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Determination of thermodynamic parameters of produced materials from (ATTz) with boron nitride nano-cages in different conditions of temperature, with DFT method

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ABSTRACT

6-Amino-1,2,4-triazolo[4,3-*b*][1,2,4,5]tetrazine (ATTz)is an explosive material, that has been synthesized from the reaction of 3,6-diaminotetrazine, with nitrous acid and then sodium azide. In the simplest terms, an explosive is defined as a substance, which on initiation by friction, impact, shock, spark, flame, heating, or any simple application of an energy pulse, undergoes a rapid chemical reaction evolving a large amount of heat and so exerting a high pressure on its surroundings. The vast majority of explosives release gaseous products on explosion.In this study the reaction of 6-Amino-1,2,4-triazolo[4,3-*b*][1,2,4,5] tetrazine (ATTz) with boron nitrideNano- cages in different conditions of temperature, by density functional theory methods was investigated. For this purpose, the material on both sides of reaction was geometrically optimized, and then the calculation of the thermodynamic parameters was performed on all of them. The values of ΔH, ΔG, ΔS for this reaction at different temperatures were obtained, and finally, the best temperature for the synthesis of explosives nano derivatives, according to the results of thermodynamic parameters were evaluated.

Keywords: Enthalpy; 6-Amino-1,2,4-triazolo[4,3-*b*][1,2,4,5] tetrazine, ATTz; boron nitride cage

INTRODUCTION

Fossil fuels are compounds produced by natural processes such as anaerobic decomposition of dead organisms, containing energy originating in photosynthesis[1]. Fossil fuels are of great importance because they can be burned (oxidized to carbon dioxide and water), producing significant amounts of energy per unit weight. but the sources of fossil fuels are exhaustible and so valuable [1]. On the other Fossil fuels during the burning usually produces a lot of pollutions and high amount of carbon dioxide (CO2), carbon monoxide (CO). These are damaging the environment [2]. 6-Amino-1,2,4-triazolo[4,3-b][1,2,4,5] tetrazine (ATTz) is an explosive material, these compounds during burning produce so much Nitrogen and water. In this research, high-energy material (ATTz) with boron nitride nano-cages in different conditions of temperature, density functional theory methods were studied. These compounds are used in various industries including military industries [3]. After combustion is produced excessive

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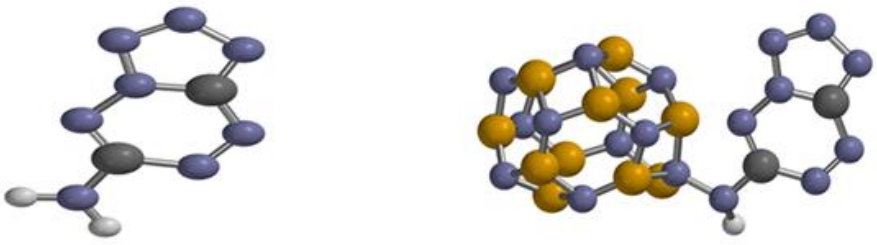
N_2gas and explosive components are green [4]. Currently, researchers around the world do investigation on energetic materials like tetrazol. Also the energetic materials are used in propellants jets [5].

CALCULATIONS AND RESULTS

Computational study material derived synthesis(ATTz) with boron nitride nano-cages in different conditions of temperature, studied by density functional theory, the operation was performed using the software Gaussian 98 and Gaussian view And Spartan. First, compounds were optimized in a series of basic using density functional theory (6-31g) and then IR studies are done in order to calculate thermodynamic parameters of the process. All calculations are done in the level B3lyp / 6-31g at 300 to 400 degrees Kelvin, and the atmospheric pressure, the studied reaction is:

Table 1. Some chemical properties calculated in the B3lyp / 6-31g tomaterial(**ATTz)**and its derivatives with boron nitride cage

	Temperature=298.15K , pressure=1 atm	
	ATTz	ATTz -$B_{12}N_{12}$
ENERGY(au)	-505.788083	-1389.69535
G° (au)	-505.714733	-1389.52637
Dipole Moment (Debye)	6.25	4.78
Weight(amu)	138.094	420.895
Volume(A^3)	103.86	335.37
Area (A^2)	129.31	299.65
ZPE (KJ/mol)	211.53	550.28
H° (au)	-505.675746	-1389.47037
CV (J/mol)	106.78	294.30
S° (J/mol)	343.31	493.07
density (amu/A^3)	1.329616792	1.255016847



ATTz **ATTz-$B_{12}N_{12}$**

Fig. 1. Optimized molecules material (ATTz) and its derivative with boron nitride nano-cages.

Calculation results

Computational Investigation of the reaction products of (ATTz) with boron nitride nano-cages in different conditions of temperature, studied by density functional theory, the operation was performed using the software Gaussian 98 and Gaussian view And Spartan. First, compounds were optimized in a series of basic using density functional theory (6-31g) and then IR studies are done in order to calculate thermodynamic parameters of the process. All calculations are done in the level B3lyp / 6-31g at 300 to 400 degrees Kelvin, and the atmospheric pressure, the studied reaction is:

$ATTz + B_{12}N_{12} \rightarrow ATTz\ B_{12}N_{12} + 1/2H_2$ (1)

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

Calculatedenthalpy values forraw materials and products in process synthesis. For calculating and obtain the change in enthalpy in the reaction A+B→C+D from the Equation 2 is used.

$$\Delta H_f = \Sigma H_{Products} - \Sigma H_{Reactants} \quad (2)$$

So Enthalpy of formation values obtained through calculation software Spartan, is as follows:

$$\Delta H_f = [H_{ATTzB12N12} + 1/2H_{H2}] - [H_{ATTz} + H_{B12N12}] \quad (3)$$

Enthalpy of formation calculated at the level B3lyp / 6-31g for derivativesmaterial (ATTz) with boron nitride nano-cages, Always Positive in all temperature range 300 to 400 degrees Kelvin.

The positive ΔHf the show, Derived synthesis process material (ATTZ) with boron nitride nano- cage insertion at temperatures ranging from 300 to 400 Kelvin And by increasing the amount of heat released exothermic reaction temperature becomes lower Fig. 2.

Table 2. Enthalpy of formation calculated at the level B3lyp / 6-31g for derivative material (ATTz) with boron nitride nano-cage

	Enthalpy(kJ/mol)
Temperature	ATTz B12N12
300	-10.63645
310	-10.60125
320	-10.59805
330	-10.61595
340	-10.63275
350	-10.65815
360	-10.70475
370	-10.75065
380	-10.79585
390	-10.83835
400	-10.87955

Calculate and assess the values of change in entropy (ΔS)

The results of the calculations show that the entropy values for raw materials and goods in process synthesis were calculated. To calculate and obtain the entropy changes in reaction A+B→C+Dthe following equation is used.

$$\Delta S_f = \Sigma S_{Products} - \Sigma S_{Reactants} \quad (4)$$

The entropy values obtained through calculation software Gaussian , generally the following

$$\Delta S_f = [S_{ATTz\ B12N12} + 1/2S_{H2}] - [S_{ATTz} + S_{B12N12}] \quad (5)$$

ΔS_f positive value indicates that the process of synthesis derived material (ATTZ) with boron nitride nano -cages at different temperatures have a negative entropy Fig. 3.

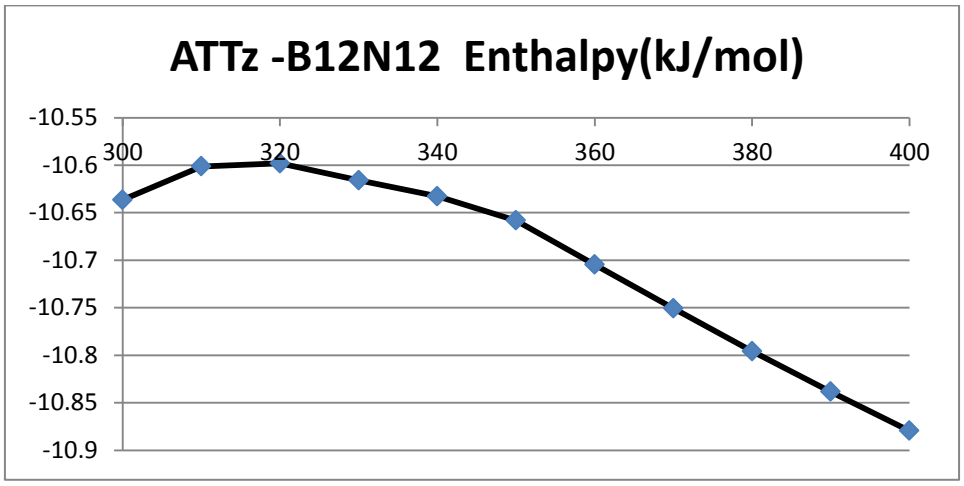


Fig. 2. Diagram the enthalpy changes for the synthesis of derivatives material (ATTZ) with boron nitride nano-cages at different temperatures.

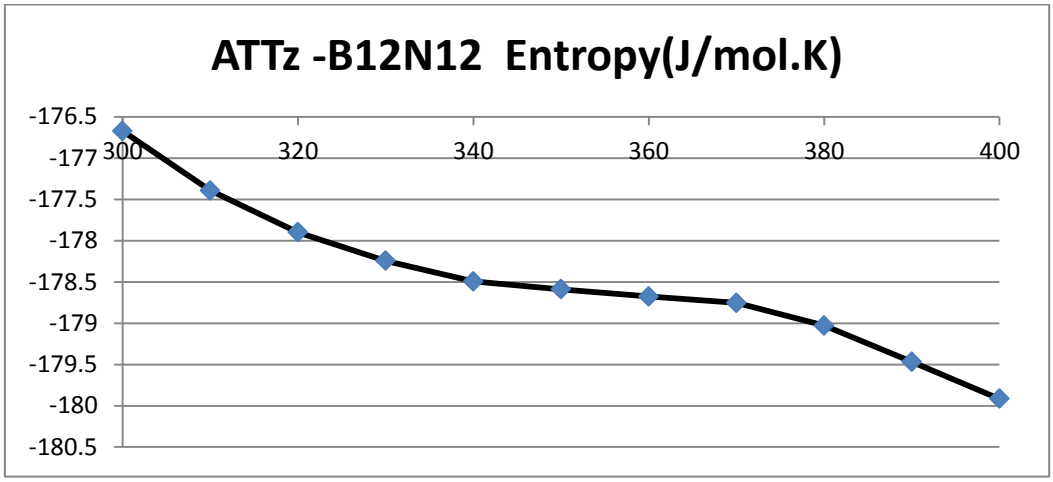


Fig. 3. Diagram of the entropy changes for the synthesis of derivatives material (ATTZ) with boron nitride nano -cages at different temperatures**.**

Calculate and verify specific heat capacity (CV)

The results of the calculations show , specific heat capacity (CV) values for raw material and product in process synthesis were calculated, That were showed the following procedure:

$CV_{B12N12\ ATTz} > CV_{ATTz}$.

Values of specific heat capacity changes, CV raw material (ATTZ), and its derivative with boron nitride nano-cages at different temperatures indicates that the product has specific heat capacity CV values higher, in the same conditions by taking more heat than the raw material, increases its temperature Fig (4).

Also density values of ATTz and ATTz B12N12 have this manner:

$$d_{ATTz} > \quad d_{ATTz\text{-}B12N12}$$

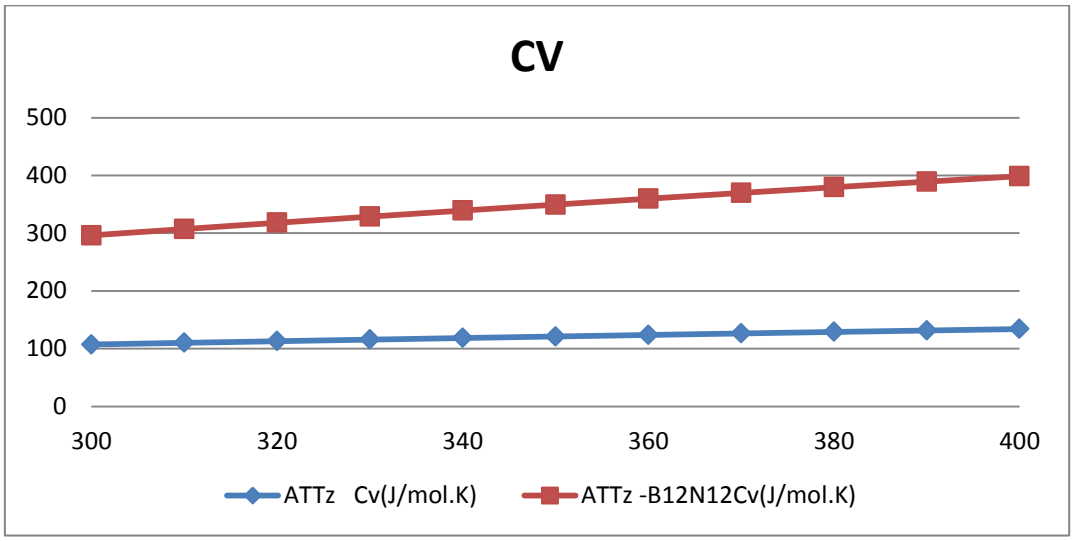


Fig. 4. Diagram changes in specific heat capacity (CV) raw material (ATTz), and its derivative with boronnitridenano-cages at different temperatures.

Table 3. Specific heat capacity calculated at the level B3lyp / 6-31g for raw material (ATTz), and its derivatives with boron nitridenano-cages at different temperatures.

	Cv(J/mol.K)	
Temperature	ATTz	ATTz B12N12
300	107.3109	296.3348
310	110.1552	307.2454
320	112.9625	318.0323
330	115.7321	328.684
340	118.4635	339.1904
350	121.1563	349.5424
360	123.8098	359.7321
370	126.4237	369.7524
380	128.9974	379.5976
390	131.5305	389.2627
400	134.0226	398.7437

DISCUSSION AND CONCLUSION

The results of the calculations show that in the process of synthesis of derivatives of (ATTz) with boron nitride nano-cages at different temperatures , the amount of ΔH_f negative at all temperatures, indicating that this process is exothermic and with increasing temperature the amount of heat released is less,So ATTz-B12N12 is stable than ATTz and has low heat content than ATTz.Thus ATTzis more active nitrogen containingenergetic material, Metastable molecules with high activity is obvious that the heat of formation is positive for these substances in the environment and sustainable divided into smaller molecules and high energy are produced. The results showsnegative entropy and decreased with increasing temperature in this reaction. The results shows specific heat capacity of ATTz and its derivative with boron nitride

cage at different temperatures are different, specific heat capacity (CV) in each temperature for ATTz is lower than ATTz B12N12. This means ATTz with less heat than ATTz B12N12 on the same condition, taking its temperature increases. Lower specific heat capacity (CV) of the ATTz represents , ATTZ is more energetic than ATTZ-B12N12. Also density values of ATTz and ATTz B12N12 have a this manner:

$$d_{ATTz} > d_{ATTz\text{-}B12N12}$$

So we can say ATTz has more explosive properties than nanostructure derivative which have studied in this paper.

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