

## Efficient preparation and comprehensive properties of thermal decomposition and detonation for 4,4'-dinitro-3,3'-azofuroxan

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### ABSTRACT

The preparation of 4,4'-dinitro-3,3'-azofuroxan (**3**) was efficiently accomplished from synthesizing the key intermediate of 4-amino-3-azidocarboxyl-furoxan (**1**) and oxidizing the precursor 4,4'-diamino-3,3'-azofuroxan (**2**). The structure of **3** and its crystal density of  $1.981 \text{ g cm}^{-3}$  were determined by single crystal X-ray diffraction studies. The crystal structure determination indicated that only **3** was obtained rather than its isomers 3,3'-dinitro-4,4'-azofuroxan (**3'**), which consistent with the results of theoretical calculations. The comprehensive thermal decomposition behaviors were fully characterized by multiple heating methods, TG–DSC–MS and original temperature-dependent/FTIR coupling technique. In addition, the experimental detonation velocity of **3** was determined to be  $9778 \text{ m s}^{-1}$  by using a developed method that only requires a small amount of samples on a network plate made of aluminum alloy, which is also well suited for other energetic compounds with high impact sensitivity ( $IS < 8 \text{ J}$ ), such as HMX, RDX and CL-20.

### 1. Introduction

Over the past decades, researchers have never stopped pursuing the design and synthesis of high energy density compounds (HEDC) with high detonation performance, such as HDNT, DNAT, CL-20, DNTF and DNAAF (Scheme 1) [1–5]. Among them, furoxan (1,2,5-oxadiazole-2-oxide) group is a unique class of energetic compounds with numerous interesting properties, such as high density, high positive heat of formation and good oxygen balance. By replacing a nitro group with a furoxan ring in HEDC molecules, the density can be increased by approximately  $0.06\text{--}0.08 \text{ g cm}^{-3}$  and the detonation velocity can also be increased by about  $300 \text{ m s}^{-1}$  [6]. Introducing furoxan rings into other energetic backbones or connecting furoxan moieties with other energetic groups has been proven to be effective to improve the crystal density and explosive performance. In addition, the synthesis of novel furoxan derivatives has also attracted considerable attentions because of their attractive biological activities [7].

Dinitroazofuroxan is a well known HEDC and has been reported in some reviews and articles [8–10]. However, its single crystal structure and properties of thermal decomposition and detonation have not been reported since their first synthesis in 1998 [11]. Therefore, it is still unclear which one is really obtained in previous researches, **3** or **3'**(3,3'-dinitro-4,4'-azofuroxan)? To the best of our knowledge, there

are several limitations, such as harsh reaction conditions, limited substrate scope and very low chemical yields in preparing HEDC bearing furoxan ring, which hinder the further studies on their structures and physicochemical properties.

In this study, in order to overcome the drawbacks mentioned above, a new efficient synthetic method was performed to prepare **3** via cyclization, azocoupling and oxidizing reaction. Both results from quantum chemistry calculations and single crystal diffraction data indicated that only **3** were obtained rather than **3'**. The thermal decomposition behaviors were further studied by TG–DSC–MS and original temperature-dependent/FTIR analysis. Finally, the experimental detonation of **3** was also evaluated by employing a convenient and efficient method.

### 2. Experimental

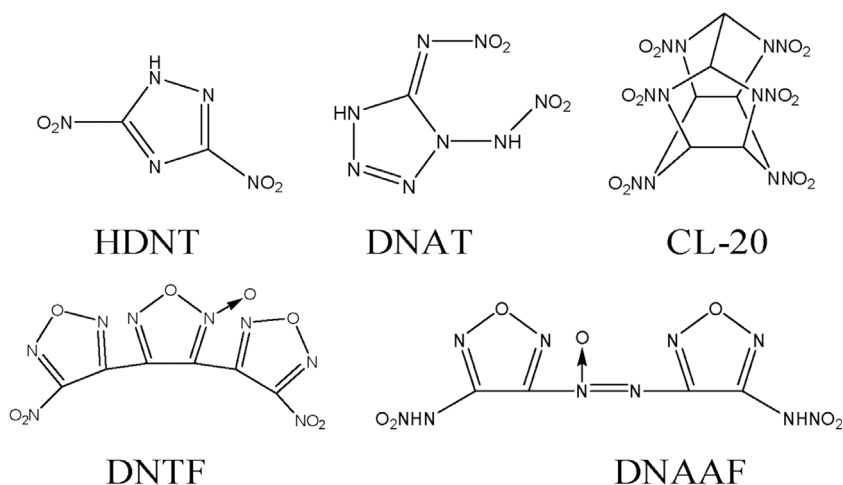
#### 2.1. Materials

##### 2.1.1. 4-amino-3-azidocarboxyl-furoxan (**1**)

First, potassium monohydrazino malonate (31.2 g, 0.2 mol) was dissolved in 6 M HCl (130 mL, 0.8 mol) and cooled to  $0\text{--}5 \text{ }^\circ\text{C}$ . Then, solution of sodium nitrite (27.6 g) in water (50 mL) was added dropwise to potassium monohydrazino malonate solution over a period of

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Scheme 1. The typical examples of high energy density compounds.

30 min, and the resulting reaction mixture was stirred at the temperature below 5 °C for 1 h. Finally, azidocarboxyl acetic acid can be easily obtained as a colorless solid in a yield of 81.7% (21.07 g) after extraction using ethyl acetate and vacuum distillation. IR (KBr,  $\text{cm}^{-1}$ ): 3277, 3016, 2891, 2305, 2272, 2158, 1699, 1628, 1433, 1418, 1256, 1184, 1159, 1018, 937, 891, 808, 748, 557.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 12.9, 3.2.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 169.2, 142.4, 43.8. Anal. Calcd (%) for  $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$ : C 27.92, H 2.34, N 32.55. Found: C 28.03, H 2.29, N 32.62.

Next, 98% nitric acid (60 mL) and sodium nitrite (10.35 g) were added to the azidocarboxyl acetic acid in acetic acid (20 mL) with vigorous stirring for 2 h at the temperature below 5 °C. The reaction mixture was poured into ice water, extracted with ethyl acetate, washed with water, dried over  $\text{MgSO}_4$  and reduced pressure evaporation below 35 °C to afford 3,4-diazidocarbonyl-furoxan. Subsequently, the resulting product was dissolved in dioxane (50 mL) and water (5 mL) mixture and was quickly heated to 80 °C with vigorously stirring for 15 min. After cooling to room temperature, a significant amount of pale yellow solid precipitated when water (100 mL) was added to the mixture in dropwise. The precipitate was filtrated off and washed with water to afford the product 1 in a yield of 63.5% (13.2 g). IR (KBr,  $\text{cm}^{-1}$ ): 3430, 3321, 2311, 2206, 2160, 1662, 1595, 1517, 1366, 1154, 1215, 972, 876, 839, 748, 650.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 6.6.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 161.7, 155.9, 104.8. Anal. Calcd (%) for  $\text{C}_3\text{H}_2\text{N}_6\text{O}_3$ : C 21.18, H 1.19, N 49.41. Found: C 21.24, H 1.22, N 49.37.

#### 2.1.2. 4,4'-diamino-3,3'-azofuroxan (2)

To the solution containing 1 (8.5 g, 0.05 mol) in dioxane (60 mL) was added trichloroisocyanuric acid (33.0 g) in portions at room temperature. The resulting reaction mixture was stirred until the complete consumption of the starting material 1 as monitored by TLC. Next, 5 mL water was added to the mixture and rapidly heated to 80 °C with vigorously stirring for 15 min. After cooling to room temperature, a significant amount of brick-red solid precipitated when water (100 mL) was added to the mixture in dropwise. The precipitate was filtered off and washed with ice water to afford product 2 in a yield of 71.93% (4.1 g). IR (KBr,  $\text{cm}^{-1}$ ): 3464, 3312, 1620, 1577, 1531, 1497, 1366, 1317, 1191, 1042, 866, 781, 698, 615.  $^1\text{H}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 7.1.  $^{13}\text{C}$  NMR (DMSO- $d_6$ ,  $\delta$ , ppm): 151.9, 124.2. Anal. Calcd (%) for  $\text{C}_4\text{H}_4\text{N}_8\text{O}_4$ : C 21.06, H 1.77, N 49.12. Found: C 21.14, H 1.74, N 49.08.

#### 2.1.3. 4,4'-dinitro-3,3'-azofuroxan (3)

A solution of compound 2 (3.0 g, 0.0132 mol) in methanesulfonic acid (40 mL) was added to a stirred suspension of sodium tungstate dihydrate (12.4 g, 0.0375 mol) in 90% hydrogen peroxide (37.5 g, 0.99 mol) in dropwise over a period of 30 min at 5–10 °C. The resulting mixture was allowed to warm to 30–35 °C, and stirring was continued

for 1.5 h at this temperature. After cooling to room temperature, the reaction mixture was poured into crushed ice. The resulting precipitate was filtrated off, washed with ice water, and dried in air to afford product 3 in a yield of 69.2% (2.6 g). IR (KBr,  $\text{cm}^{-1}$ ): 1521, 1362, 1619, 1575, 1281, 1084, 829, 658.  $^{13}\text{C}$  NMR (acetone- $d_6$ ,  $\delta$ , ppm): 155.4, 123.3.  $^{15}\text{N}$  NMR (acetone- $d_6$ ,  $\delta$ , ppm): 94.3, -9.28, -33.26, -37.87. Anal. Calcd (%) for  $\text{C}_4\text{N}_8\text{O}_8$ : C 16.68, N 38.90. Found: C 16.72, N 38.76. MS (EI),  $m/z$  (%): 288(1.72), 242(2.79), 212(6.51), 196(4.25), 196(2.48), 166(2.17), 84(66.72), 68(5.01), 44(28.36), 30(100).

## 2.2. Experimental instruments and conditions

All solvents and reagents were obtained from commercial vendors and used as received. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectroscopic data were recorded with a Bruker Advance 500 MHz spectrometer. FTIR and original temperature-dependent/FTIR spectra (differentiating rate of  $4\text{ cm}^{-1}$ , data collection rate of  $1\text{ scan s}^{-1}$  and heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ ) were obtained by using KBr pellets on a Nicolet NEXUS870 infrared spectrometer in the range of  $4000\text{--}400\text{ cm}^{-1}$ . Mass spectra (MS) with EI ion source were obtained by a Thermo Fisher SCIENTIFIC ENACTIVE. Elemental analyses (C, H, and N) were carried out with an Elementary vario EL-III microanalyzer. The TG-DSC-MS experiments were performed on 449C thermal analyzer (NETZSCH, Germany) and QMS-403C mass spectrometer (NETZSCH, Germany) under an argon atmosphere at a flow rate of  $50\text{ mL min}^{-1}$ . The heating rates used were 2.5, 5.0, 10.0 and  $20.0\text{ }^\circ\text{C min}^{-1}$  from ambient temperature to  $400\text{ }^\circ\text{C}$ . For all materials, the sensitivities towards impact and friction were determined according to BAM standards, using a ZBL-B impact sensitivity instrument (Nachen Co., China) and a MGD-036 friction sensitivity apparatus (Qingke Co., China), respectively.

## 2.3. X-ray crystallography

A thin plate was mounted on a MiteGen MicroMesh by using a small amount of Cargille immersion oil. Diffraction data were collected at 296(2) K on an Oxford Diffraction Gemini S Ultra diffract meter by using Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ). The structure was resolved by direct methods using the SHELXS-97 program [12] and refined against F2 by the full-matrix least-squares method using the SHELXL-97 program [13].

## 2.4. Theoretical study—computational details

Computations were performed with the Gaussian 09 (Revision B.01) suite of programs [14]. The geometric optimization of the structures and frequency analyses were carried out using B3LYP functional with the 6-31 + G\*\* basis set. All of the optimized structures were

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