



Original Research Article

Adsorption of 3-picrylamino-1,2,4-triazole on C₆₀ surface as a green fuel: DFT studies

Maryam Godarzi^a, Roya Ahmadi^{a,*}, Reza Ghiasi^b

^a Department of Chemistry, Yadegar-e-Imam Khomeini (RAH) Shahre Rey Branch, Islamic Azad University, Tehran, Iran

^b Department of Chemistry, Faculty of science, East Tehran Branch, Islamic Azad University, Tehran, Iran

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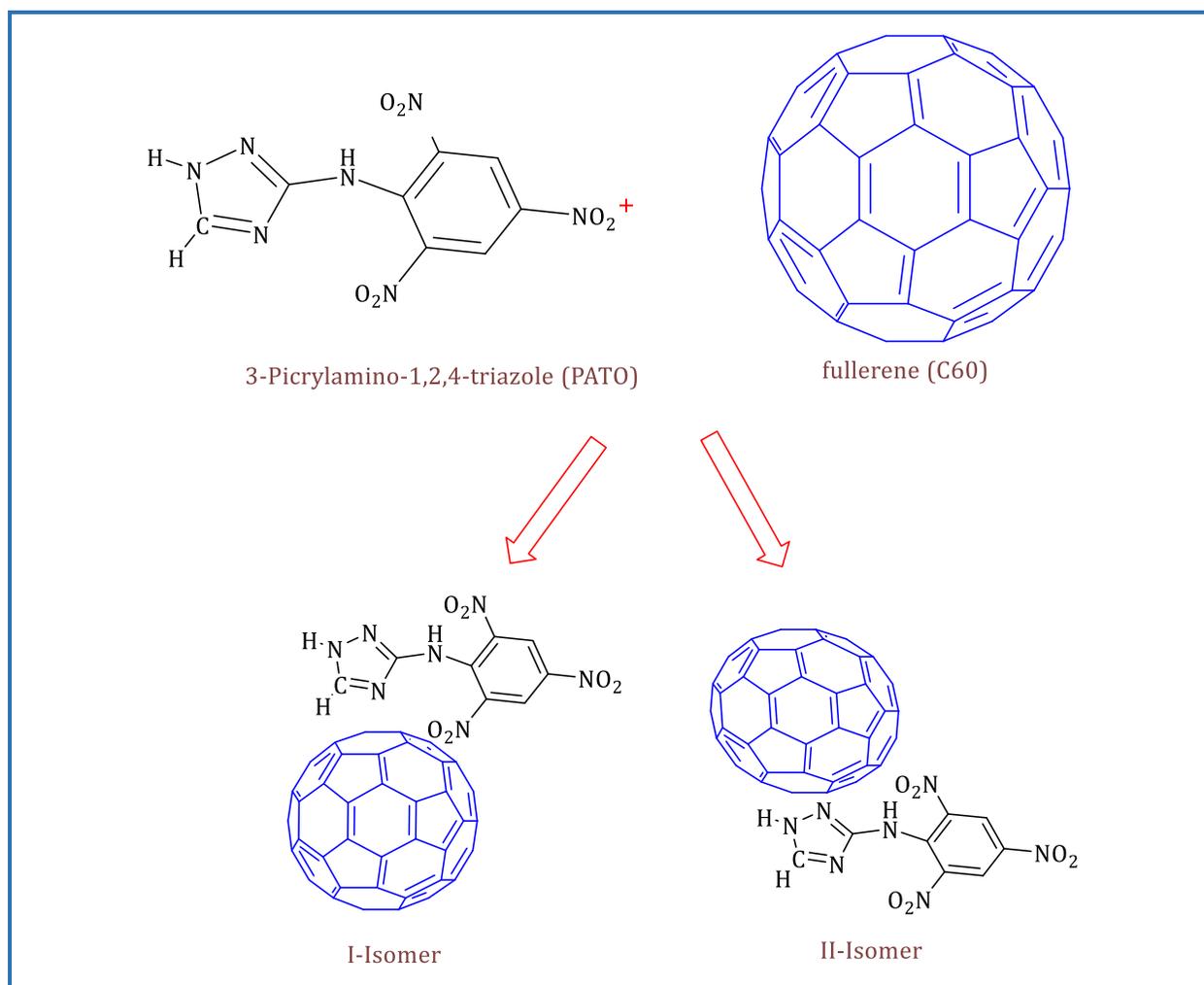
Density functional theory

ABSTRACT

In this study, the adsorption of 3-picrylamino-1,2,4-triazole (PATO) On the surface of fullerene (C₆₀) was evaluated by density functional theory using, Becke, three-parameter and Lee-Yang-Parr (B3LYP). PATO as a green fuel, is such a green material and environmental friendly, because after combustion it produces excessive amounts of N₂ gas. Due to the importance of these materials in protecting environmental pollution as well as protecting fossil fuel reserves, it is necessary to research in this field. For this purpose, the structures of PATO, C₆₀, and the PATO-C₆₀ complexes were optimized geometrically. Then, IR and Frontier molecular orbital calculations were performed on them. The calculated energies: Gibbs free energy changes (ΔG_{ad}) and adsorption enthalpy changes (ΔH_{ad}) revealed that the adsorption process of PATO-C₆₀ complexes are experimentally feasible, spontaneous and exothermic. The specific heat capacity values (C_V) showed the heat sensitivity has reduced significantly in the PATO-C₆₀ complexes. The N–O and C–N bond lengths and the density values demonstrated that PATO-C₆₀ complexes have higher explosive velocity and blasting pressure in comparison to the pure blasting materials without C₆₀. The Frontier molecular orbital parameters such as band gap, chemical hardness, electrophilicity, chemical potential and charge capacity were also studied.

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Graphical Abstract



Introduction

For the first time in 1863, 3-picrylamino-1,2,4-triazole (PATO) was synthesized, by Julius Wilbrand. After some tries, the PATO explosive properties were detected in 1891 [1]. Owing to the rather high density of PATO, it is being applied for blasting and destroying in fighting. The explosion happens by the breakdown of PATO's molecular structure [2] and the oxidation of the explosive with the participation of oxygen from the air [3]. PATO is a solid nitro aromatic compound that is synthesized from toluene with nitration (Figure 1) [4]. It is a toxic yellow solid with high adsorption heat, due to the existence of a large number of N-N and C-N bonds in its structure [5]. One of the most useful properties of PATO is that it can be safely melted and mix with other HEDM [6]. Activation energy with the exothermic reaction is very high in gas phase but the liquid or solid phases have lower activation energies. PATO mixtures with oxygen-wealthy compounds can be released more

energy in comparison with PATO alone. Therefore, often a mixture of PATO with ammonium nitrate was used in military explosive, in the 20th century [7]. Generally, the heat released from PATO explosion is considered as a reference for evaluating other explosives. Since the heat of PATO burning is generated by reaction between carbons and atmospheric oxygen [8–10], it can be considered as a green and environmentally friendly material because, after combustion of the explosives, excessive N₂ gas will be produced [9]. Adsorption energy of explosive molecules like 1,3,5-trinitro perhydro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), PATO, and so on with graphene and boron nitride (BN) sheet have been studied by density functional theory methods. The outcomes have been shown that the binding between the fiery molecules and BN sheet is firmer than that with graphene [11, 12]. The incitement of energetic materials have been studied by density functional theory (TD-DFT) [13]. 1,2,4-triazole and 3-amino-1,2,4-triazole are useful starting materials for the synthesis of many 1,2,4-triazole-based explosives. Electronic properties and blast performances of 3-picrylamino-1,2,4-triazole and its 1,3- and 1,5- tautomer are researched computationally using PM3, HF/6-31G (d, p), and B3LYP/6-31G (d, p) methods [14–17].

The aim of this study was to evaluate the effect of nano structure of fullerene on energetic properties of PATO by density functional theory (DFT) methods.

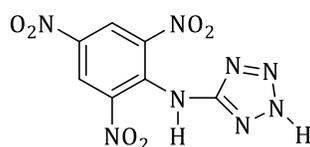


Figure 1. The chemical structure and IUPAC name of PATO

Experimental

Computational methods

Computational study of derived synthesis material of PATO with fullerene over different temperatures has been studied using B3LYP (Becke, three-parameter, Lee-Yang-Parr), method which is a density functional theory method (DFT) [18]. The operation was performed utilizing Gaussian 98 and Gauss view and Spartan computer software programs. In the level of B3LYP/6-31G in the atmospheric pressure and at 300-400 K, for studying thermodynamic parameters, IR calculating were done (Table 1). studied reactions are as bellows:



Summarize of reactions between fullerene with PATO from nitrogen (II-Isomer) (a) and from carbon (I-Isomer) (b) of its triazole ring were displayed in (Figure 2a and 2b).

When weight of compounds rises so energy decreases, also volume, area and C_v increase (Table 1). In this work some properties including, energies of HOMO & LUMO molecular orbitals (ϵ_H , ϵ_L), distance between energies of HOMO and LUMO molecular orbitals, (HLG), electrophilicity (ω), chemical potential (μ) and chemical hardness (η) were studied. Equation three displays the value of charge transferred is maximum amount of electric charge index, (ΔN_{max}), if ΔN_{max} is positive it demonstrates that compound acts equally an electron acceptor and a negative one expressions that it acts like an electron donor. The molecule electrophilicity related to its electronic charge. Equation four shows an electronic power of a molecule, which is nominated as the electrophilicity Index, ω , it is the system propensity to obtain additional electronic charge from the surround area, in the reaction between two molecules, one of them is similar a nucleophile, while other one behaves as an electrophile. Chemical hardness (η) and chemical potential (μ) are exhibited by Equations 6 and 7 [19–23].

$$HLG = \epsilon_L - \epsilon_H \quad (3)$$

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

$$\omega = \mu^2/2\eta \quad (5)$$

$$\mu \approx (\epsilon_H + \epsilon_L)/2 \quad (6)$$

$$\eta = (\epsilon_L - \epsilon_H)/2 \quad (7)$$

Table 1. Some chemical properties have been calculated in the B3LYP/6-31G for PATO and its complexes with fullerene

Chemical properties	PATO	I-Isomer	II-Isomer
Energy (au)	-1120.93	-3365.10	-3365.10
Dipole Moment (debye)	4.09	3.47	4.59
Weight (amu)	295.17	1015.83	1015.83
Volume (Å ³)	228.76	818.09	820.29
Area (Å ²)	257.24	649.96	652.36
d=m/v (amu/Å ³)	1.29	1.24	1.24

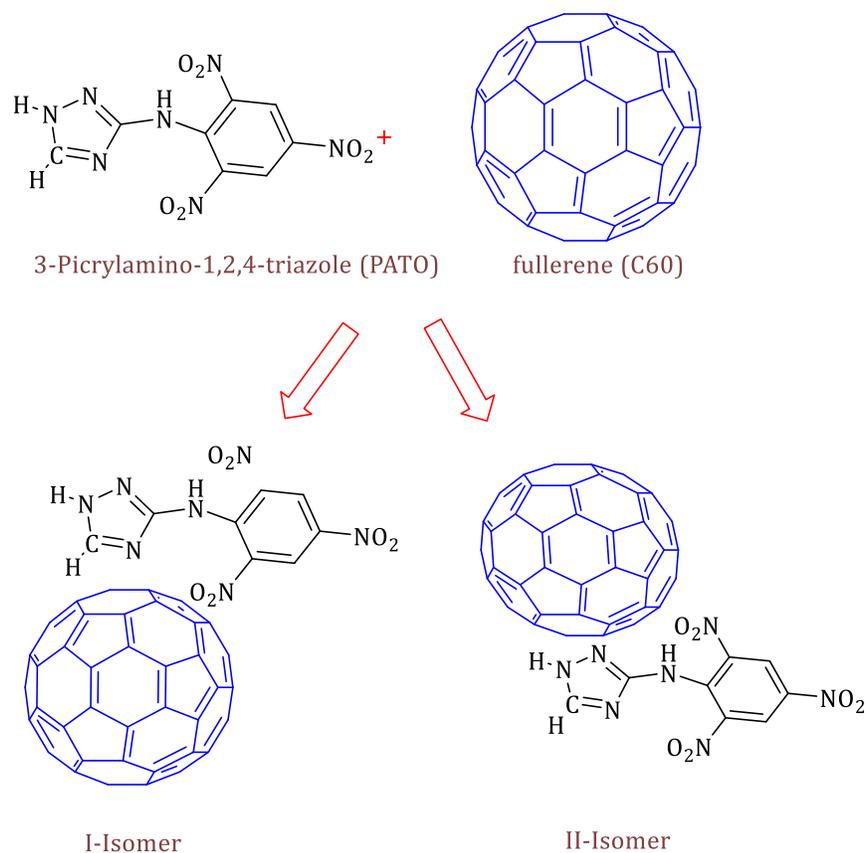


Figure 2. Schematic of 2 complexes of fullerene with PATO

The results obtained revealed that when structure of PATO is neared to nano structure C₆₀ the dipole moment in II-Isomer increased and in I-Isomer decreased (Table 1). PATO derivatives have band gap less than PATO. A small HOMO-LUMO Gap (HLG), automatically means small excitation energies to the excited states. Therefore II-Isomer and I-Isomer are more conductive than PATO (Table 2). I-Isomer, has chemical hardness less than II-Isomer, so I-Isomer is softer than II-Isomer. Soft molecules with a small gap, will have their electron density changed more easily than a hard molecule. So I-Isomer is more reactive than II-Isomer (Table 2). The results show that, the chemical potential of PATO is lower than, its nano derivatives (Table 2). Electrophilicity values in I-Isomer and II-Isomer increased. The electrophilicity index is a measure of electrophilic power of a molecule. So PATO derivatives have higher electrophilicity than PATO, therefore PATO is a weaker Lewis acid (Table 2). Maximum amount of electronic charge index (ΔN_{\max}) as above-mentioned, most electron charge which a system accepts [24–27].

The obtained results for this parameter were obtained like the previous parameters, For II-Isomer and I-Isomer, increased. If the molecular system acts an electron acceptor, the amount of ΔN_{\max} is positive and charge flows to it, but the negative amount of ΔN_{\max} shows that charge flows from system

or our system acts as an electron donor. So I-Isomer and II-Isomer are electron acceptor or a stronger Lewis acid (Table 2).

Table 2. Calculated ϵ_H and ϵ_L , HLG, Chemical hardness, η , chemical potential, μ , electrophilicity index, ω , and the maximum amount of electronic charge index, ΔN_{\max} , in electron-volt (eV) for PATO, I-Isomer and C₆₀N PATO obtained by B3LYP/6-31G level of theory

Electronic properties	PATO	I-Isomer	II-Isomer
ϵ_H (eV)	-7.31	-5.68	-5.79
ϵ_L (eV)	3.16	3.35	3.26
HLG (eV)	10.47	9.03	9.05
η (eV)	5.235	4.515	4.525
M (eV)	-2.075	-1.165	-1.265
Ω (eV)	-10.86	-5.26	-5.72
ΔN_{\max} (eV)	0.3964	0.2580	0.2796

Results and Discussion

Calculation and verifying the values of changes in the enthalpy (ΔH_{ad})

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 (8, 9) are used.

$$\Delta H_{ad} (T K) = \sum (\epsilon_0 + H_{corr})_{Products} - \sum (\epsilon_0 + H_{corr})_{Reactants} \quad (8)$$

Sum of electronic energy (ϵ_0) and thermal enthalpies (H_{corr}) = $\epsilon_0 + H_{corr} = H$

$\Delta H_{ad} = \Delta H_{adsorption}$ and temperature Kelvin = TK

$$\Delta H_{ad} (TK) = \sum (H)_{Products} - \sum (H)_{Reactants} \quad (9)$$

According to the Equations (1, 2) can be written

$$\Delta H_{ad} = [H_{I-Isomer}] - [H_{PATO} + H_{C60}] \quad (10)$$

$$\Delta H_{ad} = [H_{II-Isomer}] - [H_{PATO} + H_{C60}] \quad (11)$$

Enthalpy values obtained through calculation software Spartan, and then enthalpy of adsorption values obtained from Equations (9, 10) .

Enthalpy of adsorption calculated at the level B3LYP/6-31G for derivatives material from PATO with fullerene are always negative in all temperature range 300 to 400 Kelvin (Table 3). The negative ΔH_{ad} shows that, derived synthesis process material of PATO with C_{60} , are exothermic reaction at temperature ranging from 300 to 400 Kelvin, although with enhancing the temperature, the value of released heat from the reaction, decreases (Table 3).

Calculation and verifying specific heat capacity (C_V)

The results of the calculations show, specific heat capacity, C_V values for raw materials in process synthesis were calculated with the following procedure [28, 29]:

$$\text{II-Isomer} > \text{I-Isomer} > \text{R} \quad (12)$$

Values of specific heat capacity changes, C_V of raw material of PATO, and its derivatives with fullerene and boron nitride nano-cages at different temperatures indicate that the product have a high specific heat capacity C_V values, it means that, in the same conditions by taking more heat in rather to the raw material increasing of its temperature (Table 4). Comparing and verifying of Gibbs free energy (ΔG_{ad}), in the range of 300-400 K. The Gibbs free energy (ΔG_{ad}) of each of the reactants and products in the range of 300-400 K in synthesis reaction were calculated. And the Equations (13-16) were used:

Table 3. Enthalpy of adsorption calculated at the level B3LYP/6-31G for derivative material from PATO with fullerene

Temperature K	ΔH_{ad} (KJ/mol)	
	I-Isomer	II -Isomer
300	-1472.61	-1474.13
310	-1472.53	-1474.08
320	-1472.46	-1474.04
330	-1472.42	-1474.06
340	-1472.45	-1474.12
350	-1472.43	-1474.11
360	-1472.41	-1474.10
370	-1472.37	-1474.10
380	-1472.33	-1474.09
390	-1472.31	-1474.07
400	-1472.31	-1474.07

Table 4. changes in specific heat capacity C_v of raw material of PATO, and its complexes with fullerene C₆₀

Temperature	PATO	C _v (J/mol.K)	
		I-Isomer	II -Isomer
300	246.82	678.29	674.73
310	253.07	704.38	700.84
320	259.26	730.22	726.71
330	265.38	755.78	752.33
340	271.43	781.06	777.65
350	277.41	806.03	802.68
360	283.31	830.67	827.38
370	289.13	854.97	851.74
380	294.87	878.92	875.76
390	300.53	902.51	899.41
400	306.10	925.72	922.70

$$\Delta G_{ad} (T K) = \sum (\epsilon_0 + G_{corr})_{Products} - \sum (\epsilon_0 + G_{corr})_{Reactants} \quad (13)$$

Sum of electronic energy (ϵ_0) and Gibbs free energy (G_{corr}) = $\epsilon_0 + G_{corr} = G$

$\Delta G_{ad} = \Delta G_{adsorption}$ and temperature Kelvin = TK

$$\Delta G_{ad} (T K) = \sum (G)_{Products} - \sum (G)_{Reactants} \quad (14)$$

According to the Equations 1, 2 can be written

$$\Delta G_{ad} = [G_{I-Isomer}] - [G_{PATO} + G_{C60}] \quad (15)$$

$$\Delta G_{ad} = [G_{II-Isomer}] - [G_{PATO} + G_{C60}] \quad (16)$$

Gibbs free energy (G) values were obtained with calculation software Spartan, and then Gibbs free energy of adsorption (ΔG_{ad}) values were computed from Equations (15, 16).

ΔG_{ad} negative values of the process of synthesis derived material of PATO with fullerene at different temperatures indicate that, it can be done spontaneously and with increasing the temperature, Gibbs free energy will be higher values so at this condition the reaction has happen less (Table 5) [30, 31].

The N–O and C–N bond lengths values demonstrated that PATO-C₆₀ complexes have higher explosive velocity and blasting pressure in comparison to the pure blasting materials without C₆₀ (Figure 3, Table 6).

Table 5. The Results of Gibbs free energy in the range of 300-400 K calculated at the level B3LYP/6-31G for derivative material of PATO with fullerene

Temperature	ΔG_{ad} (KJ/mol)	
	I-Isomer	II -Isomer
300	-2330.05	-2301.57
310	-2327.73	-2299.30
320	-2325.42	-2297.05
330	-2323.09	-2294.81
340	-2320.77	-2292.57
350	-2318.44	-2290.28
360	-2316.14	-2288.01
370	-2313.81	-2285.73
380	-2311.48	-2283.43
390	-2309.15	-2281.08
400	-2306.81	-2278.75

Table 6. Bond lengths for the bonds in PATO, I-isomer and II-isomer

Bond	Bond Length(Å)		
	PATO	I-isomer	II-isomer
N ₁ -O ₁	1.27346	1.27384	1.28748
N ₁ -O ₂	1.27268	1.27254	1.28865
N ₁ -C	1.50188	1.50154	1.51694
N ₂ -O ₁	1.27319	1.27325	1.28856
N ₂ -O ₂	1.27378	1.27379	1.28918
N ₂ -C	1.49601	1.49583	1.50933
N ₃ -O ₁	1.29682	1.29705	1.30863
N ₃ -O ₂	1.26154	1.26149	1.27886
N ₃ -C	1.49901	1.49886	1.51280

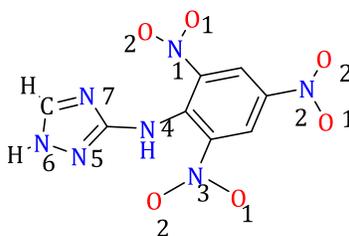


Figure 3. The location and number of the nitrogen and oxygen elements in the PATO

Conclusions

The results show that in the adsorption reaction of PATO with nano structures of fullerene (C₆₀) in the range of 300-400 K, ΔH_{ad} amounts are negative at all temperatures in the range of 300-400 K, these processes are exothermic and with increasing temperature, released heat will increase. The comparison of results of C_v shows that the heat capacity of PATO is lower than its complexes with fullerene over different temperatures. So the results of C_v calculations explain energetic properties of PATO is more than its derivatives. The ΔG_{ad} values of PATO derivations (I-Isomer, II-Isomer) indicate that, it can be done spontaneously at the 300 K to 400 K temperature range. Density values of PATO and its complexes with fullerene are as bellow:

$$\text{PATO} > \text{II-Isomer} > \text{I-Isomer}$$

Consequently PATO has more explosive properties than its complexes with fullerene, but according to produced results in this paper and considering of vibration spectra, and other results II-Isomer is more reactive than PATO and I-Isomer.

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Disclosure Statement

No potential conflict of interest was reported by the authors.

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