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Study of 5-Picrylamino-1,2,3,4-tetrazole(PAT) with nanostructures of fullerene and boron nitride nano-cages in different conditions of temperature, using density functional theory

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ABSTRACT: High Energy Materials is a term that is used for explosives, propellants and pyrotechnics. Explosives are used for military applications. 5-Picrylamino-1,2,3,4-tetrazole(PAT) is an explosive substance. In this study the reactions of the 5-Picrylamino-1,2,3,4-tetrazole(PAT) with nanostructures of fullerene and boron nitride nano-cages in different conditions of temperature, with density functional theory methods were studied. For this purpose, the material on both sides of reaction were geometrically optimized, After that calculation of the thermodynamic parameters were performed on all of them and then The values of ΔH, ΔG, ΔS the reaction at different temperatures for different products determined. Also some parameters including HOMO & LUMO levels, chemical hardness, electrophilicity Index, ΔNmax and chemical potential are investigated. And finally, the best positions and temperatures for the synthesis of explosives nano derivatives and effect of molecular weight and type of nano-cages on chemical properties and stability of PAT and nano derivatives were evaluated.

Keywords: *$B_{12}N_{12;}$ Enthalpy; Explosive; 5-Picrylamino-1,2,3,4-tetrazole; Temperature*

INTRODUCTION

Tetrazol cyclic and aromatic compounds, has four atoms of nitrogen and carbon. Which are used in military industries. These compounds are released by burning large amounts of gas N_2 so little pollution to the environment and green are the explosives (Funakoshi, *et al.*, 2016). Today, many scientists in the world are investigating the energetic materials with high density tetrazol times, Environmental hazards of these reactions are commonly used to lower fossil energy materials and has a high carbon content because during the process of burning fossil fuel carbon emissions of carbon dioxide, carbon monoxide and unburned carbon particles of such Products have a lot of soot pollution in the environment and create a lot of problems. The nitrogen-rich compounds are used in various industries. The nitrogen-rich compounds are used in various industries (Yoshimoto, *et al.*, 2016). Explosives with high temperature properties are generally considered as heat-resistant or thermally stable explosives. These are more stable at high temperatures, and find applications in modern applications. PAT is a green materials flammable, because after combustion is produced a lot of N_2 gas. In this paper are discussed about Computational calculations,

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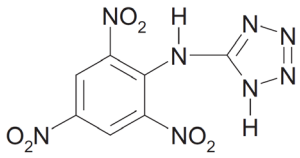

Fig. 1. 5-Picrylamino-1,2,3,4-tetrazole(PAT)

which are used to predict the energetic properties, for PAT and its derivatives (Dai, *et al.*, 2012) with nano-structures including C_{24} and $B_{12}N_{12}$.

COMPUTATIONAL METHODS

Computational study of material derived synthesis 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene and boron nitride nano-cages in different conditions of temperature has been studied by density functional theory (Baei, *et al.*, 2014). The operation was performed using the software Gaussian 98 and Gauss view and Spartan. First, compounds were optimized in a series of basic using density functional theory (6-31G). (Fig. 2a, 2b, 2c). Then IR studies, were done in order to calculate thermodynamic parameters of the process (Yoshimoto, *et al.*, 2016) (Table 1). All of these calculations were done in the level B3LYP/6-31G at 300 to 400 kelvin, and the atmospheric pressure. the studied reactions are as bellows:

$$PAT + C_{24} \rightarrow PAT\ C_{24} + 1/2H_2 \quad (1)$$

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

In this research some properties including HOMO & LUMO levels, chemical hardness and electrophilicity

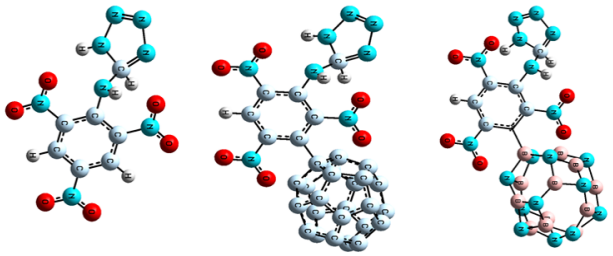

Fig. 2. optimized molecules material 5-Picrylamino-1,2,3,4-tetrazole(PAT)(a), its derivative with fullerene C_{24} (b) and boron nitride nano-cages (c)

properties, maximum amount of electronic charge index, ΔN_{max}, electrophilicity Index, ω, chemical potential and the chemical hardness are investigated, Those are calculated by following equations:

$$\Delta N_{max} = -\frac{\mu}{\eta} \quad (3)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (4)$$

$$\mu = \frac{(E_{HOMO} + E_{LUMO})}{2} \quad (5)$$

$$\eta = \frac{(E_{LUMO} + E_{HOMO})}{2} \quad (6)$$

The ΔN_{max} index describes the charge capacity of the molecule that the electrophone system may be accepted, it is given by (3) equation. A positive value of ΔN_{max} index (a.u.) Shows that acts as an electron acceptor, where as a negative value of ΔN_{max} index indicates that acts as an electron donor. The ΔN_{max} and the electrophilicity are related to electronic charge. The electrophilicity Index, ω, is a measure of electrophilic power of a molecule it is given by (4) equation. A

Table 1. Some chemical properties have been calculated in the B3LYP/6-31G for 5-Picrylamino-1,2,3,4-tetrazole(PAT) and its derivatives with fullerene and boron nitride cage

CHEMICAL PROPERTIES	PAT= $C_7H_4N_8O_6$	PAT $B_{12}N_{12}$	PAT C_{24}
ENERGY (AU)	-1145.08	-2034.75	-2047.59
DIPOLE MOMENT (DEBYE)	5.65	20.28	8.16
WEIGHT (AMU)	296.16	579.97	584.42
VOLUME (A^3)	220.67	445.23	457.66
AREA (A^2)	250.65	418.18	408.35
D= M/V (AMU/A^3)	1.34	1.30	1.28

Table 2. Calculated E-HOMO and E-LUMO (a.u.), chemical hardness, η, chemical potential, μ, electrophilicity index, ω, and the maximum amount of electronic charge index, ΔN_{max}, in atomic units and dipole moment (Debye) for PAT, PAT C_{24} and PAT $B_{12}N_{12}$ obtained by B3LYP/6-31G level of theory

ELECTRONIC PROPERTIES	PAT	PAT $B_{12}N_{12}$	PAT C_{24}
HOMO (**A**.U.)	-10.77	-11.88	-6.89
LUMO (A.U.)	-1.90	-7.78	-3.67
HLG (**A**.U.)	8.87	4.10	3.22
HARDNESS (A.U.)	4.44	2.05	1.61
CHEMICAL POTENTIAL (A.U.)	-6.34	-9.83	-5.28
ELECTROPHILICITY (A.U.)	88.99	99.04	22.44
ΔN_{MAX} (A.U.)	1.43	4.80	3.28

higher electrophilicity index shows higher electrophilic power of a molecule. So the quantity of ω describes the propensity of the system to acquire additional electronic charge from the environment, In equations (5) and (6), μ and η are the chemical potential and the chemical hardness respectively (Beheshtian, *et al.*, 2013).

The results obtained revealed that when structure of PAT is linked to nano structure C_{24} and $B_{12}N_{12}$ the dipole moment increased (Table 1). PAT derivatives have band gap less than PAT. A small HOMO-LUMO Gap (HLG) in atomic units automatically means small excitation energies to the excited states. Therefore PAT derivatives are more conductive than PAT (Table 2). PAT has chemical hardness more than C_{24} PAT and $B_{12}N_{12}$ PAT, so it is harder than its derivatives. Clearly Soft molecules with a small gap will have their electron density changed more easily than a hard molecule. So PAT $B_{12}N_{12}$ and PAT C_{24} are more reactive than PAT (Table 2). Electrophilicity value (a.u.) in PAT $B_{12}N_{12}$ increased. The electrophilicity index is a measure of electrophilic power of a molecule. So PAT $B_{12}N_{12}$ has higher electrophilicity than PAT and its nano derivatives with C_{24}, therefore PAT $B_{12}N_{12}$ is a stronger Lewis acid (Table 2). Maximum amount of electronic charge index (ΔN_{max}) as mentioned above, most electron charge which a system accepts can be calculated by ΔN_{max} parameter. The obtained results for this parameter were obtained like the previous parameters, For PAT $B_{12}N_{12}$ increased. A positive value of ΔNmax indicates that charge flows to system, or our system acts as an electron acceptor, whereas a negative value of ΔN_{max} indicates that charge flows from system or our system acts as an electron donor. So $B_{12}N_{12}$ PAT is an electron acceptor or a stronger Lewis acid (Table 2).

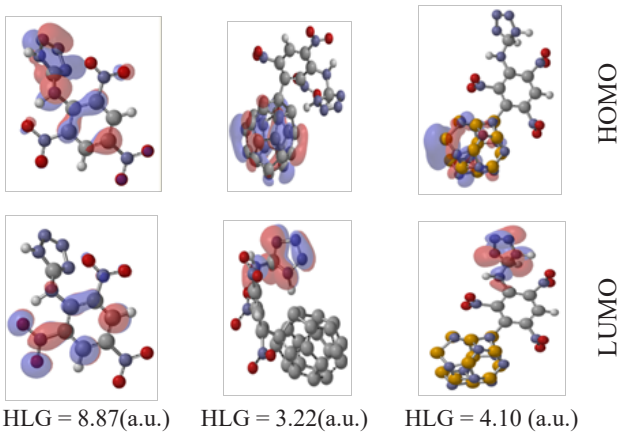

Fig. 3. LUMO and HOMO molecular orbitals of PAT, PAT C_{24} and PAT $B_{12}N_{12}$

RESULTS AND DISCUSSION

The results of the calculations are listed as follow:

Calculation and verifying the values of changes in the enthalpy (ΔH)

Eenthalpy values for raw materials and products had been calculated in process synthesis. For calculating and obtaining of any changes on the enthalpy, Equation 7 is used .

$$\Delta H_f(T\ K) = \Sigma(\varepsilon^0{}_+ H_{corr})_{Products} - \Sigma(\varepsilon^0{}_+ H_{corr})_{Reactants} \quad (7)$$

Sum of electronic and thermal enthalpies = $\varepsilon^0 + H_{corr} = H$

$$\Delta H_f(T\,K) = \Sigma(H)_{Products} - \Sigma(H)_{Reactants} \quad (8)$$

It gives the following reactions:

$$PAT + C_{24} \rightarrow PAT\,C_{24} + 1/2H_2 \quad (9)$$

$$PAT + B_{12}N_{12} \rightarrow PAT\,B_{12}N_{12} + 1/2H_2 \quad (10)$$

Enthalpy values obtained through calculation software Spartan, and then enthalpy of formation values obtained from Equation 11, 12 are as bellow:

$$\Delta H_f = [H_{PATC24} + 1/2H_{H2}] - [H_{PAT} + H_{C24}] \quad (11)$$

$$\Delta H_f = [H_{PAT\,B12N12} + 1/2H_{H2}] - [H_{PAT} + H_{B12N12}] \quad (12)$$

Enthalpy of formation calculated at the level B3LYP/6-31G for derivatives material 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene, are always negative in all temperature range 300 to 400 Kelvin , but for boron nitride nano-cages with PAT are always positive in all temperature range 300 to 400 Kelvin (Table 3).

The negative ΔH_f shows that, derived synthesis process material 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene C_{24} , is exothermic reaction at temperature ranging from 300 to 400 Kelvin, but for boron nitride nano-cages with PAT is endothermic in all temperature range 300 to 400 Kelvin (Fig. 4).

Table 3. Enthalpy of formation calculated at the level B3lyp/6-31G for derivative material 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene and boron nitride nano-cages

	ENTHALPY(KJ/MOL)	
TEMPERATURE	PAT C_{24}	PAT $B_{12}N_{12}$
300	-17172.20585	30049.38945
310	-17165.78125	30049.39019
320	-17159.52835	30049.39054
330	-17153.31585	30049.39117
340	-17147.26025	30049.39194
350	-17141.22945	30049.39274
360	-17135.20545	30049.39365
370	-17129.22325	30049.39429
380	-17123.49645	30049.39462
390	-17117.80495	30049.39459
400	-17112.16755	30049.39458

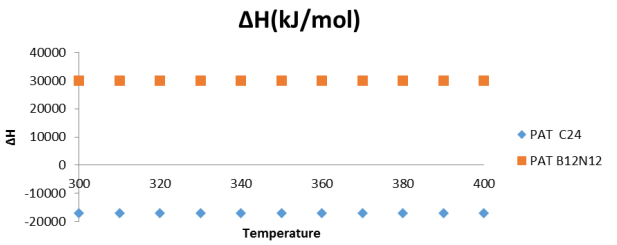

Fig. 4. diagram of the enthalpy changes for the synthesis of derivatives material 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene C_{24} and boron nitride nano-cages at different temperatures

Calculation and verifying specific heat capacity (CV)
The results of the calculations show, specific heat capacity, CV values for raw materials in process synthesis were calculated with the following procedure:

$$CV\ PAT\ B_{12}N_{12} > CV\ PAT\ C_{24} > CV\ PAT \quad (13)$$

Values of specific heat capacity changes, CV of raw material 5-Picrylamino-1,2,3,4-tetrazole(PAT), and its derivatives with fullerene and boron nitride nano-cages at different temperatures indicate that the products have a high specific heat capacity CV values, it means that, in the same conditions by taking more heat in rather to the PAT increasing of their temperature (Fig.5, Table 4).

Calculation and verifying the values of Gibbs free energy (ΔG)

The results of the calculations revealed 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

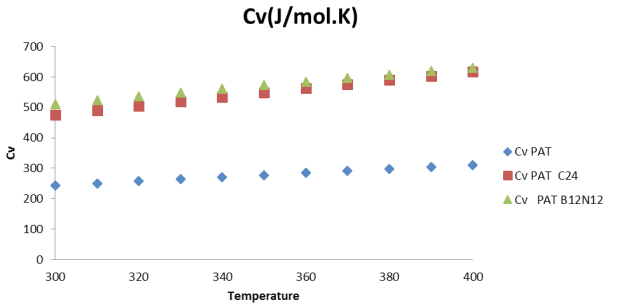

Fig. 5. Diagram changes in specific heat capacity C_V of raw material 5-Picrylamino-1,2,3,4-tetrazole(PAT), and its derivatives with fullerene C_{24} and boron nitride nano–cages $B_{12}N_{12}$ at different temperatures

Table 4. Specific heat capacity CV calculated at the level B3lyp/6-31G for derivative material 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene and boron nitride nano-cages

	CV(J/MOL.K)		
TEMPERATURE	PAT	PAT C_{24}	PAT $B_{12}N_{12}$
300	242.7485	474.6683	510.8012
310	249.9108	489.7316	523.6217
320	256.9863	504.6589	536.2501
330	263.9667	519.4255	548.6798
340	270.8444	534.0095	560.9051
350	277.6129	548.3918	572.9213
360	284.2666	562.5557	584.7248
370	290.8005	576.4871	596.3126
380	297.2108	590.1738	607.6826
390	303.4941	603.6061	618.8331
400	309.6482	616.776	629.7635

Gibbs free energy (ΔG) in the reaction A+B→C+D the following formula is used:

$$\Delta G_f(T\ K) = \Sigma\left(\varepsilon^0 + G_{corr}\right)_{Products} - \Sigma\left(\varepsilon^0 + G_{corr}\right)_{Reactants} \quad (14)$$

Sum of electronic and thermal enthalpies = $\varepsilon^0 + H_{corr} = H$

$$\Delta H_f(T\ K) = \Sigma(H)_{Products} - \Sigma(H)_{Reactants} \quad (15)$$

It gives bellow reactions:

Table 5. Gibbs Free Energy of formation calculated at the level B3lyp/6-31G for derivative material 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene and boron nitride nano-cages

	ΔG (KJ/MOL.K)	
TEMPERATURE	ΔG PAT C_{24}	ΔG PAT $B_{12}N_{12}$
300	-16950.7476	30049.81265
310	-16948.7303	30049.83061
320	-16946.67555	30049.84884
330	-16944.6264	30049.86717
340	-16942.50155	30049.8862
350	-16940.38015	30049.90515
360	-16938.24715	30049.92498
370	-16936.10935	30049.94523
380	-16933.9168	30049.96595
390	-16931.7461	30049.98624
400	-16929.6342	30050.00601

$$PAT + C_{24} \rightarrow PATC_{24} + 1/2H_2 \quad (16)$$

$$PAT + B_{12}N_{12} \rightarrow PAT\ B_{12}N_{12} + 1/2H_2 \quad (17)$$

The values of Gibbs free energy obtained through Gaussian calculation software:

$$\Delta G_f = \left[G_{PAT\ C24} + 1/2G_{H2}\right] - \left[G_{PAT} + G_{C24}\right] \quad (18)$$

$$\Delta G_f = \left[G_{PAT\ B12N12} + 1/2G_{H2}\right] - \left[G_{PAT} + G_{B12N12}\right] \quad (19)$$

ΔGf negative values of the process of synthesis derived material 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene C_{24} at different temperatures indicate that, it can be done spontaneously, but for boron nitride nano-cages with PAT is no spontaneously in all temperature range 300 to 400 Kelvin (Fig. 6).

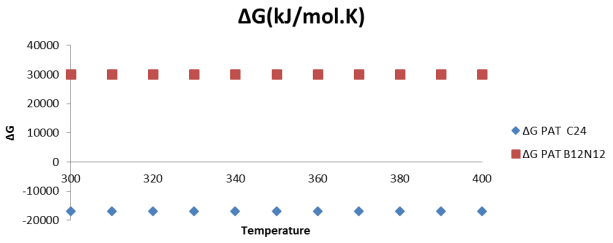

Fig. 6. Diagram of the Gibbs free energy changes for the synthesis of derivatives material 5-Picrylamino-1,2,3,4-tetrazole(PAT) with fullerene C_{24} and boron nitride nano-cages at different temperatures

CONCLUSIONS

The results of the calculations show that in the process of synthesis of 5-Picrylamino-1,2,3,4-tetrazole(PAT) with only nanostructures of C_{24} in different conditions of temperature, ΔHf and ΔGf values are negative at all temperatures which suggests that this process is exothermic and it can be done spontaneously at the 300 to 400 temperature range. The comparison of results of CV shows that the specific heat capacity of 5-Picrylamino-1,2,3,4-tetrazole(PAT) is lower than its derivatives with the $B_{12}N_{12}$ cage boron nitride and fullerene C_{24} at different temperatures, So PAT need low energy to increase its temperature, less specific heat capacity values define much energetic properties of PAT rather than its derivations. The results of the calculations show that the manner of increasing the density is according bellow equation:

$$d_{PAT} > d_{PAT\ B12N12} > d_{PAT\ C24}$$

As we know there is direct relation between energetic compound and density. Increasing trend of explosive compounds which have been predicted as follows:

$$PAT > PAT\ B_{12}N_{12} > PAT\ C_{24}$$

Consequently PAT has more explosive properties than nanostructure derivatives.

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