

Energetic Salts Based on 3,5-Bis(dinitromethyl)-1,2,4-triazole Monoanion and Dianion: Controllable Preparation, Characterization, and High Performance

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Supporting Information

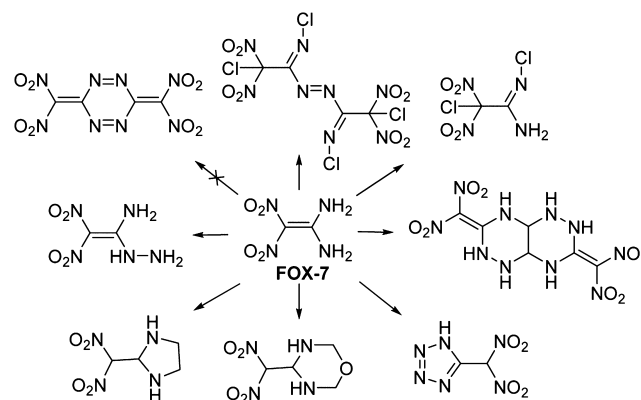
ABSTRACT: Molecular modification of known explosives is considered to be an efficient route to design new energetic materials. A new family of energetic salts based on the 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion and dianion were controllably synthesized by using 1-diamino-2,2-dinitroethene as a precursor. X-ray structure determination of monohydrazinium 3,5-bis(dinitromethyl)-1,2,4-triazolate (**5**) and monoammonium (**6**) and diammonium 3,5-bis(dinitromethyl)-1,2,4-triazolate hydrate (**8**·H₂O) further confirmed the structures of these anions. In addition, as supported by X-ray data, in the monoanion system, the roving proton on the ring nitrogen rather than on the *gem*-dinitro carbon results in extensive hydrogen-bonding interactions and higher packing coefficients. Interestingly, **5** and **6** possess the highest calculated crystal densities, 1.965 and 1.957 g cm⁻³ at 150 K, for hydrazinium and ammonium energetic salts, respectively. Energetic evaluation indicates that **5** (detonation velocity $v_D = 9086 \text{ m s}^{-1}$; detonation pressure $P = 38.7 \text{ GPa}$) and **6** ($v_D, 9271 \text{ m s}^{-1}$; $P = 41.0 \text{ GPa}$) exhibit great detonation properties, superior to those of current highly explosive benchmarks, such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).

Interest in the development of high-energy-density materials (HEDMs) has grown to a very high level.¹ As the most common source of chemical energy, HEDMs play a vital role in pyrotechnic technology, mining engineering, and aerospace exploration. Furthermore, energetic materials are of critical importance in most modern defense systems.² Among the commonly used HEDMs are cyclic nitramine compounds, such as 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), which were designed in the early 20th century.² Therefore, novel energetic materials that are nitrogen-rich and have high energy density, favorable stability, and good environmental compatibility are highly sought.

1,1-Diamino-2,2-dinitroethene (FOX-7), a star molecule that has many desirable features, is a relatively new HEDM developed by the Swedish Defense Research Agency (FOI).³

A key characteristic of FOX-7 is its insensitivity toward mechanical stimulus, while concomitantly it exhibits detonation velocity and pressure (measure of explosive power) values comparable to those of RDX.⁴ Therefore, significant work has been directed toward alternative preparation, reactivity, theoretical calculations, thermal behavior, crystal engineering, and nanoscale applications of FOX-7.⁵ In a continuing effort to expand the chemistry of FOX-7, our interest has focused primarily on structural modification. A series of FOX-7 derivatives that exhibit potentially significant energetic properties have been reported since 2010 (Scheme 1).⁵ Among all

Scheme 1. Selected Derivatives of FOX-7



target derivatives of FOX-7, the azo-bridged derivatives drew particular attention due to their very high theoretical detonation properties.⁷ We also initiated some reactions of FOX-7 with chlorine-based oxidizing reagents in which a single amino group in FOX-7 was found to be successfully converted to azo.⁶ However, all attempts to oxidize both amino groups for diazo moieties failed, and it was assumed that the nucleophilic *gem*-dinitro carbon of FOX-7 was attacked during oxidation instead of amino groups, to give amidiniformic acid.⁶

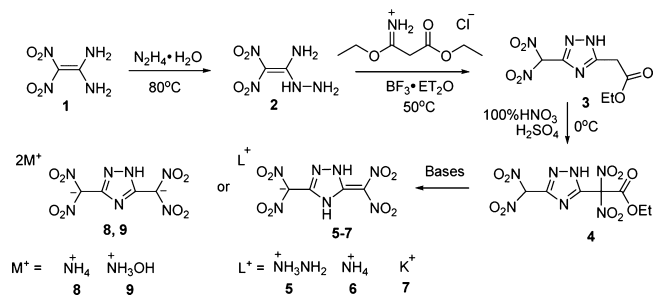
Here we describe our latest contributions to FOX-7-based heterocyclic chemistry. In this work, two FOX-7-derived

Received: April 15, 2016

Published: June 6, 2016

anions, 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion and dianion, are given. From the point of view of structure, these anions show fair similarity to diazo FOX-7 and unfold a new pathway to 1,2,4-triazole-based energetic materials. Furthermore, a series of nitrogen-rich energetic salts based on the 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion and dianion were controllably synthesized by changing the ratio of reacting bases. The synthetic pathway to the new anions and corresponding salts is shown in Scheme 2. 1-Amino-1-hydrazino-2,2-

Scheme 2. Synthesis of Energetic Salts 5–9 Based on 3,5-Bis(dinitromethyl)-1,2,4-triazole Monoanion and Dianion



dinitroethene (HFOX, 2) was synthesized from FOX-7 according to the literature.⁸ Ethyl 2-(3-(dinitromethyl)-1,2,4-triazol-5-yl)acetate (3) was readily formed through the reaction of 2 and ethyl 3-ethoxy-3-iminopropanoate hydrochloride, and was then purified by recrystallization from water (Scheme 2). When treated with a 100% nitric acid/H₂SO₄ mixture at low temperature, 3 was readily converted to the corresponding tetranitro compound 4. Consequently, a series of nitrogen-rich salts (5–9) was obtained by treating 4 with different bases in different ratios. When 4 was treated with 1 equiv of bases, monocation energetic salts 5–7 were isolated with an anion/cation ratio of 1:1. In contrast, dication energetic salts 8 and 9 were obtained by adding 2 equiv of bases. It is worth mentioning that an unknown hygroscopic product was formed when excess hydrazine hydrate was used. All salts were fully characterized by IR, ¹H NMR, and ¹³C NMR spectroscopy as well as elemental analysis (Supporting Information). In addition, ¹⁵N NMR spectra were recorded for 5 in DMSO-*d*₆ (Figure 1). Five nitrogen signals were observed in the spectrum, and they were assigned on the basis of GIAO NMR calculation by using the Gaussian 03 program.⁹

Crystals of 5, 6, and 8·H₂O suitable for single-crystal X-ray diffraction were obtained by slow evaporation of water solutions at room temperature. Compound 5 crystallizes in the triclinic space group *P* $\bar{1}$ with eight units in the lattice cell (*Z* = 4) and a density of 1.965 g cm⁻³ at 150 K. 6 has monoclinic (*P*2₁/*c*) symmetry with four units in the unit cell (*Z* = 4) and a

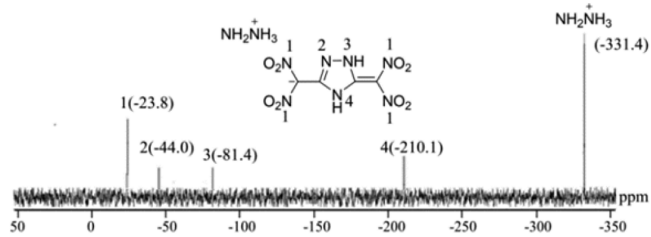


Figure 1. ¹⁵N NMR spectra of 5 in DMSO-*d*₆ with respect to CH₃NO₂ as an external standard.

crystal density of 1.957 g cm⁻³ at 150 K. Remarkably, 5 and 6 possess the highest values recorded to date for the crystal density (150 K) of hydrazinium and ammonium energetic salts, respectively. 8·H₂O has orthorhombic (*Pca*21) symmetry with four units in the unit cell (*Z* = 4) and a crystal density of 1.775 g cm⁻³ at 150 K. In crystals 5 and 6 (Figure 2a,b), the torsion

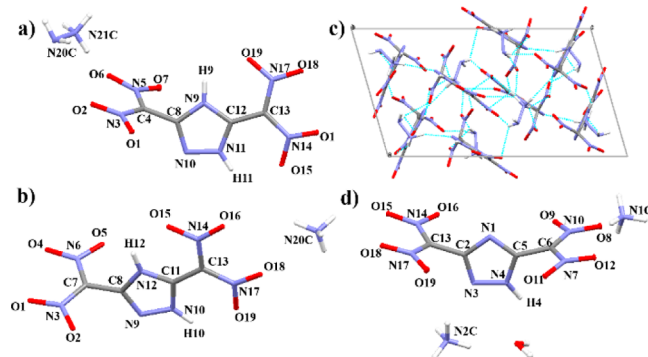
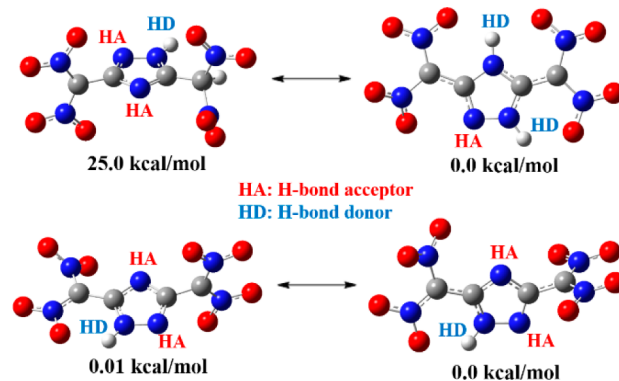


Figure 2. (a) Single-crystal X-ray structure of 5. (b) Single-crystal X-ray structure of 6. (c) Unit cell view of 5 along the *b* axis; hydrogen bonds are indicated as dotted lines. (d) Single-crystal X-ray structure of 8·H₂O.

angles of N11–C12–C13–N14, C12–C13–N14–O15, and C12–C13–N17–O19 in 5 and N10–C11–C13–N17, C11–C13–N17–O19, and C11–C13–N14–O15 are all close to 0°, which shows the same planar structure as FOX-7. In contrast, the torsion angles of N3–C4–C8–N10 and N5–C4–C8–N9 in 8 are 99.0° and 102.5°, respectively. As shown in Figure 2d, the structure of the 3,5-bis(dinitromethyl)-1,2,4-triazole dianion is distorted, and both *gem*-dinitromethyl groups are nonplanar with the triazole ring.

According to the previous study, the C=C bonds in FOX-7 (1.456 Å) and H-FOX (1.474 Å) show the intermediate values between common single and double carbon–carbon bonds.⁸ In this study, the C4–C8, C12–C13 bonds in 5, C7–C8, C11–C13 in 6, and C13–C5, C5–C6 bonds in 8·H₂O also fall in the range of 1.430–1.468 Å, and C12–C13 in 5 has even a shorter distance (1.430 Å) than that of FOX-7. Based on the variety of bonds, for each 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion and dianion, two possible tautomeric forms are suggested in Scheme 3; these tautomers have been studied at the B3LYP/6-31+G** level of theory. Theoretical study indicated that the *gem*-dinitromethylene tautomer is much more stable by 25.0

Scheme 3. Tautomeric Forms of the 3,5-Bis(dinitromethyl)-1,2,4-triazole Monoanion and Dianion



kcal mol⁻¹ than the *gem*-dinitromethyl tautomer; in addition, the crystal structure data on **5** and **6** also prefer the *gem*-dinitro methylene system. In the case of dianion, the C=C/C-N ↔ C-C/C=N tautomerism is possible because of a low energy barrier (0.01 kcal mol⁻¹). Hydrogen-bonding interactions play an important role in the enhancement of stability and density for energetic materials. In the case of the 3,5-bis-(dinitromethyl)-1,2,4-triazole monoanion, the roving proton on the ring nitrogen rather than on the *gem*-dinitro carbon results in additional hydrogen-bond-donor character on the triazole ring. Therefore, four pairs of hydrogen bonds, including an intermolecular hydrogen bonding (N11–H11···O15), were observed in these two positions for **5**. Similarly, four pairs of H-bonding interactions, including N10–H10···O19 intermolecular hydrogen bonding, were formed based on the ring N–H of **6**. Therefore, the high crystal density of **5** and **6** most likely can be attributed to the extensive H-bonding network. In contrast, because of insufficient H-bond-donor character on the ring, only two pairs of hydrogen bonds were formed through N4–H4 of 3,5-bis(dinitromethyl)-1,2,4-triazole dianion in **8**·H₂O, and yet no intermolecular hydrogen bond is observed due to the distorted structure. The packing coefficients of **5**, **6**, and **8**·H₂O are 79.2%, 78.4%, and 74.9%, respectively, which are in agreement with their crystal density order. (More details about the crystal data can be found in the [Supporting Information](#), including CIF files for **5**, **6**, and **8**·H₂O.)

The thermal stabilities of these new energetic salts were determined in sealed Al pans using a TA Instruments Q10 differential scanning calorimeter. The decomposition temperatures are given as onset temperatures in [Table 1](#). Compound

Table 1. Properties of 5–9 and Comparison with FOX-7, RDX, and HMX

material ^a	<i>T</i> _d ^b [°C]	<i>d</i> ^c [g/cm ³]	Δ _f <i>H</i> ^d [kJ/g]	<i>v</i> _D ^e [m/s]	<i>P</i> ^f [GPa]	IS ^g [J]	FS ^h [N]
5	198	1.94	0.56	9271	41.0	22	>360
6	162	1.93	0.09	9086	38.7	20	240
7	182	2.15	−0.33	8959	38.5	28	>360
8	178	1.72	−0.39	8347	29.1	22	240
9	189	1.73	−0.65	8604	31.7	30	>360
FOX-7 ⁱ	274	1.89	−0.36	8930	34.0	60	>360
RDX ^j	204	1.82	0.36	8748	34.9	7.4	120
HMX ^j	280	1.91	0.36	9320	39.5	7.4	120

^aAll the newly prepared materials are anhydrous for testing. ^bThermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C/min). ^cDensity was measured by gas pycnometer at room temperature. ^dCalculated heat of formation. ^eDetonation velocity. ^fDetonation pressure. ^gImpact sensitivity. ^hFriction sensitivity. ⁱProperties of FOX-7 are taken from ref [4b](#). ^jProperties of RDX and HMX are taken from ref [1e](#).

8·H₂O melts at 108 °C and decomposes thermally at 178 °C. The remaining salts (**5**, **6**, **7**, and **9**) decompose without melting and have thermal stabilities ranging from 162 to 198 °C. Densities of all salts were measured with a gas pycnometer and found to range between 1.72 and 2.15 g cm⁻³. The mono potassium salt **7** has the highest density (2.15 g cm⁻³) among **5**–**9**, and it is comparable with recently reported high performance primary metal explosives.¹⁰ It is noteworthy that the high densities of **5** and **6** (1.94 and 1.93 g cm⁻³, respectively), as a consequence of resonance-assisted hydrogen-bonding interactions, are even higher than that of HMX (1.91 g

cm⁻³). These two materials also rank at the top of the density series with ionic CHNO explosives such as dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50).¹¹ The heats of formation for anions and cations in this work were determined by using the Gaussian 03 suite of programs. The standard enthalpies of formation (Δ_f*H*) for **5**–**9** were obtained by employing Born–Haber energy cycles.¹² (More details about the theoretical data can be found in the [Supporting Information](#).)

With all measured room-temperature densities and calculated Δ_f*H* in hand, the detonation properties of **5**–**9** were evaluated by using the EXPLO5 6.01 program ([Table 1](#)).¹³ The calculated detonation velocities fall in the range between 8347 m s⁻¹ (**8**) and 9271 m s⁻¹ (**5**), and detonation pressures range from 29.1 GPa (**8**) to 41.0 GPa (**5**). Given the high density and good heat of formation, **5**–**7** exhibit better energetic performance than **8**, **9**, RDX, and HMX. For initial safety testing, impact sensitivity (IS) and friction sensitivity (FS) values of **5**–**9** were measured by using a BAM Fallhammer apparatus and a BAM friction tester, respectively.¹⁴ All newly prepared salts exhibit favorable IS values from 20 J to 30 J and good FS values from 240 N to above 360 N. Compound **9** possesses the lowest IS and FS (highest numbers), which can be partially attributed to the water molecule of hydration. Among all these newly prepared energetic salts, the compound that is most promising as a practical HMX replacement and an industrial scale-up candidate is the mono hydrazinium salt **5**, which has high density (1.94 g cm⁻³), acceptable sensitivities (22 J, >360 N), good detonation velocity (9271 m s⁻¹), and good pressure (41.0 GPa).

In summary, 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion and dianion were obtained in four steps by using FOX-7 as a precursor, and a series of energetic salts based on these anions were synthesized and fully characterized. The structures of **5**, **6**, and **8**·H₂O were further confirmed by single-crystal X-ray analysis. Based on the crystal data, the bond lengths of the carbon–carbon bond in the 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion and dianion exhibit intermediate values between common single and double carbon–carbon bonds. In addition, for the 3,5-bis(dinitromethyl)-1,2,4-triazole monoanion, the roving proton on the ring nitrogen rather than on the *gem*-dinitro group provides additional hydrogen-bond-donor character for the triazole ring and results in higher packing coefficients. In the case of dianion, C=C/C-N ↔ C-C/C=N tautomerism is proved to be possible because of a low calculated energy barrier. The mono hydrazinium salt **5** has the best thermal stability among these newly prepared energetic materials. The combination of high density and good performance, which are both superior to those of HMX, and its acceptable sensitivities (IS = 22 J; FS > 360 N) highlight **5** as a new HEDM and a potential HMX replacement. All of these findings also contribute to the heterocyclic *gem*-dinitro system and the ever-expanding chemistry of FOX-7.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.6b03819](https://doi.org/10.1021/jacs.6b03819).

Synthesis, characterization data, calculation detail, and crystal refinements ([PDF](#))

X-ray crystallographic file for **5** ([CIF](#))

X-ray crystallographic file for **6** (CIF)
X-ray crystallographic file for **8**·H₂O (CIF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support of the Office of Naval Research (N00014-16-1-2089), the Defense Threat Reduction Agency (HDTRA 1-15-1-0028), and CFD Research Corporation are gratefully acknowledged.

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- (14) (a) <http://www.bam.de>. (b) A 20 mg sample was subjected to a drop-hammer test with a 5 or 10 kg dropping weight. The impact sensitivity was characterized according to the UN recommendations (insensitive, >40 J; less sensitive, 35 J; sensitive, 4 J; very sensitive, 3 J).