

HFOX–1-Amino-1-hydrazino-2,2-Dinitroethylene as a Precursor to Trifluoromethyl, Dinitro, or Trinitro-Based Energetic 1,2,4-Triazoles

Ajay Kumar Chinnam, Richard J. Staples, and Jean'ne M. Shreeve*



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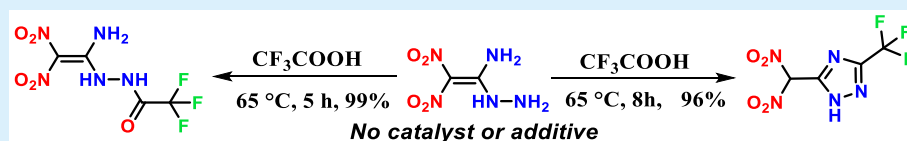
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ABSTRACT: The chemical reactivity of 1-amino-1-hydrazino-2,2-dinitroethylene with a carboxylic acid for the construction of structurally interesting energetic triazoles and their energetic salts is reported. All new compounds were fully characterized by elemental analysis, infrared spectroscopy, nuclear magnetic resonance spectroscopy, and differential scanning calorimetry. Crystal analysis, good detonation properties, and low sensitivities of these trifluoromethyl and dinitro- or trinitro-based triazoles suggest their role as potential candidates for insensitive high-energy-density materials.

Because of their wide uses for civilian and military purposes, the development of new high-energy-density materials (HEDMs) has gained considerable attention from researchers around the world.^{1,2} Generally, nitrogen-rich compounds are in high demand in the field of HEDMs, because of their high densities, high heats of formation, positive oxygen balances, and their proclivity for releasing eco-friendly gases upon detonation.^{3,4} Further energetic performance can be achieved via the addition of energetic groups (NO_2 , N_3 , NHNO_2 , NH_2 , etc.) to the nitrogen-rich compounds.⁵ However, the development of new HEDMs that exhibit high detonation performance with concomitant low sensitivity and better environmental safety is challenging. Remarkable attention was gained by 1,1-diamino-2,2-dinitroethylene (FOX-7) in the field of HEDMs, because of its high thermal stability and insensitivity toward mechanical stimulus. In addition, its detonation performance is comparable to the secondary explosive cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX).⁶ FOX-7 is an excellent example of a “push–pull ethylene”. It contains two geminal electron-donating groups on one carbon and two geminal electron-withdrawing groups on the other, which encourages strong polarization of the double bond, which has a major influence on its chemical and physical properties.⁷ Many studies have been reported on the synthesis, structure, and reactivity, theoretical calculations, and explosive properties of FOX-7 and its related energetic materials.^{8–14} Since 2010, our group has reported several high-performing energetic materials, including the highly energetic oxidizer (tetranitroacetimidic acid) based on FOX-7.^{15–20} Of the many, many offshoots of FOX-7, the halogenated derivatives of FOX-7 and azo-bridged derivatives have attracted major attention, because of their high theoretical detonation properties. Introduction of the halo dinitro methane improves the density

and high oxygen balance, resulting in potential high hypergolic oxidizers, which could react with common rocket fuels.^{21,22}

1-Amino-1-hydrazino-2,2-dinitroethylene (HFOX) is also well-known as a powerful and highly performing energetic reaction intermediate that can be obtained by nucleophilic substitution of FOX-7 by hydrazine monohydrate (Figure 1).²³ It has similar structural features as FOX-7 with the addition of an adjacent amino hydrazine, which causes it to be extremely unstable in its anhydrous form.²⁴ [Caution: HFOX should be

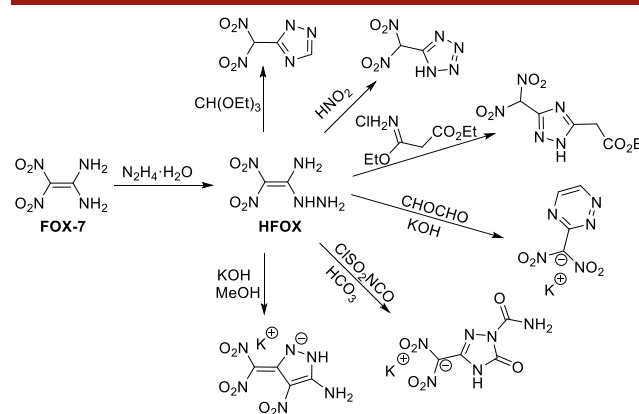


Figure 1. Selected energetic azole derivatives of HFOX.

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handled with extreme care, should not be allowed to become anhydrous, and should be used immediately upon synthesis! One interesting fact is that both FOX-7 and HFOX behave like amphoteric substances and they exhibit a variety of tautomers when they react with a base or acid.²⁵ In recent years, HFOX was used for the construction of interesting energetic heterocyclic derivatives.^{26–30} Our group has established a simple synthetic route for the high-density energetic triazoles of HFOX by reacting with ethyl 3-ethoxy-3-iminopropanoate hydrochloride.^{31,32} On another occasion, energetic triazine derivatives were synthesized via the reaction of HFOX with glyoxal in aqueous KOH solution (Figure 1).¹⁹

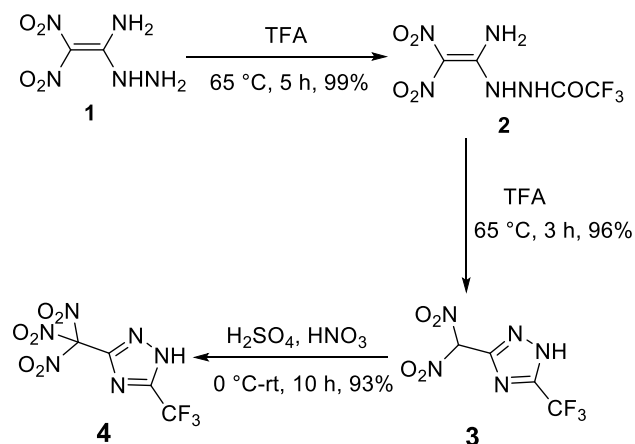
Because of the presence of the hydrazine fragment in HFOX, it exhibits high reactivity toward condensation with aldehydes and ketones, as well as acylation.³³ However, the reactivity of HFOX with carboxylic acids is still challenging, because of the electron-deficient or amphoteric nature of the amine protons or less-nucleophilic nature of the carboxylic acids. Trifluoroacetic acid (TFA) is a mono carboxylic acid that is a trifluoro derivative of acetic acid. It is very reactive, because of the presence of highly electronegative F atoms, and it has been widely used in organic chemistry for various synthetic applications.³⁴ Based on our interest in expanding the chemistry of HFOX, we reacted it with TFA in order to synthesize a new class of energetic triazoles. In this work, TFA plays a dual role as solvent as well as reactant, and it shows high reactivity with HFOX without an additional catalyst or additive to form 3-(dinitromethyl)-5-(trifluoromethyl)-1H-1,2,4-triazole (3) in excellent yields. In addition to this, structurally interesting and nonequivalent electron-withdrawing groups at the 3,5-positions of 1,2,4-triazole derivative, 5-(trifluoromethyl)-3-(trinitromethyl)-1H-1,2,4-triazole (4) was synthesized. Furthermore, nitrogen-rich energetic salts (5–8) were synthesized and well-characterized by multinuclear NMR and IR spectroscopy, differential scanning calorimetry (DSC), and elemental analyses, and the structures of 2, 4, 7, and 8 were investigated using single-crystal X-ray diffraction (XRD) analyses.

Freshly prepared HFOX 1 was dissolved in excess amounts of TFA at 65 °C for 5 h to obtain *N'*-(1-amino-2,2-dinitrovinyl)-2,2,2-trifluoroacetohydrazide 2 in 99%. Further heating of 2 in TFA at 65 °C for 3 h or treating of HFOX 1 in TFA at 65 °C for 8 h gave compound 3 in yields of 93%–96%. Later, compound 3 was treated with a mixture of concentrated sulfuric acid and 100% nitric acid at low temperature to obtain compound 4 as a yellow viscous liquid in 93% yield. After keeping the liquid compound 4 at –18 °C, it was solidified as a pale-yellow solid (Scheme 1).

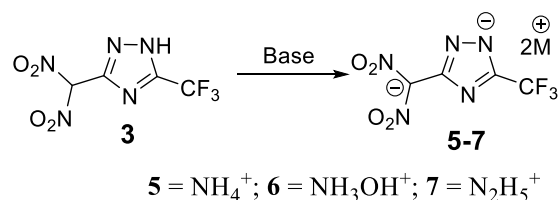
In addition, a series of nitrogen-rich energetic salts (5–7) was based on the 3-(dinitromethyl)-5-(trifluoromethyl)-1H-1,2,4-triazole dianion by simple neutralization of 3 with nitrogen-rich bases. Compound 3 was suspended in acetonitrile or ethyl alcohol and a corresponding base was added. The suspension was stirred at room temperature for 30 min. The yellow solid salts 5–7 were collected by filtration and purified by recrystallization from ethyl alcohol (see Scheme 2).

Nitration of the ammonium salt 5 in a mixture of concentrated sulfuric acid and 100% nitric acid gives the yellow viscous liquid 4. In attempts to obtain the energetic salts of 4, we have tried a series of reactions using aqueous nitrogen-rich bases. In all cases, because of the high reactivity of the trinitromethyl group, we synthesized dianionic salts of 3-(dinitromethyl)-5-(trifluoromethyl)-1H-1,2,4-triazole (5–7).

Scheme 1. Synthesis of Triazole Derivatives 3 and 4

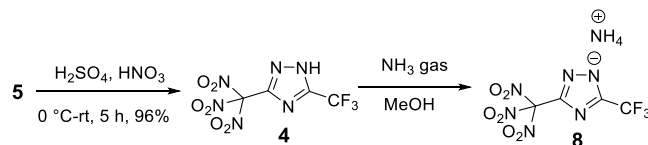


Scheme 2. Synthesis of Energetic Salts 5–7



Finally, the ammonium salt of 4 was synthesized successfully as a pale-yellow solid in 98% yield (Scheme 3), using gaseous ammonia in methanol.

Scheme 3. Synthesis of Energetic Salt 8



The reactivity of HFOX 1 with nonfluorinated acetic acid under optimized reaction conditions was also studied (Table 1). No reaction product was obtained (Table 1, entries 1–3),

Table 1. Reactivity of HFOX with Acetic Acid

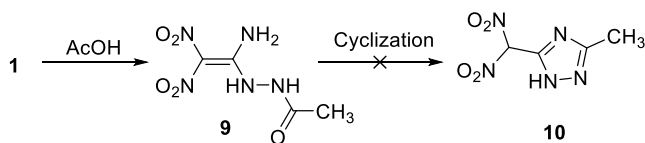
entry	reagent	time (h)	temperature (°C)	yield of product 9 (%)
1	CH ₃ COOH	24	60	—
2	CH ₃ COOH	12	80	—
3	CH ₃ COOH, BF ₃ ·OEt ₂	12	25	—
4	CH ₃ COOH, BF ₃ ·OEt ₂	8	65	80

which indicates the modest electrophilic nature of acetic acid and poor nucleophilic nature of the amine protons. The reactivity of acetic acid is enhanced by the addition of catalytic amounts of Lewis acid (BF₃·OEt₂) at 65 °C to obtain *N'*-(1-amino-2,2-dinitrovinyl) acetohydrazide 9 in 80% (see Scheme 4, as well as Table 1, entry 4).

Further attempts to cyclize 9 in the presence of excess acetic acid—reflux, acetic anhydride—reflux, or acetylchloride—reflux to form triazole derivative 10 were unsuccessful (see Scheme 4).

Similarly, no triazole product was observed when HFOX was treated with benzenecarboxylic acid, which clearly supports

Scheme 4. Attempts To Synthesize 10



that it has poor reactivity with simple carboxylic acids or acetic acid, because of its minimal nucleophilicity. The trifluoromethyl connected carboxylic acid (TFA) shows high reactivity, because of the presence of the highly electronegative CF_3 , and, subsequently, it helped with the cyclization of compound 2.

Single-crystal X-ray analyses were used to verify the compounds 2 and $4 \cdot 0.5\text{H}_2\text{O}$, along with two energetic salts ($7 \cdot \text{H}_2\text{O}$ and 8) (see Figures 2a–d). Compound 2 was

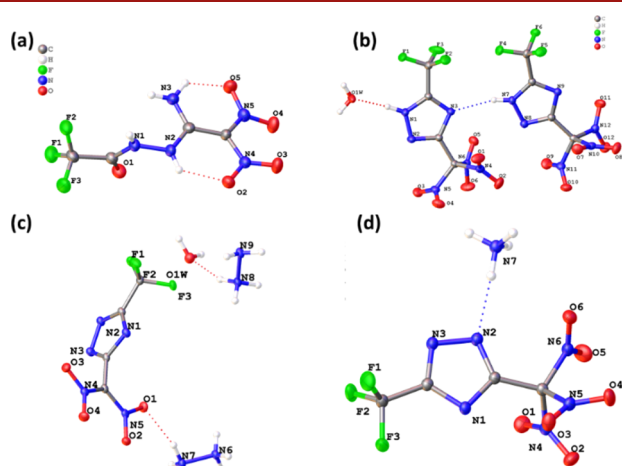


Figure 2. (a) Thermal ellipsoid plot (50%) and labeling scheme for 2. (b) Thermal ellipsoid plot (50%) and labeling scheme for $4 \cdot 0.5\text{H}_2\text{O}$. (c) Thermal ellipsoid plot (50%) and labeling scheme for $7 \cdot \text{H}_2\text{O}$. (d) Thermal ellipsoid plot (50%) and labeling scheme for 8.

crystallized by slow evaporation in TFA at room temperature. It crystallized in the monoclinic space group $P2_1/n$, (four molecules per unit cell) with a calculated crystal density of 2.039 g cm^{-3} at 100 K (see Figure 2a). The $\text{C4}=\text{C5}$ bond length is $1.455 \text{ \AA}$ in 2, compared with the $\text{C}=\text{C}$ bond length

of $1.456 \text{ \AA}$ in FOX-7 and the $\text{C}=\text{C}$ bond length of $1.476 \text{ \AA}$ in HFOX, respectively. Compound 4 was crystallized in small amounts of Et_2O at -18°C by using refrigerator, and it was crystallized in the monoclinic space group $P2_1/c$, four molecules per unit cell with a calculated crystal density of 1.943 g cm^{-3} at 100 K, respectively (Figure 1b). The triazole ring atoms were found to be planar and the bond lengths of $\text{N1}-\text{N2} = 1.3432(16) \text{ \AA}$, $\text{N1}-\text{C1} = 1.3328(18) \text{ \AA}$, $\text{N2}-\text{C2} = 1.3217(18) \text{ \AA}$, $\text{N3}-\text{C1} = 1.3229(17) \text{ \AA}$, and $\text{N3}-\text{C2} = 1.3594(17) \text{ \AA}$ are in the expected range. The bond length of $\text{C1}-\text{C3} = 1.5018(18) \text{ \AA}$ is slightly higher than that of $\text{C2}-\text{C4}$ ($1.4899(18) \text{ \AA}$).

Two energetic salts, $7 \cdot \text{H}_2\text{O}$ and 8, were crystallized using a mixture of methanol/water; $7 \cdot \text{H}_2\text{O}$ crystallized in the orthorhombic space group $Pbca$ and 8 crystallized in the monoclinic space group $P2_1/c$, with calculated densities of 1.880 g cm^{-3} and 1.861 g cm^{-3} at 100 K, respectively (see Figures 2c and 2d). From the previous study of the 3,5-bis(dinitromethyl)-1,2,4-triazole and 5-(dinitromethyl)-3-(trinitromethyl)-1,2,4-triazole-based energetic salts,³² the triazole- $\text{C}(\text{NO}_2)_2$ and triazole- $\text{C}(\text{NO}_2)_3$ bond distances between $\text{C2}-\text{C4}$ in $7 \cdot \text{H}_2\text{O}$ and $\text{C1}-\text{C3}$ in 8 were found to be 1.467 and $1.484 \text{ \AA}$, whereas their triazole- CF_3 bond distances $\text{C1}-\text{C3}$ and $\text{C2}-\text{C4}$ were found to be 1.485 and $1.497 \text{ \AA}$, respectively (see the Supporting Information).

The physicochemical properties for all the structures and standard energetic properties, for comparison, are reported in Table 2. The thermal stabilities (onset temperature) of all compounds were measured via DSC. All new compounds thermally decompose without melting. Both neutral compounds 3 and 4 are less thermally stable (3, $T_{\text{dec}} = 78^\circ\text{C}$; 4, $T_{\text{dec}} = 109^\circ\text{C}$) than their energetic salts (5, $T_{\text{dec}} = 158^\circ\text{C}$; 6, $T_{\text{dec}} = 151^\circ\text{C}$; 7, $T_{\text{dec}} = 138^\circ\text{C}$; 8, $T_{\text{dec}} = 111^\circ\text{C}$) (recall Table 2). Densities were measured by using a gas pycnometer at 25°C and were found to be in the range of $1.82\text{--}1.93 \text{ g cm}^{-3}$. All new compounds have higher densities than TNT and RDX. The heats of formation for both neutral compounds 3 and 4, and their energetic salts (5–8), were determined by using the Gaussian 03 suite of programs.³⁵ As given in Table 2, most of the new compounds exhibit negative heats of formation, because of the presence of the $\text{C}-\text{F}$ bonds, whereas the hydrazinium salt 7 has a positive heat of formation, because of the $\text{N}-\text{N}$ bonds in the cation.

Table 2. Physicochemical and Energetic Properties of 3, 4 and Energetic Salts 5–7, and 8, in Comparison with FOX-7, TNT, and RDX

compound	ρ^a (g cm^{-3})	v_D^b (m s^{-1})	P^c (GPa)	$\Delta_f H^\circ$ ($\text{kJ mol}^{-1}/\text{kJ g}^{-1}$) ^d	$\Delta_c H^\circ$ (kJ mol^{-1}) ^e	T_{dec}^f ($^\circ\text{C}$)	impact sensitivity, IS (J)	friction sensitivity, FS (N)	oxygen balance, OB ^g (%)
3	1.90	7497	24.4	−515/−2.13	−1505	78	35	>360	−33.2
4	1.93	7780	26.1	−471/−1.64	−1406	109	32	>360	−14.0
5	1.82	8261	30.1	−278/−1.01	−2600	158	>40	>360	−46.5
6	1.85	8683	34.3	−144/−0.46	−2734	151	>40	>360	−31.3
7	1.83	8799	33.6	59/0.19	−3222	138	>40	>360	−47.2
8	1.83	8292	31.4	−575/−1.89	−1732	111	>40	>360	−21.1
FOX-7 ^h	1.89	8930	34.0	−53.1/−0.36	—	274	60	>360	−21.6
TNT ⁱ	1.65	6824	19.4	−59.3/−0.26	—	300	15	353	−74.0
RDX ⁱ	1.80	8801	33.6	70.3/0.32	−2108	204	7.4	120	−21.6

^aDensity measured by a gas pycnometer at 25°C . ^bCalculated detonation velocity. ^cCalculated detonation pressure. ^dCalculated molar enthalpy of formation in solid state. ^eCalculated molar enthalpy of combustion. ^fTemperature of decomposition (onset). ^gBased on CO_2 . For a compound with the molecular formula of $\text{C}_a\text{H}_b\text{N}_c\text{O}_d$, $\text{OB}_{\text{CO}_2} (\%) = 1600 [(d - 2a - b/2)/\text{MW}]$, where MW represents the molecular weight. ^hData taken from ref 21. ⁱData taken from ref 7.

Using the measured densities and calculated heats of formation, the detonation performances were calculated by using the EXPLOS program (version 6.01).³⁶ All compounds have better detonation properties than TNT. Energetic salts **6** and **7** have comparable detonation properties with FOX-7 and RDX, with detonation velocities of 8683 m s⁻¹ (**6**) and 8799 m s⁻¹ (**7**) and detonation pressures of 34.33 GPa (**6**) and 33.59 GPa (**7**). Impact sensitivity (IS) and friction sensitivity (FS) values were measured by using BAM drop hammer and friction tester techniques.³⁷ The IS value of **3** is 35 J and that of **4** is 32 J, and they exhibit low sensitivity to friction (>360 N). All the energetic salts were found to be insensitive (IS > 40 J, FS > 360 N) to both impact and friction.

In summary, the chemical reactivity of HFOX **1** with a strong carboxylic acid was studied to obtain a new class of energetic 1,2,4-triazole derivatives **3**, **4**, and their energetic salts. All new compounds were comprehensively characterized by advanced spectroscopic techniques. Single X-ray crystallographic analysis were used to confirm the structures of **2**, **4**, **7**, and **8**. All new compounds have excellent crystal densities, good detonation performances, and low mechanical sensitivities than TNT and the energetic salts **6** ($v_D = 8683 \text{ m s}^{-1}$, $P = 34.33 \text{ GPa}$) and **7** ($v_D = 8799 \text{ m s}^{-1}$, $P = 33.59 \text{ GPa}$) have comparable detonation properties to those of FOX-7 and RDX, respectively. The low sensitivities and good detonation properties of these trifluoromethyl- and dinitro- or trinitro-based triazole compounds open a new chapter in the field of energetic materials.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.orglett.0c03736>.

X-ray crystal diffraction data and crystal structures for compounds **2**, **4**, **7**, and **8** (PDF)

Accession Codes

CCDC 2039067–2039070 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Jean'ne M. Shreeve – Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, United States;
✉ jshreeve@uidaho.edu

Authors

Ajay Kumar Chinnam – Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343, United States;
✉ ajaykumar@uidaho.edu
Richard J. Staples – Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, United States;
✉ rjstaples@msu.edu

Complete contact information is available at:
<https://pubs.acs.org/doi/10.1021/acs.orglett.0c03736>

Notes

The authors declare no competing financial interest.

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