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The thermodynamic parameters of the formation of derivatives of 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) with Boron Nitride nano-cage structure in different temperature conditions, the DFT method

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ABSTRACT: In this study, the response is derived, high-energy material 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) with boron nitridenano-cages in different conditions of temperature, density functional theory methods were studied. for this purpose, the material on both sides were geometrically optimized, then the calculation of the thermodynamic parameters were performed on all of them. The amount of ΔH, ΔS and ΔG of this reaction at different temperatures for different products together, these parameters in the raw material is obtained. And finally, the best temperatures for the synthesis of derivatives, according to the results of thermodynamic parameters were evaluated.

Keywords: *Boron nitride; Enthalpy of formation;Nano-cage; 1-(4-nitrophenyl)-1H-Tetrazole (NPHT); Temperature; Thermodynamic*

INTRODUCTION

Tetrazole cyclic and aromatic compounds, has four atoms of nitrogen and carbon (Antonelli, *et al.*, 2015). These compounds are used in various industries including military industries. Tetrazole N_2 released large quantities of gas after combustion and little pollution to the environment due to the explosive component are green (Nader, *et al.*, 2013). Enter the Tetrazole energetic properties of polymers in the structure of the polymer chains can be increased. Currently, researchers around the world many times on high-density energetic materials do Tetrazole investigation This energetic materials in the manufacture of pyrotechnics with Smoke less, and propellant gas generators are used and less sensitive to heat and shock of the show and have many applications in the military field (Majidi, 2014). Many different methods for the synthesis of poly Tetrazole (PTZ) reported that the majority of them are if you are overhanging branches and attached to the main chain. If you are using Tetrazole rings as monomers can be functionalized polymer backbones structure will Rings. Environmental hazards these reactions were less fossil energy than the materials that are commonly used and has a high carbon content During the burning process large amounts of carbon gases, carbon dioxide, carbon monoxide and unburned carbon particles such

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Table 1. Some chemical properties calculated in the B3lyp/6-31g to article 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) and its derivatives with boron nitride cage

	Temperature=298.15K, Pressure=1atm		
	R=$C_7H_4N_8O_6$	1-$B_{12}N_{12}$ NPHT	2-$B_{12}N_{12}$ NPHT
ENERGY(au)	-680.94	-1563.83	-1564.12
E HOMO(eV)	-7.72	-3.00	-3.66
E LUMO (eV)	3.70	1.65	1.88
Dipole Moment (Debye)	2.41	6.41	7.56
Weight(amu)	191.15	473.95	473.95
Volume(A^3)	167.71	396.49	393.40
Area (A^2)	191.28	356.20	348.80
ZPE (KJ/mol)	383.38	703.80	719.14
H° (au)	-680.78	-1563.54	-1563.83
CV (J/mol)	150.42	403.23	380.71
S° (J/mol)	390.50	607.80	581.88
G° (au)	-680.83	-1563.61	-1563.90

as soot and pollution generated in the environment that create a lot of problems (Haiying, *et al.*, 2014). Nitrogen-rich compounds propulsion systems, fire suppression systems and systems for car air bags as well as rocket fuels and military systems are used. In this study, derived synthesis of 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) with cage $B_{12}N_{12}$ in different conditions of temperature, density functional theory method is studied (Minoru, *et al.*, 2016).

COMPUTATIONAL DETAILS

Computational Investigation of the reaction products of 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) with boron nitride nano-cages in different conditions of temperature, studied by density functional theory, the operation was performed using thes of tware Gaussian 98 and Gaussian view And Spartan. 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 (Beheshtian, et al., 2013). All calculations are done in the level B3lyp/6-31g at 300 to 400 degrees Kelvin, and the atmospheric pressure, the studied reactions are:

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

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

RESULTS AND DISCUSSION

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

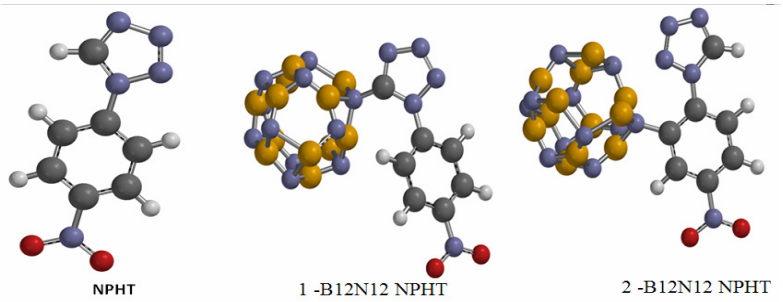

Fig. 1. Optimized molecules article, 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) and its derivatives with boron nitride nano-cages

The enthalpy values for raw materials and products in process synthesis were calculated. For calculating and obtain the change in enthalpy in the reaction A+B→C+D from the Equation 3 is used.

$$\Delta H_f = \sum H_{Products} - \sum H_{Reactants} \quad (3)$$

Given the following reactions

$$NPHT + B_{12}N_{12} \rightarrow 1 - B_{12}N_{12}NPHT + 1/2H_2$$

$$NPHT + B_{12}N_{12} \rightarrow 2 - B_{12}N_{12}NPHT + 1/2H_2$$

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

$$\Delta H_f = [H_{B12N12NPHT} + 1/2H_{H2}] - [H_{NPHT} + H_{B12N12}] \quad (4)$$

Enthalpy of formation calculated at the level B3lyp/6-31g for derivatives article 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) with boron nitride nano-cages, Always negative in all temperature range 300 to 400 degrees Kelvin. ΔH_f shows a negative amount, the synthesis of derivatives article 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) with boron nitride nano-cages Insert at temperatures ranging from 300 to 400 Kelvin , is exothermic And by increasing the reaction temperature is less than the amount of heat released Fig. (2). The results show for the derivative 1-$B_{12}N_{12}$ NPHT Enthalpy of formation is more negative derivative 2-$B_{12}N_{12}$ NPHT, Which shows create derivative 1-$B_{12}N_{12}$ NPHT the more heat is released (Fig.2, Table 2).

Table 2. Enthalpy of formation calculated at the level B3lyp/6-31g for derivatives article 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) with boron nitride nano-cages

Enthalpy(kJ/mol)		
Temperature	1-$B_{12}N_{12}$ NPHT	2-$B_{12}N_{12}$ NPHT
300	-17.5117	-5.9696
310	-17.2354	-5.8007
320	-16.9812	-5.6729
330	-16.7761	-5.5606
340	-16.5795	-5.4635
350	-16.3847	-5.3942
360	-16.2377	-5.3610
370	-16.1176	-5.3441
380	-16.0489	-5.3432
390	-16.0017	-5.3789
400	-15.9753	-5.4415

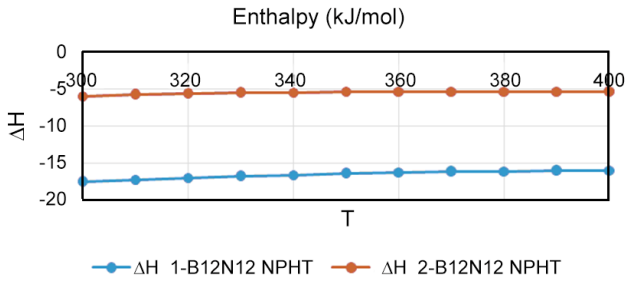

Fig. 2. Diagram the enthalpy changes for the synthesis of derivatives material 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) with boron nitride nano-cages at different temperatures

Calculate and verify specific heat capacity (CV)

The results of the calculations show, specific heat capacity CV values for raw materials and goods in process synthesis were calculated to show, the specific heat capacity of the initial explosion is less than 1 and 2 (Fig. 3, Table 3).

Values of specific heat capacity change, CV raw material 1-(4-nitrophenyl)-1H-Tetrazole, and its derivatives with boron nitride nono-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.3).

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

The results of the calculations show were calculated

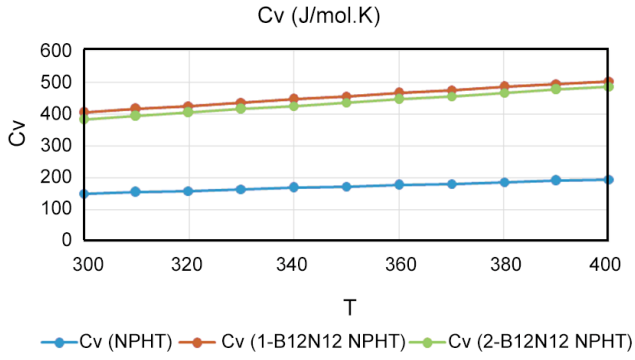

Fig. 3. Diagram changes in specific heat capacity CV raw material 1-(4-nitro-phenyl)-1H-Tetrazole (NPHT), and its derivatives with boron nitride nano-cages at different temperatures

Table 3. Specific heat capacity calculated at the level B3lyp/6-31g for raw material 1-(4-nitro-phenyl)-1H-Tetrazole (NPHT) and its derivatives with boron nitridenano-cagesat different temperatures.

Cv(J/mol.K)			
Temperature	NPHT	1-$B_{12}N_{12}$ NPHT	2-$B_{12}N_{12}$ NPHT
300	151.2549	405.1948	382.7571
310	155.7707	415.7012	393.723
320	160.2774	426.0535	404.553
330	164.7685	436.2502	415.2414
340	169.2379	446.2896	425.7833
350	173.6799	456.1706	436.1747
360	178.089	465.8925	446.4116
370	182.4601	475.4544	456.491
380	186.7886	484.856	466.4101
390	191.0702	494.0968	476.1665
400	195.3012	503.1768	485.7584

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→C+D from the following formula is used:

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

Given the reaction

$$NPHT + B_{12}N_{12} \rightarrow 1-B_{12}N_{12}NPHT + 1/2H_2$$

$$NPHT + B_{12}N_{12} \rightarrow 2-B_{12}N_{12}NPHT + 1/2H_2$$

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

$$\Delta G_f = [G_{B12N12NPHT} + 1/2G_{H2}] - [G_{NPHT} + G_{B12N12}] \quad (6)$$

ΔG_f negative values indicate that the process of synthesis of derivatives of 1-(4-nitrophenyl)-1H-Tetrazole with boron nitride nano-cages at different temperatures, it can be done spontaneously and with increasing temperature, Gibbs free energy so more negative, therefore the reaction does better at higher temperatures (Fig. 4, Table.4).

Table 4. Gibbs free energy of formation calculated at the level B3lyp/6-31g for raw material 1-(4-nitro-phenyl)-1H-Tetrazole (NPHT) and its derivatives with boron nitride-nano-cagesat different temperatures

Free Gibbs Energy (kJ/mol.K)		
Temperature	1-$B_{12}N_{12}$ NPHT	2-$B_{12}N_{12}$ NPHT
300	15.2469	34.5461
310	16.9192	36.3331
320	18.53595	38.05295
330	20.1177	39.7866
340	21.68865	41.48025
350	23.23985	43.11755
360	24.80065	44.73915
370	26.40985	46.43275
380	27.9979	48.2201
390	29.6437	49.9967
400	31.3288	51.772

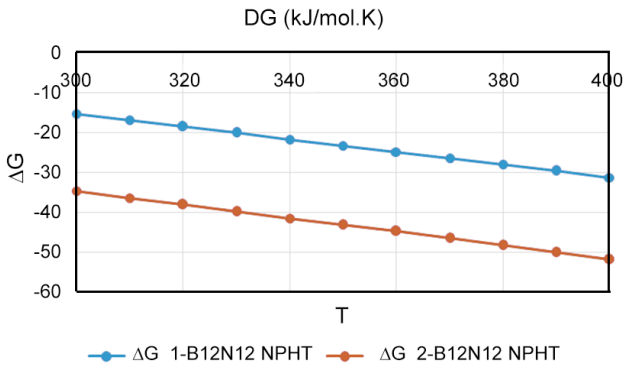

Fig.4. Diagram of the ΔGf changes for the synthesis of derivatives material 1-(4-nitrophenyl)-1H-Tetrazole with boron nitride nano-cages at different temperatures

CONCLUSIONS

The results of the calculations show that in the process of synthesis of derivatives of 1-(4-nitrophenyl)-1H-Tetrazolewith boron nitride nano-cages at different temperatures, the amount of ΔHf negative at all temperatures, which suggests that this process is exothermic and by increasing the reaction temperature is less than the amount of heat released, The process of formation of negative entropy and entropy rate decreased with increasing temperature. Changes in specific heat capacity CV shows specific heat capacity of raw material 1-(4-nitrophenyl)-1H-Tetrazole (NPHT) compared to cage its derivatives with lower doses of boron nitride at different temperatures , is less than in the same condition by taking heat Product its temperature increases. The specific heat capacity is less than the second derivative of the derivative 1. The specific heat CV represents more energetic than the material of the derivative is NPHT. The values of Gibbs free energy changes ΔGf also show that the process is calculated at various temperatures 300 to 400 Kelvin, are spontaneously. Gibbs free energy gets more negative by increasing temperature so the reaction does better in higher temperatures.

REFERENCES

Antonelli, M., Baccioli, A., Francesconi, M., Psaroudakis, P. and Martorano, L.; (2015). Small Scale ORC Plant Modeling with the AMESim Simulation Tool: Analysis of Working Fluid and Thermodynamic Cycle Parameters Influence, Energ. Procedia, 81: 440-49.

Nader, H., Stelzl, J., Weinberger, P., Molnar, G., Bousseksou, A., Kubel, F., Mereiter, K., Boca, R. and Linert, W.; (2013). Spectroscopic, structural and magnetic investigations of iron(II) complexes based on 1-isopropyl- and 1-isobutyl-substituted tetrazole ligands, Inorg. Chim. Acta, 396: 92-100.

Al-Majidi, Suaad M.H.; (2014). Synthesis of some new 4-oxo-thiazolidines, tetrazole and triazole derived from 2-SH-benzothiazole and antimicrobial screening of some synthesized, J. Saudi Chem. Soc., 18: 893-901.

Haiying, Z., Zhu, Y., Chen, C. and Zheng, J.; (2014). Photophysical properties and potential application in photocurrent generation of porphyrin-(60) fullerene polymer linked by metal axial coordination, Polymer, 55: 1913-16.

Minoru, Y., Matsunaga, T., Tanaka, M. and Kurosawa, Sh.; (2016). Determination of thermodynamic parameters for enolization reaction of malonic and metylmalonic acids by using quartz crystal microbalance, Anal. Chem. Res., 8: 9-15.

Beheshtian, J., Ahmadi Peyghan, A., BigdeliTabar, M. and Bagheri, Z.; (2013). DFT study on the functionalization of a BN nanotube with sulfamide, Appl. Surf. Sci., 266: 182-87.

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