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ORIGINAL ARTICLE

Study of thermodynamic parameters of (TATB) and its fullerene derivatives with different number of Carbon (C_{20}, C_{24}, C_{60}), in different conditions of temperature, using density functional theory

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Abstract

In this research 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) were attached with different nano structures of fullerene with 20, 24 and 60 carbons producing nano structures with diverse molecular weights. Then by the use of density functional theory methods, thermodynamic parameters of TATB with foregoing nanostructures, in wide of temperature, between 300-400 °K were computed. To this purpose, the materials on both sides of suggested synthesis reactions were geometrically optimized, and then, the calculations of the thermodynamic parameters were performed on all of them. The values of enthalpy, Gibbs free energy and Specific heat capacity for these reactions were obtained. Also important parameters such as energy levels, the amount of HOMO/LUMO values and related parameters including electrophilicity scale, chemical hardness, chemical potential, and the maximum amount of electronic charge transferred were derived. Finally, the effect of type and molecular weight of nano structure fullerene (C_{20}, C_{24}, C_{60}) on explosion properties and other chemical properties of TATB were evaluated.

Keywords: *Density Functional Theory (DFT); Enthalpy; Fullerene; TATB; Thermodynamic parameters.*

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INTRODUCTION

1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) is a combustible substance, that was firstly prepared in 1888 by Jackson and Wing, that remain stable at temperatures at least as high as 250 °C, with a high melting point and thermal stability (Fig. 1) [1-2]. TATB is bright yellow color, insoluble in organic solvents. The chemistry of the nitro group has been widely investigated. Aromatic nitro compounds are important in pharmaceutical drugs, agrochemicals, polymers, solvents, perfumes, and etc [3-4].

TATB has been developed for use in lead free primary compositions, many of the high explosives are sensitive to shock and heat, but TNT is insensitive to shock or fire so it is commonly used as a safety weapon. Research is being done to develop non-toxic and environmentally acceptable smoke, because we need to have a clean environment. TATB is a green material and environmentally friendly with less harmful effect, because after combustion of TATB, is produced excessive N_2 gas [5-8].

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EXPERIMENTAL

Computational study of 1, 3, 5-trichloro-2, 4, 6-trinitrobenzene (TATB) with nanostructures of fullerene with 20, 24 and 60 carbons, in different conditions of temperature were done by density functional theory [9]. The operation was performed using the software Gaussian 98 and Gauss view and Spartan. First, compounds were optimized in a series of basic (6-31G) using density functional theory (Fig. 2). Then IR studies were done in order to calculate thermodynamic parameters of the process (Table 1) [10-11]. All of these calculations were done in the level B3LYP/6-31G at 300 to 400 Kelvin, and the atmospheric pressure.

When molecular weight of compounds increased, energy decreased but volume, area and C_V increased (Fig. 3, Table 1). In this article some properties including energetic levels, HOMO & LUMO levels (ε_H, ε_L), electrophilicity (ω), chemical hardness (η). ΔN_{max} and chemical potential properties were investigated. The maximum amount of electronic charge index, ΔN_{max}, describes the charge capacity of the molecule that the electrophone system may accept, it is given by (1) equation. A positive value of ΔN_{max} index (a.u.) for a compound reveals that acts as an electron acceptor, where as a negative value of ΔN_{max} index indicates that acts as an electron donor. The maximum amount of electronic charge and the electrophilicity and indices are related to electronic charge. The electrophilicity Index, ω, in atomic units is a measure of electrophilic power of a molecule it is given by (2) equation. When two molecules react with each other, one molecule behaves as a nucleophile, whereas the other one acts as an electrophone. A higher electrophilicity index shows higher electrophilic power of a molecule. So the quantity of ω describes the propensity of the system to acquire additional electronic charge from the environment, which is described by (2) equation. In equations (3) and (4), respectively μ and η are the chemical potential and the chemical hardness [12-13].

$$\Delta Nmax = -\mu/\eta \quad (1)$$

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

$$\mu \approx (\varepsilon H + \varepsilon L)/2 \quad (3)$$

$$\eta = (\varepsilon L - \varepsilon H)/2 \quad (4)$$

The results obtained show that when structure of TATB is Connected to nanostructures of Fullerene with 20, 24 and 60 carbons, the dipole moment of The resulting derivatives are increased (Table 1) [14]. In TATB derivatives HOMO- LUMO Gap (HLG) are less than TATB (Table 1). A small HOMO-LUMO Gap (HLG) means small excitation energies to the excited states. Therefore TATB derivatives are more conductive than TATB (Table 1, Fig 4).

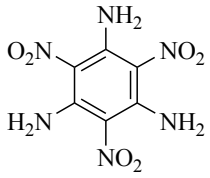


Fig. 1: 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB).

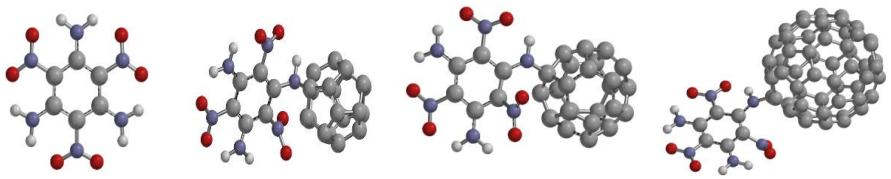


Fig. 2: optimized molecules TATB (a) and its fullerene derivatives with different number of Carbon, C_{20} TATB (b), C_{24} TATB(c) and C_{60} TATB (d).

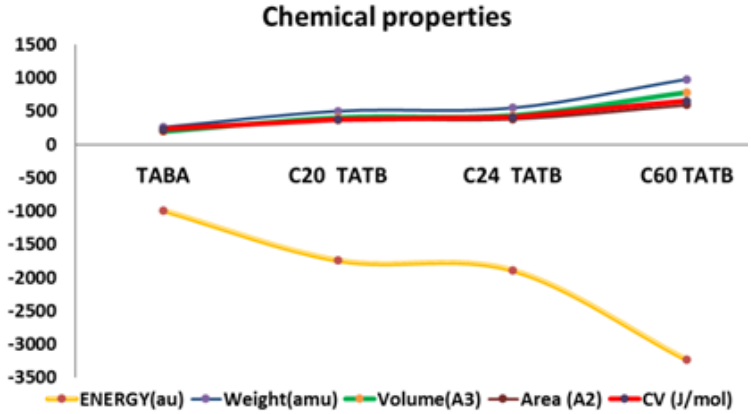


Fig. 3: Compare of some chemical properties, were done for 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) and its derivatives with C_{20}, C_{24} and C_{60}, in the computational level B3LYP / 6-31G.

Chemical hardness for TATB derivatives are less than TATB, so these are softer than TATB. Soft molecules with a small gap, can change their electron density more easily than a hard molecule. So they are more reactive than TATB (Table 1). Electrophilicity values (a.u.) in C_{60} TATB increased. The electrophilicity index is a measure of electrophilic power of a molecule. When two molecules react with each other, one molecule behaves as a nucleophile system, whereas the other one acts as an electrophone system. A higher electrophilicity index shows higher electrophilicity of a molecule; therefore C_{60} TATB is more strong Lewis acid than TATB (Table 1). Maximum amount of electronic charge index (ΔN_{max}) as mentioned, most electron charge that a system accepts can be calculated by ΔNmax parameter. The obtained results for this parameter were obtained like the previous parameter, For C_{60} TATB increased. A positive value of ΔN_{max} indicates that charge flows to system, or our system acts as an electron acceptor, whereas a negative value of ΔNmax indicates that charge flows from system or our system acts as an electron donor. So TATB derivatives are electron acceptor or a stronger Lewis acid (Table 1) [15-16].

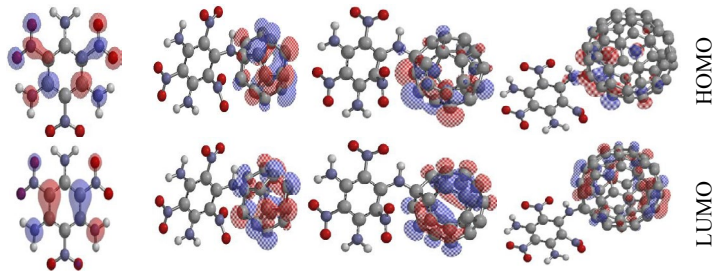
RESULTS AND DISCUSSIONS

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

$$d_{TATB} > d_{C24\ TATB} > d_{C60\ TATB} > d_{C20\ TATB}$$

As we know the power of explosion in high-energy compound depends on the density directly. Increasing trend of explosive compounds which were investigated is as follows:

$$TATB > C_{24}\ TATB > C_{60}\ TATB > C_{20}\ TATB$$



HLG =11.91(a.u.) HLG =7.92 (a.u.) HLG = 6.90(a.u.) HLG = 6.31(a.u.)

TATB a | C_{20} TATB b | C_{24} TATB c | C_{60} TATB d

Fig. 4: HOMO and LUMO molecular orbitals and HOMO- LUMO Gap (HLG) of TATB (a), C_{20} TATB(b), C_{24} TATB (c), and C_{60} TATB (d).

Table 1: Some chemical properties were calculated in the B3LYP / 6-31G for of TATB, C_{20} TATB, C_{24} TATB and C_{60} TATB.

	TATB	C_{20} TATB	C_{24} TATB	C_{60} TATB
Energy(au)	-992.92	-1740.25	-1889.78	-3236.26
E HOMO(eV)	-7.05	-4.85	-4.79	-9.06
E LUMO (eV)	4.86	3.07	2.11	-2.75
Dipole Moment (Debye)	0.00	1.35	2.58	2.48
Weight(amu)	258.15	498.37	546.41	977.80
Volume(Å^3)	190.63	401.30	434.31	779.48
Area (Å^2)	209.96	371.03	378.71	589.50
ZPE (KJ/mol)	460.56	825.00	893.99	1546.28
H° (au)	-992.73	-1739.92	-1889.42	-3235.64
C_V (J/mol)	227.66	373.69	406.10	650.00
S° (J/mol)	444.27	566.29	589.06	724.29
G° (au)	-992.78	-1739.99	-1889.48	-3235.72
d=m/v	1.35	1.24	1.26	1.25
HLG (a.u.)	11.91	7.92	6.90	6.31
Chemical Hardness (a.u.)	5.96	3.96	3.45	3.16
Chemical Potential (a.u.)	-1.10	-0.89	-1.34	-5.91
Electrophilicity (a.u.)	3.57	1.57	3.10	55.01
ΔN_{max} (a.u.)	0.18	0.22	0.39	1.87

Calculation and verifying the values of changes in enthalpy (ΔH)

The way to calculate enthalpies of reaction is to calculate heats of formation, and operation of the appropriate sums and difference. Enthalpy values for raw materials and products calculated in process synthesis. For calculating and obtaining of any changes on the enthalpy, Equation 5 is used.

$$\Delta H_f\,(T\ K)=\Sigma(\varepsilon^0{}_+H_{corr})_{Products}-\Sigma(\varepsilon^0{}_+H_{corr})_{Reactants} \quad (5)$$

Sum of electronic and thermal enthalpies = $\varepsilon^0{}_+H_{corr}=H$

$$\Delta H_f\,(T\ K)=\Sigma(H)_{Products}-\Sigma(H)_{Reactants} \quad (6)$$

Yielding the following reactions

$$TATB+C_{20}\rightarrow C_{20}TATB+1/2H_2 \quad (7)$$
$$TATB+C_{24}\rightarrow C_{24}TATB+1/2H_2 \quad (8)$$
$$TATB+C_{60}\rightarrow C_{60}TATB+1/2H_2 \quad (9)$$

Enthalpy values obtained through calculation software Spartan, and then enthalpy of formation values obtained from Equation 10, 11, 12.

$$\Delta H_f=[H_{C_{20}\ TATB}+1/2H_{H2}]-[H_{TATB}+H_{C20}] \quad (10)$$
$$\Delta H_f=[H_{C24\ TATB}+1/2H_{H2}]-[H_{TATB}+H_{C24}] \quad (11)$$
$$\Delta H_f=[H_{C60\ TATB}+1/2H_{H2}]-[H_{TATB}+H_{C60}] \quad (12)$$

Enthalpy of formation calculated at the level B3LYP / 6-31G for derivatives of 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) with C_{60} TATB is always positive in all temperature range 300 to 400 Kelvin but for C_{20} TATB and C_{24} TATB are always negative in all temperature range 300 to 400 Kelvin (Table 2).

The negative ΔH_f shows that, derived synthesis process material 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) with C_{20} and C_{24} are exothermic reaction, but with C_{60} is endothermic reaction at temperature ranging from 300 to 400 Kelvin (Fig. 5, Table 2).

Table 2: Enthalpy of formation calculated at the level B3LYP / 6-31G for derivatives of 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) with C_{20} , C_{24} and C_{60}..

	Enthalpy(kJ/mol)		
Temperature	C_{20} TATB	C_{24} TATB	C_{60} TATB
300	-1951.697378	-1957.521115	639.8432584
310	-1951.841878	-1952.819715	639.7231584
320	-1951.986978	-1948.099715	639.6040584
330	-1952.141878	-1943.406815	639.4615584
340	-1952.296678	-1938.717315	639.3030584
350	-1952.475278	-1934.054415	639.1786584
360	-1952.661678	-1929.390715	639.0665584
370	-1952.847778	-1924.726115	638.9313584
380	-1953.033678	-1920.060015	638.7928584
390	-1953.223678	-1915.392415	638.6512584
400	-1953.362778	-1910.660715	638.5686584

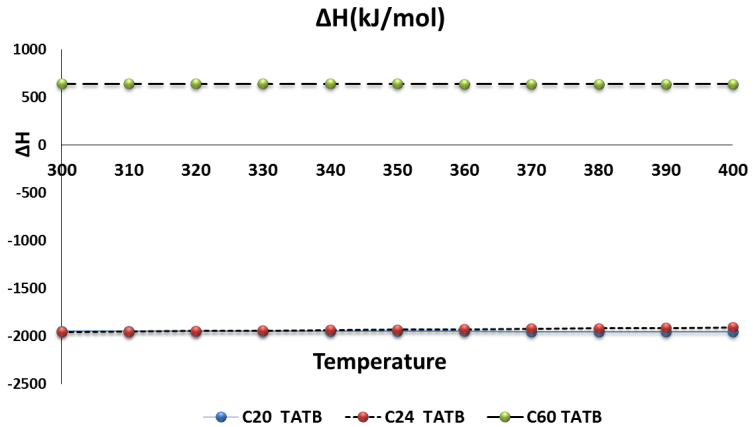


Fig. 5: Diagram of the Enthalpy of formation calculated at the level B3LYP / 6-31G for C_{20} TATB and C_{24} TATB C_{60} TATB at different temperatures.

Table 3: 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 C_{20} , C_{24} and $C_{60.}$

	Cv(J/mol.K)			
Temperature	TATB	C_{60} TATB	C_{24} TATB	C_{20} TATB
300	228.7532	654.8054	408.6298	375.9792
310	234.5778	680.6436	422.2397	388.3011
320	240.3017	706.2027	435.7092	400.4961
330	245.9244	731.459	449.0265	412.5541
340	251.4458	756.3921	462.1811	424.4664
350	256.8658	780.9846	475.1642	436.2251
360	262.185	805.2217	487.9678	447.8234
370	267.4039	829.0911	500.5851	459.2551
380	272.5232	852.5823	513.0104	470.5149
390	277.5438	875.6866	525.2385	481.5984
400	282.4665	898.3971	537.2654	492.5015

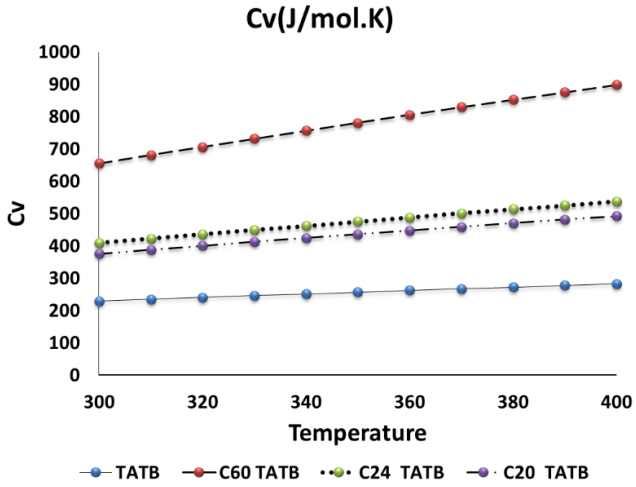


Fig 6. Diagram changes in specific heat capacity Cv of TATB, and C_{20} TATB and C_{24} TATB C_{60} TATB at different temperatures.

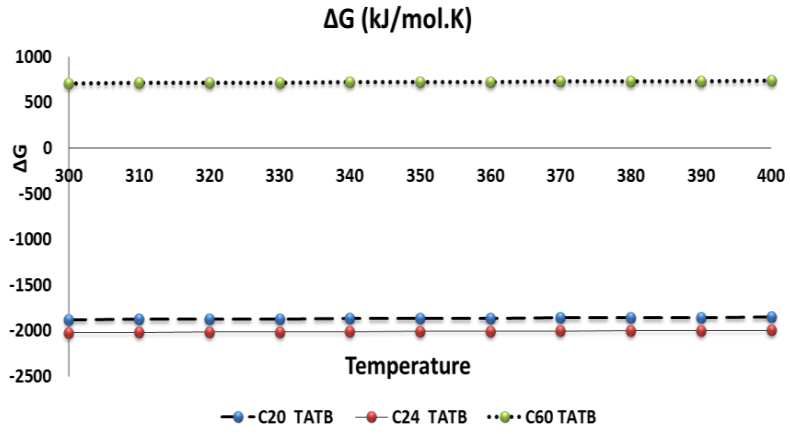


Fig. 7: diagram of the Gibbs Free Energy changes for the synthesis of derivatives material 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB), with C_{20}, C_{24} and C_{60} at different temperatures (300-400K).

Table 4: Gibbs Free Energy of formation calculated at the level B3LYP / 6-31G for derivative material 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB), with C_{20} , C_{24} and C_{60} at different temperatures.

	ΔG (kJ/mol.K)		
Temperature	C_{20} TATB	C_{24} TATB	C_{60} TATB
300	-1880.919478	-2025.131715	709.0778584
310	-1878.196778	-2022.286815	711.7868584
320	-1875.456678	-2019.386315	714.5174584
330	-1872.678078	-2016.500015	717.2449584
340	-1869.835578	-2013.553815	719.9762584
350	-1867.013578	-2010.609115	722.8166584
360	-1864.374578	-2007.766415	725.5041584
370	-1861.832278	-2005.020115	728.1708584
380	-1859.325978	-2002.338015	730.8370584
390	-1856.769878	-1999.601415	733.5212584
400	-1854.156578	-1996.770815	736.3471584

Calculation and verifying specific heat capacity(Cv)

The results of the calculations show that specific heat capacity, Cv values calculated for TATB and its derivatives with C_{20}, C_{24} and C_{60} increased following

$$\text{TATB } C_{60} > \text{TATB } C_{24} > \text{TATB } C_{20} > \text{TATB} \quad (13)$$

Values of specific heat capacity changes, Cv of raw material 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB), and its derivatives with C_{20}, C_{24} and C_{60} at different temperatures indicate that the products have a high specific heat capacity Cv values than TATB (Fig.6, Table 3).

Calculation and verifying the values of Gibbs free energy (ΔG)

The results of the calculations display 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 formula is used

$$\Delta G_f = \Sigma G_{Products} - \Sigma G_{Reactants} \quad (14)$$

Given the reactions (7, 8, 9), the values of Gibbs free energy obtained through a Gaussian calculation software:

$$\Delta G_f = [G\ C_{20\ TATB} + 1/2 G_{H2}] - [G_{TATB} + G_{C20}] \quad (15)$$

$$\Delta G_f = [G_{C24\ TATB} + 1/2 G_{H2}] - [G_{TATB} + G_{C24}] \quad (16)$$

$$\Delta G_f = [G_{C60\ TATB} + 1/2 G_{H2}] - [G_{TATB} + G_{C60}] \quad (17)$$

ΔG_f negative values of the process of synthesis derived material 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) with C_{20} and C_{24} at different temperatures indicate that, they can be done spontaneously, but this process with C_{60} at different temperatures is non spontaneously because ΔG_f values are positive at different temperatures (Fig. 7, Table 4).

CONCLUSION

The results of the calculations show that in the process of synthesis of 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) with C_{20} and C_{24} at different temperatures, ΔG_f and ΔH_f amounts are negative at all temperatures which suggests that, they are exothermic and spontaneously. (Tables 2 and 4). In contrast to ΔH_f and ΔG_f of C_{60} TATB which are positive and its procedure is endothermic at all temperatures and no spontaneously. The comparison of results of C_V shows that the Heat capacity of 1, 3, 5-triamino-2, 4, 6-trinitrobenzene (TATB) is lower than its derivatives with C_{20} , C_{24} and C_{60} at different temperatures. The specific heat capacity 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. Heat capacity is increased with increasing molecular weight.

$$CV_{C60TATB} > CV_{C24TATB} > CV_{C20TATB} > CV_{TATB}$$

Density value of TATB and its derivatives with $C_{20,}$ C_{24} and C_{60} have this manner:

$$d_{TATB} > d_{C24\ TATB} > d_{C60\ TATB} > d_{C20\ TATB}$$

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

Novelty of this study

The main objective of this work is to discover the effect of the fullerene with different weight on the chemical properties of TATB by DFT method; many investigators can use the results in their similar work.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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