Journal of Physical and Theoretical Chemistry
of Islamic Azad University of Iran, 14 (2) 143-148: Summer 2017
(J. Phys. Theor. Chem. IAU Iran)
ISSN 1735-2126

Adsorption of Bis(1,4-dinitro toprop-2-yl) Nitramine on Boron Nitride Nano-cages Surfaces: DFT Studies

Roya Ahmadi[*,1], Maryam Ebrahimikia[2] and Elham Pournamdar [2]

[1] Department of chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch, Islamic Azad University, Tehran, Iran
[2] Department of chemistry, Islamshahr Branch, Islamic Azad University, Islamshahr, Iran

Received October 2017; Accepted December 2017

ABSTRACT

In this study Bis(1,4-dinitro toprop-2-yl) Nitramine, BNA, was attached to boron nitride nano- cages (B12N12). , thermodynamic parameters of BNA with B12N12 have been computed using one of the methods of density functional theory (B3LYP) In the temperature variety 300 to 400 K each 10 degree one times, were calculated. So these materials were geometrically optimized. After that thermodynamic parameters were calculated. Enthalpy values (ΔH), Specific heat capacity (Cv) and Gibbs free energy (ΔG) were computed for these reactions. Finally, the effect of nano structures on explosion properties and other chemical attributes of BNA were evaluated.

Keywords: Enthalpy; BNA; Boron nitride nano cage; Temperature

INTRODUCTION

Recently scientists are interested in compounds with a high-nitrogen content for the reason that they are considered the best candidates for 'green'' energetic materials because the approximate stability of nitrogen as a reaction product [1]. The design of new energetic molecules is based on compounds exhibiting a high density and have high formation enthalpy and good thermal stability. Some of them have shown potential as energetic materials for explosive, propellant or gas generators formations [2]. Previous studies showed that the number of nitrogen atoms joined together is straightly proportional to the act of the compound. The nitrogen atom of high nitrogen compounds can be increased over than 75% by substitution of useful functional groups [3]. Generally tetrazole derivatives are very useful constituent in the chemistry of highly nitrogen rich compounds [4].

Tetrazoles as high-nitrogen compounds have interested in combination with energetic substituent. Such as nitro groups ($R–NO_2$) [5] or nitramine functionalities (R_2N-NO_2) [6]. Herein, we report the energetic properties of Bis(1,4-dinitro toprop-2-yl) Nitramine as example of these compounds.

Optimization of molecules with density and high energy is the firstly step in the search for high energy materials [7]. By the reason of difficulties in the preparation of those materials, theoretical computations are useful to design high-

[*]Corresponding author: roya_ahmadi_chem@yahoo.com

energy density compounds [8]. Latterly, nanostructure materials have attracted much attention Due to their different properties that classify them from the other substances.

In this work, the stimulation of Bis(1,4-dinitro toprop-2-yl) Nitramine as an explosive molecules with boron nitride (BN) nano sheet have been researched by density function theory (TD-DFT), (Fig.1).

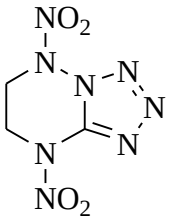

Fig. 1. Bis (1,4-dinitro toprop-2-yl) Nitramine

THEORETICAL Method

Computational DFT-based study of derived synthesis material of BNA with boron nitride nano-cages in different temperatures has been carried out using the B3LYP (Becke, three-parameter, Lee-Yang-Parr) method (Fig.2)[9-12]. The operation was performed using Gaussian 98, Gauss view and Spartan computer software programs. In the level of B3LYP/6-31G, the atmospheric pressure and at 300-400 K, for studying thermodynamic parameters, IR calculation were performed (Table 1). The reaction studied is as follows:

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

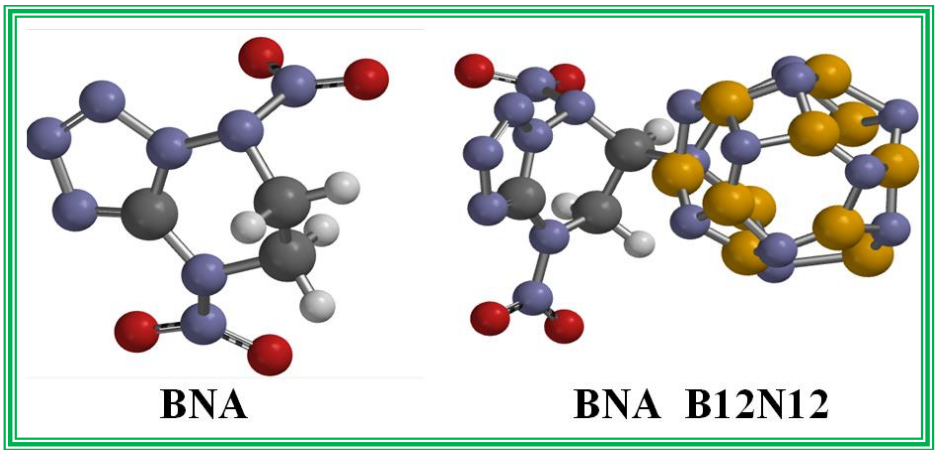

Fig. 2. Optimized molecules material **BNA** and its derivative with boron nitride nano-cages

Table 1. Some chemical properties calculated in the B3lyp / 6-31g for BNA and its derivatives with boron nitride nano cage

Chemical properties	BNA	BNA-$B_{12}N_{12}$
ENERGY(au)	-839.474212	-1722.59184
E HOMO (eV)	-8.83	-4.47
E LUMO (eV)	4.05	0.95
Dipole Moment (debye)	5.73	5.54
Weight(amu)	216.117	498.918
Volume($Å^3$)	157.57	382.21
Area ($Å^2$)	189.01	348.93
ZPE (KJ/mol)	352.19	689.29
C_v (J/mol.K)	170.15	405.41

RESULTS AND DISCUSSION

The results of the calculations show that the manner of increasing the density is according bellow:

$$BNA > BNA\ B_{12}N_{12}$$

As we know there is direct relation between energetic compound and density. Increasing trend of the explosive compounds would be as follows [13]:

$$BNA > BNA\ B_{12}N_{12}$$

Calculation and Verifying the Values of Enthalpy Changes (ΔHs)

Enthalpy values (H) for raw materials and products had been calculated in process synthesis. For calculating and obtaining of any changes on the enthalpy, Equations (2,3) is used**:**

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

$$BNA + B_{12}N_{12} \rightarrow BNA\ B_{12}N_{12} + 1/2H_2 \quad (3)$$

Enthalpy values obtained through calculation software Spartan, and then enthalpy of formation values obtained from Equations (4).

$$\Delta H_f = [H_{BNA\ B12N12} + 1/2H_{H2}] - [H_{BNA} + H_{B_{12}N_{12}}] \quad (4)$$

Table 2 . Enthalpy formation calculated at the level B3LYP / 6-31g for derivative material BNA with boron nitride nano-cages

	ΔH (kJ/mol)
Temperature	**BNA $B_{12}N_{12}$**
300	-3.87365
310	-3.69905
320	-3.54455
330	-3.43155
340	-3.34395
350	-3.27525
360	-3.22465
370	-3.19255
380	-3.20395
390	-3.23975
400	-3.31935

Enthalpy of formation calculated at the level B3LYP / 6-31G for Bis(1,4-dinitro toprop-2-yl) Nitramine (BNA) boron nitride nano-cages are always negetive in all temperature range 300 to 400 Kelvin (Table 2).

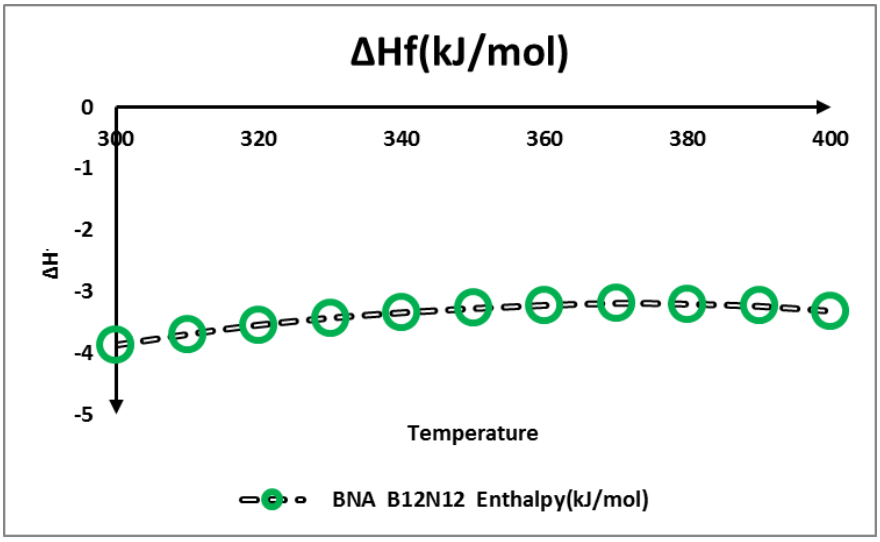

Fig. 3. Diagram the enthalpy changes for the synthesis of derivatives material BNA with boron nitride nano-cages at different temperatures.

The negative ΔH_f shows that, synthesis process Bis(1,4-dinitro toprop-2-yl) Nitramine (BNA) boron nitride nano-cages are exothermic reaction at temperature ranging from 300-400 Kelvin, although with enhancing the temperature, the value of released heat from the reaction, increases(Fig.3)

Calculate and verify specific heat capacity (C_V)

The results of the calculations show, specific heat capacity, C_V values for these materials were calculated with the following procedure (5).

$$B_{12}N_{12}\ \ BNA\ > BNA \qquad (5)$$

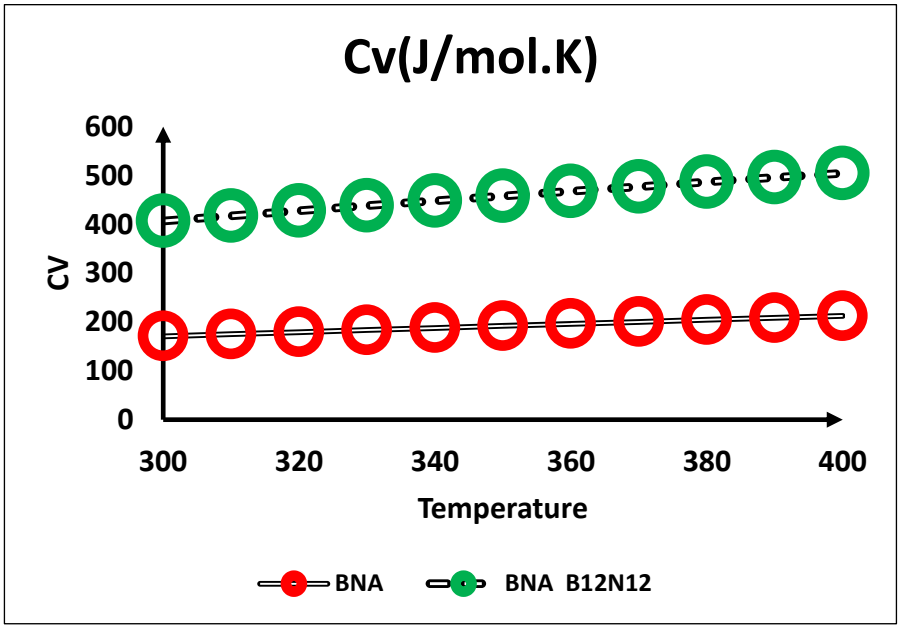

Fig. 4. Diagram changes in specific heat capacity C_V raw material BNA, and its derivatives with boron nitride nano -cages at different temperatures.

Table 3. Specific heat capacity calculated at the level B3lyp / 6-31g for raw material BNAits derivatives with boron nitride nano -cages at different temperatures

	Cv(J/mol.K)	
Temperature	**BNA**	**BNA $B_{12}N_{12}$**
300	170.9595	407.3614
310	175.2957	417.8315
320	179.5976	428.1464
330	183.8638	438.3059
340	188.0926	448.3103
350	192.2821	458.1594
360	196.4303	467.8534
370	200.535	477.3924
380	204.5942	486.7763
390	208.6057	496.0052
400	212.5676	505.0792

Values of specific heat capacity changes, C_V of Bis (1,4-dinitro toprop-2-yl) Nitramine (BNA) with boron nitride nano-cages at different temperatures, indicate that the BNA-$B_{12}N_{12}$ have a high specific heat capacity C_V values ; it means that in the same conditions by taking more heat in rather to raw material increasing of its temperature (Fig. 4), (Table .3).

Calculating and Verifying the values of Gibbs free energy (ΔG) in the Range of 300-400 K

The results of the calculations show 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 equations (6-8) are used:

$$\Delta G_f = \Sigma G_{Products} - \Sigma G_{Reactants} \quad (6)$$

$$BNA + B_{12}N_{12} \rightarrow BNA\ B_{12}N_{12} + 1/2H2 \quad (7)$$

$$\Delta G_f = [G_{BNA\ B12N12} + 1/2G_{H2}] - [G_{BNA} + G_{B12N12}] \quad (8)$$

Gibbs free energy (G) values were obtained with calculation software Spartan, and then Gibbs free energy of formation (ΔG_f) values were computed from Equations (8).

Table 4. Gibbs free energy of formation calculated at the level B3lyp / 6-31g for raw material BNA and its derivatives with boron nitride nano -cages at different temperatures

	ΔG (kJ/mol)
Temperature	BNA B12N12
300	-3.87365
310	-3.69905
320	-3.54455
330	-3.43155
340	-3.34395
350	-3.27525
360	-3.22465
370	-3.19255
380	-3.20395
390	-3.23975
400	-3.31935

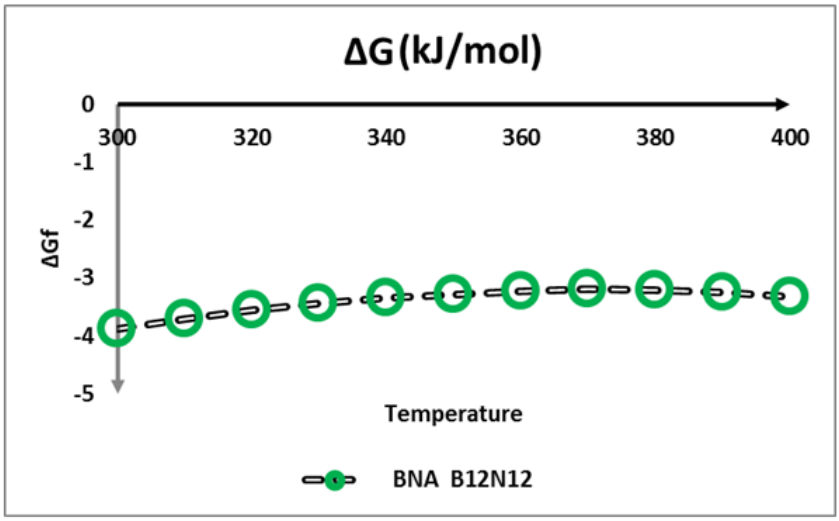

Fig. 5. Diagram of the ΔG_f changes for the synthesis of derivatives material BNA with boron nitride nano -cages at at the range temperatures 300-400K.

The negative values of ΔG_f from the synthesis of BNA with boron nitride nano-cages indicate that, it be spontaneously performed in the temperature range 300-400 K and with increasing the temperature Gibbs free energy will have higher values, so at this condition the reaction has less occurred (Table. 4) (Fig. 5).

CONCLUSION

The results of the calculations show that in the process of synthesis of derivatives of BNA with boron nitride nano- cages at different temperatures, the amounts of ΔG_f and ΔH_f are negative at all temperatures which suggests that these process are exothermic and spontaneously. The heat released by increasing the reaction temperature becomes lower. In other word, the heating process is reduced as the temperature rise. The comparison of results of specific heat capacity C_V shows that the C_V of Bis(1,4-dinitro toprop-2-yl) Nitramine (BNA) is lower than its derivatives with boron nitride nano- cages in these temperatures. The specific heat 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 BNA rather than BNA $B_{12}N_{12}$. Density values of BNA and its derivatives with boron nitride nano-cages have this manner:

$$BNA > BNA\ B_{12}N_{12}$$

Novelty of this study is to discover the effect of the nanostructures on chemical attributes of BNA by DFT method, so we can say BNA has more explosive properties than nanostructure derivatives as studied in this paper.

ACKNOWLEDGMENT

We are appreciating and thanking Islamic Azad University of Yeager-e-Imam Khomeini (Rah) Share Rey.

REFERENCES

[1] M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A.K. Sikder, B.R. Gandhe and A. S. Rao, J. Hazard. Mater. 161 (2009) 589-595.

[2] N. Fischer, K. Karaghiosoff and T. M. Klapötke, J. Stierstorfer *Z. Anorg. Allg. Chem. 636 (*2010) 735–749.

[3] G. Singh, I. P. S. Kapoor, S. M. Mannan and S. K. Tiwari, J Hazard Mater 68 (1999) 155-162.

[4] J.G. Zhang, X.Q. Niu, S.w. Zhang, T.L. Zhang, H.S. Huang and Z.N. Zhou Computational and Theoretical Chemistry 964 (2011) 291–297.

[5] T. M. Klapötke, C. M. Sabaté, Dalton Trans. 10 (2009) 1835–1841

[6] S. Berger, K. Karaghiosoff, T. M. Klapötke, P. Mayer, H. Piotrowski, K. Polborn, R. L. Willer and J. J. Weigand, J. Org. Chem. 71(2006) 1295–1305.

[7] J. K. Cooper, C. D. Grant, and J. Z. Zhang, J. Phys. Chem. A, 117(2013) 6043-6051.

[8] H. Muthurajan, R. Sivabalan, M.B. Talawar, M. Anniyappan and S. Venugopalan, J. Hazard. Mater. A133 (2006) 30-38.

[9] K. Kim and K. D. Jordan. J. Phys. Chem. 98(1994) 10089-10094.

[10] P.J. Stephens, F. J. Devlin, C. F. Chabalowski and M.J. Frisch, J. Phys. Chem. 98 (1994) 11623-11627.

[11] A. D. Becke. Phys. Rev. A.38 (1988) 3098-3100.

[12] C. Lee, W. Yang and R.G. Parr, Phys. Rev. B. 37(1988) 785-789.

[13] N. Zohari, F. Abrishami and M. Ebrahimikia, Zeitschrift Für Anorganische und Allgemeine Chemie. 642 (2016) 642, 749-760.