

# Synthesis and Crystal Structure of 1-Methoxymethyl-3,4,5-trinitropyrazole

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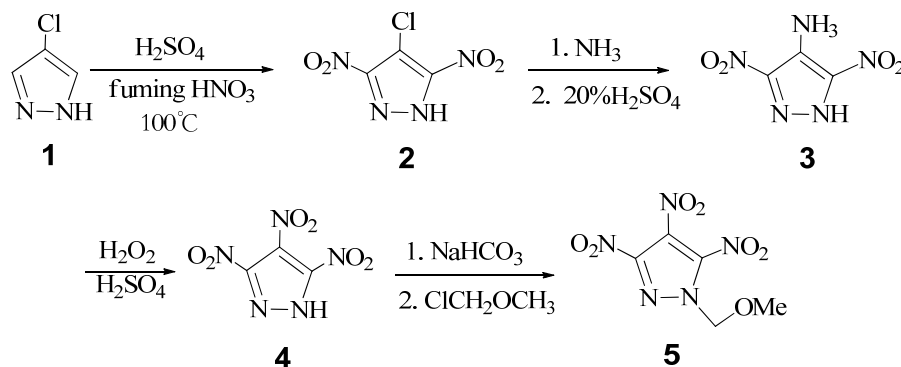
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**Abstract.** The title compound has been synthesized and its crystal has been cultivated. The crystal structure was determined by single crystal X-ray diffraction. Crystal data:  $C_5H_5N_5O_7$ , trigonal system, space group  $R\bar{3}$ ,  $a = 22.881(13)\text{\AA}$ ,  $b = 22.881(13)\text{\AA}$ ,  $c = 9.506(4)\text{\AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 120^\circ$ ,  $V = 4310.1(4)\text{\AA}^3$ ,  $M_r = 247.14$ ,  $Z = 18$ ,  $F(000) = 2268$ ,  $D_c = 1.714\text{g}\cdot\text{cm}^{-3}$ ,  $\mu = 0.161\text{mm}^{-1}$ ,  $R = 0.0491$  and  $wR = 0.1082$  for 3339 observed reflections with  $I > 2\sigma(I)$ .

## 1. Introduction

Polynitropyrazole and its derivatives are important energetic materials, which have been widely used as anion precursors of energetic ionic salts. 1-methoxymethyl-3,4,5-trinitropyrazole is a key intermediate for the synthesis of 5-substituted-3,4-dinitropyrazole derivatives. Herein, we reported the synthesis and crystal structure of compound **5** (Scheme 1). This title compound was prepared from 4-chloro pyrazole **1** by nitration, amination, oxidation and nucleophilic substitution reaction. Its structure was characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS and X-ray diffraction.



Scheme 1. Synthesis of 1-methoxymethyl-3,4,5-trinitropyrazole.

## 2. Experimental

### 2.1 Apparatus and Reagents

The melting points were measured on an XT-4B melting point apparatus (uncorrected).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker 500 MHz nuclear magnetic resonance spectrometer operating at 500 MHz and 125 MHz, respectively. Electrospray ionization mass spectra were recorded on a Bruker Apex IV FTMS spectrometry. Infrared spectra were recorded on Bruker Alpha spectrophotometer with an ATR-Ge device. The diffraction data was collected with a Bruker SMART CCD diffractometer using a graphite monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71070\text{\AA}$ ) at 100(6) K. The starting material and all reagents were commercially available and were used without further purification.

### 2.2 4-chloro-3,5-dinitropyrazol (2)

4-chloro pyrazole (1.537 g, 15 mmol) was added to a concentrated sulfuric acid (18.75 mL) at

0-5 °C. After complete dissolution, fuming nitric acid (1.95 mL, 29.9 mmol) was added dropwise. The mixture was heated to 105 °C, then kept for 5 h. After cooling to room temperature, the mixture was poured into iced water, extracted with EtOAc (100mL×3), washed with saturated brine and dried over Mg<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum and **2** was obtained as white solid (2.48 g, 85.8%). M.p:156-158 °C (lit.: 157-159 °C)<sup>[1]</sup>.

### 2.3 4-amino-3,5-dinitropyrazol (**3**)

A solution of **2** (1.0 g, 5.2 mmol) and 25% ammonia (9.3 mL) was stirred at 150 °C in a thick-walled sealed tube for 12 h. After cooling to room temperature, a lot of yellow crystal formed was filtered off, put into 20 mL H<sub>2</sub>O, and acidified with 20% H<sub>2</sub>SO<sub>4</sub> to pH = 1. Stirred for another 2 h at room temperature, the precipitate formed was filtered off and dried to yield **3** as yellow solid (0.71 g, 79.4%).

### 2.4 3,4,5-trinitropyrazol (**4**)

A concentrated solution of H<sub>2</sub>SO<sub>4</sub> (23.6 mL) was added dropwise with stirring into the solution of hydrogen peroxide (30%, 11.8 mL) at 0-5 °C. The mixture was stirred for 30 min, and then **3** (1.5 g, 8.6 mmol) was added in batches. After stirring at room temperature for 24 h, the reaction mixture was poured into iced water, extracted with Et<sub>2</sub>O (100mL×3), washed with saturated brine and dried over Mg<sub>2</sub>SO<sub>4</sub>. The solvent was removed under vacuum to provide yellow thick liquid. After standing overnight, **4** was obtained as yellow crystal (1.52 g, 86.4%). M.p:185-187 °C (lit.: 185 °C)<sup>[2]</sup>.

### 2.5 1-methoxymethyl-3,4,5-trinitropyrazole (**5**)

Sodium bicarbonate (1.2 g, 15 mmol) was added to a solution of **4** (2.03 g, 10 mmol) in MeCN (25 mL) at room temperature, the mixture was stirred for 10 min, followed by addition of methoxymethyl chloride (1.2 g, 15 mmol). The reaction mixture was stirred for 1 h, a precipitate was filtered off, the solvent was evaporated under vacuum, the residue was recrystallized from CHCl<sub>3</sub> to obtain compound **5** (1.68 g, 68%), M.p:104-106 °C (lit.: 104-105 °C)<sup>[3]</sup>. IR,  $\nu_{\text{max}}/\text{cm}^{-1}$ : 1539, 1339, 1247, 1115, 889, 805, 720, 555. <sup>1</sup>H NMR(500 MHz, CDCl<sub>3</sub>)  $\delta$ : 3.55(s, 3H, CH<sub>3</sub>), 5.99(s, 2H, CH<sub>2</sub>). <sup>13</sup>C NMR(125 MHz, CDCl<sub>3</sub>)  $\delta$ : 58.9(OCH<sub>3</sub>), 86.3(CH<sub>2</sub>), 123.5(C<sub>4</sub>), 137.4(C<sub>5</sub>), 143.4(C<sub>3</sub>). ESIMS (m/z): 202[M-CH<sub>2</sub>OMe]<sup>-</sup>.

### 2.6 Crystal structure determination

We selected the size of 0.60 mm × 0.55 mm × 0.55 mm crystals under the microscope. The diffraction data was collected with a Bruker SMART CCD diffractometer using a graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71070$  Å) at 100(6) K. The structures were solved by direct methods with SHELXS-97 program and refinements on F<sup>2</sup> were performed with SHELXL-97<sup>[4]</sup> program by full-matrix least-squares techniques. Complete crystallographic data and collection parameters are listed in Table 1. The structure of title molecular and its arrangement in crystal are shown respectively in Fig 1. and Fig 2. Crystallographic data (CCDC 1409014) can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).

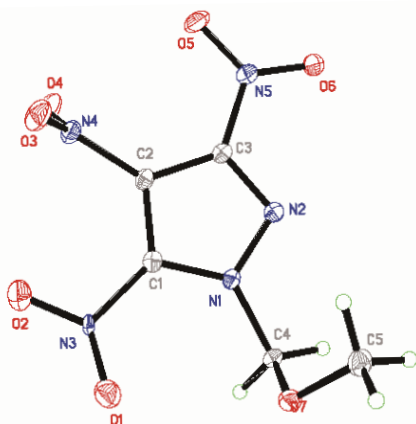


Fig. 1 Displacement ellipsoid plot (30%)

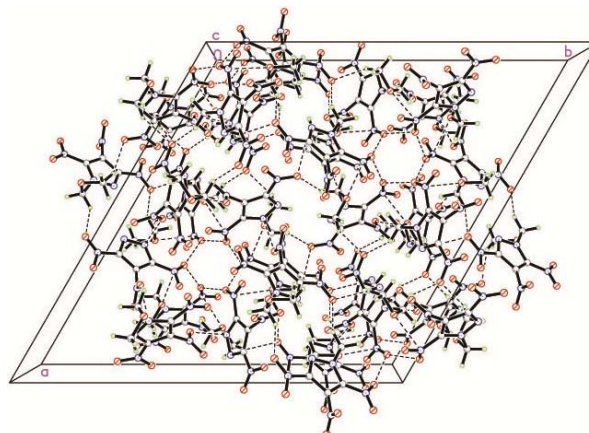


Fig. 2 Packing diagram of title compound of title compound

Table 1. Crystallographic data and structure refinement for the title compound.

|   |   |   |   |
|---|---|---|---|
| Formula                                   | C <sub>5</sub> H <sub>5</sub> N <sub>5</sub> O <sub>7</sub>   | Crystal size / mm                             | 0.60 × 0.55 × 0.55                          |
| Formula weight                            | 247.14  | θ range for data collection                   | 3.36 to 26.00°                              |
| Temperature / K                           | 100(6)  | Limiting indices                              | -28 ≤ h ≤ 18, -13 ≤ k ≤ 23,<br>-10 ≤ l ≤ 11 |
| Wavelength / Å                            | 0.71073   | Reflections collected / unique                | 3339 / 1885 [R(int) = 0.0255]               |
| Crystal system                            | trigonal  | Completeness to theta = 29.14                 | 99.7 %                                      |
| space group                               | R3  | Absorption correction                         | None  |
| Unit cell dimensions                      | $a = 22.8807(13) \text{ Å}$ $\alpha = 90^\circ$<br>$b = 22.8807(13) \text{ Å}$ $\beta = 90^\circ$<br>$c = 9.5063(4) \text{ Å}$ $\gamma = 120^\circ$ | Refinement method                             | Full-matrix least-squares on $F^2$          |
| Volume / Å <sup>3</sup>                   | 4310.1(4)   | Data/restraints/parameters                    | 1885/0/155                                  |
| Z   | 18  | Goodness-of-fit on $F^2$                      | 1.064                                       |
| Calculated density / Mg·m <sup>-3</sup>   | 1.714   | Final R indices [ $I > 2\sigma(I)$ ]          | $R^1 = 0.0491$ , $wR^2 = 0.1082$            |
| Absorption coefficient / mm <sup>-1</sup> | 0.161   | R indices (all data)                          | $R^1 = 0.0665$ , $wR^2 = 0.1181$            |
| $F(000)$                                  | 2268  | Largest diff. peak and hole/e.Å <sup>-3</sup> | 0.359 and -0.367                            |

### 3. Results and discussion

The structure of title molecular and its arrangement in crystal are shown in Fig. 1 and 2, respectively. The selected bond lengths and torsion angles are shown in Table 2 and 3.

Table 2. Selected bond lengths (Å) .

| Bond  | Dist/ Å  | Bond  | Dist/ Å  | Bond  | Dist/ Å  |
|-------|----------|-------|----------|-------|----------|
| N1—C1 | 1.357(3) | N4—C2 | 1.451(3) | N3—O1 | 1.167(2) |
| N2—C3 | 1.322(3) | N5—C3 | 1.441(3) | N3—C1 | 1.478(3) |
| N1—C4 | 1.487(3) | O6—N5 | 1.222(3) | N4—O4 | 1.209(3) |

Table 3. Selected torsion angles (°) .

| Angle       | (°)     | Angle       | (°)       | Angle       | (°)        |
|-------------|---------|-------------|-----------|-------------|------------|
| N2—N1—C1—C2 | 0.0 (2) | C1—C2—N4—O3 | 76.0 (3)  | O5—N5—C3—N2 | -176.6 (2) |
| N1—N2—C3—C2 | 0.2 (2) | O1—N3—C1—C2 | -171.5(2) | O2—N3—C1—N1 | -170.6(2)  |

Single-crystal X-ray diffraction analysis reveals that the title molecular is composed of one pyrazole ring substituted by three nitro groups respectively in 3-, 4-, 5-position and one methoxymethyl group in 1- position of the pyrazole ring. Based on table 3, the torsion angles N1-N2-C3-C2 (0.2°) and N2-N1-C1-C2 (0.0°) proved that the atoms N1,N2,C3,C2 and C1 in the pyrazole ring are almost coplane. In addition, the same result was observed that the nitro groups in 3- and 5-positiond are nearly coplanar with the ring, demonstrated by the torsion angles C2-C3-N5-O6 (-173.9°) and O1-N3-C1-C2 (-171.5°), respectively. On the contrary, the nitro gooup in 4-position is approximately perpendicular to pyrazole ring, shown by the torsion angle of C1-C2-N4-O3 (76.0°). The methoxymethyl group in 1- position is a twist chain stretching out of pyrazole ring plane. The C-N bond lengths in the pyrazole ring are 1.357 Å (C1—N1) and 1.322 Å (C3—N2), which are shorter than the normal C—N single bond length (1.472 Å) and longer than the normal C=N bond (1.269 Å). This fact indicates that there exists electron delocalization in the ring. Compared to C1—N1 bond length, C3—N2 bond length is shorter. The reason may be attributed to the fact there exist a pair of electrons in one  $sp^2$  hybridized p-orbital of N2 atom, which increase electron delocalization between N2—C3 atoms. From Fig. 2, the weaker untypical hydrogen bond C—H...O and  $\pi$ - $\pi$  stacking

interaction between molecules were observed, which link the title molecule to form its three-dimensional crystal lattice.

#### 4. Conclusion

In summary, 1-methoxymethyl-3,4,5-trinitropyrazole was prepared from 4-chloro pyrazole by nitration, amination, oxidation and nucleophilic substitution reaction according to literatuers . It was recrystallized with  $\text{CHCl}_3$  instead of  $\text{CCl}_4$  and the yield was increased. Its structure was characterized by IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS and X-ray diffraction. Its crystal structure was reported for the first time.

#### References

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