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Computational investigation of the influence of carbon nanostructures on the properties of energetic TATB substance by DFT method

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ABSTRACT: In this study, computational synthesis of carbon nanostructures' derivatives with TATB or 2,4,6-triamino-1,3,5- trinitrobenzene , which is an energetic substance in the temperature range of 300-400 K were evaluated by density functional theory method. In this regard, at the outset, the substances in the both sides of intended reactions for forming the desired products were optimized geometrically; afterward pertinent calculations to thermodynamic parameters were implemented on all of them. Then, the values of Enthalpy changes (ΔH_f) and Gibbs free energy changes (ΔG_f) of this reaction were calculated in various temperatures (300-400 K) by minusing the sum of these parameters in the products from reactants. Also Finally, The energy gaps between the HOMO and LUMO of the studied compounds were also explored. The computations results for every one of nanostructures have been compared with each other and their effect on the chemical attributes of TATB highly energetic material were inspected.

Keywords: *Carbon nanostructures; Density functional theory method; Enthalpy; Gibbs free energy; TATB*

INTRODUCTION

TATB or 2,4,6-triamino-1,3,5- trinitrobenzene was synthesized at 1996 for the first time, and owing to its outstanding performance and low sensitivity, it was considered as one of the components of explosive compounds. Moreover, its high energy and density accentuate TATB as an eruptive material (Boddu, *et al.*, 2010). In the recent years, energetic substances such as TATB that have a prominent density gathered a huge attention and have been found numerous applications in military field because of its special traits. The mentioned materials have remarkable usages and demonstrate less sensibility to heat and shock and in comparison to conventional highly-energetic matters, they have less environmental perils. On the other hand, powerful fossil substances which are commonly utilized are potential contaminants due to their extreme amounts of carbon so that, in the incineration procedure large quantities of carbon dioxide, carbon monoxide and soot particles have been produced that can cause a lot of problems. Whilst, nitrogen-rich compounds are classified as green fuels and are widely used in various industries,

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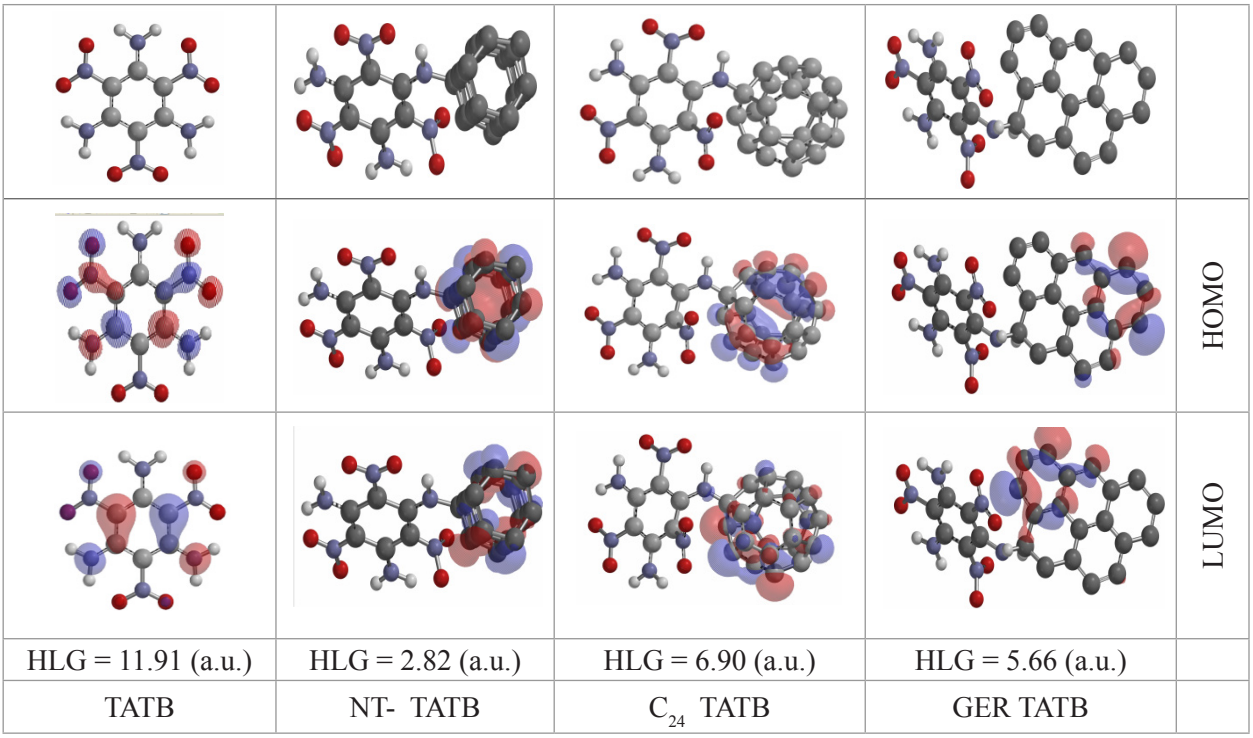

Fig. 1. TATB explosive material and its derivatives with different carbon nanostructures Note: The abbreviation terms (NT, C24 and GER) that were used in this article are as follows (NT = Nanotube, C24 = Fullerene and GER = Graphene)

because of their environmental friendly behavior (Akhavan, 2010). In this research, synthesis of derivatives NT-TATB, GER TATB and C_{24} TATB with TATB energetic substance in various temperature conditions were investigated by using density functional theory (Xing, *et al.*, 2014).

CALCULATIONS AND RESULTS

In this research, the computational study of the synthesis of nanostructures' derivatives with TATB energetic material was carried out by applying density functional theory method. The operation was accomplished

Table1. Some calculated chemical properties at B3lyp / 6-31g * levels for TATB substance and derivatives GER TATB, NT-TATB and C24 TATB

	Chemical Properties			
	TATB	NT-TATB	C_{24} TATB	GER TATB
ENERGY(au)	-992.92	-1888.71	-1889.78	-1702.35
E HOMO(eV)	-7.05	-4.20	-4.79	-4.82
E LUMO (eV)	4.86	-1.38	2.11	0.84
Dipole Moment (Debye)	0.00	2.07	2.58	10.30
Weight(amu)	258.15	546.41	546.41	486.36
Volume(A^3)	190.63	477.91	434.31	428.39
Area (A^2)	209.96	433.86	378.71	420.41
d=m/V	1.35	1.14	1.26	1.14
HLG (a.u.)	11.91	2.82	6.90	5.66
Hardness (a.u.)	5.96	1.41	3.45	2.83
Chemical Potential (a.u.)	-1.10	-2.79	-1.34	-1.99
Electrophilicity (a.u.)	3.57	5.49	3.10	5.60
ΔN_{max} (a.u.)	0.18	1.98	0.39	0.70

by exerting Gaussian 09 (Frisch, *et al.*, 2009), Spartan and Gaussian view software. At the beginning, the compounds were optimized in the series of basic by the density functional theory method (6-31g) and in the next step; IR studies were conducted to calculate the thermodynamic parameters of the process. All calculations were fulfilled in the level B3lyp / 6-31g at 300 to 400 degrees Kelvin, and the atmospheric pressure (Ahmadi, *et al.*, 2017), the studied reaction is:

$$TATB + N \rightarrow N - TATB + \frac{1}{2}H_2 \quad (1)$$

Calculate and examine the values of alterations in enthalpy (ΔH)

The enthalpy values for reactants and products in the synthesis procedure were calculated via Gaussian 09 software. In order to calculate and acquire the enthalpy variations in the reaction A+B→AB the following equation would be used.

$$\Delta H = \sum H_{products} - \sum H_{reactants} \quad (2)$$

Given to the reaction (1) the derived value of formation enthalpy that was acquired via the Gaussian software is as follows:

$$\Delta H_f = [H_{N-TATB} + 1/2H_{H2}] - [H_N + H_{TATB}] \quad (3)$$

In the written equations for calculating the enthalpy of forming reaction of nanostructures with energetic TATB, the alphabet N is an overall symbol of nanostructure (Ahmadi, *et al.*, 2016).

The pertinent data to formation's enthalpy variations for synthesis of derivatives of nanostructures are presented in figure (1) and table (2), and the results indicate that the values of formation's enthalpy are negative for NT- TATB and C_{24} TATB. However, this parameter for GER TATB has been reported positive in the temperature range of 300 to 400 K.

Calculate and inquire specific heat capacity (Cv)

The specific heat capacity (Cv) values for raw materials and products in the intended synthesis process were calculated by the means of Gaussian 09 software.

The values of specific heat capacity alterations for GER TATB, NT-TATB and C_{24} TATB derivatives in the temperature scope of 300-400 K illustrate that all

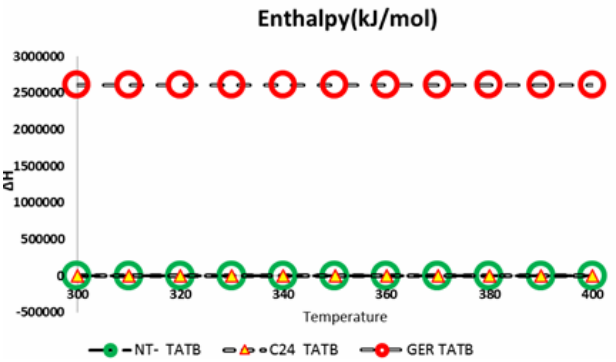

Fig. 2. Formation enthalpy changes for the synthesis of derivatives GER TATB, NT-TATB and C_{24} TATB in the temperature range of 300-400 ° K

Table 2. Formation's enthalpy changes for the synthesis of derivatives GER TATB, NT-TATB and C24 TATB in the temperature range of 300-400 K.

	Enthalpy(kJ/mol)		
Temperature (K)	NT- TATB	C_{24} TATB	GER TATB
300	-1960.266373	-1957.521115	2605317.627
310	-1960.337773	-1952.819715	2605317.14
320	-1960.398473	-1948.099715	2605316.628
330	-1960.503773	-1943.406815	2605316.099
340	-1960.628773	-1938.717315	2605315.554
350	-1960.761173	-1934.054415	2605314.995
360	-1960.894973	-1929.390715	2605314.447
370	-1961.046073	-1924.726115	2605313.882
380	-1961.178973	-1920.060015	2605313.313
390	-1961.305573	-1915.392415	2605312.727
400	-1961.370873	-1910.660715	2605312.19

Table 3. Specific heat capacity variations for the energetic TATB and GER TATB, NT-TATB and C24 TATB derivatives in the temperature range of 300-400 K

	Cv(J/mol.K)			
Temperature (K)	TATB	NT- TATB	C_{24} TATB	GER TATB
300	228.7532	504.5391	408.6298	461.2548
310	234.5778	519.2389	422.2397	472.0123
320	240.3017	533.6124	435.7092	482.5832
330	245.9244	547.6563	449.0265	492.9676
340	251.4458	561.3696	462.1811	503.166
350	256.8658	574.7523	475.1642	513.1791
360	262.185	587.806	487.9678	523.0075
370	267.4039	600.5334	500.5851	532.6523
380	272.5232	612.9378	513.0104	542.1142
390	277.5438	625.0237	525.2385	551.3944
400	282.4665	636.7956	537.2654	560.494

nanostructure products possess higher specific heat capacity than TATB energetic material. It means in the same conditions they need higher heat for increasing their temperature in comparison to the reactant, therefore, the originated derivatives from carbonic nanostructures have lesser energy than TATB (Shemshaki, *et al.*, 2017).

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

The values of Gibbs free energy (ΔG) in the mentioned synthesis process for both reactants and products were computed through Gaussian 98 software. For calculating and acquiring Gibbs free energy alterations (ΔG) in the reactions A+B→AB the succeeding equation would be applied.

$$\Delta G_{AB} = [G_{AB}] + [G_A + G_B] \quad (4)$$

Now, according to the reaction, the values of formation's Gibbs free energy that were eventuated from calculation of Gaussian software would be placed in the subsequent formula in order to obtain Gibbs free energy changes (ΔG).

$$\Delta G_f = [H_{N-TATB} + 1/2G_{H2}] - [G_N + G_{TATB}] \quad (5)$$

The values of ΔG_f that are given in Table (4) and Fig. (4) exhibit that relevant data to formation's Gibbs free energy changes for synthesis of NT- TATB and C_{24} TATB nanostructure derivatives are negative in all studied temperature range. While, this variable for GER TATB derivative has been reported positive in the temperature scope of 300-400 K.

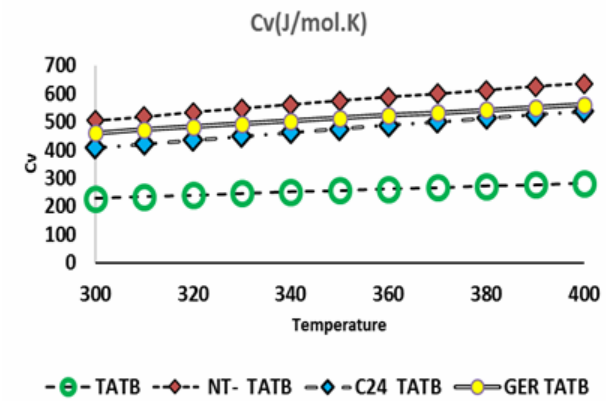

Fig. 3. Diagram of Specific Heat Capacity (Cv) Changes in TATB the Highly Energetic substance and GER TATB, NT-TATB and C_{24} TATB derivatives in the temperature range of 300-400 K

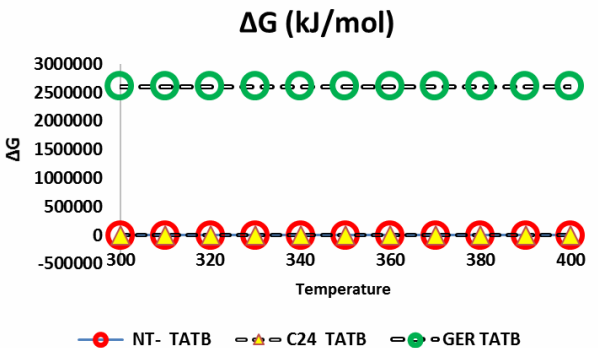

Fig. 4. Values of ΔG_f for synthesis GER TATB, NT- TATB and C_{24} TATB derivatives in temperature range of 300-400 K.

Table 4. ΔG_f changes TATB energetic substance and GER TATB, NT- TATB and C_{24} TATB synthesized derivatives in temperature range of 300-400 K.

	ΔG(kJ/mol)		
Temperature (K)	NT- TATB	C_{24} TATB	GER TATB
300	-1884.617273	-2025.131715	2605384.063
310	-1881.914973	-2022.286815	2605386.864
320	-1879.201573	-2019.386315	2605389.712
330	-1876.532573	-2016.500015	2605392.664
340	-1873.805973	-2013.553815	2605395.727
350	-1871.100073	-2010.609115	2605398.813
360	-1868.543473	-2007.766415	2605401.767
370	-1866.142673	-2005.020115	2605404.64
380	-1863.740873	-2002.338015	2605407.544
390	-1861.288073	-1999.601415	2605410.486
400	-1858.679573	-1996.770815	2605413.517

DISCUSSION AND CONCLUSIONS

The results of calculations display that in the synthesis process of GER TATB, NT- TATB and C_{24} TATB derivatives in the temperature scope of 300 to 400 Kelvin with the high energetic TATB material formation's enthalpy changes and formation's Gibbs free energy variations, In the state of TATB connection to the Nanotube and Graphene at the checked out different temperatures in the range of 300-400 have been reported negative, which prove that the both procedures are spontaneous and exothermic. However the referred parameters for Graphene bonding reaction were positive, hence, it can be deduced that this phenomenon is endothermic and Non-spontaneous. Specific heat capacity (Cv) variations in the nanostructure derivatives products with high energetic TATB substance in all binding states reveals that products own higher specific heat capacity (Cv) values than the raw materials, it means in the same conditions, in order to rising their temperature by one degree, they require more heat in comparison to primary reactants. This matter clarifies that the obtained products are less energetic than primary materials.

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