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Calculation of Thermodynamic Parameters of [2.4.6] Three Nitro Toluene (TNT) with Nanostructures of Fullerene and Boron Nitride Nano-cages over Different Temperatures, Using Density Functional Theory

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In this study the explosive substance, [2.4.6] three nitro toluene (TNT), was attached with nanostructures of fullerene (C_{24}) and boron nitride nano-cages ($B_{12}N_{12}$). In various temperatures, thermodynamic parameters of TNT with aforementioned nanostructures (C_{24} and $B_{12}N_{12}$) have been calculated using one of the density functional theory methods (B3LYP). Thus, these materials were optimized. Then, the thermodynamic parameters were calculated. Enthalpy values (ΔH), Specific heat capacity (C_v) and Gibbs free energy (ΔG) were computed for these reactions. Different parameters such as the amount of HOMO/LUMO molecular orbital levels, chemical hardness (η), electrophilicity scale (ω), charge transferred (ΔN_{max}) and chemical potential (μ) were also computed. Finally, the effect of type and molecular weight of nano structure fullerene (C_{24} , $B_{12}N_{12}$) on explosion properties and other chemical attributes of TNT were evaluated.

Keywords: Enthalpy, Explosive, TNT, Boron nitride cage, Temperature

INTRODUCTION

For the first time in 1863, [2.4.6] three nitro toluene (TNT) was synthesized, by Julius Wilbrand. After some tries, the TNT explosive properties were detected in 1891 [1]. Owing to the rather high density of TNT, it is being applied for blasting and destroying in fighting. The explosion happens by the breakdown of TNT's molecular structure [2] and the oxidation of the explosive with the participation of oxygen from the air [3]. TNT is a solid nitro aromatic compound synthesized from toluene with nitration (Fig. 1) [4]. It is a toxic yellow solid with high formation heat, due to the existence of a large number of N-N and C-N bonds in its structure [5]. One of the most useful properties of TNT is that it can be safely melted and mixed with other HEDM [6]. Activation energy with the exothermic reaction is very high in gas phase, while the liquid or solid phases have lower activation energies. TNT mixtures with oxygen-

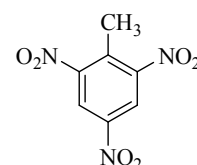


Fig. 1. [2.4.6] three nitro toluene (TNT).

wealthy compounds can release more energy in comparison with TNT alone. Therefore, often a mixture of TNT with ammonium nitrate has been used in military explosive, in the 20th century [7]. Generally, the heat released from TNT explosion is considered as a reference for evaluating other explosives. Since the heat of TNT burning is generated by reaction between carbons and atmospheric oxygen [8], it can be considered as a green and environmentally friendly material, because after combustion of the explosives, excessive N_2 gas will be produced [9]. Adsorption energy of explosive molecules like 1,3,5-trinitroperhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), TNT, and so on with boron nitride (BN)

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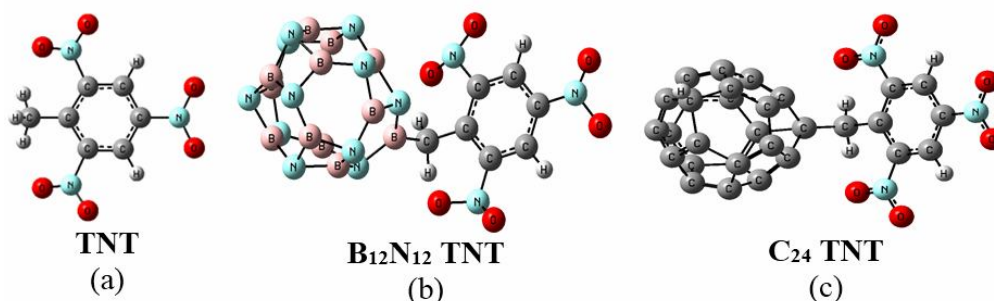


Fig. 2. Optimized molecules of TNT (a), its derivative with boron nitride nano-cages (b) and fullerene (c).

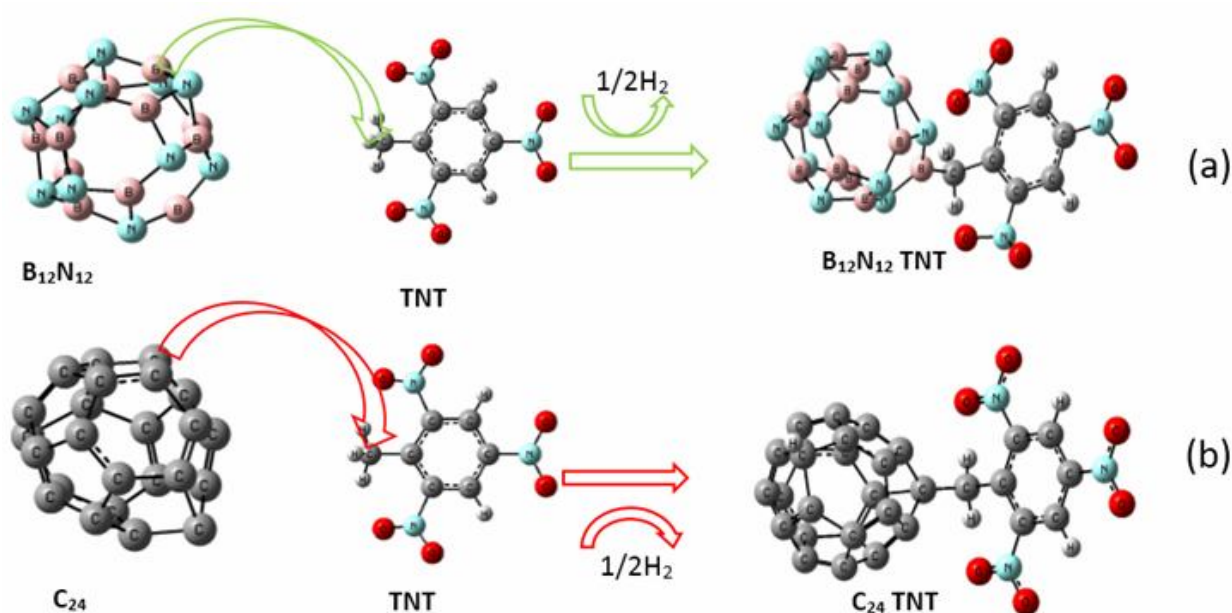


Fig. 3. Schematic of reactions between TNT with (a) boron nitride nano-cages (B₁₂N₁₂) and (b) fullerene (C₂₄).

sheet and graphene have been researched by density functional theory methods. The results have shown that the binding between the explosive molecules and BN sheet is stronger than that with graphene [10-11]. The stimulation of energetic materials have been researched by density function theory (TD-DFT) [12].

COMPUTATIONAL METHODS

Computational DFT-based study of derived synthesis material of TNT with fullerene and boron nitride nano-cages over different temperatures has been carried out using the

B3LYP (Becke, three-parameter, Lee-Yang-Parr) method [13-17] (Figs. 2a, 2b and 2c).

The operation was performed using Gaussian 98, Gauss view and Spartan computer software programs. In the level of B3LYP/6-31G, the atmospheric pressure and at 300-400 K, for studying thermodynamic parameters, IR calculation were performed (Table 1). The reactions studied are as follows:

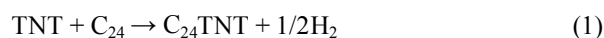


Table 1. Some Chemical Properties Calculated in B3LYP/6-31G for TNT and its Derivatives with Fullerene and Boron Nitride Cage

Chemical properties	TNT	C ₂₄ TNT	B ₁₂ N ₁₂ TNT
Energy (a.u.)	-1069.271	-1765.5594	-1752.55147
Dipole moment (debye)	2.75	1.73	9.59
Weight (amu)	272.129	515.396	509.933
Volume (Å ³)	207.25	428.65	410.87
Area (Å ²)	240.35	386.87	370.64
H° (kJ mol ⁻¹)	-2806940.642	-4634590.845	-4600540.602
C _V (J mol ⁻¹ K ⁻¹)	230.42	362.75	386.51
G° (kJ mol ⁻¹)	-2807079.790	-4634755.359	-4600708.634
D = m/v (amu Å ⁻³)	1.313047045	1.202370232	1.241105459

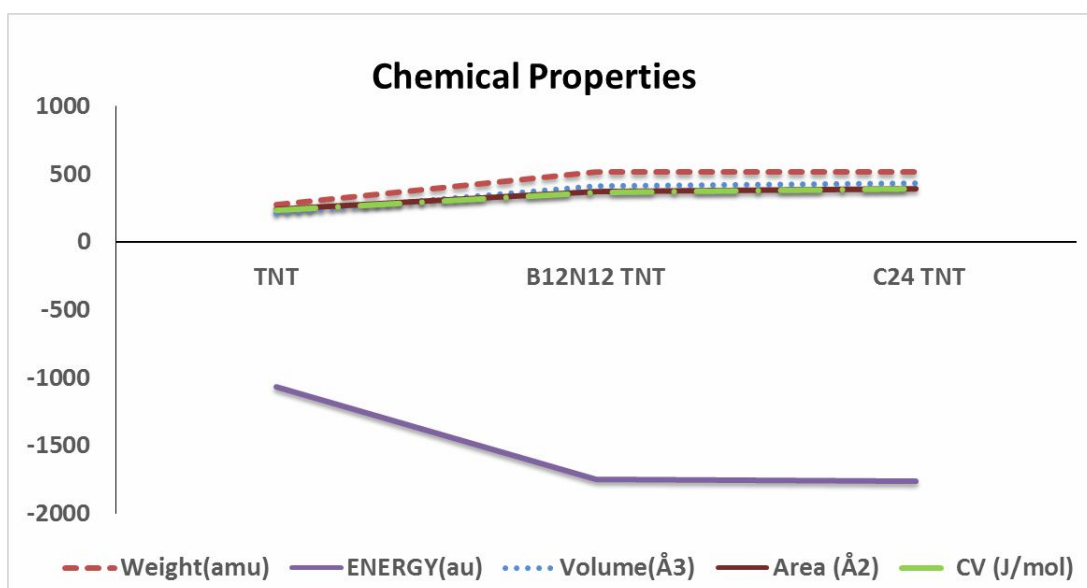


Fig. 4. Comparison of some chemical properties calculated in B3LYP/6-31G for TNT and its derivatives with fullerene and boron nitride cage.

The summary of reactions between TNT with (a) boron nitride nano-cages ($B_{12}N_{12}$) and (b) fullerene (C_{24}) for formation a bond between TNT and nano structure are displayed in (Figs. 3a and 3b).

When weight of compounds increases so energy decreases in the other hand volume, area and C_V increase (Fig. 4). In this work some properties including, energies of HOMO and LUMO (ϵ_H , ϵ_L), distance between energies of HOMO and LUMO, (HLG), electrophilicity (ω), chemical potential (μ) and chemical hardness (η) were studied. Equation (3) displays the value of charge transfer is the maximum amount of electric charge index, (ΔN_{max}). The positive value of ΔN_{max} demonstrates that compound acts as an electron acceptor and a negative one expresses that it acts like an electron donor. Electrophilicity is related to electronic charge of the molecule. Equation (4) shows an electronic power of a molecule, nominated as the electrophilicity index, ω , which is defined the system propensity to obtain additional electronic charge from the surrounding area, in the reaction between two molecules, one of them is similar to a nucleophile, while the other one behaves as an electrophile. Chemical hardness (η) and chemical potential (μ) are exhibited by Eqs. (5) and (6) [18].

$$\Delta N_{max} = -\mu/\eta \quad (3)$$

$$\omega = \mu^2/2\eta \quad (4)$$

$$\mu \approx (\epsilon_H + \epsilon_L)/2 \quad (5)$$

$$\eta = (\epsilon_L - \epsilon_H)/2 \quad (6)$$

The results obtained revealed that when structure of TNT is linked to the nano structures of C_{24} and $B_{12}N_{12}$ the dipole moment is increased in $B_{12}N_{12}$ TNT and decreased in C_{24} TNT (Table 1). TNT derivatives have band gap less than TNT. A small HOMO-LUMO Gap (HLG), automatically means small excitation energies to the excited states. Therefore, $B_{12}N_{12}$ TNT is more conductive than C_{24} TNT (Fig. 5, Table 2).

$B_{12}N_{12}$ TNT has a chemical hardness less than C_{24} TNT, so $B_{12}N_{12}$ TNT is softer than C_{24} TNT. Electron density is changed in soft molecules, with a small gap, more easily than in a hard molecule. So, $B_{12}N_{12}$ TNT is more reactive

than C_{24} TNT (Table 2). The results show that the chemical potential of TNT is lower than its nano derivatives (Table 2). Electrophilicity values in C_{24} TNT and $B_{12}N_{12}$ TNT decreased. The electrophilicity index is a measure of electrophilic power of a molecule. So, TNT has higher electrophilicity than its nano derivatives, therefore TNT is a stronger Lewis acid (Table 2). Maximum amount of electronic charge index (ΔN_{max}), as mentioned above, is the most electron charge which a system accepts. The results for this parameter were obtained like the previous parameters, for $B_{12}N_{12}$ TNT increased. If the molecular system acts as an electron acceptor, the amount of ΔN_{max} is positive and charge flows to it, but the negative amount of ΔN_{max} shows that charge flows from system, or the system acts as an electron donor. So, $B_{12}N_{12}$ TNT is an electron acceptor or a stronger Lewis acid (Table 2).

RESULTS AND DISCUSSIONS

The results of the calculations show that the manner of increasing the density is according bellow:

$$TNT > B_{12}N_{12} \text{ TNT} > C_{24} \text{ TNT}$$

As we know there is direct relation between energetic compound and density. Increasing trend of the explosive compounds would be as follows:

$$TNT > B_{12}N_{12} \text{ TNT} > C_{24} \text{ TNT}$$

The IR spectra of the compounds are shown in Fig. 6. Overall comparison of vibration spectra shows that vibrated peaks of TNT-fullerene compound have higher frequencies than TNT-boron nitride. It is clear that if the frequency goes higher, the bonds become stronger, so it could be broken more easier than C_{24} -TNT is expected, the results of DFT methods confirmed it. (Fig. 6).

Calculation and Verifying the Values of Enthalpy Changes (ΔH s)

Enthalpy values (H) for raw materials and products had been calculated in the process synthesis. For calculating and obtaining of any changes on the enthalpy, Eqs. ((7) and (8)) are used.

Table 2. Calculated ϵ_H and ϵ_L , HLG, Chemical Hardness, η , Chemical Potential, μ , Electrophilicity Index, ω , and the Maximum Amount of Electronic Charge Index, ΔN_{max} , in Electron-volt (eV) for TNT, C₂₄ TNT and B₁₂N₁₂ TNT Obtained by the B3LYP/6-31G Level of Theory

Electronic properties	TNT	C ₂₄ TNT	B ₁₂ N ₁₂ TNT
ϵ_H (eV)	-8.08	-5.07	-3.69
ϵ_L (eV)	2.67	3.04	0.62
HLG (eV)	10.75	8.11	4.31
η (eV)	5.38	4.06	2.16
μ (eV)	-2.71	-1.02	-1.54
ω (eV)	19.66	2.09	2.54
ΔN_{max} (eV)	0.50	0.25	0.71

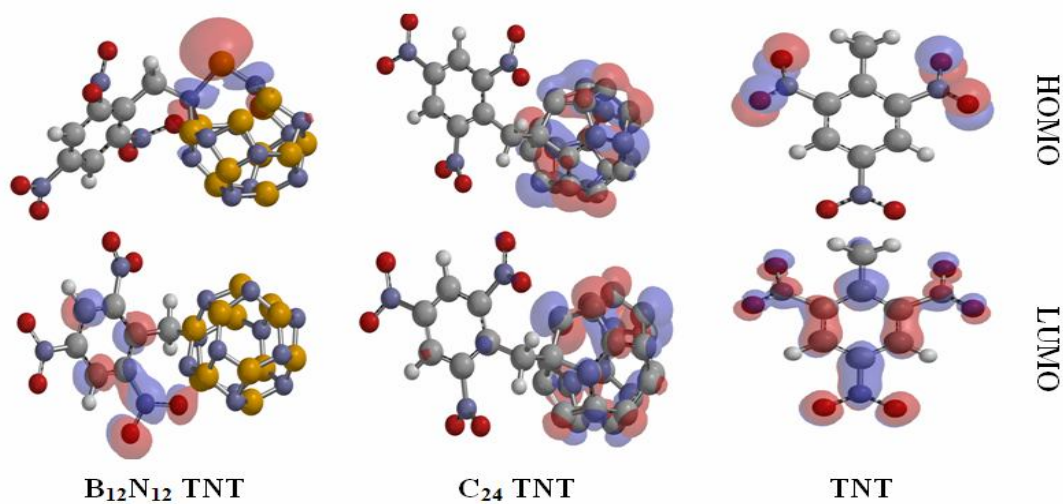


Fig. 5. LUMO and HOMO molecular orbitals of TNT, C₂₄ TNT and B₁₂N₁₂ TNT.

$$\Delta H_f(T\text{ K}) = \sum(\epsilon_0 + H_{\text{corr}})_{\text{Products}} - \sum(\epsilon_0 + H_{\text{corr}})_{\text{Reactants}} \quad (7) \quad \Delta H_f = \Delta H_{\text{formation}} \text{ and Temperature Kelvin} = T\text{ K}$$

Sum of electronic energy (ϵ_0) and thermal enthalpies (H_{corr}) = $\epsilon_0 + H_{\text{corr}} = H$

$$\Delta H_f(T\text{ K}) = \sum(H)_{\text{Products}} - \sum(H)_{\text{Reactants}} \quad (8)$$

According to the Eqs. ((1)-(2)), it can be written

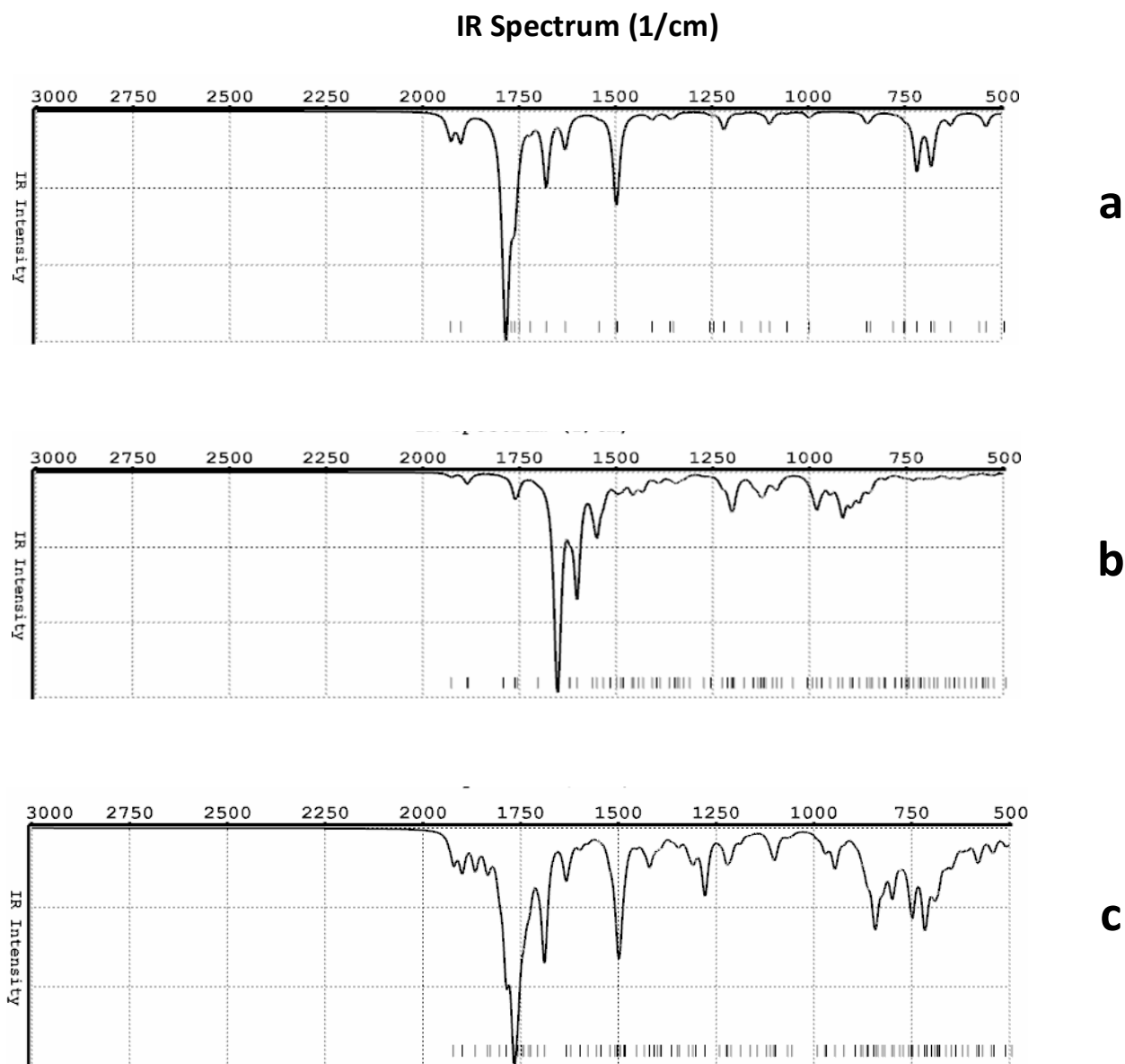


Fig. 6. IR spectra of TNT (a), its derivatives with boron nitride nano-cages, and (b) fullerene (c) Overall comparison of vibration spectra shows that vibrated peaks of TNT-fullerene compound have higher frequencies than TNT-boron nitride. It is clear that if the frequency goes higher, the bonds become stronger, so it could be broken more easier than C₂₄-TNT is expected, the results of DFT methods confirmed it (Fig. 6).

$$\Delta H_f = [H_{C_{24}TNT} + 1/2H_{H_2}] - [H_{TNT} + H_{C_{24}}] \quad (9)$$

$$\Delta H_f = [H_{B_{12}N_{12}TNT} + 1/2H_{H_2}] - [H_{TNT} + H_{B_{12}N_{12}}] \quad (10)$$

Enthalpy of formation calculated at the B3LYP/6-31G level for the derivatives of [2.4.6] TNT with fullerene, and with boron nitride nano-cages are always negative in all temperature ranges 300-400 K (Table 3).

Table 3. Enthalpy of Formation Calculated at the B3lyp/6-31G Level for Derivative Materials of [2.4.6] TNT with Fullerene and Boron Nitride Nano-cages

Temperature (K)	Enthalpy of formation (kJ mol ⁻¹)	
	C ₂₄ TNT	B ₁₂ N ₁₂ TNT
300	-2403.225437	-2370.798466
310	-2403.438937	-2370.940966
320	-2403.646837	-2371.088766
330	-2403.849137	-2371.232566
340	-2404.045837	-2371.361166
350	-2404.228237	-2371.445766
360	-2404.440337	-2371.511266
370	-2404.622437	-2371.562666
380	-2404.795637	-2371.596466
390	-2404.962537	-2371.617466
400	-2405.118937	-2371.641766

The negative ΔH_f shows that, derived synthesis process material of TNT with boron nitride nano-cages and fullerene C₂₄, are exothermic reaction at temperature ranging from 300-400 Kelvin, although with enhancing the temperature, the value of released heat from the reaction, decreases (Fig. 7).

Calculation and Verifying Specific Heat Capacity (C_v)

The results of the calculations show specific heat capacity, C_v values for raw materials in process synthesis were calculated with the following procedure:

$$R-B_{12}N_{12} > R-C_{24} > R \quad (11)$$

Values of the specific heat capacity changes, C_v of raw material of TNT, and its derivatives with fullerene and boron nitride nano-cages at different temperatures indicate that the products have a high specific heat capacity C_v values; it means that in the same conditions by taking more heat in rather to the raw material increasing of its temperature (Fig. 8).

Comparing and Verifying of Gibbs Free Energy (ΔG), in the Range of 300-400 K

The Gibbs free energy (ΔG) of each of the reactants and products in the range of 300-400 K in synthesis reaction were calculated. The Eqs. ((12)-(15)) used are:

$$\Delta G_f(T K) = \sum(\epsilon_0 + G_{corr})_{Products} - \sum(\epsilon_0 + G_{corr})_{Reactants} \quad (12)$$

Sum of electronic energy (ϵ_0) and Gibbs free energy

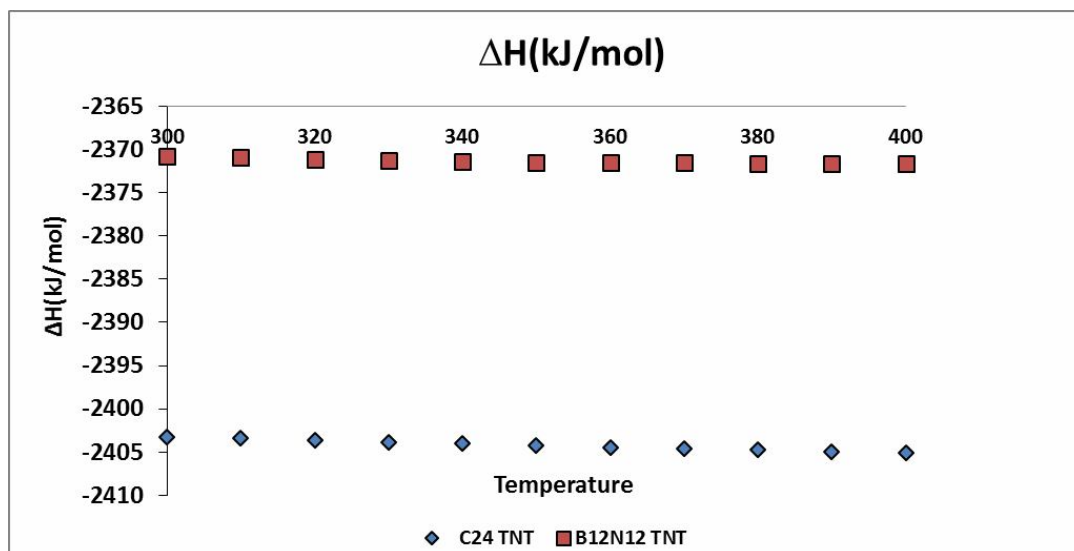


Fig. 7. Chart of enthalpy changes for the synthesis reaction of nano derivative materials of TNT with fullerene C_{24} and boron nitride nano-cages at different temperatures.

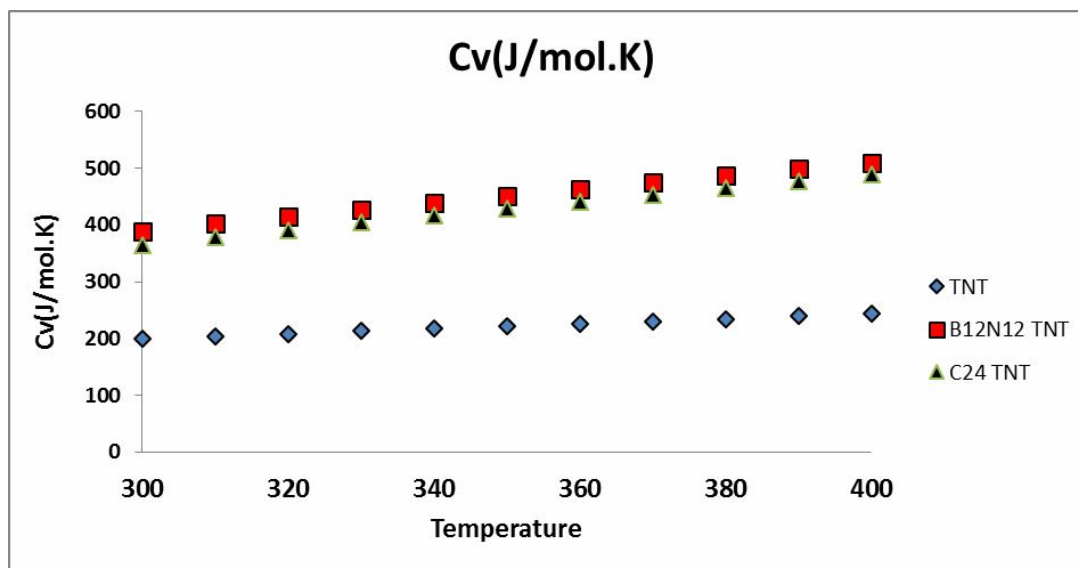


Fig. 8. Diagram changes in specific heat capacity C_v of raw material of TNT, and its derivatives with fullerene C_{24} and boron nitride nano-cages $B_{12}N_{12}$ at different temperatures.

$$(G_{\text{corr}}) = \varepsilon_0 + G_{\text{corr}} = G$$

$$\Delta G_f (T K) = \sum (G)_{\text{Products}} - \sum (G)_{\text{Reactants}} \quad (13)$$

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

According to the Eqs. ((1)-(2)) can be written

Table 4. The Results of Gibbs Free Energy in the Range of 300-400 K Calculated at the B3lyp/6-31G Level for Derivative Materials of TNT with Fullerene and Boron Nitride Nano-cages

Temperature	ΔG (kJ mol ⁻¹)	
	C24 TNT	B12N12 TNT
300	-2330.050387	-2301.571716
310	-2327.734387	-2299.304116
320	-2325.415637	-2297.053966
330	-2323.094587	-2294.813016
340	-2320.770937	1-2292.570766
350	-2318.437137	-2290.283366
360	-2316.136937	-2288.006966
370	-2313.811237	-2285.732066
380	-2311.481187	-2283.431316
390	-2309.149987	-2281.079916
400	-2306.813587	-2278.745516

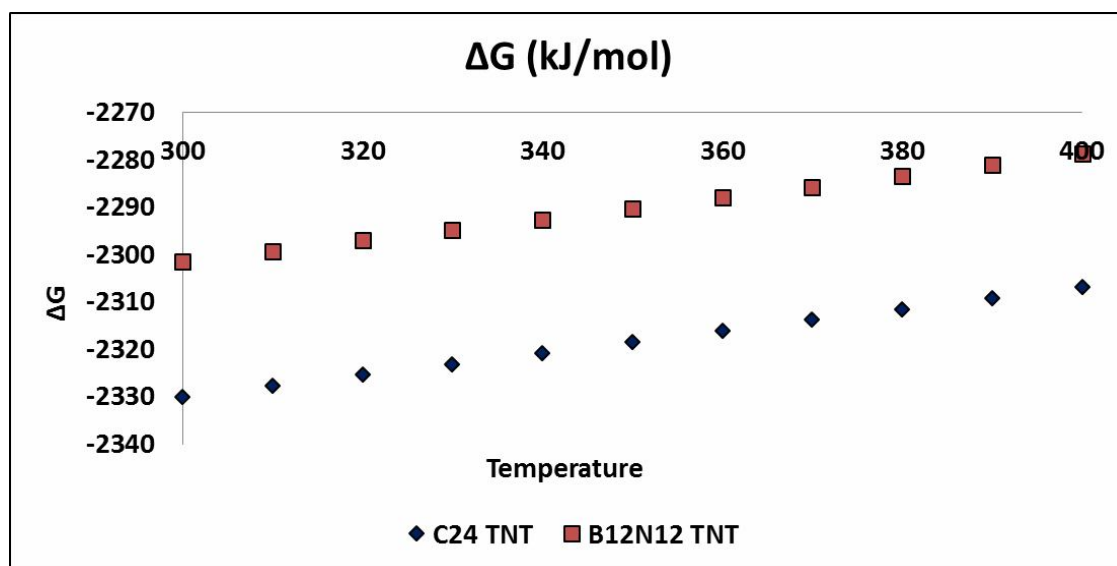


Fig. 9. Chart of Gibbs free energy changes for the synthesis reaction in the range of 300-400 K for derivative materials of TNT with fullerene C₂₄ and boron nitride nano-cages at different temperatures.

$$\Delta G_f = [G_{C_{24}TNT} + 1/2G_{H_2}] - [G_{TNT} + G_{C_{24}}] \quad (14)$$

$$\Delta G_f = [G_{B_{12}N_{12}TNT} + 1/2G_{H_2}] - [G_{TNT} + G_{B_{12}N_{12}}] \quad (15)$$

Gibbs free energy (G) values were obtained with calculation software Spartan, and then Gibbs free energy of formation (ΔG_f) values were computed from Eqs. ((14) and (15))

ΔG_f negative values of the process of synthesis derived materials of TNT with fullerene and boron nitride nano-cages at different temperatures indicate that it can be done spontaneously and with increasing the temperature Gibbs free energy will have higher values, so at this condition the reaction has less occurred (Fig. 9).

CONCLUSIONS

The results show that in the synthesis reaction of TNT with nanostructures of boron nitride nano-cages, ΔH_f amounts are negative at all temperature ranges, 300-400 K. These processes are exothermic and with increasing temperature released heat will increase. The comparison of C_v results shows that the heat capacity of TNT is lower than that in derivatives with the cage boron nitride and fullerene over different temperatures. So, the results of C_v calculations explain that energetic properties of TNT are more than those in derivatives. The ΔG_f values of TNT derivations (C_{24} TNT, $B_{12}N_{12}$ TNT) indicate that it can be done spontaneously at the 300-400 K temperature range. Density values of TNT and nanostructures of fullerene and boron nitride nano-cages are as follows:

$$TNT > B_{12}N_{12} TNT > C_{24} TNT$$

Consequently, TNT has more explosive properties than its derivatives with nanostructures. However, according to the produced results in this paper, and considering of vibration spectra, and also other results $B_{12}N_{12}$ TNT is more reactive than TNT and C_{24} TNT.

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