

New Roles for 1,1-Diamino-2,2-dinitroethene (FOX-7): Halogenated FOX-7 and Azo-bis(diahaloFOX) as Energetic Materials and Oxidizers

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S Supporting Information

ABSTRACT: The syntheses and full characterization of two new halogenated 1,1-diamino-2,2-dinitroethene (FOX-7) compounds and three halogenated azo-bridged FOX-7 derivatives are described. Some of these new structures demonstrate properties that approach those of the commonly used secondary explosive RDX (cyclo-1,3,5-trimethylene-2,4,6-trinitramine). All the compounds display hypergolic properties with common hydrazine-based fuels and primary aliphatic amines (ignition delay times of 2–53 ms). This is a new role that has yet to be reported for FOX-7 and its derivatives. Their physical and energetic properties have been investigated. All compounds were characterized by single-crystal X-ray crystallography, elemental analysis, infrared spectra, and differential scanning calorimetry. These new molecules as energetic materials and hypergolic oxidizers contribute to the expansion of the chemistry of FOX-7.

Materials that can store and release large amounts of chemical energy on demand have a wide variety of applications.^{1–4} These materials must possess properties that allow them to be handled safely and avoid accidents during transport and storage. New energetic materials that are nitrogen-rich and have high density, high heat of formation, and positive oxygen balance are highly sought, as they exhibit good detonation performance suitable for roles as propellants, pyrotechnics, or explosives. Superior energetic performances may potentially be achieved by incorporation of explosives, thus increasing the nitrogen content. However, achieving a fine balance between high detonation performance and low sensitivity is an interesting but challenging task, as the detonation performance enhancements most often come at the expense of molecular stability.

1,1-Diamino-2,2-dinitroethene (FOX-7, **1**; Scheme 1) has captured a major role in energetic materials research. A key characteristic of the thermally stable FOX-7 is its insensitivity to

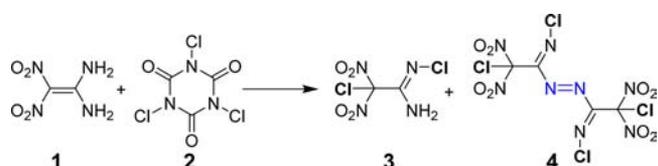
impact and friction, while it exhibits a detonation performance comparable to that of the currently commonly used secondary explosive RDX (cyclo-1,3,5-trimethylene-2,4,6-trinitramine).^{1–5} Perhaps the single most stimulating attribute of FOX-7 is that it is chemically unpredictable, which makes its reaction behavior extremely challenging. In spite of that, a rather broad range of chemical reactions has been reported, including alkylation, acylation, acetylation, electrophilic halogenation, and nitration.^{1,5} More recently, the metal chemistry of FOX-7 has been explored.^{6,7,8a,b}

Pursuing our interests in extending the chemistry of FOX-7 and its derivatives, and based on calculations which suggested it might be possible to improve the detonation performance properties relative to FOX-7 and RDX, we initiated work to develop azo-bridged FOX-7 derivatives.^{5c,8d} The reactions of FOX-7 with chlorine-based oxidizing reagents *N*-chloro-succinimide and trichloroisocyanuric acid (TCICA)⁹ (**2**) were found to be very successful in converting a single diamine group in FOX-7 to a new azo-bridged product, (*E*)-1,2-bis{(*E*)-2-chloro-1-(chloroimino)-2,2-dinitroethyl}diazene (**4**), in addition to the previously known dichloro substrate, 1-chloro-1,1-dinitro-2-(*N*-chloroamidino)ethane (**3**).^{1c} Now we report some new fully characterized energized halogenated derivatives of FOX-7—some with extraordinary properties.

When FOX-7 was reacted with a slight excess of **2** for 2 h, dichloro compound **3**^{1c} (major) and azo complex **4** (minor) were isolated. Extending the reaction time, e.g., to 24 h did not result in total conversion of **1** to **4**. However, using a larger excess (5 equiv) of **2** with **1** led to the formation of **4** as the major product. It is likely that **3** is formed initially and subsequently reacts with **2** to generate **4** (Scheme 1). To verify this, it was shown that when **3** was isolated and then reacted with additional amounts of **2**, compound **4** was formed as the major product.

Based on these results, analogous reactions of the dibromo substrate 1-bromo-1,1-dinitro-2-(*N*-bromoamidino)ethane (**5**)^{1c} with **2** were explored, and the products formed were a function of the quantity of **2** used (Scheme 2). The azo complex, (*E*)-1,2-bis{(*E*)-1-(bromoimino)-2-chloro-2,2-dinitroethyl}diazene (**6**), was obtained as the major product when a slight excess of **2** was reacted with **5**. When 3 equiv of **5** was reacted with 1 equiv of **2**, it was believed initially that three products—azo compounds **7** and **8** and the bromochloro compound **9**—were formed. However, only **7**, (*E*)-1-[(*E*)-2-bromo-1-(bromoimino)-2,2-dinitroethyl]-2-[(*E*)-2-bromo-1-(chloroimino)-2,2-

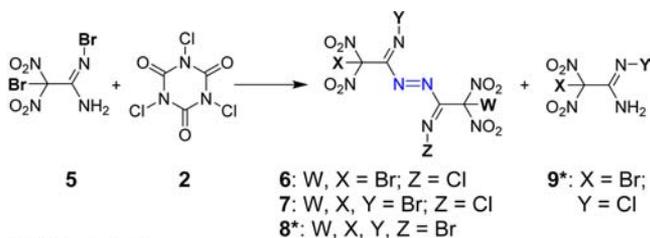
Scheme 1. Synthesis of Dichloro Substrate **3** and Compound **4**



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Scheme 2. Synthesis of Azo Compounds 6 and 7

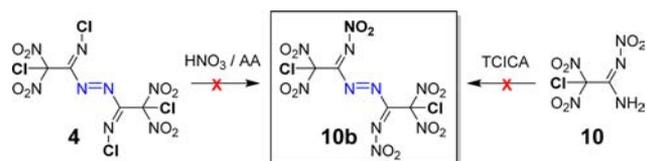


(* Not isolated)

dinitroethyl]diazene, could be isolated as determined by elemental analysis. ^{13}C NMR indicated a mixture of the starting material **5** (δ 157.4 C–NH₂, δ 112.8 Br–C–NO₂) and **9** (δ 157.5 C–NH₂, δ 114.3 Br–C–NO₂). Because their polarities are similar, it was not possible to separate the two compounds. As in the case with the preparation of **3** and **4**, the quantity of products formed was a function of the quantity of **2** used (Scheme 2). Compound **8** was not found.

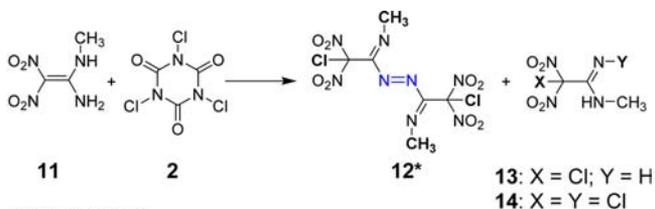
Attempts to enhance the energetic performance of azo-bridged compounds via the incorporation of additional nitro groups, e.g., into **4** via reaction with 100% HNO₃/acetic anhydride (AA) or into substrate^{1c} **10** via reaction with **2** to form **10b**, failed (Scheme 3).

Scheme 3. Attempts To Enhance the Energy of Azo Substrate 4



Based on this lack of success, no further efforts were made to nitrate the other halogenated FOX-7 derivatives. Due to the rather high impact sensitivity of azo compounds (vide infra), introduction of a methyl group would be expected to help stabilize the azo derivatives. However, when substrate **11**¹⁰ was reacted with **2**, azo product **12** was not detected; rather only the chlorinated compounds, 2-chloro-*N*-methyl-2,2-dinitroacetimidamide (**13**) and (*E*)-*N'*-2-dichloro-*N*-methyl-2,2-dinitroacetimidamide (**14**), resulted as a function of the quantity of **2** used (Scheme 4).

Scheme 4. Synthesis of Chlorinated Compounds 13 and 14



(* Not isolated)

The physical properties of the halogenated FOX-7 derivatives and the properties of some standard energetics for comparison are summarized in Table 1. The thermal decomposition temperatures of the halogenated FOX-7 derivatives range from 127 to 147 °C; thus, these derivatives are significantly less stable

thermally than **1** ($T_d = 274$ °C). The incorporation of bromine atoms tends to destabilize the azo complex relative to **4**.

Densities of the halogenated FOX-7 derivatives were determined at 25 °C using a gas pycnometer. Each compound was measured three times, and the average values are reported in Table 1. Densities range from 1.70 g/cm³ for **13** to 2.47 g/cm³ for **5**. Although the halo compounds have densities that are greater than or equal to that of **1**, the detonation performances for the derivatives are not competitive with **1**; however, they exceed those of TNT. The calculated detonation velocity values range from 8406 ms⁻¹ for **10** to 7102 ms⁻¹ for **6**, and detonation pressures lie between 23 GPa for **13** and 37 GPa for **5**, exceeding those of PETN (except **13** and **14**). The performances of compounds **5** and **7** exceed that of RDX. The sensitivities of halogenated FOX-7 derivatives range from 2 to >40 J, with the azo compounds having the highest sensitivity toward impact. The remaining compounds are less sensitive than PETN and RDX.

Oxygen balance is a measure of how much oxygen is required for complete combustion of hydrogen to water and carbon to carbon monoxide. A positive or negative oxygen balance signifies that there is an excess or a deficiency of oxygen in the molecule for complete combustion. Of the compounds, **10** has the highest and **13** the lowest oxygen balance. All halo FOX-7 derivatives compare well with TNT (–74.0%), but **1**, PETN, RDX, and HMX have superior oxygen balance values relative to the methyl derivatives **13** and **14**.

All the compounds were structured by single-crystal X-ray crystallography (see Supporting Information). Although **3** and **5** are previously known compounds, their crystal structures had not been obtained due to reported difficulty in obtaining crystals.^{1c} We now have grown suitable crystals of these materials, and for completeness their structures are reported. All the crystals were obtained by slow evaporation of a 50:50 mixture of hexane and dichloromethane. The azo compounds, **4** (Figure 1a) and **6**, both crystallize as dark purple prisms consisting of a monoclinic $P1_2/n1$ space group with two molecules per unit cell, while **7** crystallizes as dark green prisms with a monoclinic $P2_1/n$ space group with two molecules per unit cell. The absence of hydrogen bonding in these structures may contribute to their impact sensitivity. The azo –N=N– bond distances for azo complexes **4**, **6**, and **7** agree with the average bond distance for –N=N– (1.20 Å).¹³ The bond angle of C–(NO₂)₂ is decreased in **4** (N7–C5–N10, 102.5°), **6** (N1–C1–N3, 102°), and **7** (N1–C2–N2, 103°) compared to that in **3** and **5** (104°). This may be attributable to the steric repulsion of the nitro moieties and the chlorine atoms for both compounds. Compound **6** has some compositional disorder (85%/15%). This is a common phenomenon in which different atoms can occupy the same site in different molecules in the crystal.¹⁴

Dichloro compound **14** crystallizes as colorless needles in a monoclinic Cc space group containing four molecules per unit cell (Figure 1b). As in chlorinated derivatives **3** and **13**, the C3–C6 bond distance in **14** is the expected average bond distance for C–C bonds. The sp³-hybridized C6 atom is also observed (C3–C6–N8, 109°), as well as the deviation of the bond angle for C3–C6–Cl7 (115°) due to the steric repulsion of the chlorine and nitro moieties, similar to that observed with compounds **3** and **5**. Compression of the bond angle N8–C6–N11 (103° instead of 116°) is also observed. The bond angle of N4–C3–C6 (119°) is increased compared to the bond angle of N1–C1–C2 (115°) in **13** due to the presence of the additional chlorine atom on N2. Similar to **3**, **5**, and **13**, it is the hydrogen atom of the

Table 1. Physical Properties of FOX-7 Derivatives

compd	T_m^a (°C)	T_d^b (°C)	d^c/d^d (g/cm ³)	ΔH_f^e (kJ/mol)/(kJ/g)	P^f (GPa)	D^g (ms ⁻¹)	IS^h (J)	OB ⁱ (%)	I_{sp}^j (s)
1 ^k	– ^l	274	1.89	–53.1/–0.36	34.0	8930	60	0	–
3	91	127	1.86/1.84	274.1/1.26	32.5	8389	10	7.4	250
4	– ^l	139	1.97/1.99	1010.3/2.35	32.4	8348	3.5	14.9	246
5	70	128	2.47/2.48	872.8/2.85	36.7	7159	7.5	5.2	238
6	– ^l	136	2.08/2.10	1315.3/2.53	25.4	7102	<2	12.3	234
7	– ^l	133	2.39/2.33	707.7/1.32	34.3	7403	<2	11.4	238
10	129 ^m	147	1.92/1.93	–42.2/–0.19	30.3	8406	≤9	21.1	235
13	131	136	1.70/1.74	–64.4/–0.33	22.9 ⁿ	7382 ⁿ	>40	–12.2	219
14	125	141	1.79/1.77	297.4/1.29	27.5	8013	32.0	–6.9	254
TNT	81	295	1.65	–67/–0.29	19.5	6881	15.0	–24.7	205 ^o
PETN ^{o,p}	143	160	1.78	–502.8/–1.59	31.4	8564	2.9	15.2	–
RDX	206	230	1.82	92.6/0.42	35.2	8977	7.4	0	258
HMX ^{o,q}	282	287	1.94	116.1/0.39	41.5	9221	7.0	0	258

^aMelting point. ^bThermal decomposition temperature under nitrogen gas (DSC, 5 °C/min). ^cDensity (measured). ^dCrystal density. ^eHeat of formation (Gaussian 03). ^fDetonation pressure (Cheetah 6.0). ^gDetonation velocity (Cheetah 6.0). ^hImpact sensitivity (BAM Drophammer, 10 kg); ref 11. ⁱOxygen balance (% based on CO formation). ^jSpecific impulse, calculated isobarically at 68 atm (Cheetah 6.0). ^kRef 3. ^lDecomposed prior to melting. ^mRef 1c. ⁿDetonation performance calculated by Explo 5.05. ^oRef 12. ^pPETN = pentaerythritol tetranitrate. ^qHMX = Cyclotetramethylenetetranitramine.

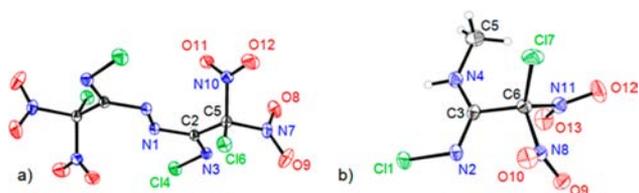


Figure 1. Thermal ellipsoids shown at 50% of (a) azo compound 4 and (b) chloro compound 14.

secondary amine of 14 that participates in hydrogen bonding with the nitrogen of the *N*-chloroamidino moiety.

One of the interesting features in this work was the discovery that the halo FOX-7 derivatives behaved as hypergolic oxidizers. While derivatives of FOX-7 have been studied extensively for their energetic properties, their role as oxidizers had yet to be explored. Hypergolicity is a term used to describe a spontaneous combustion reaction between a fuel and an oxidizer.¹⁵

Ongoing efforts continue in the development of new sources of fuels to replace the carcinogenic hydrazine and its derivatives; alternatives to commonly used oxidizers are of great interest due to the poor shelf life, highly corrosive nature, and moisture sensitivity of ones in current use.^{16,17} Although much research has been and continues to be focused on fuels, less attention has been directed toward the development of new or improved oxidizers. However, while the oxidizing properties of halo FOX-7 moieties are of chemical interest, it is anticipated that the disadvantage of using solid oxidizers with liquid fuels should not be underestimated.

Reactions of the pure halogenated FOX-7 derivatives were examined with two common fuels, hydrazine hydrate (HH) and monomethylhydrazine (MMH), in order to determine if these materials were potential hypergolic oxidizers. Additionally it had been demonstrated that a variety of aliphatic amines are hypergolic with white fuming nitric acid (WFNA).¹⁸ These hypergolic systems with ethylenediamine (EN) and tripropylamine (TPA) were determined to have ignition delay times (ID, the time from when the fuel first comes into contact with the oxidizer until the initial flame appears) of 90 and 50 ms, respectively.¹⁸ Therefore, these two amines were also investigated as fuels with the halogenated FOX-7 derivatives. The ID

was measured by using a droplet test with a high-speed camera recording 500 frames/s. One drop of the fuel (HH, MMH, EN, TPA, or DAP (1,3-diaminopropane)) was dropped into a glass vial that contained 10 mg of the solid oxidant. However, in our case it was difficult to see the flame for some of the tests because the fuel pushed the solid oxidizer against the walls of the vial. Therefore, the first sign of smoke formation was used as the end point of the measurements. Thus, the times reported are not traditional ignition delay times, but the precision of the recorded times measured three times for each halo FOX-7 compound with the average values given in Table 2 is very good. An example of the hypergolic testing can be found in Figure 2.

Table 2. ID Times for Halo FOX-7 Derivatives with HH, MMH, EN, and DAP

compd	HH (ms)	MMH (ms)	EN (ms)	DAP (ms)
3	20.7	3.3	53.3	53.3
4	13.3	4.6	14.7	14.7
5	4.7	2.7	4.7	8
6	4	2	2	3
7	6	2	6	5.3
10	NH ^a	10.7	NH	NH
13	NH	31.3	NH	NH
14	NH	10	NH	NH
WFNA ^b	19	20	90 ^c	–

^aNot hypergolic. ^bWhite fuming nitric acid. ^cRef 18.

Compounds 10,^{1c} 13, and 14 are only hypergolic with MMH; this may arise from the absence of an electrophilic N–Cl bond in



Figure 2. Hypergolic testing of azo substrate 4 with MMH.

compound **13** and the reduced electrophilicity of the N–Cl bond due to the presence of the methyl group in **14**. With the exception of **13**, all of the compounds displayed ID times that were significantly faster than WFNA with MMH and excluding **3**, for HH. The ID times ranged from 2 to 31 ms with the hydrazine-based fuels tested.

Similar to the hypergolic tests with HH and MMH, **10**, **13**, and **14** are not hypergolic with the aliphatic amines tested. It has been reported that the ID times of hypergolic systems with unbranched aliphatic amines and WFNA are enhanced when the carbon chain is increased up to five carbons.¹⁸ Thus, the expected trend was that the ID for TPA would be faster than that for EN. Interestingly, we observed no hypergolic reaction of TPA with **3** and **4**. Therefore, the remaining halo FOX-7 compounds were not investigated. Using simple primary aliphatic amines, DAP was predicted to exhibit better IDs compared to EN, based on literature data. However, the halo FOX-7 compounds that were hypergolic reacted at the same or faster rate with the shorter carbon chain (EN) than with the longer chain. EN and DAP have comparable IDs compared to HH and MMH for brominated azo compounds **6** and **7**. The IDs range from 2 to 53 ms for both fuels, exceeding the ID of WFNA with EN.

Derivatives of FOX-7 were not reported to behave as oxidizers earlier, and the discovery of this behavior is a new chapter in the chemistry FOX-7. Although these compounds are not suggested as potential replacements for current hypergolic oxidizers, this is a worthwhile discovery in the chemical life and behavior of FOX-7.

In summary, a series of new halogenated FOX-7 derivatives that are hydrolytically stable, have moderate thermal stability, and possess high densities and high heats of formation has been synthesized and characterized. Structures **4**, **6**, and **7** represent the first azo derivatives of FOX-7. Calculations indicate the energetic performances of these exceed that of TNT but are lower than that of the parent, FOX-7. The impact sensitivities of the compounds range between 2 and 40 J, making them at least competitive with or better than PETN. The new halo derivatives of FOX-7 have been found to behave as hypergolic oxidizers with common fuels, helping them to gain a new role, and us to gain a better understanding, of the chemistry of FOX-7 itself.

■ ASSOCIATED CONTENT

● Supporting Information

Experimental procedures, characterization data (single crystal X-ray, CIF files, infrared, and DSC), and heat of formation calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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