



The Effect of B₁₂N₁₂ Substitution on the Properties of TEX Energetic Materials in Different Temperature Conditions: A DFT Study

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Abstract

In this study the synthesis of the derivative of boron nitride nano- cages with energetic material (TEX) in different conditions of temperature, density functional theory methods were studied. For this purpose, the material on both sides were geometrically optimized reaction, then the calculation of the thermodynamic parameters was performed on all of them. The values of ΔH , ΔG , ΔS the reaction at different temperatures for different products together, these parameters in the raw material is obtained. And finally, the best temperature for the synthesis of derivatives of explosives, according to the results of thermodynamic parameters were evaluated.

Keywords: Thermodynamic parameters, TEX, Boron nitride cage and Density functional theory

1. Introduction

The title compound 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane – often referred to as TEX – is a very promising newcomer in the field of insensitive explosives. It is easily synthesized with good yield from cheap starting materials [1-5]. TEX offers a respectable high ambient temperature crystal density (1.985 g cm⁻³) and hence good detonation velocity and pressure but is fairly insensitive towards mechanical and thermal stimuli [6-12]. It has a large critical diameter and is advantageously used in large charges. 76 references to the public domain are given. It was first synthesized by Boyer and coworkers. Their synthesis started with form amide and glyoxal and in a two-step synthesis involving a piperazine derivative as an intermediary product, TEX is obtained. It is anitramine and additionally contains two embedded five-membered cyclic dietheric (also can be considered as acetal) structures resembling to 1,3-dioxalane [12-16].

In this study the synthesis of the derivative of boron nitride nano-cages with energetic material (TEX) in different conditions of temperature, density functional theory methods were studied.

Table 1. Some chemical properties calculated in the B3lyp / 6-31g (d) to material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX) and its derivatives with boron nitride cage.

	Temperature=298.15K , pressure=1 atm		
	TEX	B-B ₁₂ N ₁₂ TEX	N-B ₁₂ N ₁₂ TEX
	C ₆ H ₆ N ₄ O ₈	C ₆ H ₅ B ₁₂ N ₁₆ O ₈	C ₆ H ₅ B ₁₂ N ₁₆ O ₈
ENERGY(au)	-1033.38647	-1916.81	-1916.599
E HOMO(eV)	-8.45	-5.88	-4.14
E LUMO (eV)	-5.19	0.51	1.27
Dipole Moment (debye)	3.18	4.77	2.85
Weight(amu)	262.134	544.935	544.935
Volume(A ³)	182.55	406.69	411.57
Area (A ²)	199.15	362.84	367.44
Polarizability	53.01	72.85	73.48
ZPE (KJ/mol)	493.97	834.56	823.43
H° (au)	-1033.188	-1916.47	-1916.264
CV (J/mol)	185.30	410.14	419.51
S° (J/mol)	418.84	601.43	610.39
G° (au)	-1033.24	-1916.54	-1916.33

2. calculations and results

Computational study material derived synthesis 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX) 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 [17-20]. All calculations are done in the level B3lyp / 6-31g at 300 to 400 degrees Kelvin, and the atmospheric pressure, the Studied reaction is:

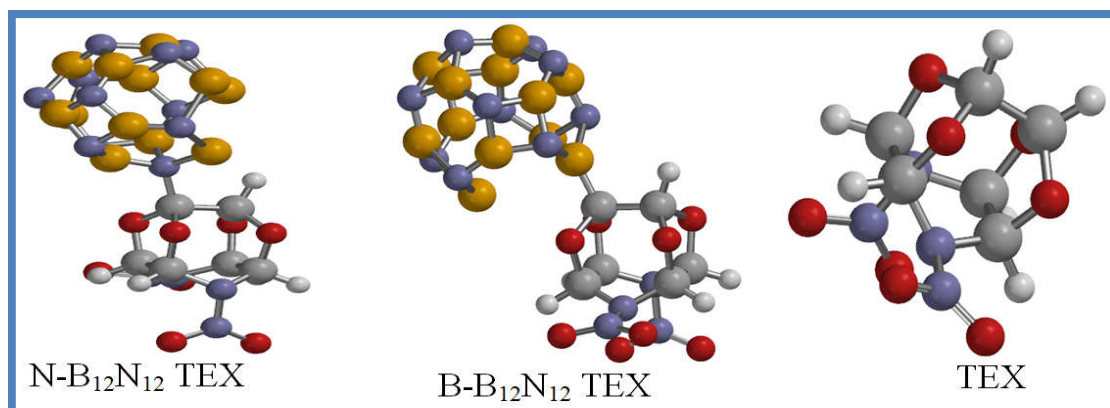


Figure 1. optimized molecules material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX) and its derivative with boron nitride nano-cage

3. Calculation results

Computational Investigation of the reaction products of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclododecane (TEX) 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:

(1)



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

calculated enthalpy values for raw materials and products in process synthesis. For calculating and obtain the change in enthalpy in the reaction $A+B \rightarrow C+D$ from the Equation 2 is used .

$$\Delta H_f = \sum H_{\text{Products}} - \sum H_{\text{Reactant}} \quad (2)$$

Given the following reactions



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

$$\Delta H_f = [H_{\text{B-B}_{12}\text{N}_{12}\text{-TEX} + 1/2\text{H}_2}] - [H_{\text{B}_{12}\text{N}_{12}} + H_{\text{TEX}}] \quad (3)$$

$$\Delta H_f = [H_{\text{N-B}_{12}\text{N}_{12}\text{-TEX} + 1/2\text{H}_2}] - [H_{\text{B}_{12}\text{N}_{12}} + H_{\text{TEX}}]$$

Table 2 . Enthalpy of formation calculated at the level B3lyp / 6-31g for derivative material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX)with boron nitride nano-cage

Temperature	Enthalpy(kJ/mol)	
	B-B12N12 Tex	N-B12N12 Tex
300	2322313.912	2322856.98
310	2322314.079	2322857.2
320	2322314.205	2322857.406
330	2322314.314	2322857.57
340	2322314.386	2322857.694
350	2322314.435	2322857.794
360	2322314.47	2322857.879
370	2322314.488	2322857.95
380	2322314.473	2322858.003
390	2322314.433	2322858.01
400	2322314.356	2322858.003

Enthalpy of formation calculated at the level B3lyp / 6-31g for derivatives material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX) with boron nitride nano-cage, Always Positive in all temperature range 300 to 400 degrees Kelvin.

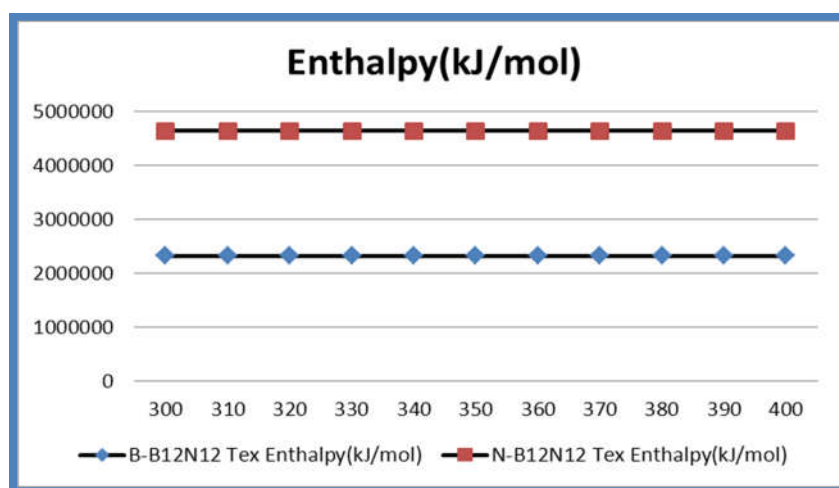


Figure 2. diagram the enthalpy changes for the synthesis of derivatives 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX) with boron nitride nono-cages at different temperatures.

The positive ΔH_f the show, Derived synthesis process material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX) with boron nitride nano- cage insertion at temperatures ranging from 300 to 400 Kelvin, figure 2).

5. Calculate and verify specific heat capacity (CV)

The results of the calculations show, specific heat capacity CV values for raw materials and goods in process synthesis were calculated showed the following procedure.

$$B_{12}N_{12} \text{ TEX} > \text{TEX} \quad (4)$$

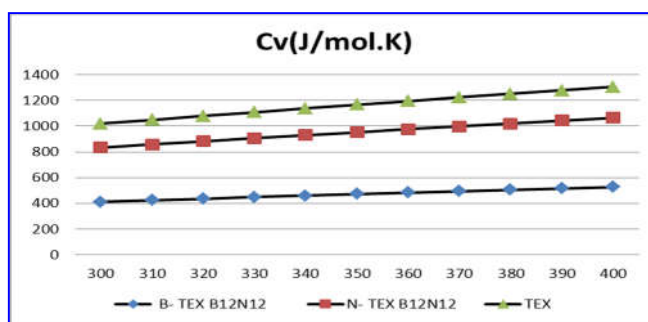


Figure 3. Diagram changes in specific heat capacity CV raw material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX), and its derivatives with boron nitride nano -cages at different temperatures.

Table 3. Specific heat capacity calculated at the level B3lyp / 6-31g for raw material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX), and its derivatives with boron nitride nano -cages at different temperatures.

Temperature	Cv(J/mol.K)		
	B- TEX B12N12	N- TEX B12N12	TEX
300	412.414	421.7757	186.3191
310	424.6109	433.9297	191.8472
320	436.6769	445.9476	197.3745
330	448.6069	457.8246	202.8957
340	460.3961	469.556	208.4049
350	472.0397	481.1374	213.8962
360	483.5332	492.5647	219.3638
370	494.8723	503.8337	224.8019
380	506.053	514.9407	230.2049
390	517.0717	525.8822	235.5672
400	527.925	536.6551	240.8838

Values of specific heat capacity, CV raw material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane (TEX), and its derivatives 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. Figure (3) .

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

The results of the calculations show were calculated the values of Gibbs free energy (ΔG) for reactants and products in process synthesis. For calculating and obtain the change in values of Gibbs free energy (ΔG) in the reaction $A+B \rightarrow C+D$ from the following formula is used:

$$\Delta G_f = \sum G_{\text{Products}} - \sum G_{\text{Reactants}} \quad (5)$$

Given the reaction



The values of Gibbs free energy obtained through calculation software Gaussian, is as follows:

$$\Delta G_f = [H_{B-B12N12-TEX} + 1/2G_{H2}] - [G_{TEX} + G_{B12N12}] \quad (6)$$

$$\Delta G_f = [H_{N-B12N12-TEX} + 1/2G_{H2}] - [G_{TEX} + G_{B12N12}]$$

Table 4 . Gibbs free energy of formation calculated at the level B3lyp / 6-31g for raw material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane inflorescences (TEX), and its derivatives with boron nitride nano -cages at different temperatures.

Temperature	(ΔG) kJ/mol	
	B-B12N12 Tex	N-B12N12 Tex
300	2322357.059	2322897.438
310	2322358.909	2322899.227
320	2322360.677	2322900.974
330	2322362.433	2322902.685
340	2322364.163	2322904.348
350	2322365.898	2322905.98
360	2322367.592	2322907.666
370	2322369.335	2322909.362
380	2322371.11	2322911.06
390	2322372.913	2322912.766
400	2322374.705	2322914.524

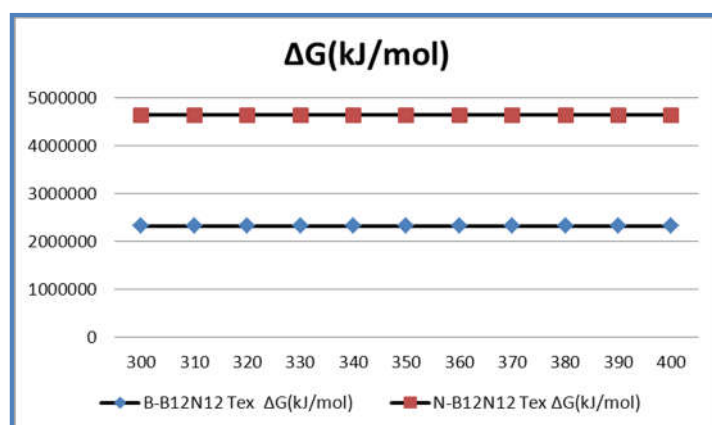


Figure 4. Diagram of the ΔG_f changes for the synthesis of derivatives material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane inflorescences (TEX) with boron nitride nano -cages at different temperatures.

ΔG_f negative values indicate that the process of synthesis derived material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane inflorescences (TEX) With boron nitride nano- cages at different temperatures, it cannot be done spontaneously and with increasing temperature, Gibbs free energy so more positive reaction than is done at higher temperatures (Figure 4) .

7. Discussion and conclusion

The results of the calculations show that in the process of synthesis of derivatives of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane inflorescences (TEX) with boron nitride nono -cages at different temperatures, the amount of ΔH_f negative at all temperatures, the amount of ΔH_f positive at all temperatures, indicating that this process is endothermic. And with increasing temperature the amount of heat released is less, the materials are thermodynamically more positive heat of formation, Unstable and thus are more active nitrogen-containing energetic materials, 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. Sometimes tensile energy release pressure release energy circles. The process of formation of explosive energy and negative entropy and entropy rate decreased with increasing temperature. Changes in specific heat capacity CV shows specific heat capacity of raw material 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-dodecane inflorescences (TEX) to its derivatives with boron nitride cage. There are at different temperatures lower doses. This means less heat than the products on the same terms by taking its temperature increases. CV lower specific heat of the material TTA represents more energetic than it is derived. The values also indicate changes in Gibbs free energy ΔG_f . That the process is calculated at various temperatures 300 to 400 degrees Kelvin, are not spontaneous. Gibbs free energy of more positive with increasing temperature so the reaction at higher temperatures, less done.

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