



# **FULL PAPER**

# A Halogen-Free Green High Energy Density Oxidizer from H-FOX

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**Abstract:** Reaction of H-FOX (1-hydrazinyl-2,2-dinitroethenamine) with 2,2,2-trinitroethanol resulted in an unexpected compound, 1,1'methylenebis(3-(2,2,2-trinitroethyl)urea) (**5**), which when treated with acetic anhydride and 100% nitric acid gave an N-NO<sub>2</sub> derivative, 1,1'methylenebis(1-nitro-3-(2,2,2-trinitroethyl)urea) (**6**) in good yield. Compound **6** exhibits a good oxygen balance (+20.4%), density (d = 1.87 g/cm<sup>3</sup>) and excellent detonation performance (vD = 8910 m/s; P = 35.8 GPa) as well as acceptable stability and sensitivity, which suggests it as an attractive replacement for ammonium perchlorate (AP).

#### Introduction

Most secondary explosives require an additional external oxygen source for complete oxidation of the hydrocarbon (fuel) portion. Ammonium perchlorate (AP) is the usual choice as a stable oxidizer in advanced explosions as well as for propellants for rockets and missiles,<sup>[1,2]</sup> but several problems are associated with AP, including release of perchlorate anion into groundwater giving rise to significant health concerns;<sup>[2,3]</sup> formation of hydrogen chloride during burning that contributes to acid rain and ozone depletion, and of chlorine that causes a white smoke that can be detected readily by radar.<sup>[4]</sup> Perchlorate-free replacements for AP are ammonium dinitramide (ADN) and hydrazinium nitroformate (HNF), but they also suffer from various drawbacks such as high sensitivity, low thermal stability, and hygroscopicity.<sup>[5,6]</sup> As a result, there remains a great need for green chlorine/perchlorate-free oxidizers with reduced sensitivity, improved thermal stability, and reduced environmental impact.<sup>[1,2]</sup>

Cyclic and acyclic polynitro compounds based on trinitromethyl and fluorodinitromethyl moieties are among the most likely materials as high energy density oxidizers (HEDOs).<sup>[7]</sup> 1,1-Diamino-2,2-dinitroethene (FOX-7) is a promising energetic material having an ideal combination of high energy content and excellent thermal stability and insensitivity towards impact and

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friction. Earlier, our group synthesized a highly promising HEDO, tetranitroacetimidic acid (TNAA) with an excellent oxygen balance (+30%). However practical application is limited because of low decomposition temperature (137 °C) and sensitivity towards friction (20 N).<sup>[2a]</sup> Replacement of the trinitromethyl group with the trinitroethyl moiety may result in compounds with improved thermal stability and sensitivity because of the additional CH<sub>2</sub> group. There are already a few known HEDOs that contain the trinitroethyl moiety but most are based on cyclic nitrogen rich heterocycles.<sup>[8]</sup>

Over the past several years, our group has synthesized several stable hypergolic oxidizers and energetic materials based on FOX-7 (**3**) and 1-hydrazinyl-2,2-dinitroethenamine (H-FOX) (**4**), which are high-energy materials themselves, but **4** suffers from spontaneous decomposition and sensitivity.<sup>[9]</sup> Now, we report the synthesis of a new promising oxidizing reagent, 1,1'- methylenebis(1-nitro-3-(2,2,2-trinitroethyl)urea) (**6**) by the reaction of trinitroethanol with H-FOX to form 1,1'-methylenebis(3-(2,2,2-trinitroethyl)urea) (**5**) followed by nitration. Compound **6** with good oxygen balance (+20.4%) and energetic performance superior to RDX is a green high energy density oxidizer and a potential replacement of perchlorate-based oxidizers.

#### **Results and Discussion**

H-FOX (4) was prepared by the nitration of 4,6-dihydroxy-2methylpyrimidine 1, followed by hydrolysis to generate FOX-7 (3), that was reacted with hydrazine monohydrate to give H-FOX (4).<sup>[9]</sup> A 1:3 molar ratio reaction of an aqueous solution of H-FOX and trinitroethanol at room temperature resulted in an unexpected compound, 1,1'-methylenebis(3-(2,2,2-trinitroethyl)urea) (5) as a pale yellow solid in 44% yield. Further N-nitration of 5 using acetic anhydride and 100% nitric acid at 0 °C resulted in 1,1'methylenebis(1-nitro-3-(2,2,2-trinitroethyl)urea) (6) as a yellow solid in 61% yield (Scheme 1).

The structure of **5** was confirmed by single crystal X-ray diffraction. Suitable crystals were obtained by slow evaporation of a methanol solution of 5 at room temperature (Fig. 1). It crystallizes in the monoclinic space group P21/c with four molecules per unit cell. The calculated density of 5 is 1.722 g cm<sup>-</sup> <sup>3</sup> at 150 K (Table S1, Supporting Information). The bond length of C10-C11 (1.529 Å) is slightly longer than the C21-C22 (1.513 Å) bond, but C11-N12 and C21-N20 are bonded at slightly shorter distances (1.421, 1.428 Å). The bond lengths of C13-O14 and C18-O19 are 1.231 and 1.228 Å, respectively. This indicates that there is no change in both the carbonyl bond lengths. The bond length of N12-C13 is 1.371 Å while that of N17-C18 is 1.343 Å. It clearly shows that there is a difference in the oxygen attached carbonyl carbon and adjacent NH group bond lengths. The nitro groups bonded to the quaternary carbon atoms are nearly coplanar with the angle between the mean plane through the attached carbon and these groups in the range [N(3)-C(10)-N(9)]

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107.2(4)° and [N(6)-C(10)-N(9)] 109.6(3)°. In the coplanar carbonyl adjacent NH groups, the bond angle is 115.4 (4)°, but the NH adjacent carbonyl and CH<sub>2</sub> group shows [C(13)-N(15)-C(16)] = 121.1(4)°. There are strong hydrogen bond interactions between the NH, CH<sub>2</sub> groups and the trinitro group, and also between the carbonyl and NH groups. The hydrogen bonding interactions are shown in [Fig. 1(b)].

Compounds 5 and 6 were characterized by <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N NMR and infrared spectroscopy, and elemental analysis. The <sup>15</sup>N NMR spectrum was measured for 5 in DMSO-d<sub>6</sub>. A signal assigned to an NH group was not observed in pure DMSO-d<sub>6</sub> but was observed after addition of one drop of D<sub>2</sub>O to the DMSO-d<sub>6</sub> solution. This can be attributed to the rapid exchange of NH protons in **5** with DMSO-d<sub>6</sub>. After the addition of one drop of D<sub>2</sub>O, the NH group is replaced with ND, and the heavier deuterium nuclei slow the exchange process and hence the signals corresponding to ND can be observed at -308 and -310 ppm. Resonances of the trinitromethyl group with an adjacent CH<sub>2</sub> species are triplets at -30.15, -30.11 and -30.07 ppm, respectively. Compound 6 has four nitrogen signals in the <sup>15</sup>N NMR spectrum. Resonances of the trinitromethyl groups and NH peaks are the same as for 5, but the nitro group bonded nitrogen peak  $(N_2)$  appears at -130 ppm and the nitrogen  $(N_3)$  at -33 ppm, respectively (Fig. 2).

Thermal stability is very important for explosive materials. The thermal stabilities of **5** and **6** were determined by differential scanning calorimetric (DSC) measurements. Compounds **5** and **6** (Table 1) decomposed at 199 and 121.5 °C, respectively. The heats of formation and detonation properties (velocity and pressure) are important parameters for newly developed materials. To evaluate the energetic properties, the heats of formation of **5** and **6** were calculated using the Gaussian03 (revision D.01) suite of programs.<sup>[10]</sup> Based on the method of isodesmic reactions (Figure S6, Supporting Information), the gas phase enthalpies of formation were computed. The solid-state heats of formation of these compounds were obtained by subtracting the sublimation enthalpies. The heat of formation of **5** and **6** are -619 kJ mol<sup>-1</sup> and -408 kJ mol<sup>-1</sup>, respectively.

Compounds 5 and 6 have good experimental densities at 1.72 g/cm<sup>3</sup>, and 1.87 g/cm<sup>3</sup> as determined from gas pycnometer measurements (25 °C). Using the values of the calculated heat of formation and measured density, the velocity of detonation (vD) and detonation pressure (P) were calculated via Explo5 v6.01 version.<sup>[11]</sup> Compound 5 has a vD of 8013 m/s and a P of 26.8 Gpa while 6 has a vD of 8910 m/s and a P of 35.8 GPa, respectively. The latter numbers are considerably higher than those of RDX (vD = 8748 m/s, P = 34.9 GPa). The oxygen balance (OB) is a measure of the amount of oxygen available for combustion of an energetic material. Compounds 5 and 6 have positive oxygen balances of OB 7% and 20.43 %, respectively. The combined nitrogen and oxygen content of 5 and 6 are 79.5, and 83% which are significantly better than AP (65%) and comparable to RDX (81.0%) and HMX (81.0%). These values indicate that 5 and 6 may be effective replacements for AP as stable chlorine free green energetic oxidizers.<sup>[7]</sup>



Scheme 1. Synthesis of 1,1'-methylenebis(3-(2,2,2-trinitroethyl)urea) (5) and 1,1'-methylenebis(1,3-dinitro-3-(2,2,2-trinitroethyl)urea) (6)



**Figure 1.** (a) Thermal ellipsoid plot (50%) of compound **5**. (b) Ball-and-stick packing diagram of **5** viewed down the a axis showing network of strong hydrogen bonds (dashed lines).



Figure 2. <sup>15</sup>N NMR spectra of 5 and 6 in DMSO-d<sub>6</sub>/D<sub>2</sub>O.

Specific impulse (Isp) is a crucial parameter which determines the efficiency of a propellant. A propellant having a high specific impulse is more efficient as it produces more thrust per unit of propellant. Compounds **5** and **6** have much higher specific impulse (Isp = 242 s and Isp = 256 s) values than AP (Isp = 157 s) and ADN

(Isp = 202 s), as calculated by EXPLO5 (version 6.01).<sup>[11]</sup> Both of Experimental Section them have acceptable nitrogen content in their backbones. Impact and friction sensitivities were obtained by using a BAM drop hammer apparatus and BAM friction tester. The impact and friction sensitivities of 5 and 6 are 18 J, 3 J, and 260 N, 20N, respectively. Compound 5 has good impact and friction sensitivities relative to AP (IS = 15 J, FS = 360 N) and superior to ADN (IS: = 3-5 J, FS: = 64-72 N) (Table 1). The overall performance of 5 suggests it as a perchlorate-free green high-energy density oxidizer with a positive combination of high detonation performance, specific impulse, low sensitivity and high thermal stability. Additionally, it should be seen that, 5 and 6 show superior energetic performance relative to PETN, and RDX.<sup>[12,7b]</sup>

Table 1. Physical Properties of 5 and 6 in comparison with AP, ADN, PETN, RDX, and HMX

	5	6	AP <sup>a</sup>	<b>ADN</b> <sup>a</sup>	PETN <sup>a</sup>	$\mathbf{RDX}^{\mathrm{b}}$	<b>ΗΜΧ</b> <sub>P</sub>
Tmº (°C)	-	-	-	93	143	-	-
Tdec <sup>d</sup> (°C)	199	121.5	>200	159	160	204	275
IS <sup>e</sup> (J)	18	3	15	3–5	2.9	7.4	7.4
FS <sup>f</sup> (N)	260	20	>360	64-72	92	120	120
Isp(s)	242	256	157	202	265.5	-	10
Nj <sup>g</sup> (%)	30.6	30.7	11.0	52.0	17.7	37.8	37.8
O <sup>h</sup> (%)	49.0	52.5	54.0	45.0	60.7	43.2	43.2
OB <sup>i</sup> (%)	7.0	20.4	26.0	25.7	15.2	0.00	0.00
N+O <sup>j</sup> (%)	79.5	83.0	65.0	97.0	78.4	81.0	81.0
HOF <sup>⊾</sup> (kj mol⁻¹)	-619	-408	-296	-150	-561	80.0	104.8
vD <sup>I</sup> (m/s)	8013	8910	6368	7860	8405	8748	9144
P <sup>m</sup> (Gpa)	26.8	35.8	15.7	23.6	31.9	34.9	39.2
d <sup>n</sup> (g cm <sup>-3</sup> )	1.72	1.87	1.95	1.81	1.78	1.80	1.90

[a] From ref. [7] and [9a]. [b] From ref. [12]. [c] Melting temperature. [d] Decomposition temperature. [e] Impact sensitivity. [f] Friction sensitivity. [g] Nitrogen content. [h] Oxygen content. [i] Oxygen balance (based on CO). [j] Combined nitrogen and oxygen content. [k] Heat of formation. [I] Calculated detonation velocity. [m] Calculated detonation pressure. [n] Density measured by gas pycnometry at 25 °C.

### Conclusions

In summary, the chemical reactivity of H-FOX has been expanded to enable the synthesis and characterization of the new energetic materials 1,1'-methylenebis(3-(2,2,2-trinitroethyl)urea) (5) and 1,1'-methylenebis(1-nitro-3-(2,2,2-trinitroethyl)urea) (6) in good yields resulting from a simple and straightforward synthetic route. Compounds 5 and 6 possess good detonation properties (vD = 8013 m/s, P = 26.8 Gpa and vD = 8910 m/s, P = 35.8 Gpa), respectively. These properties suggest that these molecules could be good replacements for AP as green high-energy density oxidizers and the latter which is superior to RDX as a high-energy density material.

Caution: While we have experienced no difficulties in syntheses and characterization of these materials, proper protective measures should be used. Manipulations must be carried out in a hood behind a safety shield. Face shield and leather gloves must be worn. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials. Special precautions should be utilized with H-FOX since it is known to detonate on standing without warning. It should be synthesized only in small amounts, used immediately upon synthesis and not be stored. Mechanical actions involving scratching or scraping (especially with metal devices) must be avoided for all of the compounds.

#### General methods

Reagents were purchased from Acros Organics and Aldrich as analytical grade and were used as received. 1H and 13C spectra were collected on a Bruker AVANCE 300 nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively. A Bruker AVANCE 500 nuclear magnetic resonance spectrometer operating at 50.69 MHz was used to collect 15N spectra data. DMSO-d6 was employed as a solvent and locking solvent. Chemical shifts are given relative to Me4Si for 1H and \_13C spectra and MeNO2 for 15N NMR. The decomposition point was measured by a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of 5 °C min<sup>-1</sup>. Infrared (IR) spectra were recorded using KBr pellets on a BIORAD model 3000 FTS spectrometer. Densities were measured using a Micromeritics AccuPyc 1330 gas pycnometer at room temperature (25 °C). Elemental analyses (C, H, N) were performed with a Vario Micro cube elemental analyzer. Impact and friction-sensitivity measurements were tested by employing a standard BAM Fallhammer and a BAM friction tester.

1,1-Diamino-2,2-dinitroethene (FOX-7, 3) and 1-hydrazinyl-2,2dinitroethenamine (H-FOX, 4) were synthesized according to literature procedures.<sup>[9]</sup>

1,1'-Methylenebis(3-(2,2,2-trinitroethyl)urea (5). H-FOX, 4 (0.200 g 1.22 mmol) was placed in a 100 mL round-bottomed flask in 10 mL distilled water. 2,2,2-Trinitroethanol<sup>[13]</sup> (0.66 g, 3.68 mmol) was added slowly to the reaction mixture over a period of 10 minutes. After complete addition, the reaction mixture was stirred overnight at room temperature. A pale yellow solid precipitated. The solid was collected, washed with cold water, and dried in air to give a pale yellow powder of pure 5 (0.250 g, 0.54 mmol, 44 %). Td: 198.6 °C. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ 7.34 (2H), 5.08 (4H). <sup>13</sup>C NMR (300 MHz, DMSO-d<sub>6</sub>): δ 156.21, 126.11, 62.21, 43.37. IR (KBr) u 3140, 3118, 1584, 1544, 1531, 1486, 1469, 1373, 1312, 1282, 1270, 1148, 1099, 1089, 1067, 997, 964, 929, 894, 825, 804, 707, 614, 557. 419 cm<sup>-1</sup>. Elemental analysis: (%) calculated for C<sub>7</sub>H<sub>10</sub>N<sub>10</sub>O<sub>14</sub> (458.21): C, 18.35; H, 2.20; N, 30.57; found C, 18.47; H, 1.77; N, 29.33.

1,1'-Methylenebis(1-nitro-3-(2,2,2-trinitroethyl)urea) (6). To a mixture of acetic anhydride (6 mL) and nitric acid (100%, 5.0 mL), 1.1'methylenebis(3-(2,2,2-trinitroethyl)urea (5) (0.500 g, 0.892 mmol) was added at 0 °C. After being stirred for 6 h at room temperature, the reaction mixture was poured into ice water and the precipitate filtered to give a yellow product 6 (0.118 g, 0.54 mmol, 61%). Td: 121.5 °C. <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>): δ 7.31 (2H), 5.06 (4H). <sup>13</sup>C NMR (300 MHz, DMSO-d<sub>6</sub>):  $\delta$  162.94, 151.01, 68.59, 62.17. IR (KBr) u 3393, 3024, 1742, 1597, 1509, 1409, 1384, 1299, 1230, 1185, 1092, 1055, 961, 902, 855, 805, 738, 596, 541, 475 cm<sup>-1</sup>. Elemental analysis: (%) calculated for C7H8N12O18 (548.21): C, 15.34; H, 1.47; N, 30.66; found C, 15.83; H, 1.56; N, 29.59.

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**Keywords:** green energetic oxidizers • density • high energy materials • heat of formation • specific impulse

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### Energetic Oxidizers

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A Halogen-Free Green High Energy Density Oxidizer from H-FOX

Development of new halogen free green energetic oxidizers 1,1'-methylenebis(3-(2,2,2-trinitroethyl)urea) (5) and 1,1'-methylenebis(1-nitro-3-(2,2,2-trinitroethyl)urea) (6) results from sensitive H-FOX (4) in good yields. Both the compounds have high nitrogen and oxygen content and exhibit high densities and good detonation properties.