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Original Research Article

TATB Interaction with Carbon Nanocone and Nanocone Sheet: A Comprehensive Computational Study

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ABSTRACT

In this study 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) interaction with carbon nanocone(NC) and nanocone Sheet (NCS) was evaluated by density functional theory. The calculated thermodynamic parameters including Gibbs free energy changes and Enthalpy alterations showed the interaction of TATB with the both nanostructures are exothermic, spontaneous, experimentally possible and irreversible. The specific heat capacity values proved the heat sensitivity of TATB decline after its adsorption on the surface of carbon nanocone and nanocone sheet. The effect of temperature on this process was also investigated and the results indicated 300 K is the optimum temperature for the interaction of TATB with the nanostructures. The frontier molecular orbital analysis was also employed and the findings indicated the reactivity and energetic traits of TATB have enhanced significantly after its interaction with carbon nanocone and nanocone sheet. Indeed, both of the nanostructures cause a substantial improvement in energetic features and a tangible decrease in the heat sensitivity.

Keywords: TATB, Carbon nanocone, Nanocone Sheet, DFT, Explosives

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Introduction

1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is an fiery substance, that first time was synthesized, by Jackson and Wing in 1888 [1]. Also again with a high-purity 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) was synthesized by Mitchell and etal in 2006. TATB is a strong explosive. It is a Heat-resistant and has a high melting point, but TATB is very non-sensitive to vibration, fire and shock, so its sensitivity is low and suitable for military purposes [2]. TATB has a benzene ring. Which three amine groups (NH_2) and three nitro groups (NO_2) alternating round it are attached. (Fig. 1) [3]. It is a bright yellow color. TATB is such as a green material and environmentally friendly, because after combustion of explosives is produced excessive N_2 gas [4-5].

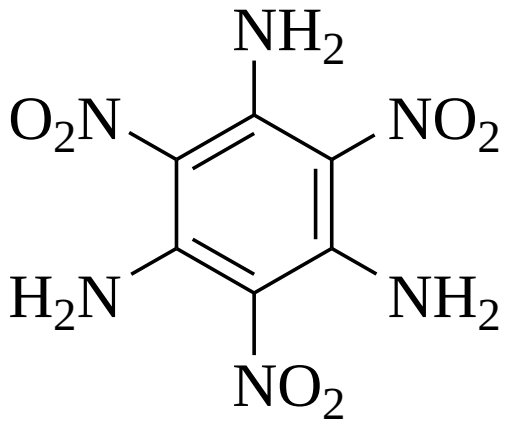


Fig. 1: 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)

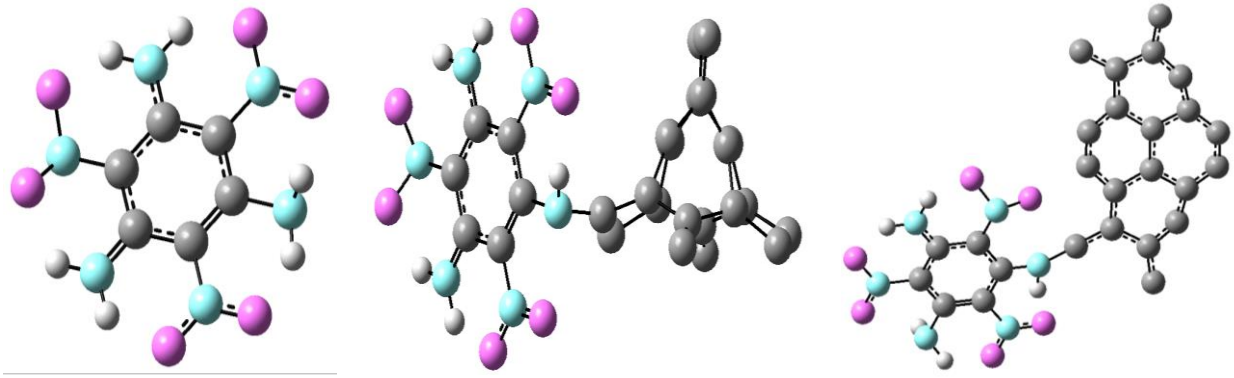
Calculations of density functional theory methods (DFT), were performed on 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) to determine the effect of fullerenes (C20, C24, C60) and on [2.4.6] Three Nitro Toluene (TNT) and 5-Picrylamino-1,2,3,4-tetrazole (PAT) to determine the effect Fullerene and Boron Nitride Nano-cages, also on 6-Amino-1,2,4-triazolo[4,3-b][1,2,4,5] tetrazine (ATTz) to determine the effect only Boron Nitride Nano-cage on energetic properties of TATB, TNT, PAT and ATTz and them nano derivatives [6-9]. interaction of explosives like TNT, octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (octogen) and 1,3,5-Trinitroperhydro-1,3,5-triazine (RDX), with graphene and boron nitride sheet have been studied and shown that the binding among BN sheet and the fiery molecules is stronger than that with graphene [10-11].The highest objective of this research is to discover the effect of the Carbon Nano cone and Nano cone sheet Surfaces on the chemical and energetic properties of TATB by DFT method.

Computational Methods

Computational study of material derived from synthesis 1,3,5-trichloro-2,4,6-trinitrobenzene (TATB) with nano cone (NC) and nano cone Sheet (NCS), in the scope from 300-400 K were carried out, by B3LYP (Becke, three-parameter, Lee-Yang-Parr), a method from density functional theory (DFT). [12] (Fig. 2a, 2b, 2c). This work was carried out by the software Gaussian 98 and Gauss view and Spartan.at First, considered molecules were optimized in a series of basic (6-31G) (Fig. 2). Then IR studies were performed in order to calculate thermodynamic parameters of the process (Table. 1). All of these assessment were accomplished in the computational level of B3LYP/6-31G [13]. The studied reactions are as following:

$$TATB + NC \rightarrow NCTATB + 1/2H_2 \quad (1)$$

$$TATB + NCS \rightarrow NCSTATB + 1/2H_2 \quad (2)$$



TATB **NC TATB** **NCS TATB**

a **b** **c**

Fig. 2: optimized molecules material TATB (a), NC TATB (NC: Nano Cone) (b), NCS TATB (NCS: Nano Cone Sheet) (c)

Summarize of reactions between TATB, Nano Cone and Nano Cone Sheet are displayed in (Fig. 3a, 3b).

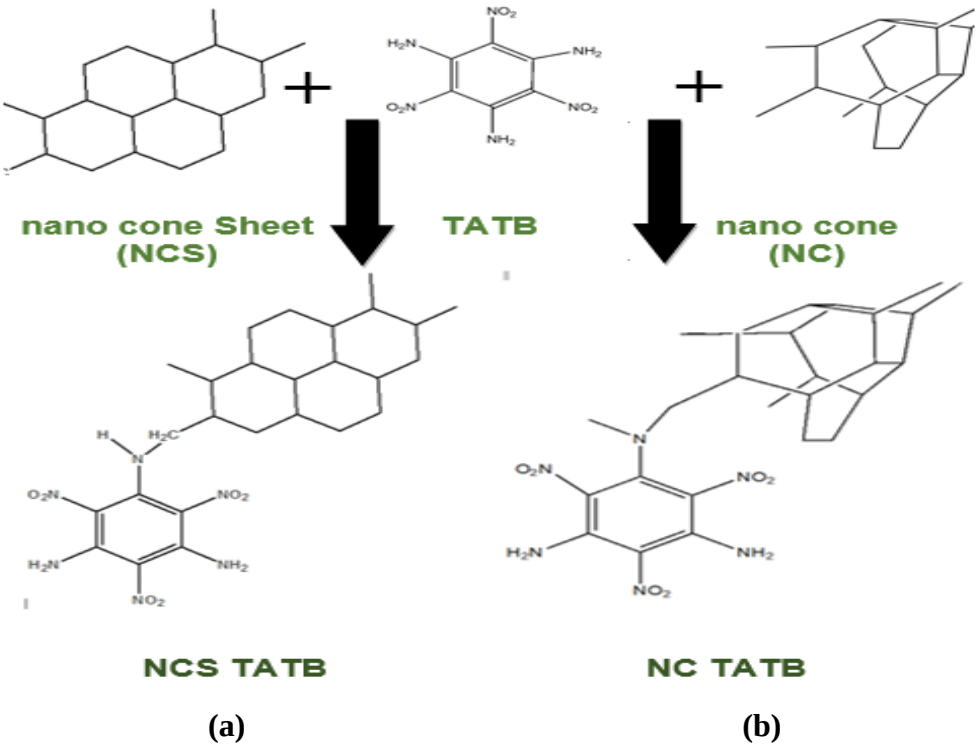


Fig. 3: Schematic of reactions between TATB, with NCS (a) and NC (b)

Table 1: Some chemical properties calculated in the B3LYP / 6-31G for of TATB, NC TATB (NC: Nano Cone) and NCS TATB (NCS: Nano Cone Sheet)

Chemical properties	TATB	NC TATB	NCS TATB
Dipole Moment (Debye)	0.00	0.7669	5.6344
d=m/V(amu/ Å^3)	1.35	1.15	0.98
Weight(amu)	258.15	486.36	499.38
Volume(Å^3)	190.63	423.96	511.77
Area (Å^2)	209.96	397.55	511.98
Cv (J/mol.K)	227.66	435.79	542.78

When Molecular Weight, Volume and Area of compounds increased SCF total energy decreased but Specific heat capacity (C_V) increased (Table 1).

Table 2: Compare of Some chemical properties calculated in the B3LYP / 6-31G for 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and its derivatives with NC and NCS

	eH (eV)	eL (eV)	HLG (eV)	h(eV)
TATB	-7.05	4.86	11.91	5.955
NCS TATB	-7.2	3.1	10.3	5.15
NC TATB	-5.7	2.2	7.9	3.95

In this work several attributes like, Energies of HOMO & LUMO molecular orbitals ($\square_H$, $\square_L$), distance among Energies of HOMO and LUMO molecular orbitals, or HOMO-LUMO Gap (HLG), and chemical hardness (η) are inquired. which are described by (3) and (4) equations. [14].

$$HLG = E_L - E_H \quad (3)$$

$$\eta = (E_L - E_H)/2 \quad (4)$$

The results obtained show that when structure of TATB is linked to nano structures of NC and NCS the dipole moment are increased (Table 1). TATB derivatives have band gap or HLG less than TATB. A small HLG means small excitation energies to the excited states. Therefore TATB derivatives are more conductive than TATB (Table 2).

NCSTATB and NC TATB have chemical hardness less than TATB, so these are softer than TATB. Soft molecules with a small gap, will have their electron density changed more easily than a hard molecule. So these are more conductive than TATB (Table 2).

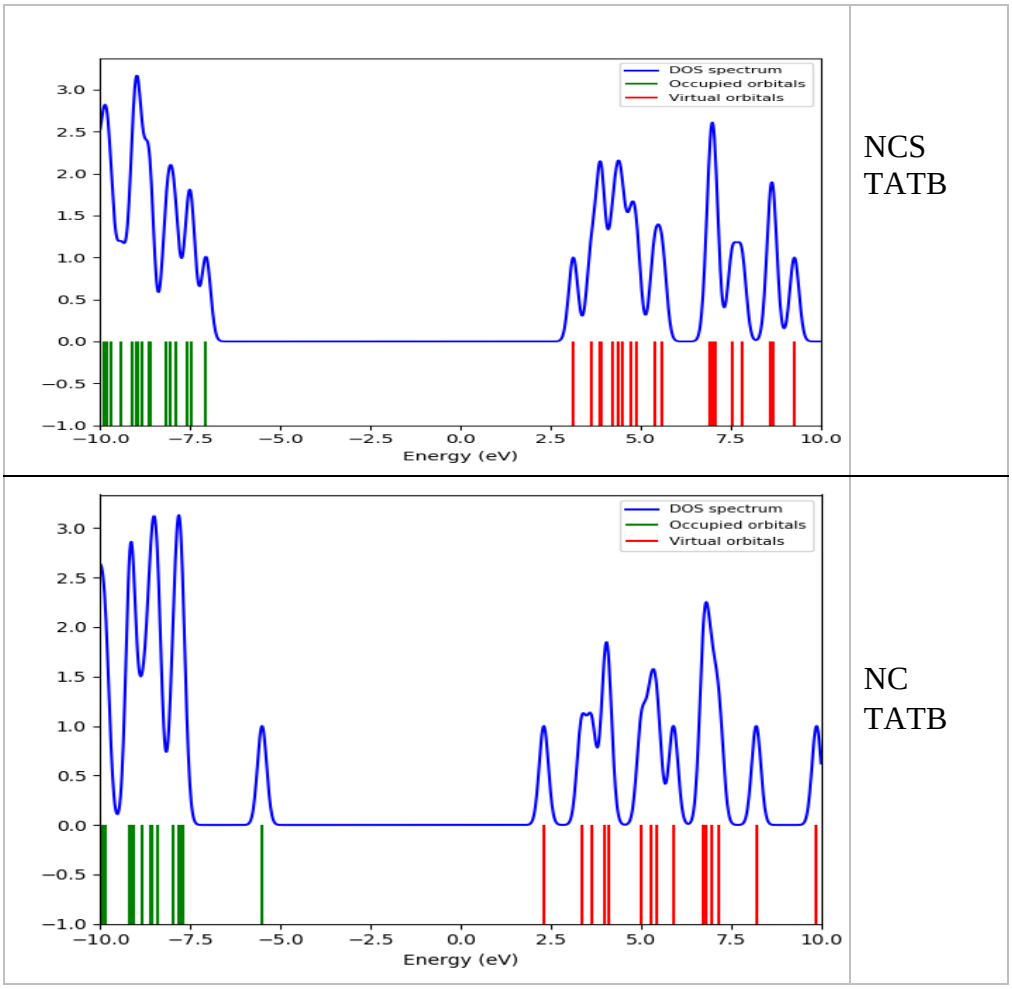


Fig. 4: LUMO and HOMO molecular orbitals of TATB (a), NC TATB (b) and NCS TATB (c)

Calculation and verifying the Adsorption energy value (Eads)

Adsorption energy is an appropriate parameter for evaluating the stability and mechanism of the adsorption process. In this regard, after optimization step was performed on all of the aforementioned derived products, the adsorption energy was calculated from the subsequent Eqs. ((5)-(6)):

$$E_{ads} = [E_{NCS\ TATB}]-[E_{NCS} + E_{TATB}] \quad (5)$$

$$E_{ads} = [E_{NC\ TATB}]-[E_{NC} + E_{TATB}] \quad (6)$$

In these formulas, E represents the total energy of the optimized structures. Then, the obtained SCF total and adsorption energy values were presented in (Table 3). As it can be witnessed from

the table, NCS TATB derivative has lower adsorption energy than NCTATB product. This fact implies that TATB has the ability to form more stable configurations with NCS because the reported adsorption energy values are negative than of its derivative with NC (Table 3).

Table 3. Calculated SCF total energy (eV) and Adsorption energy (eV) of the derived products from the reaction between alanine amino acids with pure graphene (G) and silicon-doped graphene (G*) in the temperature of 298 K**.**

	SCF total energy (eV)	ΔE_{ads} :Adsorption energy (eV)
NCS TATB	**-47354.677**	**-113.017989**
NC TATB	**-47345.817**	**-53.3846951**

Results and discussions

The results of the calculations show that the manner of increasing the density is such as the follows:

TATB> NC TATB>NCS TATB (7)

As known as in high-energy compound the power of explosion depends on the density directly [11]. Increasing trend of explosive compounds which have investigated are as follows:

TATB> NC TATB>NCS TATB (8)

Calculate and verify the values of changes in enthalpy (ΔH)

Enthalpy values (H) for raw materials and products had been calculated in process synthesis. For calculating and obtaining of any changes on the enthalpy,

Equations (9, 12) are used .

ΔH_f (T K)=$\Sigma(\varepsilon_{0+}H_{corr})_{Products}-\Sigma(\varepsilon_{0+}H_{corr})_{Reactants}$ (9)

Sum of electronic energy (ε_0) and thermal enthalpies (H_{corr}) = $\varepsilon_{0+}H_{corr}$ =H

$\Delta H_f = \Delta H_{formation}$ and Temperature Kelvin= T K

ΔH_f (T K) =Σ (H) $_{Products}-\Sigma$ (H) $_{Reactants}$ (10)

According to the equations 1-3 can be written

$\Delta H_f = [H_{NCTATB} + 1/2H_{H2}]-[H_{TATB} + H_{NC}]$ (11)

$\Delta H_f = [H_{NCSTATB} + 1/2H_{H2}]-[H_{TATB} + H_{NCS}]$ (12)

Enthalpy values obtained through calculation software Spartan, and then enthalpy of formation values obtained from Equations (11- 12).

Table 4: Enthalpy of formation calculated at the level B3lyp / 6-31G for derivative material TATB with NC and NCS.

	Enthalpy of formation changes: ΔH (eV)	
Temperature	NC TATB	NCS TATB
300	970.1085	-80.7856
310	970.0983	-80.7894
320	970.0883	-80.7932
330	970.0783	-80.7968
340	970.0681	-80.8002
350	970.0582	-80.8035
360	970.0488	-80.8063
370	970.0396	-80.8085
380	970.0306	-80.8105
390	970.0217	-80.8125
400	970.0135	-80.8135

Enthalpy of formation calculated at the level B3LYP / 6-31G for 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) with Nano Cone (NC) are always positive in all temperature range 300 to 400 Kelvin but with Nano Cone Sheet (NCS) are always negative in all temperature range 300 to 400 Kelvin (Table. 4).

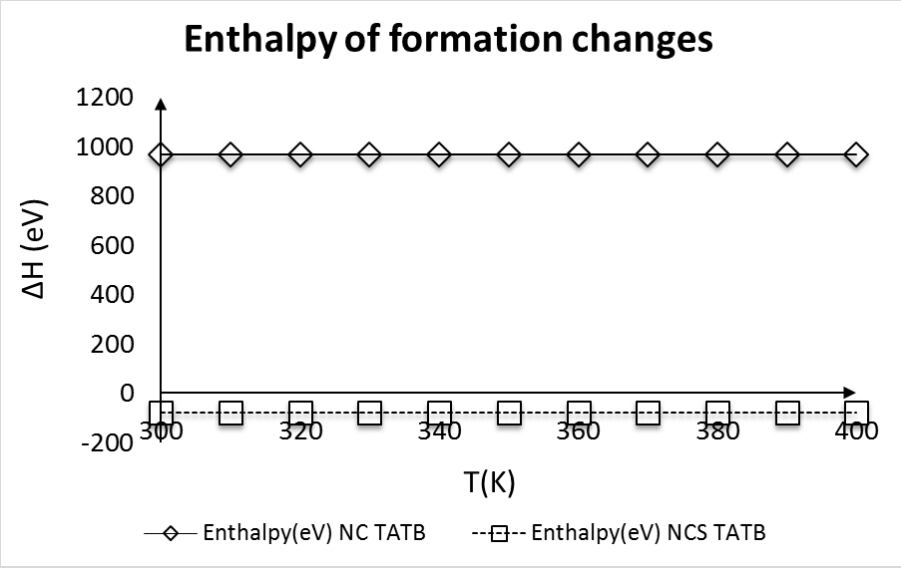


Fig. 5: diagram of the Enthalpy of formation calculated at the level B3LYP / 6-31G for derivative material 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) with NC and NCS at different temperatures

The negative ΔH_f shows that, synthesis process 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) with NCS and C_{20} are exothermic reaction, but it is endothermic at temperature ranging from 300 to 400 Kelvin, for NC with TATB because ΔH_f is positives (Fig. 5).

Calculate and verify specific heat capacity (C_V)

The results of the calculations show, specific heat capacity, C_V values for materials in process synthesis were calculated with the following procedure (14):

NCS TATB > NC TATB > TATB (14)

Table 5: Specific heat capacity (Cv) calculated at the level B3LYP / 6-31G for 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and its derivative with NC and NCS

	Specific heat capacity: Cv(J/mol.K)		
Temperature	TATB	NC TATB	NCS TATB
300	228.7532	437.9924	545.1738
310	234.5778	449.761	557.8695
320	240.3017	461.3091	570.2024
330	245.9244	472.6344	582.1785
340	251.4458	483.7362	593.8047
350	256.8658	494.6142	605.0886
360	262.185	505.2689	616.0384
370	267.4039	515.7014	626.6626
380	272.5232	525.9132	636.97
390	277.5438	535.9061	646.9695
400	282.4665	545.6825	656.6702

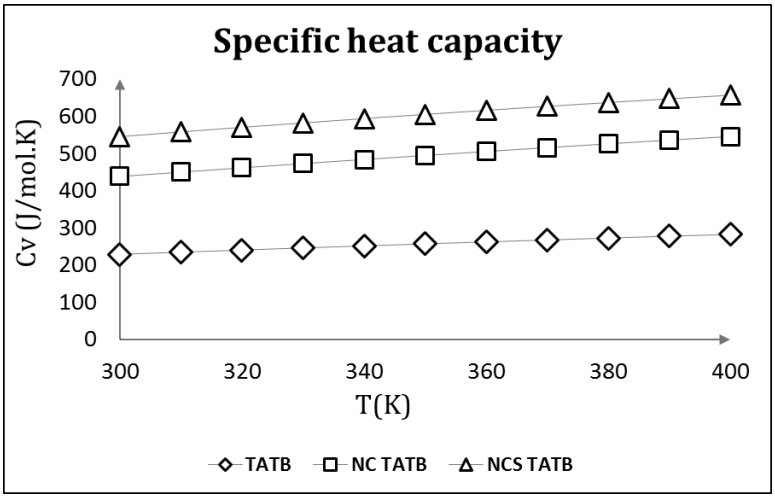


Fig 6. Diagram changes in specific heat capacity C_V of raw material 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), and its derivatives with NC: Nano Cone, NCS: Nano Cone Sheet at different temperatures

Values of specific heat capacity changes, C_V of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), and its derivatives with NC, NCS and C_{20} at different temperatures, indicate that the product have a high specific heat capacity C_V values (Fig.6, Table 5).

Calculate and verify the values of Gibbs free energy (ΔG)

The results of the calculations show that the values of Gibbs free energy (ΔG) were calculated for each of the reactants and products in process synthesis. For calculating and obtaining any changes in values of Gibbs free energy (ΔG) in the reaction A+B→C+D

The following equations (15-18) are used:

$$\Delta G_f\ (T\ K)=\Sigma(\varepsilon_{0+}\ G_{corr})_{Products}-\Sigma(\varepsilon_{0+}\ G_{corr})_{Reactants} \quad (15)$$

Sum of electronic energy (ε_0) and Gibbs free energy (G_{corr}) = $\varepsilon_{0+}\ G_{corr}$ =G

$\Delta G_f = \Delta G_{formation}$ and Temperature Kelvin= T K

$$\Delta G_f\ (T\ K) =\Sigma\ (G)_{Products}-\Sigma\ (G)_{Reactants} \quad (16)$$

According to the equations 1-2 can be written

$$\Delta G_f =[G_{NCTATB} +1/2G_{H2}]-[G_{TATB} + G_{NC}] \quad (17)$$

$$\Delta G_f =[G_{NCSTATB} +1/2G_{H2}]-[G_{TATB} + G_{NCS}] \quad (18)$$

Gibbs free energy (G) values were obtained with calculation software Spartan, and then Gibbs free energy of formation (ΔG_f) values were computed from Equations (17- 18).

Table 6: Gibbs Free Energy of formation calculated at the level B3LYP / 6-31G for 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), with NC and NCS at different temperatures

	Gibbs Free Energy changes:ΔG (eV)	
Temperature	**NC TATB**	**NCS TATB**
300	**971.1130**	**-79.7486**
310	**971.1490**	**-79.7168**
320	**971.1858**	**-79.6842**
330	**971.2233**	**-79.6510**
340	**971.2612**	**-79.6178**
350	**971.2983**	**-79.5847**
360	**971.3344**	**-79.5530**
370	**971.3712**	**-79.5215**
380	**971.4077**	**-79.4895**
390	**971.4447**	**-79.4578**
400	**971.4825**	**-79.4250**

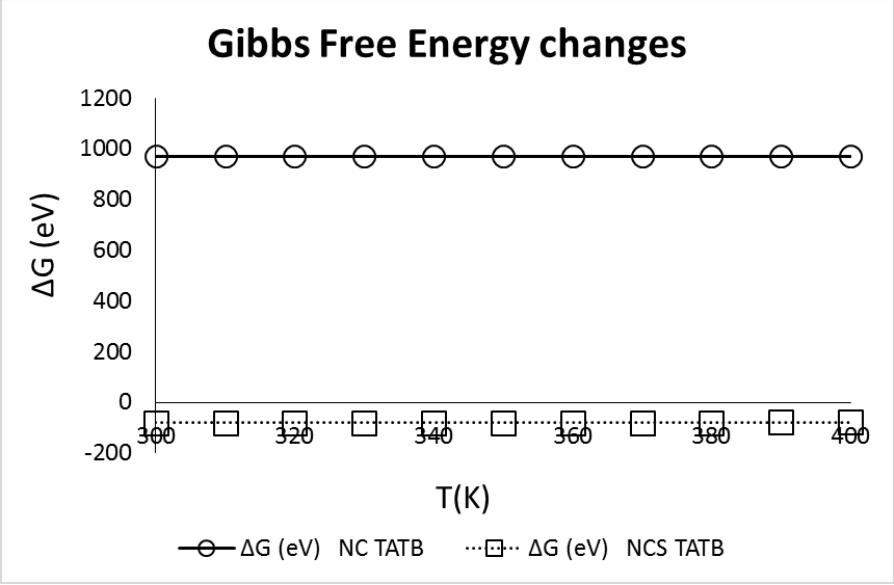


Fig. 7: diagram of the Gibbs Free Energy changes for the synthesis of derivatives 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), with NC and NCS at the range temperatures 300-400K

The negative values of ΔG_f from the synthesis of NCS TATB indicate that, it be spontaneously performed in the temperature range 300-400 K, but the process of synthesis NC TATB at same condition is non-spontaneously because ΔG_f values are positive. (Table 6, Fig.7).

Conclusion

The results of the calculations show that in the process of synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene TATB with NCS, in the temperature range 300-400 K, ΔG_f and ΔH_f amounts are negative at all temperatures which suggests that these process are exothermic and spontaneously. The heat released by increasing the reaction temperature becomes lower. In other word, the heating process is reduced as the temperature rise, in contrast to ΔH_f and ΔG_f of NC TATB which are positive and its procedure is endothermic at all temperatures and no spontaneously. The comparison of results of specific heat capacity C_V shows that C_V for TATB is lower than its derivatives with NC and NCS in this temperatures. The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius, So it cause to need low energy to increase the material temperature, less specific heat capacity values define much energetic properties of TATB rather than its derivations. Density values of TATB and its derivatives with NC and, NCS have a manner: TATB >NC TATB>NCS TATB

So we can say TATB has more explosive properties than nanostructure derivatives as studied in this paper.

Novelty of this study is to discover the effect of the different nanostructures with equal carbon number on the chemical attributes of TATB by DFT method, Many investigators can use our results in their similar work.

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