

Bis(1,2,4-oxadiazole)bis(methylene) Dinitrate: A High-Energy Melt-Castable Explosive and Energetic Propellant Plasticizing Ingredient

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Supporting Information

ABSTRACT: Discussed herein is the synthesis of bis-(1,2,4-oxadiazole)bis(methylene) dinitrate, determination of its crystal structure by X-ray diffractometry, calculations of its explosive performance, and sensitivity measurements. Steps taken to optimize the synthesis process and to improve yields of the dinitrate are also discussed. Bis(1,2,4-oxadiazole)bis(methylene) dinitrate has a calculated detonation pressure 50% higher than that of TNT. The dinitrate compound exhibits a relatively high decomposition temperature that is rarely observed for nitrate-based compounds. The dinitrate was found to have lower sensitivities to impact and friction compared with RDX. It is believed that intramolecular hydrogen bonding observed in the crystal lattice assists in the relatively high thermal stability and relatively low sensitivity of the material.

INTRODUCTION

The development of high-energy-density materials (HEDMs)¹ with excellent performance and reasonable sensitivity is an overarching goal in the field of energetic materials. High-energy-density melt-castable explosives are a particularly challenging area in which to attain this goal. Melt-cast explosives are sought because they allow for scalable and efficient manufacturing processes. However, these materials must also possess specific unique properties, which significantly narrows the range of new target materials that can be pursued.

For example, although a melt-cast material can have a melting point between 70 and 120 °C², a melting point below 100 °C is ideal. This allows steam heating to be used at ambient pressure in casting operations, which can dramatically reduce costs in manufacturing. Other meaningful properties of a melt-castable explosive include low vapor pressure, a significant difference between the melting temperature and the decomposition temperature, high density, low sensitivity, and “green” and affordable synthesis.² Traditional state-of-the-art melt-castable explosives have been TNT-based.³ However, TNT has fallen out of favor in the energetics community because of toxicity and environmental concerns. TNT is listed as a possible human carcinogen, and prolonged exposure to TNT may result in anemia and abnormal liver function.⁴

As a stand-alone ingredient, TNT suffers from a relatively high vapor pressure,⁵ is susceptible to photolytic degradation,⁶

and is sensitive to reactions in an alkaline environment.⁷ Also concerning is the generation of red water and pink water, two types of wastewater that are generated from the TNT manufacturing process, which find their ways into the waste stream.⁸ Red water is waste generated during the TNT purification process (sulfitation). It is characterized by its alkaline pH of 8 and consists of a complex mixture of nitroaromatics and inorganic salts. Pink water is wash water from the TNT finishing process following sulfitation, in which the TNT is dried, flaked, and packaged. Pink water, which is acidic (pH ~3) is typically saturated with the amount of TNT that will dissolve in water and is produced as a result of equipment washing processes following demilitarization or munitions filling operations. The U.S. Environmental Protection Agency has declared TNT a pollutant and has pushed for its removal from military munitions.⁹

The removal of TNT as an explosive ingredient has garnered some success militarily, as it has been replaced with melt-castable eutectic formulations based on dinitroanisole (DNAN).¹⁰ Unfortunately, DNAN has a low density of 1.52 g cm⁻³ and a detonation velocity of only 5670 m s⁻¹, making it a significantly less powerful explosive than TNT (density of 1.65 g cm⁻³ and a detonation velocity of 6900 m s⁻¹).¹¹ Thus, there is an interest in developing higher-performing melt-castable ingredients that are not only more powerful than DNAN but also more powerful than TNT and less environmentally problematic and less toxic to human health.

A plasticizer enhances fluidity or plasticity when added to a formulation. Energetic plasticizers are used to improve physical properties, to act as a fuel, and to improve the overall energy yield of a formulation. In designing an optimal plasticizer, understanding how chemical functional groups (e.g., alkyl substituents) affect physical properties (melting, onset of decomposition, and safety) of candidate materials becomes imperative.^{12–16} A successful energetic plasticizer must possess a good density, reasonable sensitivity, low chemical reactivity, and high thermal stability as one approaches oxygen-balanced materials.

Previously investigated materials based on *N*-nitroxyalkyl- and *N*-azidoalkyl-substituted nitro-based heterocycles^{16–19} have been found to suffer from stability issues due to the inherent

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reactivity of the electrophilic ring. To mitigate the aforementioned safety concerns, the development of materials with heterocyclic Lewis basic character toward electrophilic energetic materials such as nitrocellulose (NC) and nitramines is desired. Inclusion of alkyl nitrate pendant chains within these materials is important to ensure high miscibility with commonly used energetic plasticizers. These materials may possess better wetting and plasticization properties by allowing for softer boundaries at material interfaces. A softer boundary reduces the tendency to crack at the propellant grain–liner interface.

RESULTS AND DISCUSSION

Recently, the bis(isoxazole) ring system was potentially found to offer tandem melt-castability and energetic propellant plasticization properties. In particular, the recently synthesized bis(isoxazole)bis(methylene) dinitrate²⁰ was found to exhibit a melting point of 96.2 °C, thermal onset of decomposition at 192.7 °C, and performance slightly lower than that of TNT (Figure 1). In an effort to further improve the energetic output

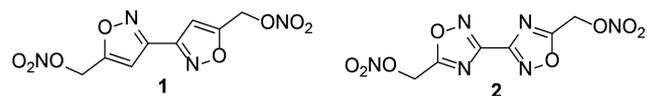


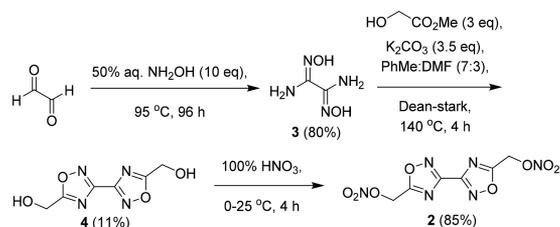
Figure 1. Molecular structures of bis(isoxazole)bis(methylene) dinitrate (1) and bis(1,2,4-oxadiazole)bis(methylene) dinitrate (2).

and oxygen balance, attention was turned toward the bis(1,2,4-oxadiazole) ring system (Figure 1). Overall, it was reasoned that the presence of more nitrogen and less carbon should lead to a higher heat of formation and a higher density, thus resulting in a higher-performing energetic material. Thus, we decided to pursue the synthesis of dinitrate 2.

The synthesis of 2 initially commenced with condensation of glyoxal with 50% aqueous hydroxylamine to afford diamino-glyoxime (DAG, 3).²¹ Use of an all-aqueous system when preparing DAG as opposed to the use of a hydroxyammonium chloride/NaOH system was found to dramatically reduce the exothermic nature of the reaction profile.²¹ Treatment of DAG with methyl glycolate in the presence of base at high temperature, analogous to the conditions described by Amarasinghe,²² afforded bis(1,2,4-oxadiazole) 4, albeit in a very low yield of 7%. It was found in subsequent experiments that the yield could be improved to 11% if a solution of DAG in DMF/toluene was added over the course of 4 h. Nitration of 4 with 100% HNO₃ yielded 2 in 85% yield. While the synthesis route was only three steps, 2 was obtained in just a 7.5% overall yield.

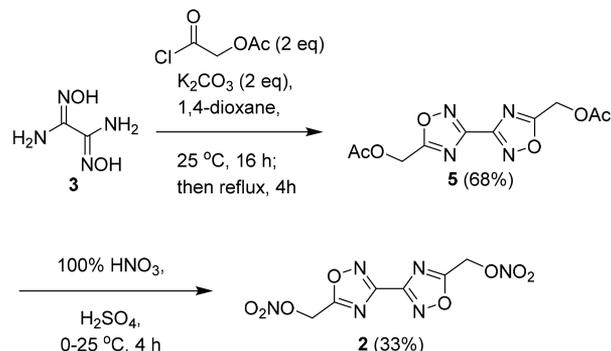
The first and third steps the synthesis in Scheme 1 were deemed acceptable, so efforts were undertaken to optimize the yield of the double cyclization reaction. Dropwise addition of

Scheme 1. First-Generation Synthesis of Bis(1,2,4-oxadiazole)bis(methylene) Dinitrate (2)



acetoxyacetyl chloride to a suspension of 3 and K₂CO₃ in 1,4-dioxane at room temperature followed by stirring overnight afforded the presumed bis(O-acyl) intermediate, which underwent double cyclization at the refluxing temperature to yield bis(1,2,4-oxadiazole) 5 (Scheme 2). The yield of the cyclization

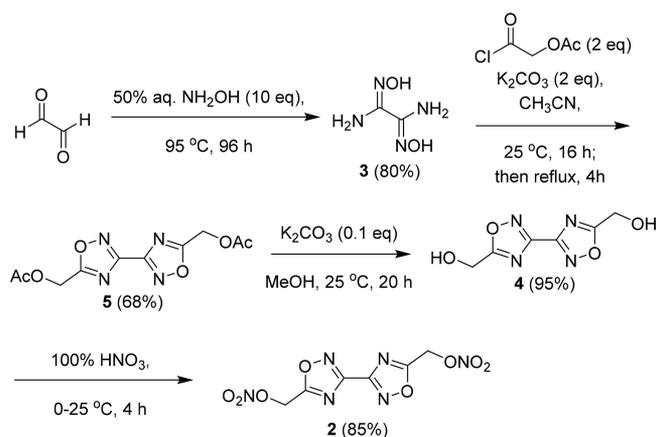
Scheme 2. Second-Generation Synthesis of 2



reaction was a much improved 68%. Attempted nitrolysis of the acetate groups with 100% HNO₃ and 100% HNO₃/Ac₂O afforded no product, and only starting material was recovered. Subjecting 5 to mixed acid conditions did afford 2, thus demonstrating that nitrolysis could be achieved. Unfortunately, the yield was only 33% for this transformation, and the reaction was significantly exothermic. The high exothermicity and low yield of the nitrolysis reaction were deemed unacceptable from a safety and scale-up standpoint. Thus, there was still room for optimization regarding both the yield and safety profile of the process.

The optimized synthesis of 2 is summarized in Scheme 3. Because of the toxicity profile of 1,4-dioxane, it was replaced

Scheme 3. Optimized Synthesis of 2



with the more environmentally acceptable acetonitrile. Even though the refluxing temperature of acetonitrile (82 °C) is lower than that of 1,4-dioxane (102 °C), cyclization still proceeded uneventfully to furnish 5 in an identical yield of 68%. The acetate moieties were easily cleaved in the presence of catalytic K₂CO₃ in MeOH to give 4, which was nitrated uneventfully to yield 2. Although the synthesis sequence in Scheme 3 adds an additional step, it is inherently safer and significantly higher-yielding, as 2 was obtained in an overall yield of 44%, allowing 25 g scale reactions to be performed multiple times without incident. It is important to mention that

while the nitrolysis of **5** to give **2** is highly exothermic, the nitration of **4** yields **2** without an exothermic event, even when 20 g of **4** is added in one portion to cold 100% HNO₃ with stirring.

The physical properties and calculated explosive performance of **2** are provided in Table 1.^{2,3} **2** is CO oxygen-balanced and

Table 1. Calculated Physical Properties of **2 Compared with Those of TNT and Composition B**

data category	2	TNT	Composition B
T_m [°C] ^a	84.5	80.4	78.0–80.0
T_{dec} [°C] ^b	183.4	295.0	200.0
Ω_{CO_2} [%] ^c	–33.3	–74.0	–
Ω_{CO} [%] ^d	0	–24.7	–
ρ [g cm ^{–3}] ^e	1.832	1.65	1.68–1.74
P_{cj} [GPa] ^f	29.4	20.5	26.0–28.0
V_{det} [m s ^{–1}] ^g	8180	6950	7800–8000
I_{sp} [s] ^h	236.0	–	–
$\Delta_f H^\circ$ [kJ mol ^{–1}] ⁱ	–79.4	–59.3	–

^a T_m = onset temperature of melting. ^b T_{dec} = onset temperature of decomposition. ^c Ω_{CO_2} = CO₂ oxygen balance. ^d Ω_{CO} = CO oxygen balance. ^e ρ = derived density from X-ray data. ^f P_{cj} = detonation pressure. ^g V_{det} = detonation velocity. ^h I_{sp} = specific impulse. ⁱ $\Delta_f H^\circ$ = molar enthalpy of formation.

has a melting point of 84.5 °C and a thermal onset of decomposition at 183.4 °C. Thus, **2** can be classified as a potential stand-alone melt-castable explosive material. **2** outperforms TNT in many categories by a wide margin, which is significant since the latter material is considered the benchmark for melt-castable explosives. The experimental density and theoretical detonation velocity of **2** are significantly higher than those of TNT, with a theoretical detonation pressure ca. 50% higher than that of TNT, even surpassing the performance of Composition B, a high-performance melt-castable formulation. The 1,2,4-oxadiazole moieties possess weak Lewis basic character as well as maximum pendant alkyl nitrate functionality. Hence, this material may also serve as an energetic plasticizer in nitrate-based formulations, potentially reducing volatility and migration during thermal and mechanical shock events.

The sensitivities of **2** toward impact, friction, and electrostatic discharge (ESD) were determined and compared with those of the commonly handled and processed explosive RDX (Table 2). **2** was found to exhibit lower sensitivities to impact

Table 2. Sensitivities of **2 Compared with Those of RDX**

compound	IS ^a	FS ^b	ESDS ^c
RDX	6.2	156	0.125
2	8.7	282	0.125

^aIS = impact sensitivity. ^bFS = friction sensitivity. ^cESDS = electrostatic discharge sensitivity.

and friction and an identical ESD sensitivity compared to RDX and is therefore deemed to be a relatively safe material to handle. The relatively low sensitivities of **2** to impact and friction are noteworthy since there is a common belief among many in the energetic materials community that nitrate-based materials possess high sensitivities to impact and friction.

Single-crystal X-ray diffractometry was used to unequivocally identify **2**, confirm its structure, provide an experimentally

determined density, and reveal its key intra- and intermolecular interactions (Figure 2). There are no unusual bond lengths or

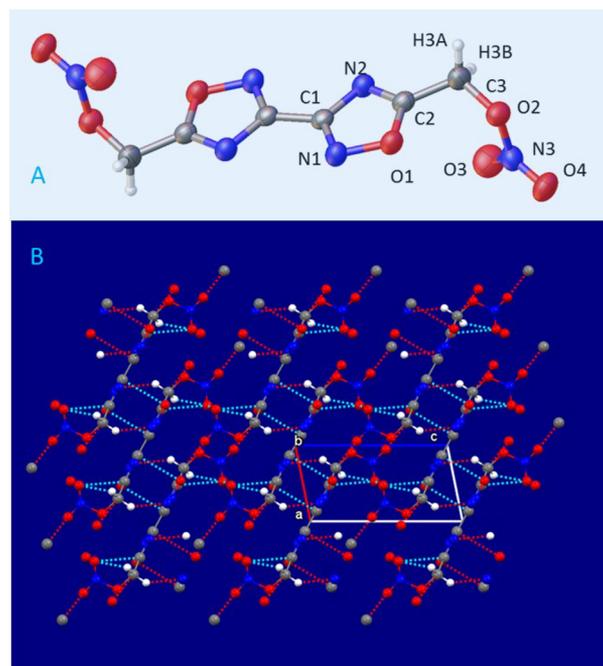


Figure 2. (A) Molecular conformation of compound **2**. The non-hydrogen atoms are shown as 50% probability displacement ellipsoids. The nonlabeled atoms result from inverting the asymmetric unit ($-x$, $-y + 1$, $-z + 2$). (B) Crystal packing viewed along the b axis. Dashed blue lines represent intramolecular interactions, whereas dashed red lines represent intermolecular contacts, including H3A...N2 and O3...O3.

angles. The 1,2,4-oxadiazole rings are planar (root-mean-square deviation = 0.0021(2) Å) and the alkyl nitrate groups adopt a trans configuration with respect to the rings. The C3 atom is nearly coplanar with the ring (atom-to-mean plane distance = 0.03 Å), whereas the C3–O2 bond is twisted slightly out of the plane, as evidenced by the torsion angles O1–C2–C3–O2 = $-21.8(3)^\circ$ and N2–C2–C3–O2 = $162.8(2)^\circ$. The dihedral angle between the oxadiazole ring and the nitrate group is $83.5(1)^\circ$. Bifurcated intramolecular contacts between the O3 atoms and the H3B and C2 atoms [O3...H3B = 2.360(2) Å; O3...C2 = 2.856(3) Å] contribute to its stability, whereas van der Waals contacts between the H3A and N2 atoms on adjacent molecules [H3A...N2ⁱ = 2.562(1) Å; symmetry code (i): $-x + 1$, $-y$, $z - 2$] and between the O3 and O3 atoms on adjacent molecules [O3...O3ⁱⁱ = 3.025(1) Å; symmetry code (ii): $-x + 1$, $-y + 1$, $-z + 1$] dominate its intermolecular interactions. In the crystal lattice, the oxadiazoles are arranged face-up in rows [centroid-to-centroid distance = 6.028(1) Å, plane-to-plane shift = 6.025(2) Å], forming planes parallel to the b axis. The rings are stacked along the a axis with some in close proximity [centroid-to-centroid distance = 3.444(2) Å; plane-to-plane shift = 1.5542(3) Å] (see Figure 2B).

The diffraction patterns of **2** are consistent with its being a member the triclinic crystal system ($P\bar{1}$) with one molecule in its unit cell. On the basis of its molecular mass and lattice constants [$a = 4.8405(4)$ Å, $b = 6.0293(4)$ Å, $c = 9.4356(7)$ Å, $\alpha = 80.399(6)^\circ$, $\beta = 77.125(7)^\circ$, and $\gamma = 78.831(6)^\circ$], we obtain a density of 1.832 g cm^{–3} at 295.9 (1) K.

CONCLUSIONS

In summary, an efficient, scalable route to bis(1,2,4-oxadiazole)-bis(methylene) dinitrate (**2**) has been developed, its crystal structure has been determined, and its explosive performance and sensitivity have been evaluated. The four-step synthesis affords **2** in an overall yield of 44%. **2** was found to have a low sensitivity to impact, friction, and ESD, and it was estimated to have energy in excess of that of Composition B and a detonation pressure 50% higher than that of TNT. The characteristics and performance properties of **2** suggest that this material has high potential to serve as a powerful stand-alone melt-castable explosive material as well as an energetic plasticizing ingredient with nitrocellulose-based propellant formulations in an effort to reduce the volatility/migration issues that arise during cookoff.

EXPERIMENTAL SECTION

General Methods. Chemicals and solvents were used as received from Sigma-Aldrich. Diaminoglyoxime (**3**) was synthesized according to the literature.²¹ ¹H and ¹³C NMR spectra were recorded using an Anasazi 90 MHz instrument. The chemical shifts quoted in parts per million in the text refer to typical standard tetramethylsilane in CDCl₃ 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 studies were performed with a SuperNova Dualflex diffractometer containing an EosS2 charge-coupled device detector and a Mo K α radiation source ($\lambda = 0.71073$ Å).

Caution! Although we did not experience any problems handling the compounds described in this paper, when handling energetic materials such as **3** and **2**, 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.

[3,3'-Bis(1,2,4-oxadiazole)]-5,5'-diylbis(methylene) Diacetate (5**).** To a 2 L round-bottom flask equipped with a stir bar were sequentially added 1 L of acetonitrile, **3** (15.0 g, 0.127 mol, 1.00 equiv), and K₂CO₃ (35.1 g, 0.254 mol, 2.00 equiv). The flask was fitted with a pressure-equalizing liquid addition funnel, and a solution of acetoxyacetyl chloride (35.4 g, 27.9 mL, 0.254 mol, 2.00 equiv) in 200 mL of CH₃CN was added dropwise over 2 h. The reaction mixture was stirred overnight at ambient temperature, and the flask was then fitted with a reflux condenser. The reaction mixture was heated to reflux, stirred for 4 h, and then cooled to room temperature. The solid was collected by Büchner filtration and discarded. The mother liquor was transferred to a 2 L round-bottom flask and concentrated in vacuo to afford a crude solid. The crude solid was purified by trituration with 500 mL of H₂O. The solid was collected by Büchner filtration and oven-dried at 60 °C overnight to afford 24.4 g of bis(1,2,4-oxadiazole) **5** (68% yield) as a white powder. $T_{\text{melt}} = 107.5$ °C; ¹H NMR (90 MHz, DMSO-*d*₆) δ 5.53 (s, 4H), 2.18 (s, 6H); ¹³C NMR (90 MHz, DMSO-*d*₆) δ 176.91, 169.84, 159.37, 56.45, 20.09; IR (neat) cm⁻¹ 1745.23 (s), 1577.13 (m), 1208.08 (s).

[3,3'-Bis(1,2,4-oxadiazole)]-5,5'-diylmethanol (4**).** To a 250 mL round-bottom flask equipped with a stir bar were sequentially added 50 mL of MeOH, **5** (24.0 g, 85.1 mmol, 1.00 equiv), and K₂CO₃ (1.18 g, 8.51 mmol, 0.100

equiv). The reaction mixture was stirred at ambient temperature for 48 h and then concentrated in vacuo to give a crude solid, which was purified by trituration with 200 mL of H₂O. The solid was collected by Büchner filtration and oven-dried at 60 °C overnight to afford 16.0 g of diol **4** (95% yield) as a white powder. $T_{\text{melt}} = 197.8$ °C; $T_{\text{dec}} = 231.5$ °C (onset), 278.2 °C (peak); ¹H NMR (90 MHz, DMSO-*d*₆) δ 6.16 (s, 2H), 4.87 (s, 4H); ¹³C NMR (90 MHz, DMSO-*d*₆) δ 178.50, 156.94, 52.74; IR (neat) cm⁻¹ 3339.57 (w), 1575.77 (m), 1431.04 (m), 1202.56 (m), 1081.27 (s).

[3,3'-Bis(1,2,4-oxadiazole)]-5,5'-diylbis(methylene) Dinitrate (2**).** To a 250 mL round-bottom flask immersed in an ice bath was added 100 mL of 100% HNO₃. After the nitric acid was chilled to 0 °C, diol **4** (20.0 g, 101.0 mmol, 1.00 equiv) was added in four equal portions over 1 h. 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 1 h, the solid was collected by Büchner filtration and air-dried in a well-ventilated fume hood to afford 24.7 g of dinitrate **2** (85% yield) as a white powder. $T_{\text{melt}} = 84.5$ °C; $T_{\text{dec}} = 183.4$ °C (onset), 214.6 °C (peak); ¹H NMR (90 MHz, DMSO-*d*₆) δ 6.16 (s, 4H); ¹³C NMR (90 MHz, DMSO-*d*₆) δ 175.48, 159.43, 64.26; IR (neat) cm⁻¹ 2950.51 (w), 1653.16 (s), 1574.20 (m), 1415.61 (m), 1350.42 (m), 1282.23 (s), 1212.83 (s), 1059.18 (m).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.8b00076.

Experimental procedures and analytical data for all new compounds (¹H, ¹³C NMR, and FT-IR spectra and DSC traces for compounds **2**, **4**, and **5**) and X-ray crystallographic data for compound **2** (PDF)

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Notes

The authors declare no competing financial interest.

The CIF file for compound **2** can be obtained from the Cambridge Crystallographic Data Centre (deposit@ccdc.cam.ac.uk) free of charge, quoting the CCDC reference number 1819160.

■ ABBREVIATIONS

TNT = trinitrotoluene; DNAN = dinitroanisole; RDX = royal demolition explosive

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