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Original Research Article

The Effect of Boron Nitride Nanocage on the Thermodynamic and Energetic Properties of TATB

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ABSTRACT

In this research, IR and frontier molecular orbital computations were employed for investigating the influence of $B_{12}N_{12}$ on the energetic and thermodynamic parameters of TATB. The Computed enthalpy changes and Gibbs free energy variations showed TATB interaction with this nanostructure is exothermic, spontaneous and experimentally possible. The specific heat capacity values (C_V) revealed the heat sensitivity of TATB has improved sharply after its interaction with BN nanocage. Some structural features like bandgap, chemical hardness, chemical potential, electrophilicity and maximum transferred charge capacity were also computed and the results indicated that the reactivity, conductance and electrophilicity of TATB enhances substantially after its reaction with $B_{12}N_{12}$. All of the computation were done by density functional theory in the B3LYP/6-31G(d) level of theory.

Keywords: TATB, Boron nitride cage, Density functional theory, Thermodynamic Parameters

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Introduction

In recent years high energy material noted more than past because they have specific properties and show potential for military industry. Now many researchers study high energy material with high density in all over the word. These high energy material have application in production of pyrothecnic material with less smoke, gas generator, propellant and exhibit less sensitivity to heat and shock [1-5]. The other advantages of these compound than common high energy compound is that they are green. For this reason, they are less dangerous and emerge better performance than the other compound [6-10]. fossil fuel as high energy compound are environment pollutant and release CO, CO2 and cause serious environmental problems. Nitrogen-rich compound extensively has been used in prepollant system, fire extinguisher, Cars Airbag and also as Missles fuel and some of the military systems [11-15]. In this research, theoretical investigating of formation reaction of TATB derivatives with different nanostructure at different temperatures were done by using density functional theory. propellant and explosive material belong to high energy compound class and is being used for gas production at high energy []. propellants is used to produce great repulsion forces and explosive cause destruction. when propellant reacted with explosive compound in reaction chamber produce gaseous product, and cause high pressure system, finally this pressure became repulsion force for propulsion or destructive force [15-20].

Computational Details

At the first step chemical structure of TATB and Boron Nitride Cage were drawn by using Gauss view and nanotube modeler. Then, these structure were transferred to Spartan software environment and also calculation about geometrical optimization, IR Studies, calculation about HOMO and LUMO on component were performed. All of the calculations were performed by using density functional theory and base series B3LYP/631G(d). these calculations were performed by considering, aqueous solution, room temperature and 1 atm pressure. In this research structural information such as energy gap(HLG), Chemical hardness(η), Electrophilicity(ω), maximum charge electron transfer(maxΔN) about a number of pharmaceutical molecule were investigated. In Chemistry HOMO and LUMO are kind of molecular orbital that difference energy level

between them, called energy gap and usually it is shown by HLG. This parameter could be obtained by using Equation NO.1. Equation NO.2 is used to calculate chemical hardness .Electrophilicity and maximum transferring electronic charge to system could be calculated by Equation NO.3 and Equation NO.4.

$$HLG=E_{LUMO}-E_{HOMO} \quad (1)$$

$$\eta= (E_{LUMO}-E_{HOMO}) \quad (2)$$

$$\omega=\mu^2/2\eta \quad (3)$$

$$\Delta N_{max}=-\mu/\eta \quad (4)$$

Results and Discussion

Calculation and investigating Enthalpy amount of formation reaction

Enthalpy amount for reactants and products in synthesis process were performed by using Spartan software. For calculating Enthalpy changes in reaction following equation is used:

ΔH=H product – H substrate (5)

Now by considering formation enthalpy amount obtained by using Gaussian software:

ΔHF=[HN-TATB+1/2H H2]-[HN+HTATB] (6)

In written Equation for calculating Formation Reaction Enthalpy of TATB High energy compound derivative, N stands for Nanostructure. After all the calculation the final result is shown in table NO.1. as it can be seen enthalpy changes for two reaction at all temperature is negative. This phenomenon reveals that synthesis of TATB derivative Is Exothermal and for synthesis progress giving heat is not necessary.

Table 1. formation enthalpy changes and derivatives ($B_{12}N_{12}$-TATB) at different temperature.

Temperature	Enthalpy(kJ/mol)
	$B_{12}N_{12}$-B-TATB
300	-643.8602252
310	-643.9058252
320	-643.9517252
330	-644.0148252
340	-644.0958252
350	-644.1846252
360	-644.2555252
370	-644.3357252
380	-644.4643252
390	-644.6064252
400	-644.7114252

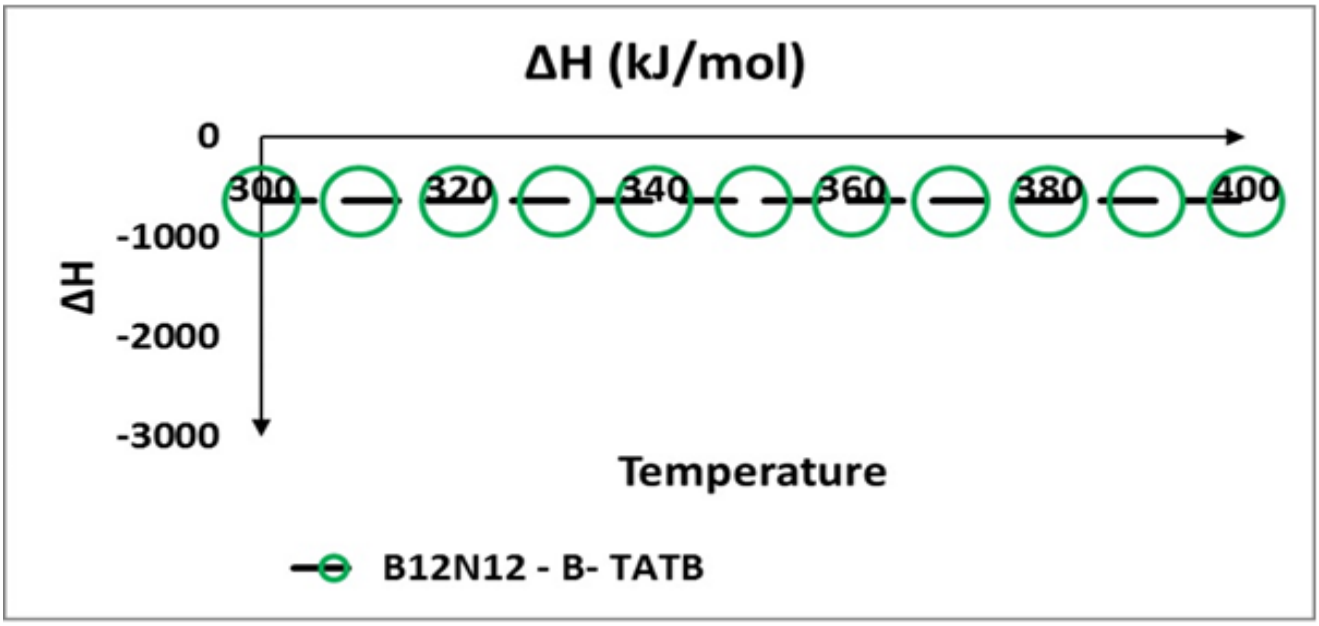

Figure 1. Calculated Enthalpy Changes Diagram at B3lyp/6-31g* for the formation of $B_{12}N_{12}$-B-TATB at different temperatures.

Gibbs free energy calculation

Gibbs free Energy for the reactant and product in synthesis process calculated by using Spartan software. For calculation of Gibbs free energy following Equation is used:

ΔGAB=[GAB]-[GA+GB] (7)

Now by considering reaction, Formation Gibbs Free Energy Amount Coul be obtained by :

ΔGf=[HN-TATB+1/2G H2]- [GN+GTATB] (8)

Obtained result from these calculations have been shown in Table and picture NO.2. as it can be seen Gibbs free Energy amount for process is negative. Therefore, TATB reaction is spontaneous.

Table 2. Changes in gibbs free energy of $B_{12}N_{12}$-TATB at different temperatures.

Temperature	ΔG(kJ/mol)
	$B_{12}N_{12}$-B-TATB
300	-577.7831252
310	-575.2574252
320	-572.6655252
330	-570.0156252
340	-567.3471252
350	-564.6523252
360	-562.1448252
370	-559.6785252
380	-557.2969252
390	-554.8563252
400	-552.3689252

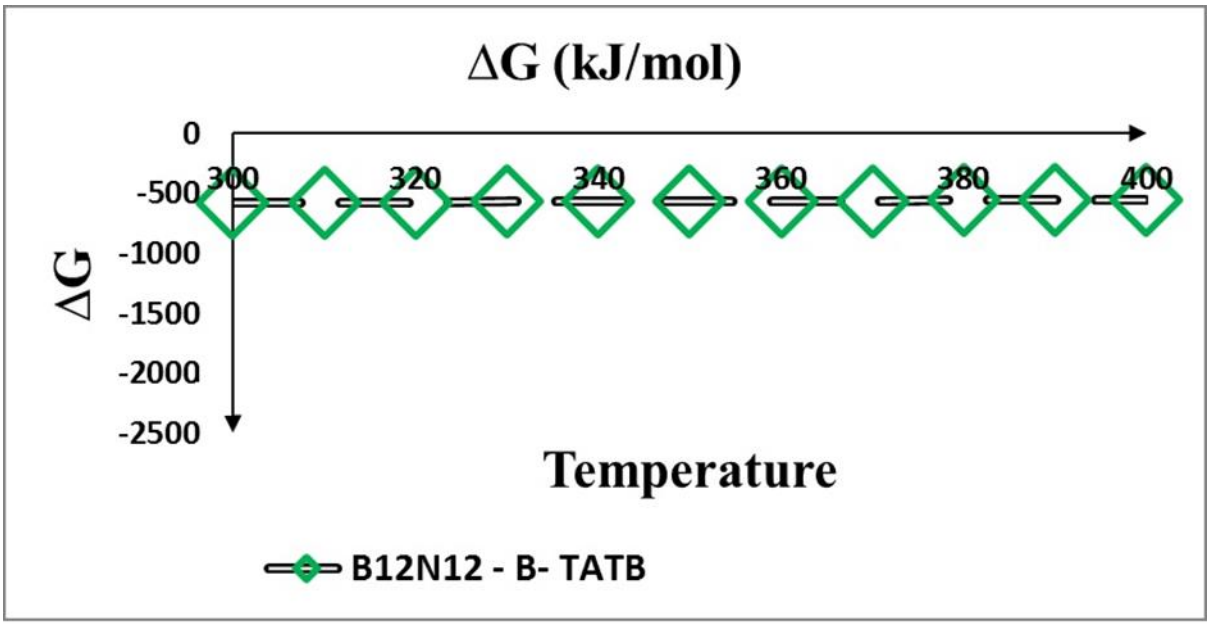

Figure 2. Changes in Gibbs Free Energy of $B_{12}N_{12}$-TATB at different Temperature at the level of b3lyp/6-31g*

Calculation and investigating of Heat Specific Capacity (Cv)

Changes in Heat Capacity is Like previous Parameters and calculated by (CV product)-(CV reactant). Result was shown in picture NO.3. obtained Number reveal that heat capacity of TATB derivative with two nanostructures is more than TATB Heat Capacity. TATB deivatives have less energy than TATB. In other words, in same situation by absorbing more heat their temperature will be increased and become safe and also they will emerge less sensitivity to heat and different shocks.

Table 3- Specific heat capacity for TATB and $B_{12}N_{12}$-TATB at different Temperature and at b3lyp/6-31g*

Temperature	Cv(J/mol.K)	
	TATB	$B_{12}N_{12}$ - B- TATB
300	228.7532	468.7242
310	234.5778	480.9502
320	240.3017	492.943
330	245.9244	504.7036
340	251.4458	516.2339
350	256.8658	527.5359
360	262.185	538.6121
370	267.4039	549.4654
380	272.5232	560.0986
390	277.5438	570.5148
400	282.4665	580.7171

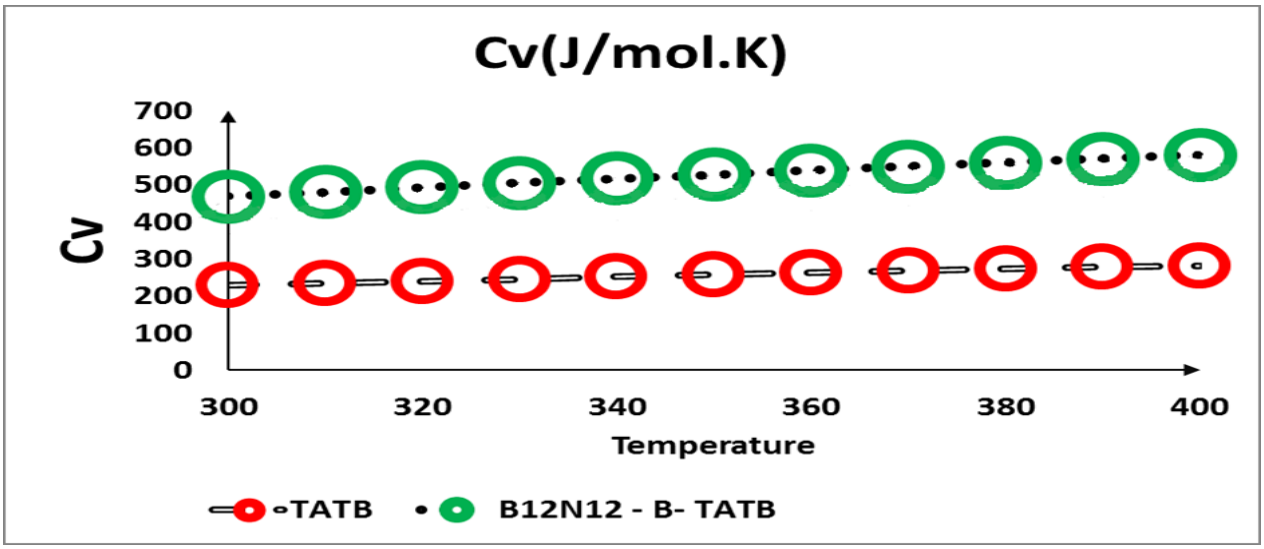

Figure 3- Changes in heat specific capacity _ TATB and B12N12-B_TATB at different temperature calculated at B3lyp/6-31g(d)

Chemical properties of TATB **and its Derivatives**

structural and chemical properties of TATB and its nano structure derivatives have been revealed in Table NO.4 And Pictures NO.4 and NO.5.

As it could be seen The Energy Gap OF TATB after reaction with boron nitride caged has been increased. It means That electrical conductance and Its reactivity became less than past. According to the fact that dipole moment has forward relation to solubility in the water after connection to nanostructures, dipole moment has been increased. It could be stated that by connecting TATB To each dope nano structure Its solubility in water and other polar solvent have been raised. Chemical hardness after connection Boron nitride caged Has been dramatically decreased. Therefore, this interaction make TATB more chemicaly soft than past. It should be noted that amount of electrophilicity of TATB is less than two deravatives and it means that TATB became more electrophile after connecting to Nano structure.

Table 4- S ome of the calculated chemical properties at B3lyp/6-31G* for TATB and its derivatives $B_{12}N_{12}$-TATB

	Chemical Properties	
	TATB	$B_{12}N_{12}$ - B- TATB
ENERGY(au)	-992.92	-1876.23
E HOMO(eV)	-7.05	-6.25
E LUMO (eV)	4.86	-0.58
Dipole Moment (Debye)	0.00	10.12
Weight(amu)	258.15	540.95
Volume(Å3)	190.63	411.87
Area (Å2)	209.96	372.59
ZPE (KJ/mol)	460.56	789.10
H° (au)	-992.73	-1875.90
CV (J/mol)	227.66	466.44
S° (J/mol)	444.27	653.93
G° (au)	-992.78	-1875.98
d=m/v (amu/Å3)	1.35	1.31
HLG (a.u.)	11.91	5.67
Hardness (a.u.)	5.96	2.84
Chemical Potential (a.u.)	-1.10	-3.42
Electrophilicity (a.u.)	3.57	16.53
ΔNmax (a.u.)	0.18	1.20

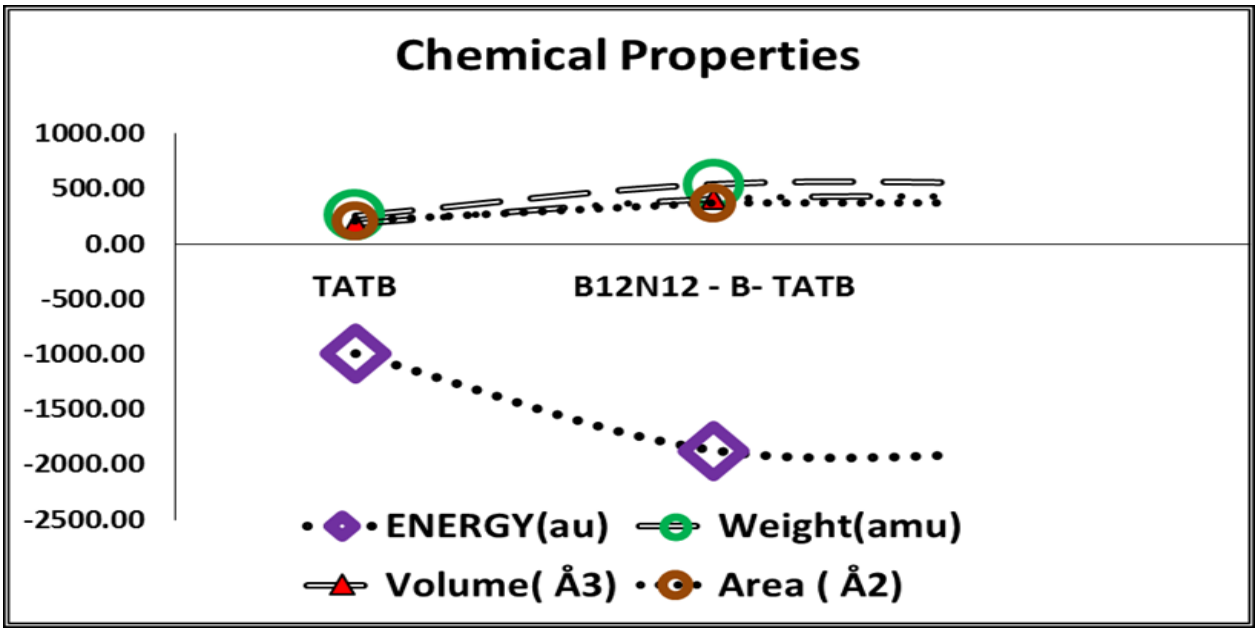

Figure 4- comparison diagram for some calculated chemical properties atB3lyp/6-31g* For TATB compound and its derivatives B12N12-b-TATB

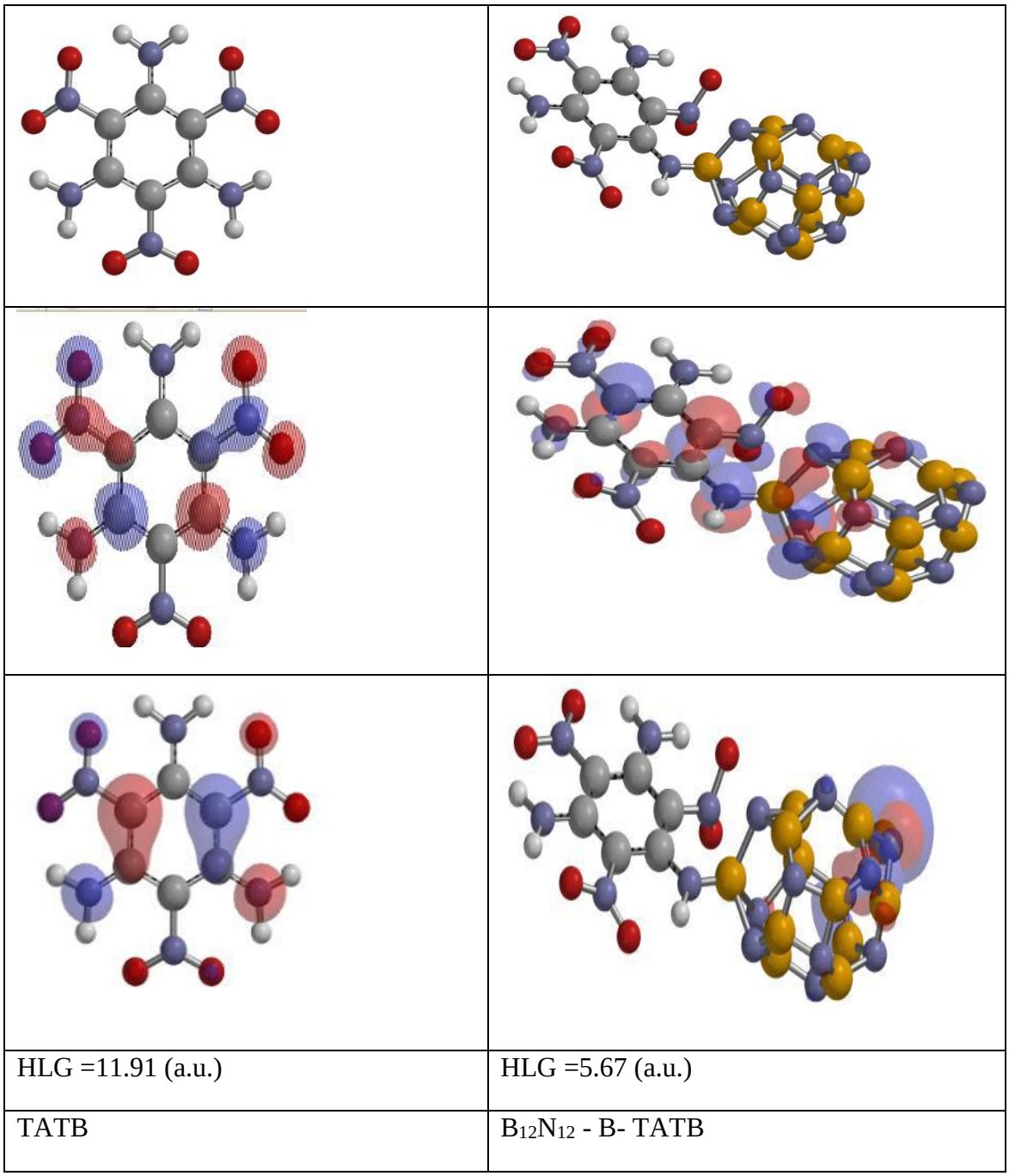

Figure 5- Optimized and HOMO, LUMO molecular orbitals for TATB and its derivatives $B_{12}N_{12}$-TATB

Conclusion

result from calculation express that in synthesis process of TATB-24C and B12N12-B-TATB at Temperature range from 300 to 400 Kelvin By using High Energy compound TATB changes in Formation Enthalpy and formation Gibbs free Energy in connected state to Boron Nitride Cage at all the Temperature from 300 to 400 Kelvin has Negative Value which reveal that the process is Exothermic And spontaneous. Changes for heat specific capacity Cv for nano structure derivatives with high energy compound in all the state emerge that, products have more value(amount) than reactant, it means that in same situation for raising the temperature by one degree they need more heat than reactant. It means that product have less energy than reactant.

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