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The Many Faces of FOX-7: A Precursor to High-Performance Energetic Materials**

Haixiang Gao and Jean'ne M. Shreeve**

Abstract: *New derivatives of 1,1-diamino-2, 2-dinitroethene (FOX-7) are reported. These highly oxygen- and nitrogen-rich compounds were fully characterized using IR and multinuclear NMR spectroscopy, elemental analysis (EA), and differential scanning calorimetry (DSC). X-ray structure determination of (E)-1,2-bis{(E)-2-chloro-1-(chloroimino)-2,2-dinitroethyl}-diazene) (**10**), N1, N2-dichloro-1, 2-diazenedicarboximidamide (**11**), and (E,E)-N,N′-1,2-ethanediylidenebis(2, 2-dinitro-2-chloro-ethanamine) (**12**) was helpful in their characterization. Heats of formation (HOF) were calculated (Gaussian 03) and combined with experimental densities to estimate the detonation velocities (D) and pressures (P) of the high-energy-density materials (HEDMs) (EXPLO5, v6.01). The compounds exhibit good thermal stability, high density, positive HOF, acceptable oxygen balances, and excellent detonation properties, which often are superior to that of 1,3,5-trinitroperhydro-1,3,5-triazine (RDX).*

The design, synthesis, and characterization of high-energy-density materials (HEDMs) have attracted considerable interest from researchers around the world.[1] In general, the raison d'etre for the search for new HEDMs is the desire to achieve a detonation performance comparable to those of the current benchmark HEDMs, such as octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20).[2,3] Furthermore, there are several criteria that new HEDMs should satisfy, such as inexpensive synthesis, safe handling, and good environmental compatibility, among others. In the quest for higher detonation-performing HEDMs, the field of HEDMs chemistry must expand the boundaries of the energy capacity of compounds, which requires new classes of functionalized compounds,[4] advanced theoretical prediction techniques,[5] and new synthetic strategies.[6] Desirable characteristics for new HEDMs include high density, positive heats of formation (HOF), positive oxygen balance (OB), high detonation velocity and pressure, high thermal stability, simple synthesis, low sensitivity toward external forces, such as impact and friction, and environmental friendliness.[1–5]

1,1-Diamino-2,2-dinitroethene (FOX-7) was first synthesized nearly 20 years ago.[7] Recently, this compound has emerged as a potential candidate for use as an insensitive HEDM, attracting substantial interest because its performance as an explosive is comparable to RDX. Furthermore, the sensitivity to impact and friction of FOX-7 and, thus to involuntary detonation, is markedly lower.[8] These properties render FOX-7 attractive because the low sensitivity of this HEDM will reduce the risk of serious and fatal accidents during its handling and application. For future applications, FOX-7 is considered an important preferred component of propellants and has attracted interest from researchers for its high potential in diverse applications. Many studies have been performed on the synthesis,[9] molecular structure,[10] reactions,[11] theoretical calculations,[12] thermal behavior,[13] explosive performance,[14] and applications of FOX-7.[15]

In a continuing effort to seek less sensitive, more powerful, eco-friendly HEDMs, our interest focused primarily on the modification of the molecular structure of FOX-7 to obtain new HEDMs that contain a high percentage of oxygen and nitrogen and lower amounts of carbon and hydrogen. We noted that the molecular structure of FOX-7 contains the functional group $=C(NH_2)_2$, similar to nitroguanidine.[16] This fact suggests that FOX-7 could be a good intermediate for reaction with nucleophiles and electrophiles, enabling the design and optimization of the molecular structure to enhance performance with respect to high energy and insensitivity. Our earlier research showed that the design approach is a practical method to improve the detonation performance properties relative to those of FOX-7 by modifying its structure with metal,[17] nitro,[18] or azo functional groups.[19] Pursuing our continuing interest to extend the chemistry of FOX-7 and its derivatives, in this study, we report the synthesis of a series of FOX-7 derivatives that display potentially significant physical and energetic properties.

The nitro group is a vital constituent of HEDMs; its presence greatly contributes to the overall energetic performance. Additionally, the nitro group enhances the OB (oxygen balance) and density which improves the detonation performance (pressure and velocity).[20] Initially, our strategy was to introduce additional nitro groups to modify FOX-7. Hexahydro-3-tert-butyl-2,2-dinitromethylene-1, 3, 5-triazine (**2**) was isolated as a light yellow crystalline solid in 91 % yield from the Mannich condensation of FOX-7 (**1**), formaldehyde, and tert-butyl amine (Scheme 1). Compound **2** was nitrated

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[*] Prof. Dr. H. Gao
Department of Applied Chemistry, China Agricultural University
Beijing, 100193 (China)
E-mail: hxgao@cau.edu.cn

Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho
Moscow, ID 83844-2343 (USA)
E-mail: jshreeve@uidaho.edu

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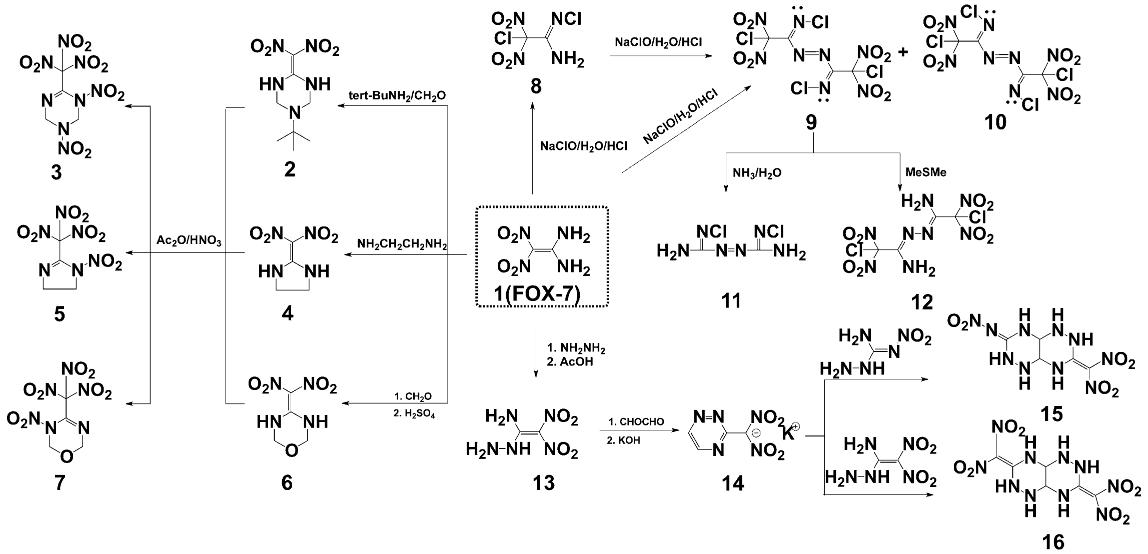

Scheme 1. Derivatives of FOX-7.

Table 1: Properties of the derivatives of FOX-7.[a]

	T_d[b] [°C]	d[c] [g cm^{-3}]	OB[d] [%]	$\Delta_f H$[e] [kJ mol^{-1}/kJ g^{-1}]	D[f] [m s^{-1}]	P[g] [GPa]	IS[h] [J]	FS[i] [N]
1	274.0	1.89	0	−53.1/−0.36	8930	34.0	60	>350
2	180.7	1.46	−75.0	125.4/0.39	6903	15.2	>40	>360
3	141.2	1.87	19.7	−60.7/−0.25	9112	38.1	6	80
4	257.0 (261–262)[j]	1.69	−27.6	−5.7/−0.02	8394	28.6	>40	>360
5	129.8	1.75	12.1	256.2/1.47	8504	31.9	3.5	40
6	209.2	1.79	−16.8	−74.2/−0.27	8280	28.9	>40	>360
7	140.4	1.83	17.1	−148.6/−0.78	8807	34.9	3.5	60
8[k]	127.0	1.86/1.84[l]	7.4	274.1/1.26	8389	32.5	10	–
9	139.0	1.97/1.99[l]	14.9	1010.3/2.35	8348	32.4	3.5	40
10	137.7	1.95/2.00[l]	14.9	1060.1/2.47	7851	30.1	3.5	40
11	159.6	1.71/1.77[l]	−35.0	348.3/1.91	6460	16.4	>40	>360
12	120.7	1.95	8.8	−94.3/0.26	8250	30.8	5	240
13[m]	124.5	1.78	−4.9	71.6/0.43	8803	33.8	6	–
14	270.0	1.88	−10.7	104.8/0.57	7252	22.1	4	240
15	123.5	1.73	−15.8	304.2/1.30	8492	29.4	8	360
16	125.6	1.85	−9.2	348.2/1.04	8862	35.2	7.5	160
RDX	204	1.82	0	80.0/0.36	8748	34.9	7.4	120
HMX	280	1.91	0	104.8/0.36	9320	39.5	7.4	120

[a] All compounds are anhydrous except **14**, which is monohydrate. [b] Thermal decomposition temperature (onset) under nitrogen gas (DSC, 5 °C min^{-1}). [c] Density measured by gas pycnometer (25 °C). [d] OB = oxygen balance (%); for $C_aH_bO_cN_d$: $1600(c-a-b/2)/M_w$; M_w = molecular weight of compound. [e] Calculated HOF. [f] Detonation velocity. [g] Detonation pressure. [h] Impact sensitivity. [i] Friction sensitivity. [j] Ref. [5b]. [k] Ref. [19]. [l] Crystal density. [m] Ref. [22c].

using mixed nitric acid and acetic anhydride as the reaction medium at 0 °C to give 1, 2, 3, 4-tetrahydro-1, 3-dinitro-6-trinitromethyl-1, 3, 5-triazine (**3**) in 89 % yield. The structure of **3** is supported by ^{1}H and ^{13}C NMR spectroscopic data as well as elemental analysis (EA) (see the Supporting Information). The nitration of other cyclic amines derived from **1** gave similar trinitromethyl derivatives, as shown in Scheme 1. Thus, 2-(dinitromethylene)-1,3-diazacyclopentane (**4**) and 4-(dinitromethylene)- tetrahydro-4*H*-1, 3, 5-oxadiazin(**6**) gave 3-3-nitro-2-(trinitromethyl)-l,3-diazacyclopent-1-ene (**5**) and 4-(trinitromethyl)-3-nitro-dihydro-2*H*-1, 3, 5-oxadiazin (**7**), respectively. Nitration of **2**, **4**, and **6** increased the number of nitro groups in forming **3**, **5**, and **7**. Thus, compound **3** has a positive OB of 19.7 %; and **5** and **7** have 12.1 % and 17.1 %, respectively, which are superior to RDX (0 %) and HMX (0 %). OB is calculated assuming all carbon is converted into carbon monoxide and all hydrogen to water. The oxygen percentages of **3**, **5**, and **7** are 49.4 %, 48.5 %, and 51.4 %, respectively, which are superior to RDX (43.2 %) and HMX (43.2 %) and nearly competitive with ammonium perchlorate (54.5 %).

Although **5** was previously synthesized from 1,1-diiodo-2,2-dinitroethylene, its physical and detonation properties were not studied.[5] In our work, **5** as well as the other newly synthesized compounds were characterized using IR and NMR spectroscopy, EA, and differential scanning calorimetry (DSC). The detonation velocities and pressures of the compounds were calculated with EXPLO5 v6.01. To further evaluate these energetic materials, impact sensitivities and friction sensitivities were measured using a BAM Fallhammer apparatus and a BAM friction tester, respectively (Table 1).

The densities of these polynitro derivatives of FOX-7 fall in the range 1.75–1.89 g cm^{-3} (compound **3**), which equal or exceed those of common explosives. The calculated detonation pressures of **3**, **5**, and **7** are over the range of P 31.9–38.1 GPa (RDX 34.9 GPa; HMX 39.5 GPa). The detonation velocities fall between 8504 and 9112 m s^{-1} (RDX 8748 m s^{-1}; HMX 9320 m s^{-1}).The calculated detonation properties coupled with the relatively high hydrolytic and thermal stabilities suggest that these oxygen-rich materials may be attractive candidates for energetic applications.

Several azo-based HEDMs have been investigated in recent years[21] for use in applications, such as insensitive munitions, gas-generating substances (for example for use in airbags) and propellant additives. The presence of the azo (−N=N−) moiety generally imparts a high endothermic HOF to a compound; thus, the decomposition energy is largely derived from this source rather than from the fuel-oxidizer reaction. The reactions of FOX-7 with chlorine-based oxidizing reagents trichloroisocyanuric acid (TCICA) and *N*-chlorosuccinimide[19] were previously studied carefully by our group, and the reagents proved successful in the synthesis of the previously known dichloro substrate, 1-chloro-1,1-dinitro-2-(*N*-chloroamidino)ethane (**8**) and in the conversion of a single diamine group in FOX-7 to an azo-bridged product, (*E*)-1,2-bis{(*E*)-2-chloro-1-(chloroimino)-2,2-dinitroethyl}diazene (**9**).

These halogenated derivatives of FOX-7 have good detonation properties, and certain derivatives have extraordinary properties as hypergolic oxidizers. However, the low yield of the reactions and the expensive oxidizing reagents required for the reactions preclude their applications and further study. Now, we have used commercial bleach (sodium hypochlorite) as an oxidizing reagent with FOX-7 to give a higher yield of **9** (42.5% vs 11% with TCICA as oxidizer)[19] and simultaneously obtained a novel isomer azo-bridged product (*E*)-1,2-bis{(*Z*)-2-chloro-1-(chloroimino)-2,2-dinitroethyl}diazene) (**10**) (yield 21.0%) (Scheme 1). Because **10** has good solubility in *n*-hexanes and **9** is insoluble, the two isomers could be easily separated by washing the products with *n*-hexanes. Compound **10** forms a brownish prism-shaped crystal, and its structure was obtained by X-ray crystallography (Figure 1). Compound **10** has physical properties similar to **9** (thermal stability, density, impact, and friction sensitivity) but has a slightly higher HOF. The ignition delay (ID) test shows that **10** has a shorter ID time with UDMH (unsymmetric dimethylhydrazine) as fuel of 3 ms compared with 11 ms for **9** (Figure 2). This result suggests that **10** would perform as a superior hypergolic oxidizer.

Further treatment of **9** with ammonia or dimethyl sulfide leads to N1, N2-dichloro-1, 2-diazenedicarboximidamide (**11**) or (*E*, *E*) -*N*, *N′*-1, 2-ethanediylidenebis (2, 2-dinitro-2-chloroethanamine, **12**; Scheme 1). These structures were determined by X-ray crystallography (Figure 1). Compared with their parent molecule **9**, compounds **11** and **12** have superior stability (thermal, impact, and friction) with less favorable detonation properties (Table 1).

Recently, we also examined the reactivity of FOX-7 and its hydrazine derivative 1-amino-1-hydrazino-2,2-dinitroethene (**13**) with a variety of bases, which led to a series of isolated salts containing FOX-7 and **13** anions.[22] Compound **13** also acts as a synthon for a number of dinitromethylene compounds.[23] The condensation of **13** with glyoxal in aqueous KOH solution gives the heterocyclic 3-(dinitromethyl)-1, 2, 4-triazine potassium salt (**14**),[24] which proved to be a reactive substrate in a condensation reaction with 1-nitro-3-aminoguanidine, forming the corresponding derivative, 3-nitrimino-7-dinitromethylene-octahydro-[1,2,4]triazino-[6,5-e][1,2,4]triazine (**15**).[24] Similarly, a similar reaction of **14** with **13** led to the new symmetric heterobicyclic material, 3,7-bis(dinitromethylene)-octahydro-[1,2,4]triazino-[6,5-e][1,2,4]triazine (**16**), which exhibits better detonation properties (density 1.85 $\mathrm{g\,cm^{-3}}$; pressure, 35.2 GPa, velocity, 8862 $\mathrm{m\,s^{-1}}$, IS = 7.5 J) than **15**, and compares favorably with RDX (density 1.80 $\mathrm{g\,cm^{-3}}$; $P = 34.9$ GPa, $D = 8748\ \mathrm{m\,s^{-1}}$, IS = 7.4 J), and thus may have potential as an HEDM (Table 1).

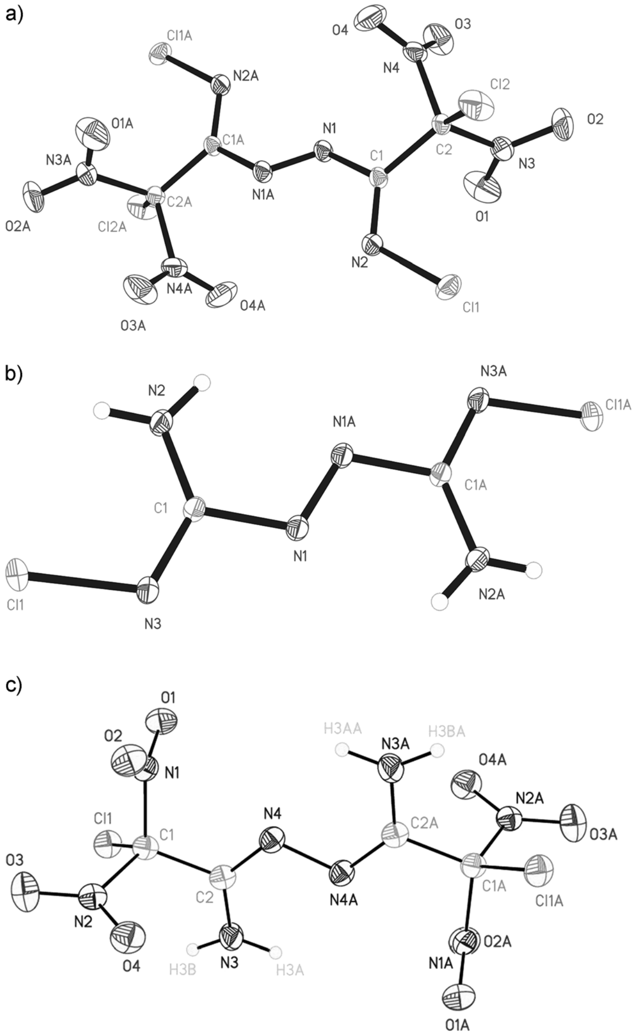

Figure 1. ORTEPs of compounds a) **10**, b) **11**, and c) **12**. Ellipsoids are set at 50% probability.[26]

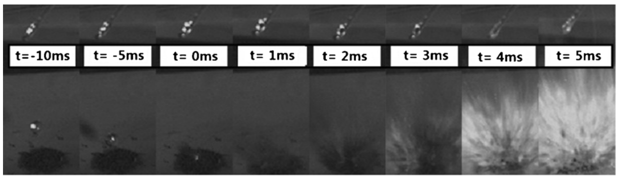

Figure 2. Hypergolic test of compound **10** with unsymmetric dimethylhydrazine (UDMH).

The syntheses of HEDMs which contain polynitro, azo, and heterobicyclic functional groups from FOX-7 were successful. The structures of these compounds were determined, and their physical and detonation properties were measured or calculated. The new compounds exhibit good physical and detonation properties, such as high densities, moderate thermal stabilities, as well as high HOF, detonation pressures, and detonation velocities. The calculated detonation values for these compounds are comparable to those of RDX. These further studies on FOX-7 highlight once again the particular reactivity of this compound. Although FOX-7 is reported to exhibit two phase transitions that are readily apparent in the DSC,[25] none of the new derivatives of FOX-7 in this research shows phase transitions (polymorphism) upon heating prior to decomposition. Among the new polynitro derivatives of FOX-7, **3** has the highest positive OB (19.7 %), an oxygen content of 48.6 %, and a decomposition temperature of 141.2 °C, which suggests its potential for use as a new stable oxidizer. Furthermore, an inexpensive and convenient method to prepare azo functional group-containing derivatives using commercial bleach as an oxidizer with FOX-7 led to a higher yield of **9** and to the formation of a new isomer **10** whose properties as a hypergolic oxidizer exceed those of **9**. X-ray structuring unambiguously characterized the unexpected compound **10**. Further study of the reactions of **9** resulted in two new azo functional group-containing derivatives of FOX-7. Compound **13** led to the new symmetric heterobicyclic product **16** with substantially better detonation properties than those of RDX and may have potential as an HDEM. All of these findings contribute to the ever-expanding chemistry of FOX-7.

Keywords: detonation performance · energetic materials · FOX-7 · nitrogen oxides · X-ray diffraction

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[26] CCDC 1048968 (**10**), CCDC 1048969 (**11**), and CCDC 1048988 (**12**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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