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Synthesis and Theoretical Studies of a New Insensitive Explosive, 2'-Methyl-3-nitro-2'*H*-[1,3'-bi(1,2,4-triazole)]-5,5'-diamine

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Abstract: A new insensitive energetic material 2'-methyl-3-nitro-2'*H*-[1,3'-bi(1,2,4-triazole)]-5,5'-diamine (**1**) was prepared by a three-step synthesis from commercially available chemicals. The energetic title compound was comprehensively characterized by various means, including FT-IR, multinuclear (¹H, ¹³C, ¹⁴N) NMR spectroscopy, elemental analysis, HPLC and thermal analysis. The sensitivities of the synthesized material towards various external stimuli (impact, friction) were determined according to the BAM method. The optimized structure and related thermodynamic parameters were obtained at the DFT-B3LYP/6-31+G** theoretical level. The detonation properties of the material were also predicted according to the Kamlet-Jacobs formulae and the Monte-Carlo method. The results show that the density, heat of formation, detonation velocity, detonation pressure, impact sensitivity and purity were 1.83 g/cm³, 369 kJ/mol, 7.52 km/s, 25.4 GPa, 82.3 J and 97.7%, respectively. In addition, the compound was an insensitive high explosive which could meet the requirements of high energetic materials.

Keywords: insensitive explosive, synthesis, theoretical studies, density functional theory, new 1,2,4-triazole derivative

1 Introduction

Energetic nitrogen-rich heterocycles have attracted much attention recently as a result of their high enthalpies of formation [1-7]. 5-Amino-3-nitro-1*H*-1,2,4-

triazole (ANTA) is an insensitive explosive, which exhibits an impact sensitivity similar to that of TATB. In addition, its molecular structure includes two active sites (1-NH and 5-NH₂), with a nucleophilic reaction site at the 1-NH position. In order to obtain insensitive materials with improved comprehensive properties, the synthesis of new high-energy and insensitive compounds from ANTA as an intermediate has already emerged as a current popular research topic [8]. 1,2,4-Triazole derivatives subjected to N-arylation appear to promote nucleophilic substitution of the nitro group located at the 3 position with various agents [9-12]. Numerous structural modifications and the synthesis of new derivatives of the 1,2,4-triazole series have been conducted [13, 14]. 1-Methyl-5-nitro-1*H*-1,2,4-triazol-3-amine (MNTA) is a typical high-density 1,2,4-triazole derivative, which also exhibits low sensitivity and excellent heat resistance.

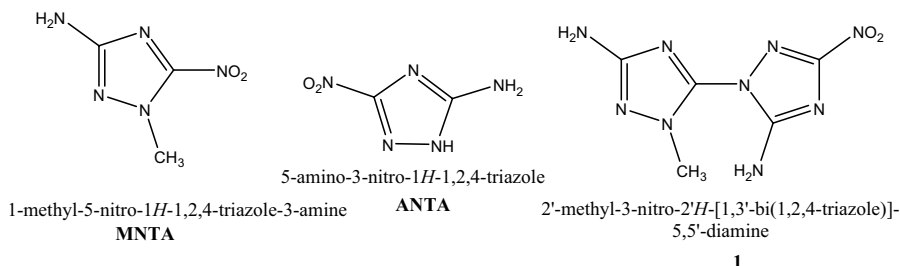


Figure 1. Structures of MNTA, ANTA and **1**

In the present study, an insensitive explosive with multiple amino and nitro groups, 2'-methyl-3-nitro-2'*H*-[1,3'-bi(1,2,4-triazole)]-5,5'-diamine (**1**) was designed and synthesized based on the ANTA and MNTA structures (Figure 1). The resultant **1** is a new, thermally stable, insensitive explosive (Figure 2). The properties of **1** were compared to those of other explosives, including FOX-7, NTO, TEX, LLM-105 and TATB.

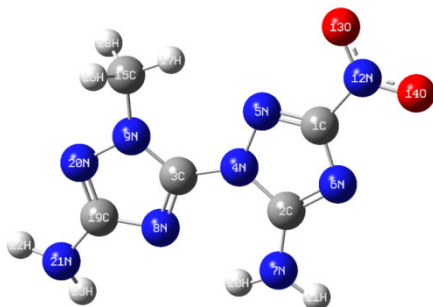


Figure 2. Molecular modelled structure of **1**

2 Experimental

2.1 Materials and methods

All reagents were of analytical grade, purchased from commercial sources, and used as received. The dicyandiamide, aqueous methylhydrazine (40%), ethyl acetate, acetone, sodium bicarbonate and sodium nitrite were purchased from Nan Tong Dong Li Corporation (China). The ANTA, hydrochloric acid (37%) and concentrated sulfuric acid (98%) were supplied by North University of China. Densities were determined experimentally using Archimedes' principle. ^1H , ^{13}C and ^{14}N NMR spectra were recorded on a Bruker-Avance DRX 500 MHz NMR instrument with CDCl_3 as a solvent. Differential thermal analysis (DTA) was recorded on a PerkinElmer model TG/DTA730 instrument. The kinetics of the thermal degradation of **1** was investigated by DTA. The heating rate was $5\text{ }^\circ\text{C}/\text{min}$ under an atmosphere of nitrogen, and the sample weight was equal to 0.7 mg. The FTIR spectra were collected on a PerkinElmer Spectrum 100 instrument. Elemental analyses were performed on a HERAEUS 1106 elemental analyzer (Germany). The impact sensitivity was recorded at room temperature using an ERL 12-drop hammer apparatus with a sample mass of 35 ± 1 mg and a drop weight of 5 ± 0.002 kg. The friction sensitivity tests were carried out according to the explosion probability method of BAM using an IDEA SCIENCE Corporation (USA) Friction Sensitivity Tester. The purity of **1** was confirmed by high-performance liquid chromatography (HPLC). The mobile phase was methanol-water in the ratio 45:55 (isocratic), at a constant flow of 1 mL/min at the UV wavelength of 246 nm. The retention time of **1** was 12 min, as shown in Figure 3. All calculations were conducted using the Gaussian 09 program package. The geometric optimization of the structures and frequency analyses were accomplished with B3LYP and the 6-31+G** basis set [15], and single point energies were calculated at the MP2/6-311++G** level. Atomization energies were calculated according to the G2 method [16].

2.2 Synthesis

2.2.1 1-Methyl-3,5-diamino-1,2,4-triazole (3)

Methylhydrazine (40%, 5.75 g, 0.05 mol) and absolute ethanol (15 mL) were transferred to a 100 mL three-necked, round-bottomed flask fitted with a mechanical stirrer, dropping funnel and condenser, in a cooling bath at $0\text{--}5\text{ }^\circ\text{C}$. Fuming concentrated hydrochloric acid (37%, 10 mL) was added dropwise while stirring. The mixture was allowed to react for 5.5 h at $20\text{ }^\circ\text{C}$, before dicyandiamide (3.7 g, 0.045 mol) and water (20 mL) were slowly added to the

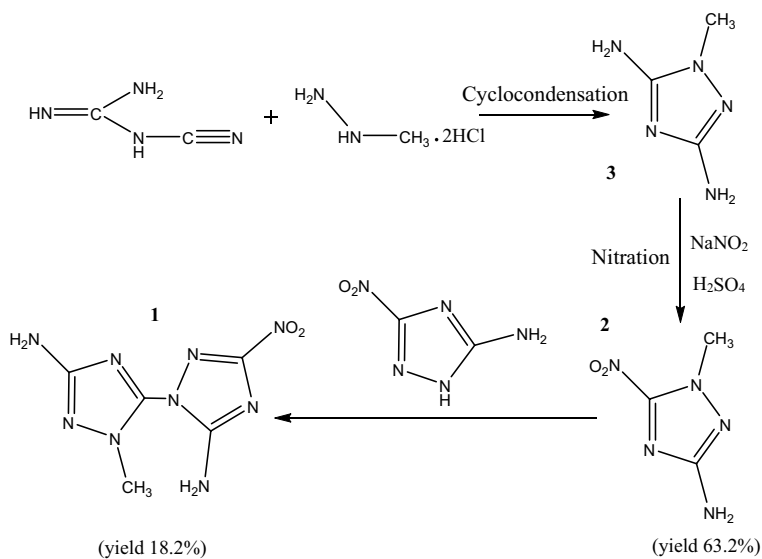
reaction mixture. After the addition was complete, the reaction mixture was heated to and maintained at 40 °C for 5 h with continuous stirring. The reaction mixture was then cooled to 20 °C and poured into a small beaker. The pH was adjusted by the addition of sodium hydroxide solution (10%) until pH 8-9. The mixture was then stored until used.

2.2.2 1-Methyl-3-amino-5-nitro-1,2,4-triazole (2)

Sodium nitrite (34.5 g, 0.5 mol) and water (50 mL) were transferred to a 250 mL three-necked, round-bottomed flask fitted with a mechanical stirrer, dropping funnel and condenser. The temperature was slowly raised to 50 °C, and the solution of **3** above mixed with sulfuric acid (2.5 mol/L, 27 mL) was slowly added dropwise into the reaction mixture during 1.5 h. Fuming sulfuric acid (98%, 25 mL) was then carefully added dropwise with continuous stirring, followed by refluxing for 0.5 h. The reaction mixture was then cooled to room temperature and ethyl acetate was used to repeatedly extract **2**. The pale yellow solid **2** (4.0 g, 63.2% yield, HPLC purity 99.4%) was obtained by concentration, followed by crystallization and drying.

2.2.3 2'-Methyl-3-nitro-2'H-[1,3'-bi(1,2,4-triazole)]-5,5'-diamine (1)

2 (0.715 g, 5 mmol) dissolved in acetone was added to a 100 mL three-necked, round-bottomed flask fitted with a mechanical stirrer. The temperature was slowly raised to 60 °C. ANTA (0.65 g, 5 mmol) was completely dissolved in sodium hydroxide solution (5 mL, 5 mol/L) with continuous stirring; the resultant solution was then slowly added dropwise to the above acetone solution, with continuous stirring, followed by refluxing for 3 h. The reaction mixture was then cooled to 0 °C. The precipitate was filtered off, washed with water and dried at 100 °C to yield a pale brown solid (0.23 g, 18.2% yield (**final step**), HPLC purity 97.7%). IR (KBr), ν (cm⁻¹): 3442, 3324, 3169, 2921, 1515, 1398, 1310; ¹H NMR (CDCl₃, 500 MHz), δ (ppm): 4.84 (s, 2H, -NH₂), 3.21 (s, 2H, -NH₂); 1.20 (s, 3H, -CH₃); ¹³C NMR (CDCl₃, 125 MHz), δ (ppm): 102.87, 104.79, 113.42, 118.05, 122.35; ¹⁴N NMR (CDCl₃, 500 MHz), δ (ppm): -5 (s, 1N, -NO₂), -98.9, 100.6 (s, 2N, -N=N=), -208, 218 (s, 1N, -N=), -340, -343 (s, 1N, -NH₂). The synthetic route was designed and described as in Scheme 1.



Scheme 1. Synthetic route to **1**

3 Results and Discussion

3.1 Chromatographic analysis

Analysis indicated that the **1** synthesised had a purity of 97.7%. Given that the pure form of **1** is not available commercially, this result is satisfactory. The HPLC analysis was shown as in Figure 3.

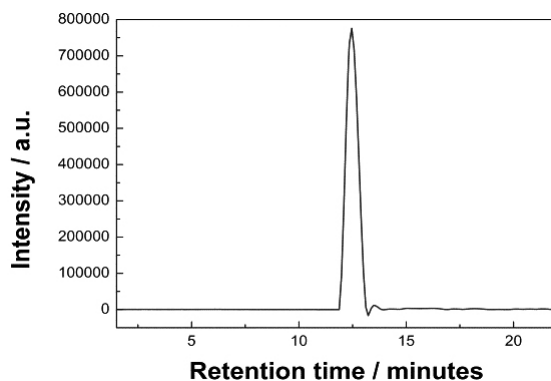


Figure 3. HPLC analysis of **1**

3.2 Spectral analysis

The FTIR spectrum of **1** indicates the presence of -NH_2 groups at 3442 cm^{-1} , 3324 cm^{-1} , 3169 cm^{-1} and 1640 cm^{-1} . The bands located at 1398 cm^{-1} correspond to the symmetrical deformation. The bands located at 2921 cm^{-1} correspond to the stretching of the methyl group. The two intense absorptions exhibited at 1515 cm^{-1} and 1310 cm^{-1} represent the characteristic frequencies for the asymmetric and symmetric vibrations of -NO_2 groups [17]. The FTIR spectrum was shown as in Figure 4.

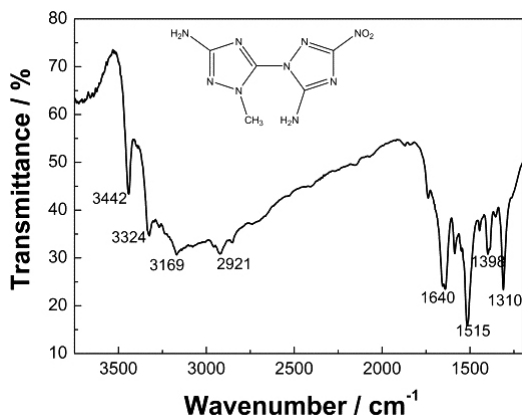


Figure 4. The infrared spectrum of **1**

The ^1H NMR spectrum of **1** exhibited a broad peak at δ 4.84 assigned to the C10-NH_2 protons of the right-hand triazole ring, and two singlets located at δ 1.20 and δ 3.21 assigned to the C4-NH_2 and -CH_3 protons respectively attached to the left-hand triazole ring. The ^{13}C NMR spectrum of **1** exhibits five different types of carbon, with peaks at 102.87 ppm, 104.79 ppm, 113.42 ppm, 117.05 ppm and 120.35 ppm for C4, C2, CH_3 , C10, and C8, respectively, in the triazole rings. The peak at -7.26172 in the ^1H spectrum was the signal from the solvent CDCl_3 . The NMR spectra was shown as in Figure 5.

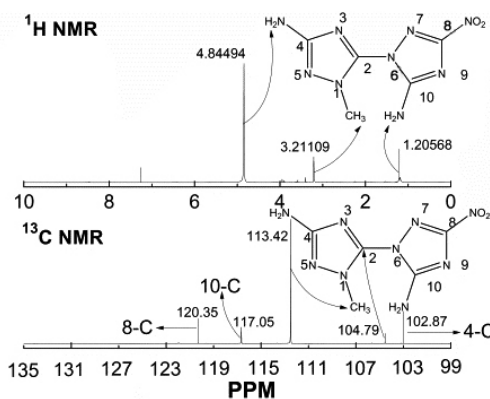


Figure 5. The ¹H NMR and ¹³C NMR spectra of **1**

3.3 Elemental analysis

Elemental analysis, calculated for C₅H₇N₉O₂ (**1**): C 26.67%, H 3.11%, N 56.00%; found C 26.59%, H 3.12%, N 55.89%. The percentages of the elements in **1** demonstrated by elemental analysis were in good agreement with the calculated values, verifying the high purity of the synthesized product.

3.4 Thermal analysis

As shown in Figure 6, **1** exhibited decomposition at a temperature of 219 °C, as indicated by the TG-DTA thermogram of the corresponding exotherm at 222.6 °C. The DTA curve indicated that the exothermic peak begins at 201.7 °C with a peak maximum at 235.6 °C. As the temperature exceeds 235.6 °C, the exotherm returns to the baseline value, and no more heat is released. The most striking result is the reported thermal stability of **1**, which is similar to that of ANTA; the value is nearly identical to that of ANTA at 201.7 °C, but differs from MNTA with a decalescence peak around 100 °C. This may indicate that the weakest link is located in the ring of the ANTA unit, which would first undergo cleavage.

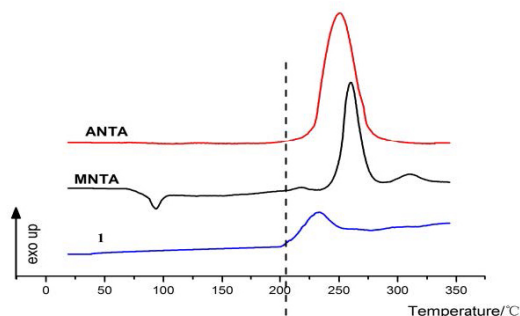
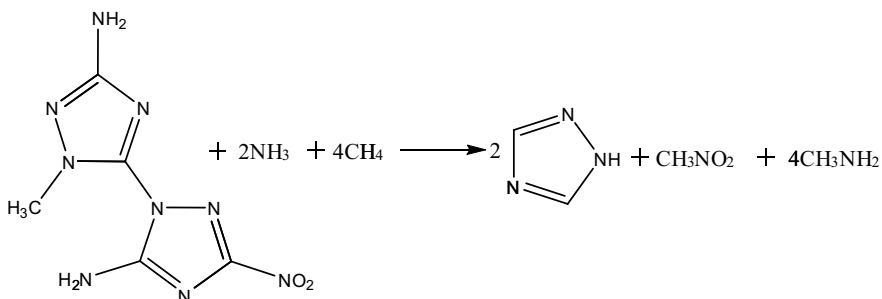


Figure 6. DTA plots for ANTA, MNTA and **1** at a heating rate of 5 °C/min. The dashed line indicates the decomposition onset for ANTA and **1**

3.5 Physical properties

3.5.1 Heat of formation (HOF)

All optimized structures were characterized as true local energy minima on the potential energy surface without imaginary frequencies. The isodesmic reaction is widely used to calculate the molar formation in the gas phase. All bond types and the number of electron pairs in the system remain the same in the design of the isodesmic reactions, and the electronic environments of the reactants and products were very similar; errors resulting from the electronic correlation energies can offset one another. In order to reduce the error, the isodesmic reaction was designed and described as in Scheme 2.



Scheme 2. Isodesmic reaction design for **1**

The heat of the isodesmic reaction (ΔH_{298}) at 298 K can be calculated based on the following equation:

$$\Delta H_{298} = \Sigma \Delta H_{f,p} - \Delta H_{f,r}$$

where $\Delta H_{f,p}$ and $\Delta H_{f,r}$ are the HOFs of the products and reactants at 298 K, respectively. The experimental HOFs of the reference compounds 1,2,4-triazole, NH_3 , CH_4 , CH_3NO_2 and CH_3NH_2 were obtained by combining the MP2/6-311++G** energies. Thus, the HOF of **1** can be calculated once the ΔH_{298} is known. The ΔH_{298} can be calculated according to the following formula:

$$\Delta H_{298} = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K, ΔZPE represents the difference between the zero-point energies (ZPE) of the products and the reactants, and ΔH_T is the thermal correction from 0 K to 298 K. ΔnRT is the work term, which is equal to zero. The heat of formation (HOF) was 369 kJ/mol.

3.5.2 Density

All density calculations were accomplished at the B3LYP/6-311++ G** (d,p) level. Based on the volumetric space wrapped by the isoelectronic density interface, the Monte-Carlo method [12, 15] was used to estimate the average molar volume V of **1**, which was equal to 115.8 cm³/mol. The calculated density value was 1.83 g/cm³, based on the average molar volume of **1**. The calculations are based on the volumetric space surrounded by the equal electron surface of 0.001 e/Bohr³. This result is very close to the experimental result using Archimedes' principle.

3.5.3 Detonation pressure and velocity

Detonation performance and detonation pressure represent two important performance parameters of energetic materials. The empirical Kamlet-Jacobs equations [18-21] are employed to estimate the detonation velocity (D) and detonation pressure (P) for high-energy materials containing C, H, O, and N, as described by the following equations:

$$D = 1.01(NM^{1/2} Q^{1/2})^{1/2}(1+1.3\rho)$$
$$P = 1.558\rho^2NM^{1/2} Q^{1/2}$$

N is the moles of gas produced per gram of explosive, M is the mean molecular weight of the gaseous detonation products, Q is the heat of detonation (cal/g), and ρ is the density of **1** which is equal to 1.83 g/cm³. For the $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$

explosive explored by the current study ($b/2 > c$). N , M , and Q were calculated according to following formulae: $[C_5H_7O_2N_9]$,

$$N = (b + d) / 2M$$

$$M = (2b + 28d + 32c) / (b + d)$$

$$Q = [57.8c + 0.239 \Delta_f H_m^\theta] / M$$

where a , b , c and d respectively represent the number of C, H, O and N atoms in the explosive molecule, and M is the molecular weight of the explosive.

3.6 Performance and sensitivity tests

The sensitivity and performance properties of FOX-7, NTO, TEX, LLM-105, **1** and TATB are presented in Table 1. An investigation of the sensitivity of **1** indicated that its sensitivities were similar to those of TATB and TEX, and less sensitive than the other materials. The calculated performance parameters of **1**, such as detonation velocity and density were similar to those of TATB and the detonation pressure was close to that of NTO, TEX and TATB. The insensitivity of nitrogen-rich and amino-rich heterocycles arises primarily from intermolecular hydrogen bonds [22], which act as molecular glue. The intermolecular hydrogen bonds are very strong, which can maintain the integrity of the molecules and prevent weaker molecular rings from breaking down when stimulated by multiple devastating attacks. The results indicated that the material will be more insensitive and not easily exploded when exposed to external stimuli, thus improving the security of the explosive.

Table 1. Comparison of explosive performance and sensitivity

Explosive	Density [g/cm ³]	Velocity [km/s]	Pressure [GPa]	Melting point [°C]	Impact H ₅₀ [J]	Friction [kg]
FOX-7 [23]	1.89	9.09	36.6	254	30.9	36
NTO [23]	1.93	8.56	31.2	270	22.8	36
TEX [23]	1.99	8.56	31.4	299	>43.4	36
LLM-105 [23]	1.91	8.56	35.0	354	28.7	36
1	1.83	7.52	25.4	--	82.3	36
TATB [23]	1.94	8.10	31.1	330	>43.4	36

FOX-7: 1,1-diamino-2,2-dinitroethylene; NTO: nitrotriazolone; TEX: tetraoxa-explosive; LLM-105: 2,6-diamino-3,5-dinitropyrazine-1-oxide; TATB: 2,4,6-trinitro-1,3,5-triaminobenzene.

4 Conclusions

An efficient procedure for the synthesis of a new insensitive energetic material, **1**, was successfully established. The results indicate that **1** is a powerful explosive with many favorable properties, including high density, thermal stability and low sensitivity. **1** was prepared via a three-step synthesis and characterized by instrumental techniques including spectral methods. Analysis of the sensitivity and performance properties of **1** demonstrates that its impact sensitivity is better than most explosives, and its detonation pressure value was next to that of NTO, TEX and TATB. Furthermore, **1** can be prepared from commercially available starting materials, demonstrating its economic value for large scale synthesis for application in propellant and explosive formulations. Moreover, as a new and energetic triazole compound, the synthesis of **1** will provide material and method references for the further development of new, insensitive, high-energy materials.

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