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Investigating the Effect of Fullerene (C_{20}) Substitution on the Structural and Energetic Properties of 3-picrylamino-1, 2, 4-triazole by Density Functional Theory

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ABSTRACT

The substitution reaction of fullerene with 3-picrylamino-1,2,4-triazole (PATO) were evaluated computationally at two configurations, in this study. For this purpose, all of the studied structures were optimized geometrically, then IR and NBO calculations were performed on them in the temperature range of 298.15-398.15 K at 10° intervals. The obtained negative values of Gibbs free energy variations(ΔG_f), formation enthalpy alterations (ΔH_f) and great values of the thermodynamic equilibrium constant (K_{th}) prove that the reaction of the fullerene with PATO is exothermic, spontaneous, one-sided and experimentally feasible. The impact of temperature on the thermodynamic parameters of the reaction was also inspected and the results indicate that 298.15 K is the optimum temperature for the synthesis of all of the derived products from the interaction of PATO and the studied nanostructures. The calculated specific heat capacity values (Cv) show that the sensitivity of PATO to the shock and heat has decreased significantly after its junction to fullerene nanostructures. The obtained density values demonstrate that C_{20} has an excellent impression on the improvement of the blasting power of PATO.

Keywords: 3-picrylamino-1, 2, 4-triazole; Fullerene; Density functional theory; Explosives.

1. INTRODUCTION

3-picrylamino-1, 2, 4-triazole which is mostly known as PATO is an energetic substance that is usually utilized in the construction of bombs and war weapons [1-3]. PATO which its chemical structure is presented in figure 1, was widely used in the construction of Ammunitions in wars [4-6]. Energetic materials have a major downside which has severely constrained their production and usage in military fields in this era and the problem is their high sensitivity to heat, shock and friction

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[11-14]. Indeed, explosive materials sometimes can react to some factors such as Heat, shock and friction and this phenomenon could lead to the explosion before the appropriate time and cause irreparable casualties [15-17]. In this regards, allocating more studies on the energetic compounds and synthesizing substances with more explosive power and less sensitivity to heat and shock is of a great importance [18-20]. But owing to the fact that working with blasting compounds is very dangerous and requires laboratories with advanced and special equipment which are not accessible in many cases due to their high prices, performing experimental research is not economical, safe and intellectual [21-23]. On the other hand, theoretical studies and computational methods provide the privilege for the scholars and scientists to carry out research activities on explosives at a very low cost and without endangering their lives and safety [24-28].

In addition, C_{20} molecule is the smallest member of the fullerene family with a dodecahedral cage structure (figure 2). This fullerene consists of only pentagonal rings and has extreme curvature. Due to the fact that former reports have proved that fullerenes from C_{20} to C_{58} have narrow HOMO- LUMO gaps and prominent reactivity. It seems these small fullerenes can have a good impression on the energetic features of explosives. Hence, the effect of C_{20} cage substitution on the structural properties and blasting power of PATO was evaluated by Ab initio calculations in this study, for the first time.

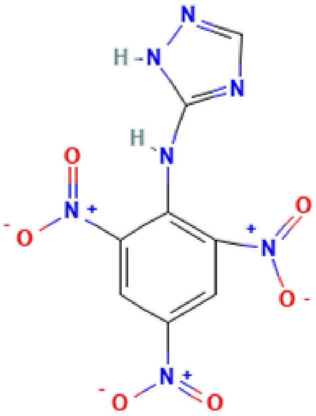


Fig. 1. Chemical structure of PATO

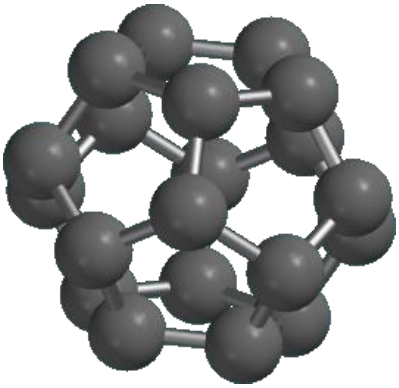
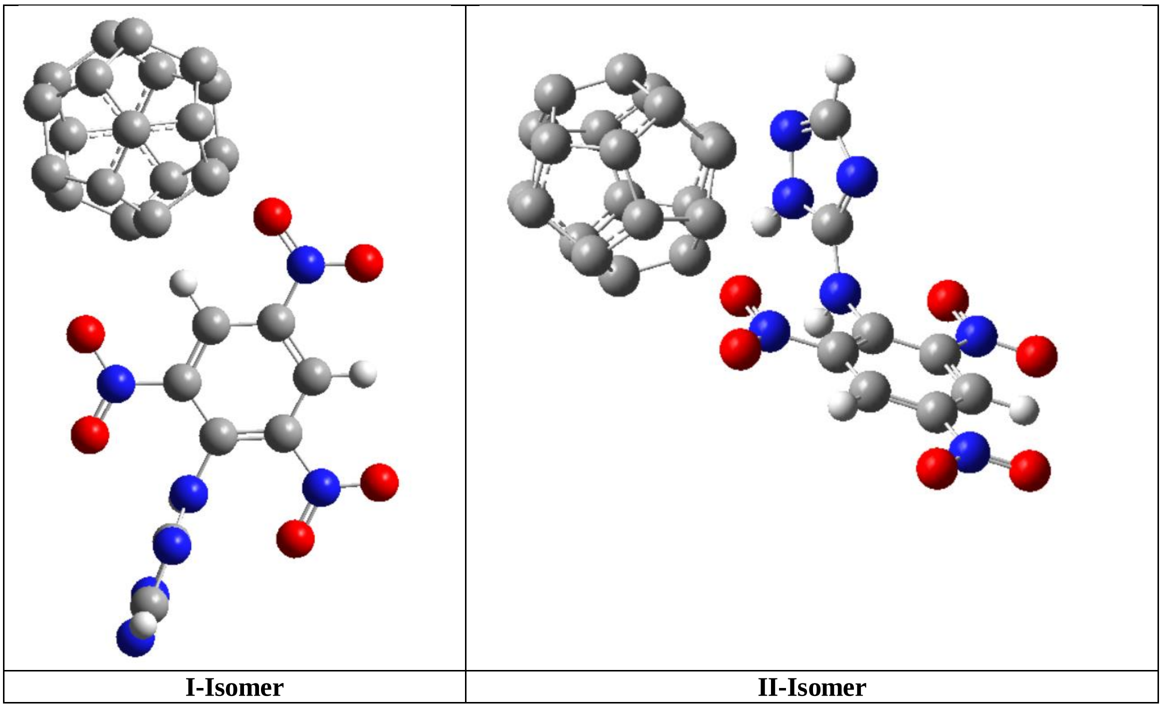


Fig. 2. Fullerene C_{20} cage structure.

2. COMPUTATIONAL METHODS

In the beginning, the structures of the C_{20} cage, PATO and the derived products of the reaction between PATO and nanostructures at two different configurations were designed primarily by nanotube modeler 1.3.0.3 and Gauss View Softwares. Then, the designed structures were optimized geometrically and in the next step, IR and FMO calculations were implemented on them in the temperature range of 298.15-398.15 K at 10° intervals by spartan software. All of the calculations were performed by density functional theory in the B3LYP/6-31G (d) basis set. The reactions were assumed in the gaseous phase and one atmosphere pressure. The studied reaction is as follows:

$$\text{PATO} + C_{20} \rightarrow \text{PATO-}C_{20} \qquad (1)$$



I-Isomer

II-Isomer

Fig. 3. The structures of PATO and its derived products with C_{20} at two configurations.

3. RESULTS AND DISCUSSIONS

3.1. Structural Analysis

As it can be seen from figure 3, the reaction of PATO with C_{20} was investigated from two sites in order to find the most stable conformer. In I-Isomer, the PATO is place near the fullerene towards its nitro functional groups but in II-Isomer, the triazole ring of PATO is located near the adsorbent in a parallel form. It should be noted that the IR calculations show that all of the structures do not have any negative frequency and the positive frequency values that are presented in the table have also confirmed this fact. The next matter that can be understood from the table is that the total energy of fullerene derivatives is lower than ordinary PATO. Given the fact that by decreasing the total energy the stability of the evaluated compound has ameliorated. So; it can be inferred that the stability of PATO has improved after the junction to the surface of fullerene.

The dipole moment is a key factor which has a direct relationship with the solubility of a compound in polar solvents. Indeed, a structure with high dipole moment has a good solubility in polar solvents like water and a substance with a low dipole moment has a poor solubility in polar solvents. The obtained results from the calculations have revealed that the solubility of PATO has reduced after its reaction with C_{20} due to the lowering of dipole moment values in the fullerene derivatives.

The next important studied parameter is the density of PATO and its derived products with fullerene. Density has an obvious relationship with the destructive and explosive power of an energetic substance. An explosive with higher density has stronger destructive and blasting power, whereas an explosive with lower density has weaker destructive and blasting power. The provided data in table 6 show that by binding of PATO to the surface of pure fullerene the density has decreased substantially. Therefore, the explosive power of pure C_{20}-PATO derivatives can be lower than single PATO.

3.2. Calculation and verifying the formation enthalpy changes values (ΔH_f)

In order to achieve formation enthalpy alterations values, the subsequent equation would be applied. In this formula, ΔE° is the symbol of variations in the total energy of the system which can be calculated by subtracting the total energy of the products from the total energy of the reactants. H_{th} also represents the thermal enthalpy values that were computed by the software for raw materials and products of the desired process.

$$\Delta H_f = \Delta E^{\circ} + (H_{th\ (PATO\text{-}C20)} - (H_{th\ (PATO)} + H_{th\ (C20)})) \qquad (2)$$

As the provided data in table 2, exhibit clearly the obtained ΔH_f values for all of the evaluated derivatives are negative. And this fact proves that the synthesis procedure is exothermic for all of the derived products from the reaction between PATO and fullerene. Indeed, the heat is transferred from the system to the environment in this process. As it can be witnessed from the table, the ΔH_f values for I-Isomers are more negative than the formation enthalpy changes values of II-isomers. Owing to the fact that temperature is one of the most important variables that can influence the synthesis mechanism and efficiency sharply. The effect of this factor on thermodynamic parameters was also inspected. As it is obvious from the table, temperature does not have a remarkable effect on the formation enthalpy changes values of all derivatives and it seems 298.15 K is the best temperature for the synthesis procedure of all derived products.

Table 1. Total energy, the lowest frequency, dipole moment, weight, volume, area, and density of PATO and its derivatives with fullerene

Chemical properties	**PATO**	**I-Isomer**	**II-Isomer**
Total Electronic Energy (au)	-1120.930	-1868.254	-1868.251
The Lowest Frequency (cm^{-1})	10.211	9.873	8.991
Dipole Moment (debye)	4.090	2.800	3.240
Weight(amu)	295.171	535.391	535.391
Volume($Å^3$)	228.760	434.680	436.680
Area ($Å^2$)	257.240	417.470	417.780
d=m/v ($amu/Å^3$)	1.290	1.232	1.226

Table 2. The formation enthalpy changes values for the synthesis of the PATO-fullerene derivatives in the temperature range of 298.15-398.15 K

Temperature(K)	I-Isomer	II-Isomer
298.15	-1900.682	-1894.448
308.15	-1900.686	-1894.516
318.15	-1900.715	-1894.600
328.15	-1900.758	-1894.688
338.15	-1900.837	-1894.780
348.15	-1900.926	-1894.884
358.15	-1901.015	-1895.008
368.15	-1901.121	-1895.124
378.15	-1901.217	-1895.230
388.15	-1901.298	-1895.319
398.15	-1901.353	-1895.381

3.3. Calculation and Verifying the Values of Gibbs Free Energy Changes (ΔG_f) and Thermodynamic Constant (K_{th})

For calculating Gibbs free energy variations, the following equation was utilized. In this formula, G_{th} is the thermal Gibbs Free energy that was computed by the software for each material in the synthesis procedure and ΔE° represents the total energy changes of the system.

$$\Delta G_f = \Delta E^{\circ} + (G_{th\ (PATO\text{-}\ C20)} - (G_{th\ (PATO)} + G_{th\ (C20)})) \qquad (3)$$

As the calculated ΔG_f in table 3 demonstrate clearly, the synthesis process of all of the studied derivatives is spontaneous because this variable is negative for all of the derived products. By a more precise glance at the table, it could be understood that the formation reaction of I-Isomers is more spontaneous than II-Isomers since the values of Gibbs free energy changes for I-Isomer are more negative than II-Isomers. The influence of temperature on this variable has also been checked out and the results indicate that the 298.15 K is the optimum temperature for the formation reaction of all of the evaluated derivatives. Because the values of Gibbs free energy alterations have increased by incrementing of temperature. This phenomenon can be attributed to the fact that PATO is unstable at high temperature since it is sensitive to heat and takes part in combustion and explosion reactions.

3.4. Calculation and inquiring the specific heat capacity values (Cv)

Specific heat capacity is defined as the amount of heat which is needed for incrementing the temperature of a certain amount of material to one degree. In this regards, this variable can be an appropriate parameter for estimating the sensitivity of an explosive compound to heat and shock. For this reason, the specific heat capacity values of all of the studied structures were computed in the temperature range of 298.15-398.15 K at 10° intervals and the obtained results were tabulated in table 5. The tabulated results in the table clearly demonstrate that the specific heat capacity values of the fullerene derivatives are considerably higher than the pure PATO ones.

This subject indicates that for raising the temperature of C_{20} derived products with PATO, more heat and energy is required in comparison to single PATO. Therefore, it can be concluded that the sensitivity of PATO has abated noticeably after its junction to the C_{20} surface. The next matter that could be seen in the table is that the Cv values of I-Isomer are higher than II-Isomer. So, the safety of I-Isomers is more than the other ones.

Table 3. The values of Gibbs free energy changes for the synthesis of PATO-C_{20} derivatives in the temperature range of 298.15-398.15 K

Temperature (K)	I-Isomer	II-Isomer
298.15	-1846.238	-1839.264
308.15	-1844.249	-1837.195
318.15	-1842.280	-1835.132
328.15	-1840.317	-1833.059
338.15	-1838.418	-1831.029
348.15	-1836.484	-1829.026
358.15	-1834.541	-1827.034
368.15	-1832.606	-1824.988
378.15	-1830.628	-1822.881
388.15	-1828.575	-1820.748
398.15	-1826.465	-1818.577

Table 5. The values of specific heat capacity (Cv) for PATO and its fullerene derivatives in the temperature range of 298.15-398.15 K

Temperature (K)	PATO	I-Isomer	II-Isomer
298.15	246.822	399.616	395.066
308.15	253.073	411.955	407.423
318.15	259.261	424.203	419.698
328.15	265.380	436.350	431.879
338.15	271.430	448.384	443.954
348.15	277.406	460.295	455.913
358.15	283.307	472.075	467.744
368.15	289.128	483.715	479.441
378.15	294.869	495.207	490.994
388.15	300.526	506.545	502.396
398.15	306.097	517.724	513.642

3.5. FMO Analysis

Some of the structural and energetic properties including the energy of HOMO and LUMO molecular orbital (E_H and E_L), the energy gap between HOMO and LUMO orbitals (HLG), electrophilicity (ω), maximum transferred charge (ΔN_{max}) and chemical hardness (η) reported at table 6. HOMO is the highest occupied molecular orbital and LUMO is the lowest unoccupied molecular orbital in chemistry and the energy difference between them is known as energy gap which is shown usually by HLG abbreviation. This parameter can be calculated by using equation 4. As it is obvious from table 6, the amount of energy gap has decreased after PATO's junction to the surface of C_{20} in all of the evaluated derivatives. And owing to the fact that the compounds with low energy gap need less energy for transferring the electron to the excited situation. It can be inferred that the conductivity of PATO has improved after its binding to the fullerene.

The next inspected variable was chemical hardness which was calculated by equation 5. Chemical hardness is an ideal standard for estimating the softness of a molecule. Indeed, if a structure has a high chemical hardness value it will be chemically harder. As it can be observed from the table, the chemical hardness of PATO-fullerene derivatives is lower than pure PATO ones and given the fact that soft molecules can change their electron density more easily, this type of compounds could undergo chemical reactions more conveniently because the electron transmission, which is essential for the implementation of chemical reaction will be done comfortably in soft materials. Thus, it can be concluded that the reactivity of the fullerene derived products with PATO is higher than the reactivity of pure PATO. In other words, C_{20}-PATO derivatives are more reactive than single PATO in terms of energetic aspects. The chemical potential values that are necessary for obtaining electrophilicity and maximum transferred charge values were also calculated by means of equation 6. This parameter has also incremented after the connection of PATO to the surface of fullerene.

$$HLG = E_{LUMO} - E_{HOMO} \quad (4)$$

$$\eta = (E_{LUMO} - E_{HOMO})/2 \quad (5)$$

$$\mu = (E_{LUMO} + E_{HOMO})/2 \quad (6)$$

$$\omega = \mu^2/2\eta \quad (7)$$

$$\Delta N_{max} = -\mu/\eta \quad (8)$$

Electrophilicity index which can be calculated by equation 7, is an excellent criterion for estimating the tendency of a substance towards electron. When two molecules take part in a reaction, one of them behaves as a nucleophile while the other one acts as an electrophile. And if a compound has a high electrophilicity value, it will have a high affinity for absorbing the electron. The maximum transferred charge index (ΔN_{max}) that was calculated by equation 8, demonstrates the charge capacity of a system. In fact, if a material has a positive value of ΔN_{max} it will act as an electron acceptor, but if a substance has a negative value of ΔN_{max} it will play the role of an electron donor. As it is clear from the table, the electrophilicity of PATO increased after its interaction with fullerene and ΔN_{max} of PATO declined after its reaction with fullerene indicating PATO-C_{20} derivatives have lower tendency for absorbing electron in comparison to pure PATO without nanostructure.

CONCLUSIONS

Performing research and development activities on energetic compounds in order to find an explosive with higher blasting power and lower sensitivity to heat and shock is of a great importance. And computational methods provide the opportunity for chemists to study this field with low cost and without endangering their health. Hence, the effect of C_{20} substitution on the energetic and structural features of PATO was evaluated in this study. The obtained thermodynamic parameters have shown that the reaction between PATO with fullerene are exothermic, spontaneous, one-sided and experimentally feasible and the best temperature for the synthesis of PATO-C_{20} derivatives is 298.15 K. The calculated specific heat capacity values have revealed that the sensitivity of PATO to heat and shock has declined drastically after its junction to the fullerene surface. Moreover, the achieved results from the

Table 6. The values of Calculated E_H and E_L, HLG, chemical hardness (η), electrophilicity index (ω), chemical potential (μ), the maximum amount of electronic charge index (ΔN_{max})

Chemical properties	PATO	I-Isomer	II-Isomer
E HOMO(eV)	-7.310	-4.950	-5.090
E LUMO (eV)	3.160	2.980	2.820
Dipole Moment (Debye)	4.090	2.800	3.240
HLG (eV)	10.470	7.930	7.910
Chemical Hardness (eV)	5.235	3.965	3.955
Chemical Potential (eV)	-2.075	-0.985	-1.135
Electrophilicity (eV)	-10.863	-3.906	-4.489
ΔN_{max} (eV)	0.396	0.248	0.287

density values have exhibited that the explosive and destructive power of fullerene derivatives is lower than pure PATO. The experimental synthesis of these compounds and checking their energetic properties is recommended to be evaluated in the future to the experts of this field.

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مجله شیمی فیزیک و شیمی نظری
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بررسی اثر جانشینی فولرن (C20) بر خواص ساختاری و انرژیتیکی ۳-پیکریل آمینو-۱، ۲، ٤-تری آزول با نظریه تابعی چگالی

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چکیده

در این مطالعه واکنش جایگزینی فولرن با ۳-پیکریل آمینو-۱، ۲، ٤-تری آزول (PATO) به صورت محاسباتی در دو پیکربندی مورد بررسی قرار گرفت. بدین منظور تمامی ساختارهای مورد مطالعه از نظر هندسی بهینه سازی شدند و سپس محاسبات IR و NBO بر روی آنها در محدوده دمایی۲۹۸/۱۵ تا ۳۹۸/۱۵ کلوین در فواصل ۱۰ درجه انجام شد. مقادیر منفی به دست آمده از تغییرات انرژی آزاد گیبس(ΔG_f) ، تغییرات آنتالپی تشکیل (ΔH_f) و مقادیر زیاد ثابت تعادل ترمودینامیکی (K_{th}) ثابت می کند که واکنش فولرن با PATO گرمازا، خود به خودی، یک طرفه و از نظر تجربی امکان پذیر است. تأثیر دما بر پارامترهای ترمودینامیکی واکنش نیز بررسی شد و نتایج نشان می‌دهد که در دمای ۲۹۸,۱۵ کلوین، دمای بهینه برای سنتز همه محصولات مشتق‌شده از برهمکنش PATO و نانوساختارهای مورد مطالعه است. مقادیر ظرفیت حرارتی ویژه محاسبه شده (Cv) نشان می‌دهد که حساسیت PATO به شوک و گرما پس از اتصال به نانوساختارهای فولرن به طور قابل توجهی کاهش یافته است. مقادیر چگالی به‌دست‌آمده نشان می‌دهد که C20 تأثیر بسیار خوبی بر بهبود قدرت انفجار PATO دارد.

کلید واژه‌ها: ۳- پیکریل آمینو-۱، ۲، ٤- تری آزول؛ فولرن؛ نظریه تابعی چگالی؛ مواد منفجره

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