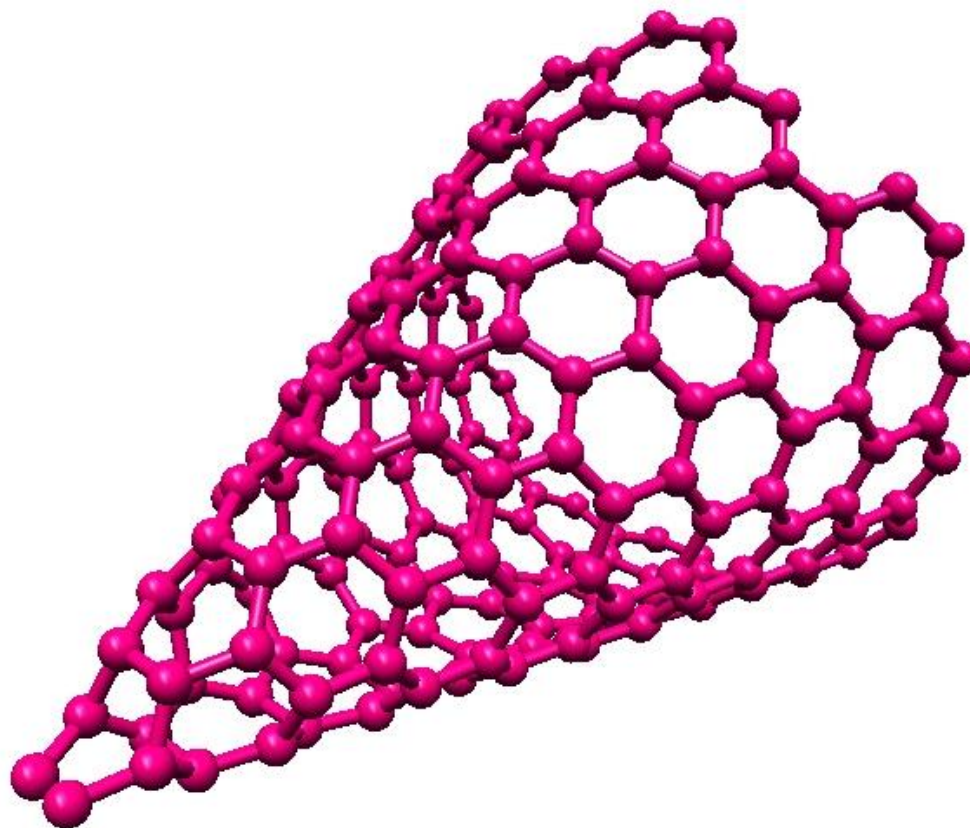
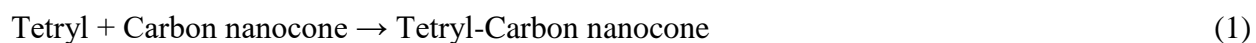


Figure 2. The structure of carbon nanocone

Computational Methods

The structures of tetryl, carbon nanocone and their complex were designed by nanotube modeler and gauss view softwares respectively. Then their structures were optimized and IR and frontier molecular orbital computations were performed on them by Spartan software. All of the computations were carried out at atmospheric pressure and aqueous phase. The evaluated process was as follows:



Results and discussion

Thermodynamic parameters

The thermodynamic parameters of the adsorption process were calculated via the following equations:

$$\Delta H_{ad} = H_{\text{tetryl-carbon nanocone}} - (H_{\text{tetryl}} + H_{\text{carbon nanocone}}) \quad (2)$$

$$\Delta G_{ad} = G_{\text{tetryl-carbon nanocone}} - (G_{\text{tetryl}} + G_{\text{carbon nanocone}}) \quad (3)$$

$$\Delta S_{ad} = S_{\text{tetryl-carbon nanocone}} - (S_{\text{tetryl}} + S_{\text{carbon nanocone}}) \quad (4)$$

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

In these formulas, H represents the sum of thermal correction of enthalpy and SCF total energy for each reactant. G denotes the sum of thermal correction of Gibbs free energy and SCF total energy for each material. S is the symbol of thermal correction of entropy, R is the ideal gas constant and T is the temperature. As can be seen from table 1, the adsorption procedure of tetryl is spontaneous, exothermic, non-equilibrium and experimentally possible due to the negative values of enthalpy changes and Gibbs free energy alterations. It seems after adsorbing of tetryl on the surface of carbon nanocone aggregations occurs owing to the negative values of entropy changes. The influence of temperature on the adsorption process was also investigated. As it is clear by increasing temperature the interaction of tetryl with the adsorbent has abated sharply because the values of thermodynamic equilibrium constants have decreased remarkably by increasing temperature. So, this nano-adsorbent has the potential to be used for removal of this toxic nitroaromatic compound.

The specific heat capacity values were also calculated and inspected and the obtained data are given in table 2. As it can be observed the C_v values have increased tangibly after tetryl adsorption on the surface of carbon nanocone. Therefore, the tetryl-carbon nanocone derivative has less heat sensitivity in comparison to pure explosive.

Table 1. The values of Gibbs free energy changes (ΔG_{ad}), enthalpy changes (ΔH_{ad}), thermodynamic equilibrium constant (K_{th}) and entropy changes (ΔS_{ad}) for the adsorption process of tetryl in the temperature range of 298-398 K.

Temperature	ΔH_{ad}	ΔG_{ad}	K_{th}	ΔS_{ad}
298	-775.827	-710.400	2.909E+124	-218.0901
308	-775.769	-708.229	1.139E+120	-217.8716
318	-775.692	-705.975	8.184E+115	-217.8656
328	-775.609	-703.575	9.964E+111	-218.2868
338	-775.546	-701.173	2.067E+108	-218.7449
348	-775.488	-698.774	6.987E+104	-219.184
358	-775.456	-696.377	3.692E+101	-219.6644
368	-775.452	-693.950	2.911E+98	-220.2771
378	-775.463	-691.548	3.376E+95	-220.8279
398	-775.483	-689.214	5.665E+92	-221.2026

Table 2. The specific heat capacity values for tetryl and its derivative with carbon nanocone

Temperature	Tetryl	Tetryl-Carbon nanocone
298	252.953	484.7947
308	258.555	496.5335
318	264.086	508.084
328	269.548	519.446
338	274.938	530.619
348	280.258	541.601
358	285.507	552.390
368	290.683	562.986
378	295.787	573.386
398	300.816	583.590

Frontier molecular orbital analysis

The frontier molecular orbital parameters were calculated by the following equations and the results are tabulated in table 3.

$$HLG = E_{LUMO} - E_{HOMO} \quad (6)$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (7)$$

$$\mu = (E_{LUMO} + E_{HOMO})/2 \quad (8)$$

$$\omega = \mu^2 / 2\eta \quad (9)$$

$$\Delta N_{max} = -\mu / \eta \quad (10)$$

In these formulas, E_{LUMO} is the energy of the lowest unoccupied molecular orbital and E_{HOMO} is the energy of the highest occupied molecular orbital. HLG is the energy discrepancy between HOMO and LUMO orbital that have a direct relationship with conductivity. As can be seen, this factor has increased after adsorption of tetryl on the surface of carbon nanocone significantly. Hence, this nanostructure can be used for construction of new electrochemical sensors for determination of tetryl and using the decline in conductivity as detection signal. The chemical hardness (ω) that have a direct relationship with chemical reactivity has decreased after interaction of tetryl with carbon nanocone. Therefore, the tetryl-adsorbent complex has lower reactivity than pure tetryl without carbon nanocone.

Table 3. The values of frontier molecular orbital parameters for tetryl adsorption process

	E_H (eV)	E_L (eV)	HLG (eV)	η (eV)	ω (eV)	ΔN_{max} (eV)	Dipole moment (deby)	Density= m/v ($\text{amu}/\text{\AA}^3$)
Tetryl	-8.22	2.68	10.90	5.45	-2.77	0.70	0.51	1.30
Carbon nanocone	-6.29	2.87	9.16	4.58	-1.71	0.32	0.37	0.96
Tetryl-Carbon nanocone	-8.16	5.52	13.68	6.84	-1.32	0.13	2.03	1.12

The electrophilicity (ω) and maximum transferred charge capacity (ΔN_{\max}) are two indices that show the affinity of a compound for absorbing electron. As it is clear from the table, both of these parameters have become more positive, so, it can be deduced that the tendency of tetryl for absorbing electron has defused after interacting with carbon nanocone.

The next evaluated parameter is dipole moment that is a good probe for estimating the solubility of the compound in water and other polar solvents. As can be seen, this parameter has increased after tetryl adsorbing on the surface of carbon nanocone. Therefore, tetryl-carbon nanocone complex has better solubility in water in comparison to pure tetryl.

The density of the evaluated structures was also checked out. As can be observed, the tetryl-carbon nanocone derivative has lower density than pure tetryl. Hence, the explosion velocity and detonation pressure have decreased after adsorption of tetryl on the surface of carbon nanocone.

Conclusion

In this paper, the adsorption of tetryl on the surface of carbon nanocone was evaluated by density functional theory. The obtained thermodynamic parameters proved that the adsorption process of tetryl is exothermic, spontaneous, one-sided and non-equilibrium. So, carbon nanocone is an ideal candidate for removal of this toxic nitroaromatic explosive from the environmental specimens. The C_V values showed that the heat sensitivity of tetryl has abated after interaction of tetryl with carbon nanocone. The frontier molecular orbital parameters substantiate that carbon nanocone can be used as a prominent recognition element for fabrication of new electrochemical sensors for determination of tetryl. In addition, the affinity of tetryl for absorbing electron has improved after interacting with carbon nanocone. The density values have also shown that tetryl-adsorbent complex has lower explosion velocity than pure tetryl. the effect of temperature was also investigated, the results indicated the ambient temperature is the optimum temperature for the interaction of tetryl with carbon nanocone.

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