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Bis-1,2,4-Oxadiazole-bis-Methylene Dinitrate: A High-Energy Melt-Castable Explosive and Energetic Propellant Plasticizing Ingredient

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ABSTRACT: Based on environmental and performance factors, there is a strong need for new melt-castable explosives to serve as higher-energy replacements for dinitroanisole (DNAN) and trinitrotoluene (TNT), as well as a need for new energetic plasticizers to improve the range of double-base rocket propellants. 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. This material is unique in that it has both melt-castable explosive and energetic plasticizing potential, with a calculated detonation pressure in excess of Composition B. Bis-1,2,4-oxadiazole-bis-methylene dinitrate has a calculated detonation pressure 50% higher than TNT; the latter of which considered to be the benchmark of melt-castable explosives. 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 as compared to 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.

Keywords: Energetic Materials, Explosives, Propellants, Heterocycles, Process Chemistry, Synthesis

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 is a particularly challenging area in which to attain this goal. Melt cast explosives are sought after because they allow for scalable and efficient manufacturing processes. But 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 70–120 °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 a low vapor pressure, a significant difference between the melting temperature and the

decomposition temperature, a high density, a low sensitivity, as well as a “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 due to 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 standalone ingredient, TNT suffers from a relatively high vapor pressure⁵, is susceptible to photolytic degradation⁶, 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 US 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 gcm⁻³ and a detonation velocity of only 5670 ms⁻¹, making it a significantly less powerful explosive than TNT (density of 1.65 gcm⁻³ and a detonation velocity of 6900 ms⁻¹).¹¹ Thus, there is an interest in developing higher performing melt-castable ingredients that are not only more powerful than DNAN, but that are also more powerful than TNT and less environmentally problematic and less toxic to human health.

A plasticizer, when added to a formulation, enhances fluidity or plasticity. 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 imperative¹²⁻¹⁶. A successful energetic plasticizer must possess a good density, reasonable sensitivity, low

chemical reactivity, and a high thermal stability as one approaches oxygen balanced materials.

Previously investigated materials based on nitroxyalkyl- and azidoalkyl-*N*-substituted nitro-based heterocycles¹⁶⁻¹⁹ have been found to suffer from stability issues due to the inherent reactivity of the electrophilic ring. To mitigate the aforementioned safety concerns, development of materials with heterocyclic Lewis basic character towards 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 of cracking at the propellant grain/liner interface.

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

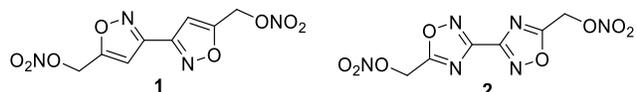
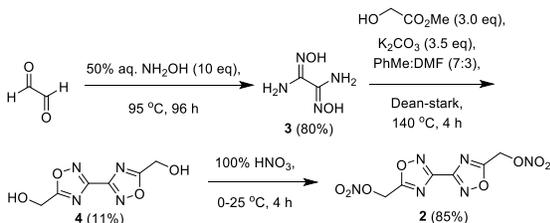


Figure 1. Molecular structures of *bis*-isoxazole-*bis*-methylene dinitrate (**1**) and *bis*-1,2,4-oxadiazole-*bis*-methylene dinitrate (**2**).

The synthesis of **2** initially commenced with condensation of glyoxal with 50% aqueous hydroxylamine to afford diaminoglyoxime (DAG, **3**).²¹ Treatment of DAG with methyl glycolate in the presence of base at high temperature analogous to the conditions described by Amarasinghe²² 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 (11%) if a solution of DAG in DMF/toluene was added over the course of 4 hours. 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% yield overall.

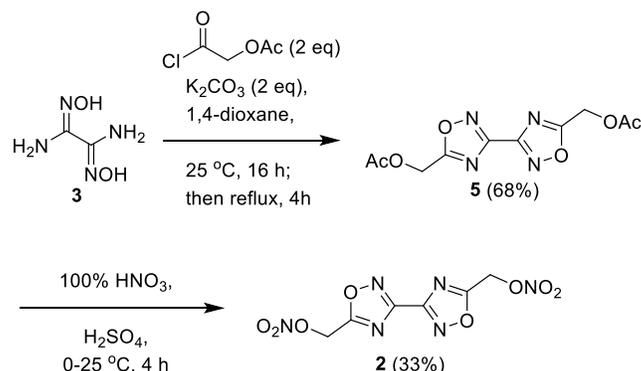
Scheme 1. First generation synthesis of *bis*-1,2,4-oxadiazole-*bis*-methylene dinitrate (**2**).



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 acetoxyacetyl chloride to a suspension of **3** and

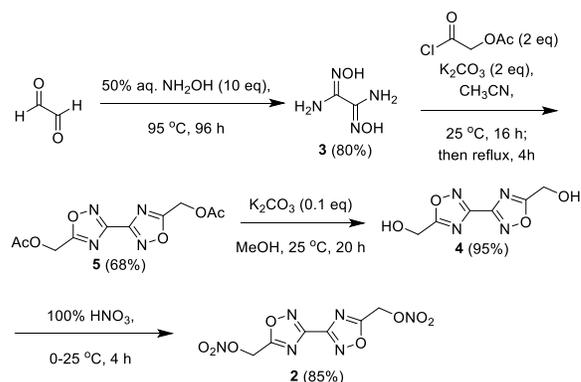
K₂CO₃ in 1,4-dioxane at room temperature, followed by stirring overnight afforded the presumed *bis*-O-acyl intermediate, which underwent cyclization at the refluxing temperature to yield *bis*-1,2,4-oxadiazole **5**. The yield of the cyclization reaction was a much improved 68%. Attempted nitrolysis of the acetate groups with 100% HNO₃ and 100% HNO₃/Ac₂O afforded no product, and only starting material was recovered. Subjection of **5** to mixed acid conditions did afford **2**, thus demonstrating that nitrolysis could be achieved. Unfortunately, the reaction was highly exothermic and the yield was only 33% for this transformation. Thus, the process detailed in Scheme 2 afforded **2** in an overall yield of 21.1%. While this was an improvement, there was still room for optimization regarding both the yield and safety profile of the process.

Scheme 2. Second generation synthesis of *bis*-oxadiazole-*bis*-methylene dinitrate (**2**).



The optimized synthesis is summarized in Scheme 3. Because of the toxicity profile of 1,4-dioxane, it was replaced with acetonitrile. Even though the refluxing temperature of acetonitrile (82 °C) is lower than 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 in a non-exothermic fashion to yield **2**. Although the synthesis sequence in Scheme 3 adds an additional step, it is inherently safer, and is significantly higher yielding, as **2** was obtained in an overall yield of 44%, allowing 25-gram scale reactions to be performed multiple times without incident.

Scheme 3. Optimized synthesis of *bis*-oxadiazole-*bis*-methylene dinitrate (**2**).



The physical properties and explosive performance of **2** are provided in Table 1. **2** is CO oxygen balanced, has a melting point of 84.5 °C and a thermal onset of decomposition of 183.4 °C. Thus, **2** can be classified as a potential standalone 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** is significantly higher than TNT, with a theoretical detonation pressure ca. 50% higher than TNT, even surpassing the performance of Composition B, a high performance melt-castable formulation. The 1,2,4-oxadiazole moiety possesses weak Lewis basic character, while also possessing 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.

Table 1. Physical properties and performance of **2** compared to 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 [gcm ⁻³] ^[e]	1.832	1.65	1.68-1.74
P_{ej} [GPa] ^[f]	29.4	20.5	26.0-28.0
V_{det} [ms ⁻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 melting; [c] Ω_{CO_2} = CO₂ oxygen balance; [d] Ω_{CO} = CO oxygen balance; [e] ρ = derived density from X-ray data; [f] P_{ej} = detonation pressure; [g] V_{det} = detonation velocity; [h] I_{sp} = specific impulse; [i] $\Delta_f H^\circ$ = molar enthalpy of formation.

The sensitivity of **2** toward impact, friction, and electrostatic discharge (ESD) were determined and compared to the commonly handled and processed explosive RDX (Table 2). **2** was found to exhibit lower sensitivities to impact and friction, with an identical ESD sensitivity compared to RDX, and has therefore been deemed as a relatively safe material handle. The relatively low sensitivities of **2** to impact and friction are noteworthy since there is a commonly belief amongst many in the energetic materials community that nitrate-based materials possess high sensitivities to impact and friction.

Table 2. Sensitivities of **2** as compared to RDX.

Compound	IS ^a	FS ^b	ESD ^c
RDX	6.2	156	0.125
2	8.7	282	0.125

[a] IS = impact sensitivity; [b] FS = friction sensitivity; [c] ESD = electrostatic discharge sensitivity

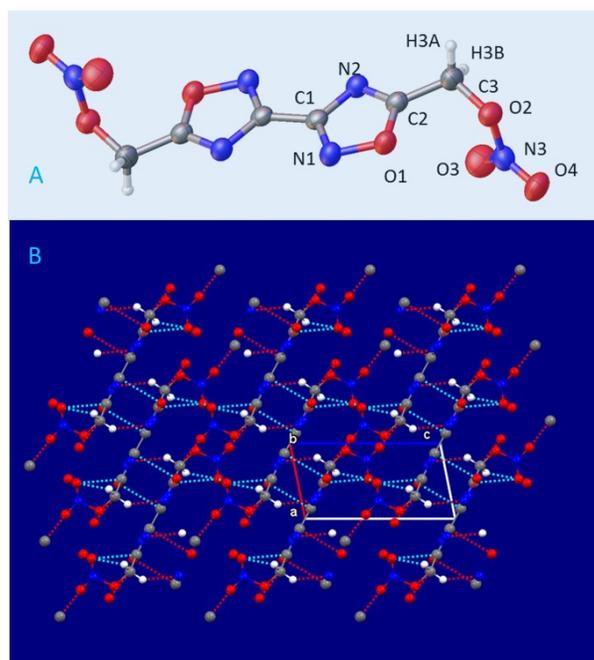


Figure 2. (A): Molecular conformation of compounds **2**, showing the non-hydrogen atoms as 50% probability displacement ellipsoids. The non-labeled atoms result from inverting the asymmetric unit (-x, -y+1, -z+2); and (B): crystal packing viewed along the *b* axis. Dashed blue lines represent intramolecular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

Single crystal X-ray diffractometry was used to unequivocally identify **2**, confirm its structure, and to reveal its key intra- and intermolecular interactions (Figure 2). The 1,2,4-oxadiazole rings adopt a near planar configuration (r.m.s deviation = 0.0021 (2) Å) with *trans* alkyl nitrate groups. 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)° and N2—C2—C3—O2 = 162.8 (2)°. The dihedral angle between the oxadiazole ring and the nitrate group is 69.58 (9)°. Bifurcated intramolecular contacts between the O3 atoms and the H3A and C2 atoms [O3⋯H3A = 2.360 (2) Å; O3⋯C2 = 2.856 (3) Å] contribute to its stability, whereas van der Waals contacts between the H3A atoms 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 (x) Å; symmetry code (ii): -x+1, -y+1, -z +1] dominate its intermolecular interactions. In the crystal lattice, the oxadiazole 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 it being a member the triclinic crystal system (P-1) with one molecule in its unit cell. Based on its molecular mass and the following lattice constants: *a* (Å) = 4.8405 (4), *b* (Å) = 6.0293 (4), *c* (Å) = 9.4356 (7), α /° = 80.399 (6), β /° = 77.125 (7), and γ /° = 78.831 (6), we obtain a density of 1.832 g/cc at 295.9 (1) K.

In summary, an efficient, scalable route to *bis*-1,2,4-oxadiazole-*bis*-methylene dinitrate (**2**) has been developed,

its crystal structure determined, and its explosive performance and sensitivity evaluated. It features a four step synthesis in an overall yield of 44%. **2** was found to have a low sensitivity to impact, friction and ESD, and was estimated to have energy in excess of Composition B, with a detonation pressure 50% higher than TNT. The characteristics and performance properties of **2** suggest that this material has high potential to serve as a powerful standalone 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 cook-off.

EXPERIMENTAL

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 ppm 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 (XRD) studies were performed with a SuperNova Dualflex diffractometer containing an EosS2 charge-coupled device detector and a molybdenum Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation source.

*Caution! Although we did not experience any problems handling the compounds described in this paper, when handling energetic materials such as diaminoglyoxime (**3**) and dinitrate **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'-bi(1,2,4-oxadiazole)]-5,5'-diylbis(methylene) diacetate (5**)**. To a 2 L round-bottom flask equipped with a stir bar was sequentially added 1 L of acetonitrile, diaminoglyoxime (**3**) (15.0 g, 0.127 mol, 1.00 eq), and K₂CO₃ (35.1 g, 0.254 mol, 2.00 eq). 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 eq) in 200 mL of CH₃CN was added dropwise over 2 h. The reaction mixture was stirred overnight at ambient temperature, the flask was then fitted with a reflux condenser. The reaction mixture was heated to reflux, stirred 4 h, and was then cooled to room temperature. The solid was collected by Büchner filtration and was discarded. The mother liquor was transferred to a 2 L round-bottom flask and was 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 was oven-dried at 60 °C overnight to afford 24.4 g of bis-1,2,4-oxadiazole **5** (68%) as a white powder; T_{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'-bi(1,2,4-oxadiazole)]-5,5'-diyldimethanol (**4**)**. To a 250 mL round-bottom flask equipped with a stir bar was sequentially added 50 mL of MeOH, diacetate **5** (24.0 g, 85.1 mmol, 1.00 eq), and K₂CO₃ (1.18 g, 8.51 mmol, 0.100 eq). The reaction mixture was stirred at ambient temperature for 48 h, and concentrated *in vacuo* to give a crude solid. The crude solid was purified by trituration with 200 mL of H₂O.

The solid was collected by Büchner filtration, and was oven-dried at 60 °C overnight to afford 16.0 g of diol **4** (95%) as a white powder; T_{melt} = 197.8 °C; T_{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'-bi(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 eq) was added in four equal portions over 1 hour. 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 was air dried in a well-ventilated fume hood to afford 24.7 g of dinitrate **2** (85%) as a white powder; T_{melt} = 84.5 °C; T_{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).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

TNT = Trinitrotoluene; DNAN = Dinitroanisole; RDX = Royal Demolition Explosive

ASSOCIATED CONTENT

Supporting information:

The supporting Information is available free of charge on the ACS Publication Website at DOI: xxxx.

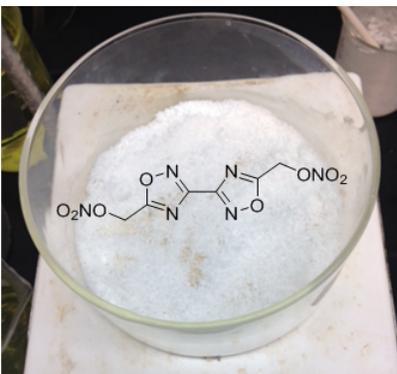
Experimental procedures and analytical data for all new compounds (¹H, ¹³C NMR, FT-IR, and DSC traces for compounds **2**, **4** and **5**. X-ray crystallographic data of compound **2** found in the SI pdf (CIF). The CIF file of compound **2** can also be obtained from the Cambridge Crystallographic Data Centre (deposit@ccdc.cam.ac.uk) free of charge quoting the CCDC reference number 1819160.

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TOC Graphic-



- Melt-Castable Explosive
 - 50% Better Performance than TNT
 - Energetic Propellant Plasticizer
 - 4 steps, 44% overall yield, 25 g scale
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