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Bis(Nitroxymethylisoxazolyl) Furoxan: A Promising Standalone Melt-Castable Explosive

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The synthesis and crystal structure of the heterocyclic explosive bis(nitroxymethylisoxazolyl) furoxan, $C_{10}H_6N_6O_{10}$, are described. In addition, we report its physical properties and theoretical performance. This material was found to exhibit standalone melt-castable explosive properties, with a melting point of 89.8 °C and an onset decomposition temperature of 193.8 °C. Bis (nitroxymethylisoxazolyl) furoxan features an insensitive behavior to impact, friction, and electrostatic discharge, with a calculated detonation pressure about 25 % higher than the state-of-the-art melt-castable explosive TNT.

Introduction

The development of high-energy-density materials (HEDMs)[1] with high performance and low sensitivity is a main goal in the synthesis of new energetic materials. Due to the US Army's continued interest in melt-castable explosives, one focal point of our research is the synthesis of such materials. While it has been stated that energetic materials possessing melting points between 70–120 °C constitutes a good melt-castable material,[2] it is best if melting points of such materials are below 100 °C so that steam can be used for low-cost melting operations. Current state-of-the-art melt-castable technologies have centered around TNT.[3] Unfortunately, TNT presents an occupational health hazard due to its high vapor pressure,[4] and is now questioned as an environmentally acceptable material.[5–7] Although dinitroanisole (DNAN) has been investigated heavily as a melt-castable material in insensitive munitions technologies,[8] the performance of DNAN is significantly worse than TNT. Therefore, despite its environmental and human health hazards, TNT remains the optimal choice for performance-based melt-castable explosive technologies. Thus, there is a continued interest in developing higher-performing melt-castable ingredients that significantly outperform TNT in explosive performance.

Results and Discussion

Recently, the biisoxazole ring system was found to offer standalone melt-castable properties, as biisoxazole bi(methylene) dinitrate (**1**)[9] was synthesized and found to exhibit a melting point of 92.0 °C and a thermal onset of decomposition at 189.2 °C (Figure 1). Unfortunately, the performance was calculated to be slightly lower than that of TNT. Materials containing the furoxan moiety have, at times, been found to have melt-castable properties, while further boosting the energy, due to the high density and high heat of formation of this explosophore.[10] In an effort to further improve the energetic output of melt-castable biisoxazole-based systems, we decided to synthesize a molecule (**2**), which exhibits both the functional groups of these systems and the furoxan heterocyclic ring functionality.

The synthesis of **2** (Scheme 1) commenced by treating cyanoacetic acid with mixed acid in an improved process to yield dicyanofuroxan (DCFO, **3**) in 72 % yield and 84 % purity, as we published previously.[11] The impurity was inconsequential, as DCFO was converted uneventfully to diamidoxime **4** in 68 % yield.[12] **4** was isolated in very high purity via Büchner filtration, while the aforementioned impurity remained in the mother liquor. Double diazotization of **4** gave dihydroximoyl chloride **5**,[11,12] which was then converted to biisoxazole **6** in reasonable yield. Employing an excess of propargyl alcohol, coupled with slow addition of **5**, were critical in obtaining good yields. Otherwise, significant amounts of undesired water-soluble byproducts were obtained. Nitration of the resulting alcohols followed by recrystallization of the solid from isopropanol yielded dinitrate **2**. Overall, the synthesis proceeded in 23 % overall yield in 5 steps.

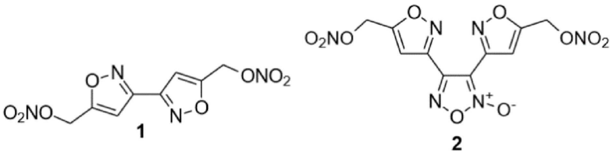

Figure 1. Molecular structures of energetic dinitrates **1** and **2**.

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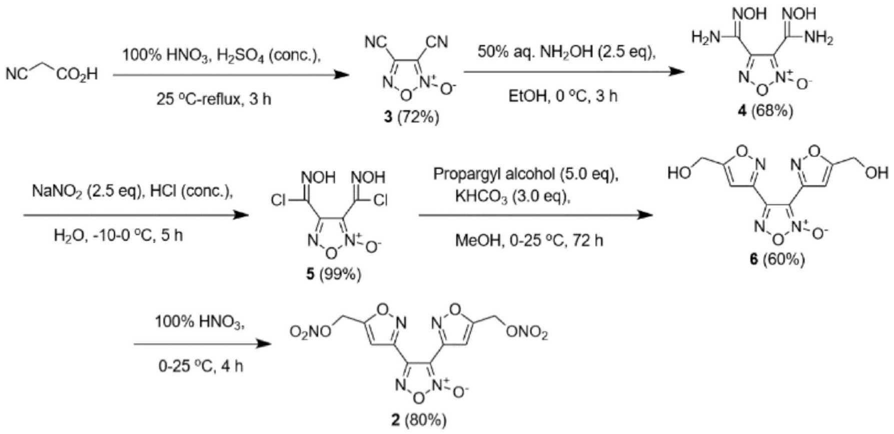

Scheme 1. Synthesis of nitrate **2** from cyanoacetic acid.

The physical properties and CHEETAH 8.0-derived calculated explosive performance of **2** compared to TNT and biisoxazole **1** are provided in Table 1.[13] Single crystal X-ray diffraction data of **2** and its analysis helped verify the structure, as well as to reveal its molecular configuration and key intra- and intermolecular interactions.[14] The details of the data acquisition and structure solution are provided in the Supporting Information. **2**, as observed by the DSC trace in Figure 2, possesses melting and decomposition temperatures in a range that, like TNT, makes it ideal as a potential standalone melt-castable explosive. **2** significantly outperforms TNT and **1** in oxygen balance, density, and detonation velocity compared to TNT. **2** also has a positive heat of formation, whereas the heat of formations of TNT and **1** are negative. Relative to TNT and **1**, **2** has a detonation pressure that is ca. 25% higher. Detonation pressure is an important metric, as higher values typically equate in a better ability to push metal, which can make metal fragments fly farther distances. Although **2** is more sensitive to impact and friction as compared to TNT and **1**, it still has lower sensitivities to impact and friction compared to the commonly processed explosive RDX (IS = 6.2 J, FS = 156 N). Thus, **2** could be considered as a potential TNT replacement in melt-castable explosive formulations. Interestingly, **1** and **2** differ only by a single furoxan moiety, and yet this moiety accounts for about 6 GPa of detonation pressure. This explains why the furoxan ring is such a popular explosophore to the energetic materials community.

Table 1. Physical and explosive properties of **2**.

Data category	TNT	**1**	**2**
T_m [°C][a]	80.4	92	89.8
T_{dec} [°C][b]	295.0	189.2	193.8
Ω_{CO2} [%][c]	−74.0	−61.5	−56.2
Ω_{CO} [%][d]	−24.7	−16.8	−13.0
ρ [g cm^{-3}][e]	1.65	1.585	1.712
P_{cj} [GPa][f]	20.5	19.3	25.1
V_{det} [m s^{-1}][g]	6950	7060	7374
I_{sp} [s][h]	–	206.2	224.0
$\Delta_f H°$ [kJ mol^{-1}][i]	−59.3	−139.0	49.5
IS[j] [J]	15.0	11.2	7.8
FS[k] [N]	> 360	> 360	240
ESD[l] [J]	> 0.25	0.125	0.125

[a] T_m = onset temperature of melting; [b] T_{dec} = onset temperature of decomposition; [c] Ω_{CO2} = CO_2 oxygen balance; [d] Ω_{CO} = CO oxygen balance; [e] ρ = experimentally determined density; [f] P_{cj} = theoretical detonation pressure; [g] V_{det} = theoretical detonation velocity; [h] I_{sp} = theoretical specific impulse; [i] $\Delta_f H°$ = theoretical molar enthalpy of formation; [j] IS = impact sensitivity; [k] FS = friction sensitivity; [l] ESD = -electrostatic discharge sensitivity.

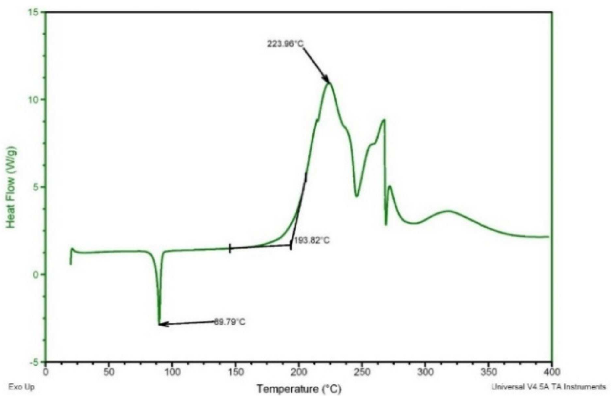

Figure 2. DSC trace of dinitrate **2**.

Conclusion

In summary, an nitric ester 2 was synthesized in 5 steps in 23% overall yield, and was found to melt and decompose within an ideal temperature range that makes this material suitable as a potential TNT replacement in melt-castable explosive operations. 2 was found to outperform TNT in many performance categories, including having a ca. 25% higher detonation pressure. The furoxan moiety was found to contribute about 6 GPa toward the detonation pressure of this material, which explains why this explosophore is such a popular choice amongst energetic materials chemists.

Experimental Section

Caution! Although we did not experience any problems handling the compounds described in this paper, proper laboratory precautions should be taken. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast shields are necessary for all energetic transformations, and in handling any material that is determined to be energetic.

Chemicals and solvents were used as received from Oakwood Chemicals. Diol **6** and dinitrate **2** were synthesized according to the literature.[8,9] ^{1}H and ^{13}C NMR spectra of **6** and **2** were recorded using an Bruker 400 MHz and 101 MHz instrument, respectively. The chemical shifts quoted in ppm in the text refer to typical standard tetramethylsilane in DMSO-d_6 or acetone-d_6 as the solvent. Infrared spectra were measured with a Bruker Alpha-P FTIR instrument. Melting and decomposition temperatures were measured at a heating rate of 5 °C/min using a TA Instruments Q10 DSC instrument. Single-crystal X-ray diffraction (XRD) studies were performed with a SuperNova Dualflex diffractometer containing an EosS2 charge-coupled device detector and a molybdenum Mo–Kα ($\lambda = 0.71073$ Å) radiation source.

3,4-bis(5-hydroxymethylisoxazol-3-yl)-1,2,5-oxadizole 2-oxide (**6**): To a 2 L round-bottom flask equipped with a stir bar were sequentially added 500 mL of MeOH, 49.0 mL of propargyl alcohol (46.5 g, 0.830 mol, 5.00 eq.), and $KHCO_3$ (49.9 g, 0.498 mol, 3.00 eq.). The reaction mixture was cooled to 0 °C, the flask was fitted with a pressure-equalizing liquid addition funnel, and a solution of **5** (40.0 g, 0.166 mol, 1.00 eq.) in 500 mL of MeOH was added dropwise over 4 h. After addition was complete, the ice bath was removed, and the reaction mixture was stirred for 72 h at ambient temperature. The reaction mixture was filtered, the mother liquor was transferred to a 2 L round-bottom flask, and was concentrated *in vacuo* to afford a brown, viscous oil. The liquid was triturated with 1.5 L of H_2O, and a solid appeared. The solid was collected by Büchner filtration and dried under suction overnight to afford 27.9 g (60 %) of *bi*isoxazole **6** as a light brown powder. $T_m = 90.8$ °C (onset), 96.9 °C (peak); $T_{dec} = 255.1$ °C (onset), 269.1 °C (peak); ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.94 (s, 1 H), 6.93 (s, 1 H), 5.84 (s, 1H), 5.83 (s, 1 H), 4.70 (s, 2H), 4.69 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.77, 174.68, 151.50, 148.70, 147.58, 108.03, 102.39, 101.44, 54.69, 54.66; IR (neat) cm^{-1} 3314.65 (w), 1589.38 (s), 1223.38 (w).

3,4-bis(5-nitroxymethylisoxazol-3-yl)-1,2,5-oxadiazole 2-oxide (**2**): To a 100 mL round-bottom flask immersed in an ice bath was added 100 mL of 100 % HNO_3. After the nitric acid was chilled to 0 °C, the inseparable mixture of alcohol **6** (5.00 g, 17.9 mmol, 1.00 eq.). After the addition was complete, the reaction mixture was stirred for 4 h, during which time the ice bath was allowed to melt, and the reaction mixture was allowed to warm to ambient temperature. The reaction mixture was poured onto crushed ice with stirring. After 3 h, the solid was collected by Büchner filtration. Recrystallization of the solid from hot isopropanol afforded 5.29 g (80 %) of nitric ester **2** as a white solid. $T_{melt} = 87.5$ °C (onset), 89.8 °C (peak); $T_{dec} = 193.8$ °C (onset), 224.0 °C (peak); ^{1}H NMR (400 MHz, acetone-d_6) δ 7.36 (s, 1H), 7.33 (s, 1H), 5.96 (s, 2H), 5.94 (s, 2H); ^{13}C NMR (101 MHz, acetone-d_6) δ 166.92, 166.87, 153.26, 150.58, 147.94, 108.40, 107.28, 106.11, 64.74, 64.68; IR (neat) cm^{-1} 3141.42 (w), 1642.12 (s), 1612.15 (s), 1523.71 (m), 1420.54 (m), 1281.11 (s).

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Keywords: cycloaddition reactions · energetic materials · explosives · furoxans · heterocycles

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[14] CCDC 1969496 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

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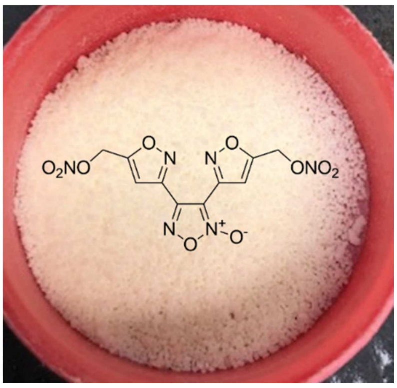
COMMUNICATIONS

More potential than TNT? The synthesis, characterization and x-ray crystal structure of bis(nitroxymethylisoxazolyl) furoxan is described. This energetic material was made on a 25 g scale in a five-step process in 23 % overall yield and was determined to exhibit standalone melt-castable explosive properties. This material was found to possess a theoretical detonation pressure of 25.1 GPa, 25 % higher than TNT, while exhibiting good sensitivity values to impact, friction and electrostatic discharge.



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