



## Synthesis and Property of 1,4-Diamino-3,6-dinitropyrazolo[4,3-c]pyrazole and Its Derivatives

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**Abstract:** A synthetic procedure has been developed for the synthesis of 1,4-diamino-3,6-dinitropyrazolo[4,3-c]pyrazole (DADNP) via N-amination reaction. Its derivatives, 4,4'-(triaz-1-ene-1,3-diyl)bis(1-amine-3,6-dinitropyrazolo[4,3-c]pyrazole) (TBADNP) and 1,4-dinitramino-3,6-dinitropyrazolo[4,3-c]pyrazole (DNADNP), were first designed and synthesized by the diazotization and nitration of amino group, and their structures were characterized by IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR, elementary analysis and MS. The thermal properties of target compounds were studied by means of differential scanning calorimetry (DSC) and thermogravimetry (TG). The thermal decomposition peak temperatures of DADNP, TBADNP and DNADNP are 227, 236 and 288 °C, respectively. Results show that the derivatives of 1,4-diamino-3,6-dinitropyrazolo[4,3-c]pyrazole have better thermal stability.

**Keywords:** 3,6-dinitropyrazolo[4,3-c]pyrazole (DNPP), 1,4-diamino-3,6-dinitropyrazolo[4,3-c]pyrazole (DADNP), 4,4'-(triaz-1-ene-1,3-diyl)bis(1-amine-3,6-dinitropyrazolo[4,3-c]pyrazole) (TBADNP), N-amination reaction, synthesis, property

### 1 Introduction

N-heterocyclic ring compounds, such as pyrazole, pyrazine, triazole, tetrazine and furazan derivatives, have often been utilized in energetic compounds due to their high positive heats of formation, density, nitrogen content and better

thermal stability than those of their cyclic carbon analogues. This has been attributed to the large number of C–N, C=N, N–N and N=N bonds in their molecular structures [1-9]. The large amount of nitrogen gas generated as an end product of the nitrogen-rich compounds listed above is highly favored both for the enhancement of energy output and the avoiding of environmental pollution [3, 7]. In order to develop environmentally friendly explosives, a number of heterocyclic-based energetic compounds have been developed and extensively used as high-energy explosives and ingredients of propellants [1, 2, 4, 10]. 1,4-Diamino-3,6-dinitropyrazolo[4,3-c]pyrazole (DADNP) is a nitrogen-rich energetic compound. Its density is 1.85 g/cm<sup>3</sup>, its nitrogen content is 49.12%, and its predicted detonation energy is 101% of HMX. The structure of DADNP has been previously described [11, 12], but the characterization data, synthetic condition and performance have not been reported.

In this paper, 1,4-diamino-3,6-dinitropyrazolo[4,3-c]pyrazole (DADNP) was synthesized using 3,6-dinitropyrazolo[4,3-c]pyrazole (DNPP) as the starting material *via* N-amination reaction [12]. Using the amino group of DADNP, two derivatives: 4,4'-(triaz-1-ene-1,3-diyl)bis(1-amino-3,6-dinitropyrazolo[4,3-c]pyrazole) (TBADNP) [13] and 1,4-dinitramino-3,6-dinitropyrazolo [4,3-c]pyrazole (DNADNP) were designed and obtained for the first time. The properties of DADNP, TBADNP and DNADNP were estimated by a B3LYP method on a 6-31G+(d,p) basis set of Gaussian 09 procedure [14, 15]. Their thermal properties were analyzed by differential scanning calorimetry (DSC) and thermogravimetric (TG) techniques.

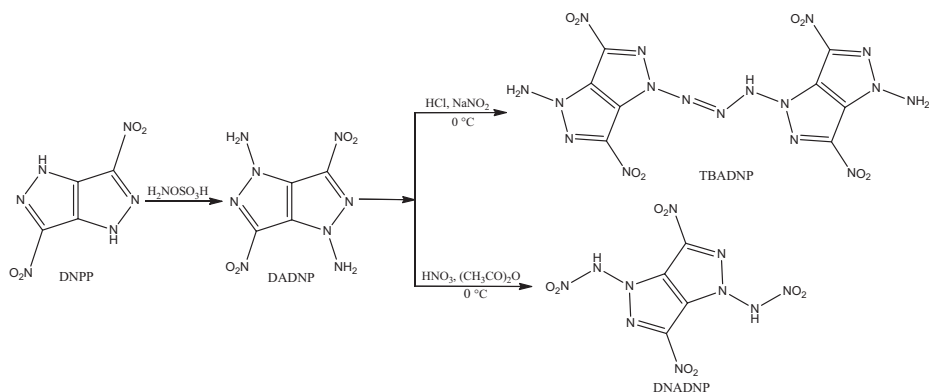
## 2 Experimental

### 2.1 Materials and methods

We synthesized 3,6-dinitropyrazolo[4,3-c]pyrazole (DNPP). Other reagents (of analytic grade) were obtained from commercial suppliers and used without further purification. Their IR spectra were recorded utilizing a NEXUS 870-based Fourier infrared spectrometer employing a KBr matrix. <sup>1</sup>H NMR (500 MHz) and <sup>13</sup>C NMR (125 MHz) spectra were recorded with an AV 500-type superconducting NMR instrument. DMSO-*d*<sub>6</sub> was used as the solvent and tetramethyl silane (TMS) as the internal standard. Elemental analysis was performed using a Vario EL-III Elemental Analyzer. DSC was performed in a platinum sample container using a Shimadzu DSC-60, the 0.5-1.0 mg sample being heated at a rate of 5 °C/min. TG was performed in a platinum sample container using a Nicolet TA 2950, the 0.5-1.0 mg sample being heated at a rate of 5 °C/min. The purity

of products was recorded using an LC-2010A ht liquid chromatographer.

The synthetic routes for DADNP, TBADNP and DNADNP are outlined in Scheme 1. The starting material (DNPP) can be easily obtained according to the method previously reported [16-18]. The synthesis of DADNP was performed via N-amination of DNPP. Then TBADNP and DNADNP were prepared by diazotization and nitrification of DADNP.



**Scheme 1.** Synthesis of 1,4-diamino-3,6-dinitropyrazolo[4,3-c]pyrazole and its derivatives.

## 2.2 Synthesis of 1,4-diamino-3,6-dinitropyrazolo[4,3-c]pyrazole

A solution of 1.0 g ( $8.84 \times 10^{-3}$  mol) of hydroxylamino-*O*-sulfuric acid in 3.0 mL of water was added over a period of 5 min to a solution of 0.5 g ( $2.53 \times 10^{-3}$  mol) DNPP and 0.74 g ( $6.95 \times 10^{-3}$  mol) sodium carbonate in 12.0 mL water at  $70\text{--}75^\circ\text{C}$ . Meanwhile, the pH was carefully adjusted to 8-9 by adding sodium bicarbonate. The mixture was kept at  $70\text{--}75^\circ\text{C}$  for 2 h and then cooled to room temperature. The precipitate was filtered off, washed with water, and dried to give 0.122 g of a brown solid with a yield of 21.1%; m.p.:  $227^\circ\text{C}$  (DSC, decomposed),  $^1\text{H}$  NMR (DMSO- $d_6$ , 500 MHz),  $\delta$ : 7.221 (s, 4H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 125 MHz),  $\delta$ : 128.49 (d), 131.94 (d); IR (KBr,  $\text{cm}^{-1}$ ),  $\nu$ : 3319, 3272, 1638 ( $-\text{NH}_2$ ), 1532, 1395 ( $-\text{NO}_2$ ), 1229, 1112, 1019 (pyrazole ring); Anal. Calcd for  $\text{C}_4\text{H}_4\text{N}_8\text{O}_4$  (%): C 21.05, H 1.753, N 49.12; found C 21.09, H 1.749, N 49.15; MS (EI)  $m/z$ : 228 ( $\text{M}^+$ ).

## 2.3 Synthesis of 4,4'-(triaz-1-ene-1,3-diyl)bis(1-amine-3,6-dinitropyrazolo[4,3-c]pyrazole)

0.3 g ( $1.32 \times 10^{-3}$  mol) DADNP was suspended in 1.9 mL 36-38% hydrochloric acid at room temperature, then 0.11 g ( $1.59 \times 10^{-3}$  mol)  $\text{NaNO}_2$  in 1.1 mL  $\text{H}_2\text{O}$

was added at 0-2 °C. The reaction mixture was stirred at 0-2 °C for 1 h. The resulting grey precipitate was filtered, washed with water, and dried in air to give 0.19 g of a grey solid with a yield of 61.9%; m.p.: 236 °C (DSC, decomposed), <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz), δ: 7.236 (s, 4H, 2NH<sub>2</sub>), 15.064 (s, 1H, NH); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz), δ: 128.94, 132.11, 132.39, 138.39; IR (KBr, cm<sup>-1</sup>), ν: 3601, 3513 (-NH), 3319, 3271, 3171 (-NH<sub>2</sub>), 1638 (C=N), 1609 (N=N), 1531, 1393 (-NO<sub>2</sub>), 1246, 1142, 1039 (pyrazole ring); Anal. Calcd for C<sub>8</sub>H<sub>5</sub>N<sub>17</sub>O<sub>8</sub> (%): C 20.56, H 1.08, N 50.96; found C 20.60, H 1.06, N 50.99; MS (EI) m/z: 451 [M-NH]<sup>+</sup>.

## 2.4 Synthesis of 1,4-dinitroamino-3,6-dinitropyrazolo[4,3-*c*]pyrazole

0.1 g (0.44 × 10<sup>-3</sup> mol) DADNP was suspended in 10.0 mL acetic anhydride at room temperature, then 6.0 mL 98% nitric acid was added dropwise at 0-5 °C. The reaction mixture was stirred at 0-10 °C for another 3 h. The solution was poured into ice water, extracted with ether (3 × 40.0 mL), dried with magnesium sulfate, and the ether evaporated under reduced pressure to give 0.089 g of a yellow solid with a yield of 63.8%; m.p.: 288 °C (DSC, decomposed), <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz), δ: 15.110 (s, 2H, 2-NH); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 125 MHz), δ: 131.99 (s), 138.34 (s); IR (KBr, cm<sup>-1</sup>), ν: 3597, 3510, 1604 (-NH), 1544, 1518, 1385, 1361 (-NO<sub>2</sub>), 1246, 1142, 1039 (pyrazole ring); Anal. Calcd for C<sub>4</sub>H<sub>2</sub>N<sub>10</sub>O<sub>8</sub> (%): C 15.10, H 0.63, N 44.03; found C 15.07, H 0.66, N 43.96; MS (EI) m/z: 336 [M+H<sub>2</sub>O]<sup>+</sup>.

## 3 Results and Discussion

### 3.1 Synthesis

#### 3.1.1 Synthesis of DNPP

The synthesis of DNPP has been reported in numerous papers [16-20], but the total yield was found to be very low (only 9.3%). In our initial study [21], the post-treatment method of a key-intermediate of DNPP (4-diazonium-3,5-dimethylpyrazole salt) was improved. Using freezing crystal techniques instead of extractive techniques led to an increase in yield from 42.9% to 86.1%. This could avoid the use of organic reagents and shorten the operation process. The total yield of DNPP reached up to 17.9%.

### 3.1.2 Synthesis of DADNP

The structure of DADNP has been previously published in the literature [11, 12], but data on characterization, synthetic conditions and performance have not been reported. The synthetic procedure for DADNP was reported in our initial paper [21], but the yield was only 10.4%. In the research reported in this paper, the yield of DADNP reached up to 21.1% by improving the synthetic method and optimization of the synthetic conditions. The effects of the molar ratio of hydroxylamino-*O*-sulfuric acid and DNPP, pH value and reaction temperature on the yield of DADNP have been investigated and the results are summarized in Table 1.

**Table 1.** The optimization of synthetic conditions for DADNP

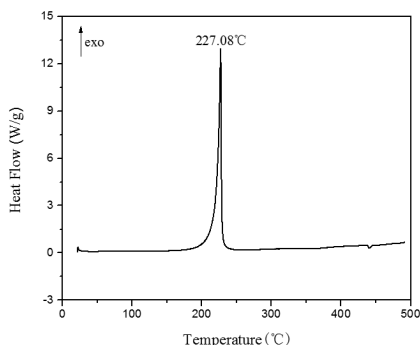
Molar ratio	Yield [%]	pH value	Yield [%]	Temperature [°C]	Yield [%]
2.5:1	13.1	7	12.1	50	15.9
3:1	15.2	8	19.9	60	16.5
3.5:1	19.6	9	20.1	70	21.1
4:1	19.5	10	16.5	80	17.3
4.5:1	19.8	11	14.2	90	14.4

The most suitable synthetic conditions we found for DADNP (producing a yield of 21.1%) are as follows: a molar ratio of hydroxylamino-*O*-sulfuric acid and DNPP of 3.5:1, pH value 8-9, reaction temperature 70 °C.

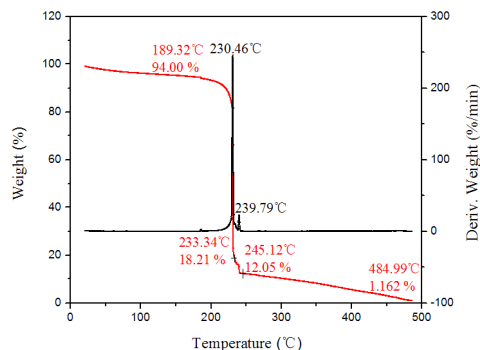
## 3.2 Thermal behavior of the compounds

### 3.2.1 Thermal behavior of DADNP

DSC and TGA analyses revealed that DADNP is thermally stable up to 207 °C. The DSC curve (Figure 1) of DADNP exhibits a melting point with a main concomitant decomposition at 227 °C. In the TGA curves (Figure 2), DADNP shows one stage decomposition. DADNP showed a mass loss of 81.8% up to 233 °C, and a 1.16% residue at 485 °C.



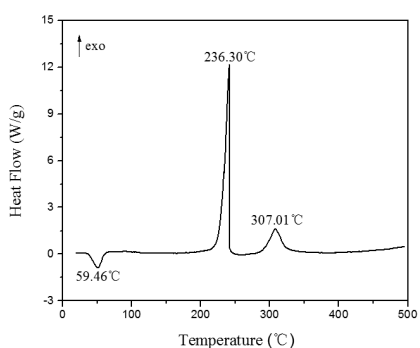
**Figure 1.** DSC curve of DADNP.



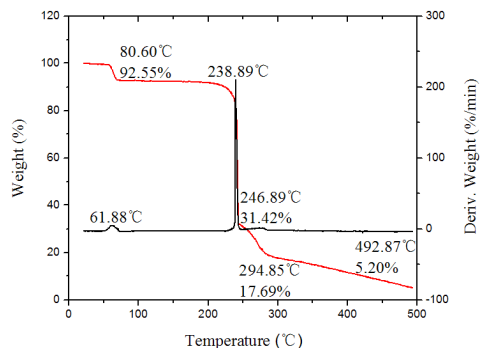
**Figure 2.** TGA curves of DADNP.

### 3.2.2 Thermal behavior of TBADNP

DSC and TGA analyses revealed that TBADNP is thermally stable up to 223 °C. The DSC curve (Figure 3) of TBADNP exhibits a volatilizable peak at 59 °C and two thermal decomposition peaks at 236 °C and 307 °C, respectively. In the TGA curves (Figure 4), the thermal behaviors of TBADNP can be described in two stages. The first stage is an obvious exothermic decomposition process with a mass loss of 68.6% up to 247 °C. The second stage is the continued decomposition of the compound with a total mass loss of 82.3% up to 295 °C, and a 5.2% residue at 493 °C.



**Figure 3.** DSC curve of TBADNP.



**Figure 4.** TGA curves of TBADNP.

### 3.2.3 Thermal behavior of DNADNP

DSC and TGA analyses revealed that DNADNP is thermally stable up to 220 °C. The DSC curve (Figure 5) of DNADNP exhibits a melting point with a main concomitant decomposition at 288 °C. In the TGA curves (Figure 6), DNADNP shows one stage decomposition. DNADNP showed a mass loss of 70.1% before

317 °C, and a 22.3% residue at 443 °C.

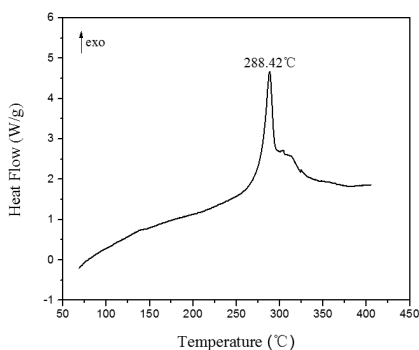


Figure 5. DSC curve of DNADNP.

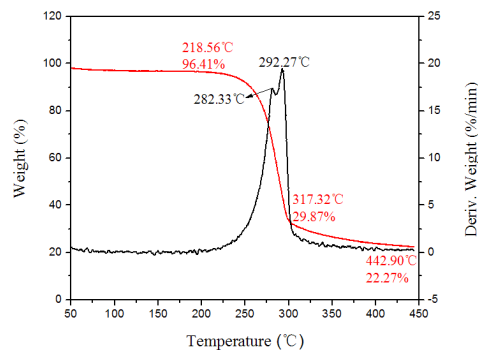


Figure 6. TGA curves of DNADNP.

### 3.3 Properties of the compounds

The thermal stability of DADNP, TBADNP and DNADNP were determined by DSC measurements at a heating rate of 5 °C/min. As shown in Table 2, the decomposition temperatures of TBADNP and DNADNP are 236 °C and 288 °C, which are both higher than the precursor DADNP (207 °C).

Density is one of the most important physical properties of energetic compounds. The detonation pressure is dependent on the square of the density and the detonation velocity is proportional to the density [22]. The structures of DADNP, TBADNP and DNADNP were optimized using Gaussian 09 in order to obtain their stable geometric configuration, and their densities were then calculated [15]. The densities of DADNP (1.85 g·cm<sup>-3</sup>), TBADNP (1.91 g·cm<sup>-3</sup>) and DNADNP (1.92 g·cm<sup>-3</sup>) fall in the range for high-performance energetic materials (1.8-2.0 g·cm<sup>-3</sup>) [23] and are superior to that of RDX (1.82 g·cm<sup>-3</sup>).

The heat of formation is another important parameter that needs to be considered when designing energetic compounds. The heats of formation of target compounds were calculated based on their stable geometric configurations, which were optimized using Gaussian 09 [15]. As shown in Table 2, the results show that DADNP (431.5 kJ·mol<sup>-1</sup>), TBADNP (1131.1 kJ·mol<sup>-1</sup>) and DNADNP (505.7 kJ·mol<sup>-1</sup>) exhibit higher heats of formation than RDX (92.6 kJ·mol<sup>-1</sup>) and HMX (104.8 kJ·mol<sup>-1</sup>).

The detonation parameters of TBADNP and DNADNP were calculated using the empirical VLW equation [14]. The calculated detonation pressure and detonation velocity were 38.6 GPa and 8997.6 m·s<sup>-1</sup> (TBADNP), 49.7 GPa and 9347.2 m·s<sup>-1</sup> (DNADNP), which are superior to RDX (33.7 GPa, 8712.5 m·s<sup>-1</sup>).

The sensitivities of all the explosives studied were determined experimentally

according to standard BAM methods [24]. All of the compounds were found to have impact sensitivities ranging from 14 J to 20 J, and are therefore less sensitive than RDX (7.5 J) and HMX (7 J). The friction sensitivity of DADNP was measured as 280 N, dropping to > 360 N for TBADNP. Thus, according to the UN recommendations [25], compounds DADNP and DNADNP are to be classified as sensitive towards impact and friction, whereas compound TBADNP is sensitive towards impact and insensitive towards friction.

DADNP and TBADNP are soluble in dimethyl sulfoxide, N,N-dimethylformamide, and concentrated sulfuric acid but insoluble in water, acetone, ether and petroleum ether. DNADNP was soluble in dimethyl sulfoxide, acetonitrile, water, and ether but insoluble in petroleum ether. The performance data of DADNP, TBADNP, DNADNP compared with RDX and HMX are listed in Table 2.

**Table 2.** Properties of DADNP, TBADNP, DNADNP compared with RDX and HMX

Performances	DADNP	TBADNP	DNADNP	RDX [26]	HMX [26]
Formula	$C_4H_4N_8O_4$	$C_8H_5N_{17}O_8$	$C_4H_2N_{10}O_8$	$C_3H_6N_6O_6$	$C_4H_8N_8O_8$
Appearance	brown solid	grey solid	yellow solid	white crystal	colorless crystal
Density [ $g \cdot cm^{-3}$ ]	1.85	1.91	1.92	1.82	1.91
Nitrogen content [%]	49.1	51.0	44.0	37.8	37.8
Melting point [ $^{\circ}C$ ]	227 (dec.)	236 (dec.)	288 (dec.)	203	276
Thermal decomposition peak [ $^{\circ}C$ ]	227	236, 307	288	244	287
Detonation velocity [ $m \cdot s^{-1}$ ]	8733.9	8997.6	9347.2	8712.5	9010.4
Detonation pressure [GPa]	33.7	38.6	49.7	33.7	39.6
Heat of formation [ $kJ \cdot mol^{-1}$ ]	431.5	1131.1	505.7	92.6	104.8
Detonation energy [ $kJ \cdot kg^{-1}$ ]	5739.4	6034.0	6683.0	5355.3	5695.2
Impact sensitivity [J]	14	20	17	7.5	7
Friction sensitivity [N]	280	>360	300	120	112
Electrostatic discharge sensitivity [J]	0.75	0.8	0.6	0.2	0.2



## 4 Conclusions

- (1) 1,4-Diamino-3,6-dinitropyrazolo[4,3-c]pyrazole (DADNP) and its derivatives: 4,4'-(triaz-1-ene-1,3-diyl)bis(1-amine-3,6-dinitropyrazolo[4,3-c]pyrazole) (TBADNP) and 1,4-dinitramino-3,6-dinitropyrazolo[4,3-c]pyrazole (DNADNP) were synthesized and structurally characterized for the first time.
- (2) The thermal behaviors of target compounds were studied using DSC and TG. The thermal decomposition peak temperature of DADNP, TBADNP and DNADNP were found to be 227 °C, 236 °C and 288 °C, respectively. These results show that these compounds have acceptable thermal stability.
- (3) The heats of formation and detonation properties of the target compounds were calculated using Gaussian 09 and the empirical VLW equation. All the compounds exhibited higher heats of formation than RDX and HMX. The detonation pressure and detonation velocity of TBADNP and DNADNP are superior to RDX.

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