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Enforced Planar FOX-7-like Molecules: A Strategy for Thermally Stable and Insensitive π-Conjugated Energetic Materials

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KEYWORDS: Energetic Materials, Planar molecules, Thermally stable, Insensitive, π-Conjugated

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ABSTRACT: Exploring new energetic derivatives of 1,1-diamino-2,2-dinitroethylene (FOX-7) is still a key aspect in the field of energetic materials. However, so far most of the attention has been focused on modification of FOX-7 via different reaction strategies. Now we report the design of three new FOX-7-like compounds (**3**-**5**) where one nitro group in FOX-7 is replaced by a nitrogen-rich heterocyclic ring. Each of them is characterized by single-crystal X-ray crystallography. Electronic structures are studied through computational methods in comparison with FOX-7. In addition, the chemical reactivity of **3** was also investigated. Its hydroxylammonium (**7**), hydrazinium (**8**), and ammonium (**9**) salts were prepared and the nitrate product (**10**) was also isolated. Compound **10** has a C-N bond length of 1.577 Å that is one of the longest values found for the C-NO_2 bond. It was found that the incorporation of a tetrazole or triazole ring into the backbone of a conjugated nitroenamine does lead to a planar structure, which not only enhances the thermal stability but also improves the sensitivity of the product.

INTRODUCTION

Push-pull ethylene-containing compounds (Figure 1a), which contain electron-donating and electron-withdrawing substituents, have been investigated widely in recent years.[1] This gives rise to interesting changes in the chemical and physical properties of these compounds due to the conjugative interaction between the donor and acceptor moieties. In the field of energetic materials, 1,1-diamino-2,2-dinitroethene (FOX-7, Figure 1b) is a typical push-pull ethylene. The nitro group (-NO_2) is one of the strongest electron-withdrawing groups and the amino group (-NH_2) is an electron- donating group. FOX-7 shows promising properties such as a detonation performance and insensitivities toward mechanical stimuli that are comparable to that of the commonly used secondary explosive RDX.[2]

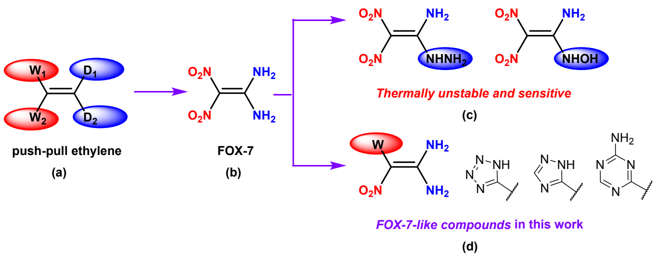


Figure 1. (a) Push–pull ethylenes (W =electron-withdrawing group; D = electron-donating group). (b) The molecular structure of FOX-7. (c) Thermally unstable and sensitive FOX-7 derivatives. (d) FOX-7-like compounds in this work

Inspired by the good performance of FOX-7, exploring new fascinating energetic molecules which result from FOX-7 has been an important research topic since its discovery. Molecular modification has been utilized to generate many energetic derivatives based on FOX-7 and many synthetic strategies have been developed.[3] It is worth noting that these methods typically involve FOX-7 as a starting material.[4] However, such an approach does not always provide competitive alternatives relative to FOX-7. FOX-7 is a push-pull ethylene molecule, but it is not strictly planar given that the nitro groups are twisted out of the plane by the two amino groups and C=C bond, no matter if it is in the α phase, β phase or γ phase.[5] In addition, its derivatives, the well-studied 1-amino-1-hydrazino-2,2-dinitroethene[6] and 1-amino-1-hydroxyamino-2,2-dinitroethene[7] (Figure 1c) that were prepared by transamination of FOX-7 with amines have shown that they are sensitive and thermally unstable. To overcome this problem, formation of a planar structure could lead to an advanced insensitive energetic material as shown in previous studies.[8]

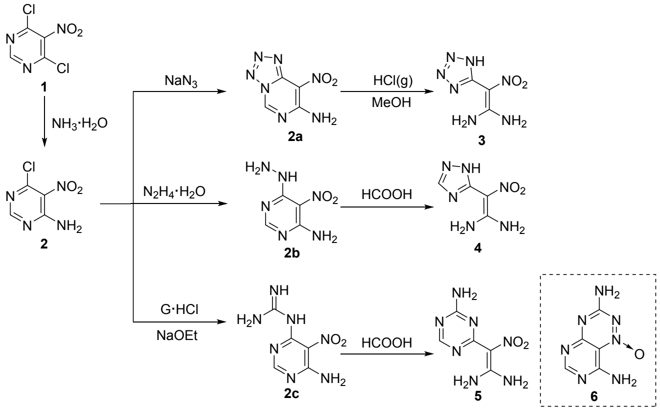
Motivated by the advantages of potential intramolecular hydrogen bond interactions of adjacent nitro group and nitrogen-rich heterocyclic rings,[9] we anticipated that a FOX-7-like compound with replacement of a nitro group with a nitrogen-rich heterocyclic ring would show promising possibilities. Now we report the design of three new FOX-7-like compounds (Figure 1d) and studies leading to their syntheses. These FOX-7-like compounds have conjugated ethylene structures where one nitro group is replaced by a heterocyclic ring (tetrazole, triazole or triazine ring). They were prepared from a commercially available reagent 4,6-dichloro-5-nitropyrimidine (**1**). All of them were fully characterized and confirmed by single crystal X-ray diffraction. Their covalent bonding interactions and physiochemical properties were also studied. In addition, the chemical reactivity of compound **3** involving acid-base neutralization and nitration reactions was also investigated.

Results and Discussion

Synthesis

The synthetic route is shown in Scheme 1. Although compound **3** was reported previously, only limited characterization was given and the synthetic procedure was also very tedious; in fact, we were unable to synthesize **3** based on the literature.[10] Therefore, we modified the synthetic route. Compound **2a** was prepared by reacting **2** with sodium azide in an improved yield. Then **2a** was treated with a methanol HCl gas mixture to give **3**. Treatment of chloro-substituted **2** with hydrazine monohydrate gave the hydrazine-substituted product **2b**,[11] which was further treated with formic acid under reflux to give **4**. Compound **5** was obtained by reacting **2c**[12] with formic acid, although a previous study[13] showed that it was possible to form **6** with a triazine N-oxide moiety under such conditions. The structures of **3**-**5** were confirmed by single crystal X-ray diffraction.

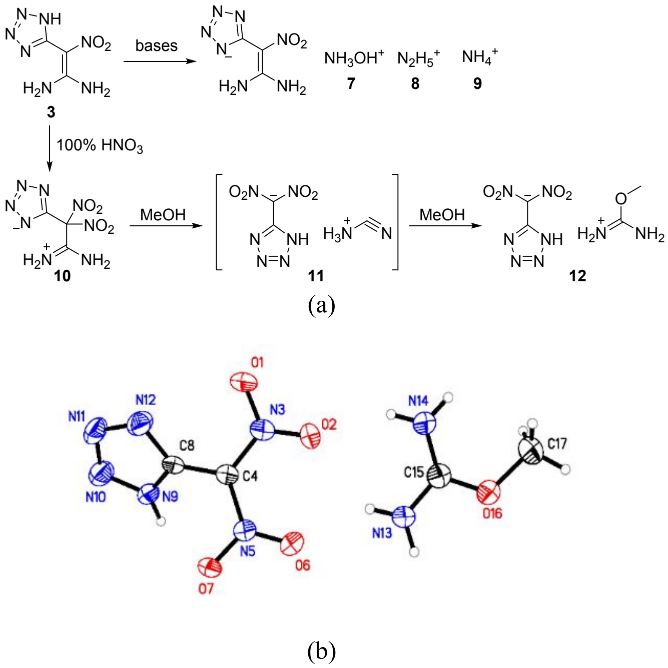
Scheme 1. Synthesis of 3at.



In order to extend the chemical reactivity of those FOX-7-like compounds, especially the potential nitrogen-rich energetic **3**, covalent bonding interactions were investigated. The charge concentrations associated with covalent bonds are clearly shown by deformation maps depicted in Figure 2. The deformation densities along the C=C bond paths in these compounds feature similar shapes. Furthermore, the topology of the total electron density was analyzed using Multiwfn.[14] All (3, -1) bond critical points (BCPs) have been characterized (Supporting Information, Figures 1-4) and the relevant data and derived properties for intramolecular covalent bonds are given in Table 1. The negative Laplacians at the BCPs with high electron densities indicate the covalent character of a bond. The ellipticity $\varepsilon = \lambda_1/\lambda_2-1$ at BCP is viewed as an indicator of asymmetric distribution of electron density around the bond; the higher deviation to axisymmetric distribution, the larger the ε value at BCP. It is found that **3** has the lowest value of $\varepsilon = 0.303$, indicating the C=C double bond in **3** has a lower π-contribution than the other three compounds. This is also supported by an additional indicator, $\eta = |\lambda_1|/\lambda_3$, which becomes smaller with decreasing covalent character. Compound **3** has a $\eta = 1.807$, which is comparable to that of **4** and lower than those of FOX-7 and **5**. The low covalent character results in the nitrated product being stabilized at room temperature.

Previous studies have shown that the nitrated products of FOX-7 are difficult to isolate since they are very unstable at room temperature.[15] In 2014, Vo isolated tetranitroacetimidic acid (TNAA) accompanied by the hydrolysis of one amino group.[16] Meanwhile, another nitrated product was stabilized by formation of the triflate salt. After analyzing these covalent bonding interactions, it was thought that the nitration of **3** could lead to a neutral compound. Treatment of **3** with 100% nitric acid gave the zwitterionic salt **10** (Scheme 2a), which was confirmed by single crystal X-ray diffraction analysis. Compound **10** can be stored for several weeks at room temperature; however, it is not stable in organic solvents. During the recrystallization of **10** in methanol, **12** was formed, which was confirmed by single crystal X-ray diffraction (Scheme 2b). It is believed that the C-C bond in **10** is easily broken to form the intermediate **11** which reacted with methanol to give **12**. In addition, reactions of **3** with 50% hydroxylamine, hydrazine monohydrate or aqueous ammonia resulted in the formation of salts **7**, **8**, or **9**, respectively.

Scheme 2. (a) Synthetic routes to energetic derivatives (7-12) from 3; (b) Molecular structure of 12



(a)

(b)

^{15}N NMR spectra

The ^{15}N NMR spectra of **3**, **7** and **10** were recorded in d_6-DMSO and are given in Figure 3. In **3**, only two signals were found and assigned to the nitrogen atoms in the nitro group (N5, δ = -20.1 ppm) and amino groups (N6/N7, δ= -289.0 ppm), respectively. For the hydroxylammonium salt (**7**), the chemical shifts for the nitro and amino groups (N5, δ = -20.8 ppm; N6/N7, δ = -288.9 ppm, respectively) are nearly the same as those in **3**. The nitrogen signals (N1, N2, N3 and N4) in the tetrazole ring are seen (N2/N3: δ = -4.8 ppm; N1/N4: δ = -96.2 ppm). The N8 signal of the hydroxylammonium cation is found at δ = -282.2 ppm. In comparison with **7**, the nitrogen signals of the tetrazole ring and amino groups in **10** are shifted to lower field (N2/N3: δ = 18.3 ppm; N1/N4: δ = -53.7 ppm; N7/N8: δ = -261.1 ppm), while the N5/N6 signal (δ = -21.2 ppm) assigned to the nitro groups are comparable to those found in **3** and **7**.

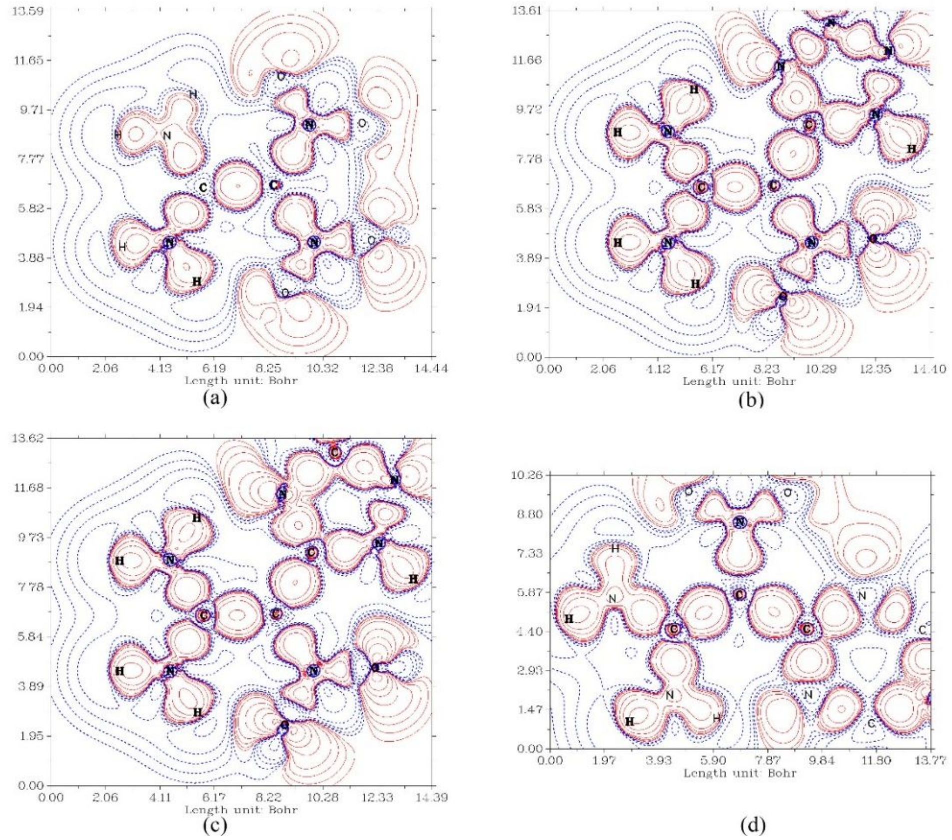


Figure 2. Deformation density maps for (a) FOX-7 and (b-d) **3-5**. Contours are drawn. Positive deformation density is in solid red; negative in dashed blue.

Table 1. Topological parameters of the bond critical points in FOX-7, 3, 4, 5 (BCPs, 3,−1) from Multiwfn.

Comp.	Bond	d_{BP} (Å)[a]	$d1_{BP}$ (Å)[b]	$d2_{BP}$ (Å)[c]	ρ (au)[d]	$\nabla^2\rho$ (rBCP)[e]	λ_1[f]	λ_2[f]	λ_3[f]	ε[g]	η[h]
FOX-7	C5-C4	1.421	0.734	0.686	0.293	-0.759	-0.630	-0.464	0.336	0.357	1.875
3	C5-C4	1.435	0.750	0.685	0.287	-0.742	-0.611	-0.469	0.338	0.303	1.807
4	C5-C4	1.435	0.752	0.683	0.287	-0.742	-0.611	-0.468	0.337	0.305	1.813
5	C17-C18	1.420	0.747	0.673	0.293	-0.764	-0.626	-0.467	0.329	0.340	1.901

[a] d_{BP} the total length of the bond path (BP); [b] $d1_{BP}$ the distance of the first named atom to the BCP; [c] $d2_{BP}$ the distance of the BCP to the second named atom; [d] ρ: the electron density; [e] $\nabla^2\rho$： the Laplacian; [f] λ_1, λ_2 and λ_3 are the Hessian eigenvalues; [g] ε is the bond ellipticity ($\varepsilon = \lambda_1/\lambda_2-1$); [h] $\eta = |\lambda_1|/\lambda_3$.

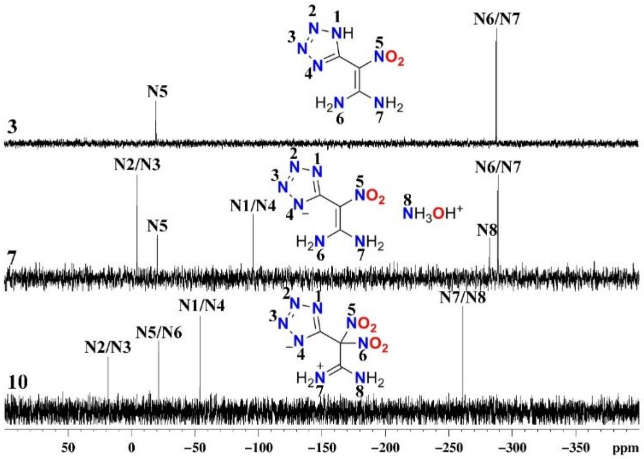
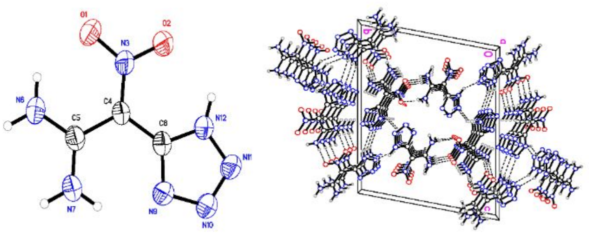


Figure 3. ^{15}N NMR spectra of **3**, **7** and **10**

Crystal structures

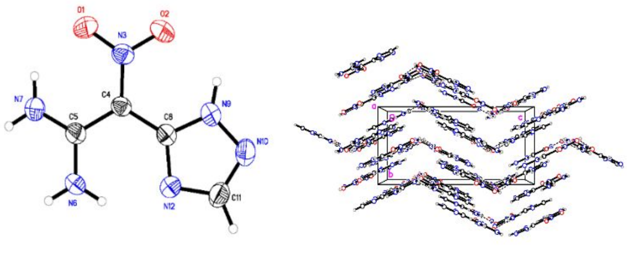
Compound **3** crystallizes in the triclinic space group P-1 with six moieties in the unit cell at 293 K. The crystal structure is shown in Figure 4a. There are three kinds of molecules in the unit cell (Figure 4b). The C4=C5 bond length is 1.481 Å in **3** compared with the C=C bond length of 1.446 Å in FOX-7. Bonds C16-C17 and C28-C29 are 1.463 and 1.436 Å, respectively (Supporting Information). Unlike the nonplanarity of FOX-7, the atoms in **3** are coplanar with torsion angles of O(2)-N(3)-C(4)-C(8) = 0.5(5)°, N(3)-C(4)-C(5)-N(6) = 2.8(5)° and N(3)-C(4)-C(8)-N(9) = 179.3(3)°, respectively. (O14-N12-C4-C5 = 20.84°, O2-N3-C4-C5 = -158.10° are the values found for FOX-7, Figure S1 in SI) The structure of **3** is mainly dominated by many intermolecular hydrogen bonds (N6–H6A···O13 and N7–H7A···O14) and intramolecular bonds (N6–H6B···O1, N12–H12···O2 and N7–H7B···N9) (SI).



(a) (b)

Figure 4. (a) Molecular structure of **3**. (b) Packing diagram of **3** viewed down the *a*-axis. Unit cell indicated, and dashed lines represent hydrogen bonding.

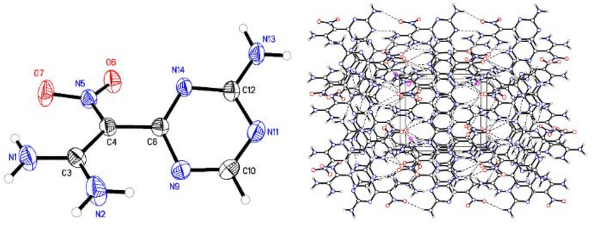
Compound **4** crystallizes in the orthorhombic space group Pbca with eight moieties in the unit cell at 293 K. The crystal structure is shown in Figure 5a. The bond length of C4=C5 is 1.459 Å. Compound **4** is also planar with torsion angles O(2)-N(3)-C(4)-C(8) = 0.6(2)^{o} and C(8)-C(4)-C(5)-N(6) = -0.8(2)^{o}, respectively. In addition, intramolecular hydrogen bonds involving N7-H7B···O1, N9-H9···O2 and N6-H6B···N12 are observed (Figure 5b).



(a) (b)

Figure 5. (a) Molecular structure of **4**. (b) Packing diagram of **4** viewed down the *a*-axis. Unit cell indicated and dashed lines represent hydrogen bonding.

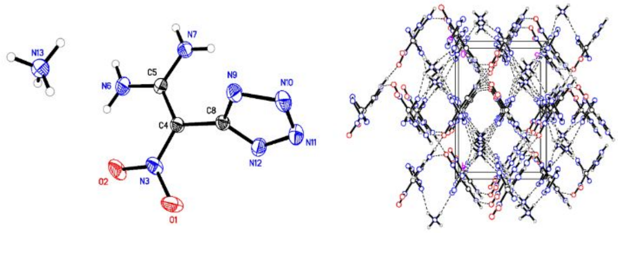
Compound **5** crystallizes in the monoclinic space group P2/n with four moieties in the unit cell at 293 K. The crystal structure is shown in Figure 6a. The bond length of C4=C8 is 1.477 Å, which is slightly longer than that in **4**. However, due to the steric hindrance of the six-membered triazine ring, it is caused to rotate out of the plane by the nitro and amino groups. The torsion angle of N(14)-C(8)-C(4)-N(5) is 33.8(3)^{o}. There are two kinds of intramolecular hydrogen bonds N1-H1B···O7 and N2-H2B···N9 and several intermolecular hydrogen bonds (Supporting Information).



(a) (b)

Figure 6. (a) Molecular structure of **5**. (b) Packing diagram of **5** viewed down the *c*-axis. Unit cell indicated and dashed lines represent hydrogen bonding.

Compound **9** crystallizes in the orthorhombic space group Pna2$_1$ with four moieties in the unit cell and a crystal density of 1.674 g cm^{-3} at 293 K (Figure 7a). The bond length of C4=C5 is 1.471 Å. The C4=C5 double bond linked amino and nitro groups are nearly planar with a torsion angle of N(3)-C(4)-C(5)-N(7) = -174.6(2)^{o}. The plane forms a dihedral angle of 69.18^{o} with the tetrazole ring. In the packing diagram, the ammonium cation is coordinated with the adjacent nitrogen atoms in the tetrazole rings (N13–H13A···N9, N13–H13B···N11, N13–H13C···N12, N13–H13D···N10). In addition, the N6 atom forms an intramolecular hydrogen bond with the O2 atom (N6–H6B···O2).



(a) (b)

Figure 7. (a) Molecular structure of **9**. (b) Packing diagram of **9** viewed down the *a*-axis. Unit cell indicated and dashed lines represent hydrogen bonding.

Compound **10** crystallizes as a zwitterion structure in the triclinic space group P-1 with two moieties in the unit cell and a crystal density of 1.741 g cm^{-3} at 293 K (Figure 8). The bond lengths of C13-N14 and C13-N15 are 1.289 and 1.300 Å, respectively. The bond length of C6-C13 is 1.540 Å. It is worth noting that the bond length of C6-N10 is 1.577 Å. Overall the mean length for a C-NO$_2$ bond is 1.528 Å with a standard deviation of 0.02. This is from a collection of 1694 C-NO$_2$ distances in the Cambridge Structural Database. The bond length of 1.577 Å is one of the largest reported values for the C-NO$_2$ bond.

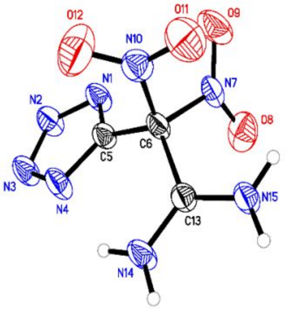


Figure 8. Molecular structure of **10**

Physical and Detonation Properties

The physicochemical properties are summarized in Table 2. The onset decomposition temperature of these new compounds was determined using a TA Instruments Q2000 differential scanning calorimeter at a heating rate of 5 ^{o}C min^{-1}. As can be seen, the FOX-7-like compounds **3**-**5** have much higher decomposition temperatures (**3**: 275 ^{o}C; **4**: 267 ^{o}C; **5**: 276 ^{o}C) than FOX-7 (T_d: 220 ^{o}C). Energetic salts **7** and **8** are more thermally stable than **3**, while the ammonium salt **9** decomposes at 242 ^{o}C, which is lower than the parent molecule **3**. The nitrated product **10** decomposes at 120 ^{o}C, which is the lowest of any of the new compounds in this work.

Table 2. Energetic properties and detonation parameters

Comp	ρ[a] (g·cm^{-3})	Dv[b] (m s^{-1})	P[c] (GPa)	ΔH_f[d] (kJ mol^{-1}/kJ g^{-1})	T_{dec}[f] (°C)	IS[g] (J)	FS[h] (N)
3	1.83	8499	26.7	181.5/1.06	275	30	>360
4	1.71	7427	19.0	46.2/0.27	267	36	>360
5	1.70	7488	19.3	54.0/0.27	276	40	>360
7	1.76	9016	30.4	71.1/0.32	286	30	>360
8	1.80	9596	34.0	398.4/1.96	275	35	>360
9	1.66	8446	25.2	255.4/1.36	242	40	>360
10	1.73	8445	29.0	354.5/1.64	120	8	240
FOX-7	1.845	8613	31.6	-134.1/-0.91	220[i]	24.7[i]	>360[i]
TNT	1.654	6824	19.4	-59.3/-0.26	300	15	353
RDX	1.80	8801	33.6	70.3/0.32	204	7.4	120
HMX	1.905	9193	37.8	74.8/0.25	275	7.4	120

[a] Density measured by a gas pycnometer at 25 °C; [b] Calculated detonation velocity from EXPLO5_V6.05.02; [c] Calculated detonation pressure from EXPLO5_V6.05.02; [d] Calculated molar enthalpy of formation in solid state; [e] Melting point; [f] Temperature of decomposition (onset); [g] Impact sensitivity; [h] Friction sensitivity [i] Ref 8d.

The densities were measured with a gas pycnometer at room temperature. Replacement of a nitro group by a tetrazole ring led to a slightly lower density (**3**: 1.83 g cm^{-3} vs FOX-7: 1.845 g cm^{-3}). The densities of **4** and **5** are 1.71 and 1.70 g cm^{-3}, respectively. The hydrazinium salt **8** is more dense (1.80 g cm^{-3}) than the hydroxylammonium (**7**: 1.76 g cm^{-3}) and the ammonium salt (**9**: 1.66 g cm^{-3}). The heats of formation were calculated by using the Gaussian 03 suite of programs. As expected, the introduction of nitrogen rich rings (tetrazole, triazole, amino-triazine) results in **3**-**5** having higher heats of formation than FOX-7. Compounds **7**-**10** also show high positive heats of formation.

With the measured densities and calculated heats of formation, the detonation performances were calculated by using the EXPLO5 6.05.02 program.[17] Compound **3** has a detonation velocity of 8499 m s^{-1} and a detonation pressure of 26.7 GPa, which are lower than those of FOX-7. However, the hydrazinium salt **8** has the best detonation performance with a detonation velocity of 9596 m s^{-1} and a detonation pressure of 34.0 GPa, which are comparable to those of HMX. The hydroxylammonium salt **7** also has good detonation properties (Dv: 9016 m s^{-1} and P: 30.4 GPa).

For initial safety testing, the mechanical sensitivities toward impact (IS) and friction (FS) were measured according to standard BAM technology. As can be seen, compound **10** is sensitive with an impact sensitivity of 8 J and a friction sensitivity of 240 N. The other compounds show friction sensitivities comparable to FOX-7. These FOX-7-like compounds (**3**-**5**) are less sensitive than FOX-7. Among these newly prepared energetic compounds, the hydrazinium salt **8** is the most promising one as a practical HMX replacement with a moderate density (1.80 g cm^{-3}), acceptable sensitivities (35 J, >360 N), and good detonation properties (9596 m s^{-1} and 34.0 GPa). In addition, the FOX-7-like compound **3** shows promising properties with increased thermal decomposition temperature and improved impact sensitivity as a replacement for FOX-7. Due to its high nitrogen content (N: 57.3%), it also has a potential application as a gas generator.

In order to balance performance and safety, the design and synthesis of novel energetic molecules requires tuning properties by the incorporation of energetic moieties into known compounds. While this is a usual method to obtain more energetic derivatives, it is not an efficient design concept to obtain energetic molecules with high performances and low sensitivities. In this study, we focused on the design and syntheses of FOX-7-like compounds where a nitro group in FOX-7 was replaced by a tetrazole or a triazole ring. An apparent advantage of this strategy is an enforced overall planar conformation (Figure 9), which results in significant enhancement in thermal stability and sensitivity. Although the triazine ring is twisted out of the plane, compound **5** is still thermally stable and insensitive.

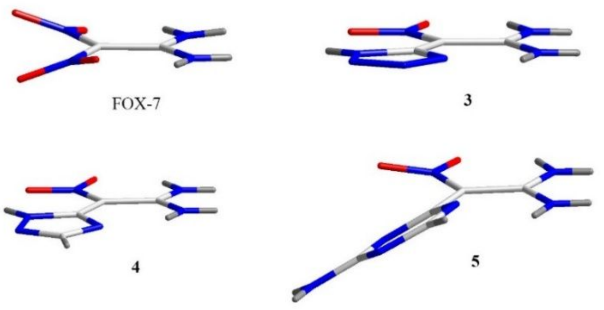
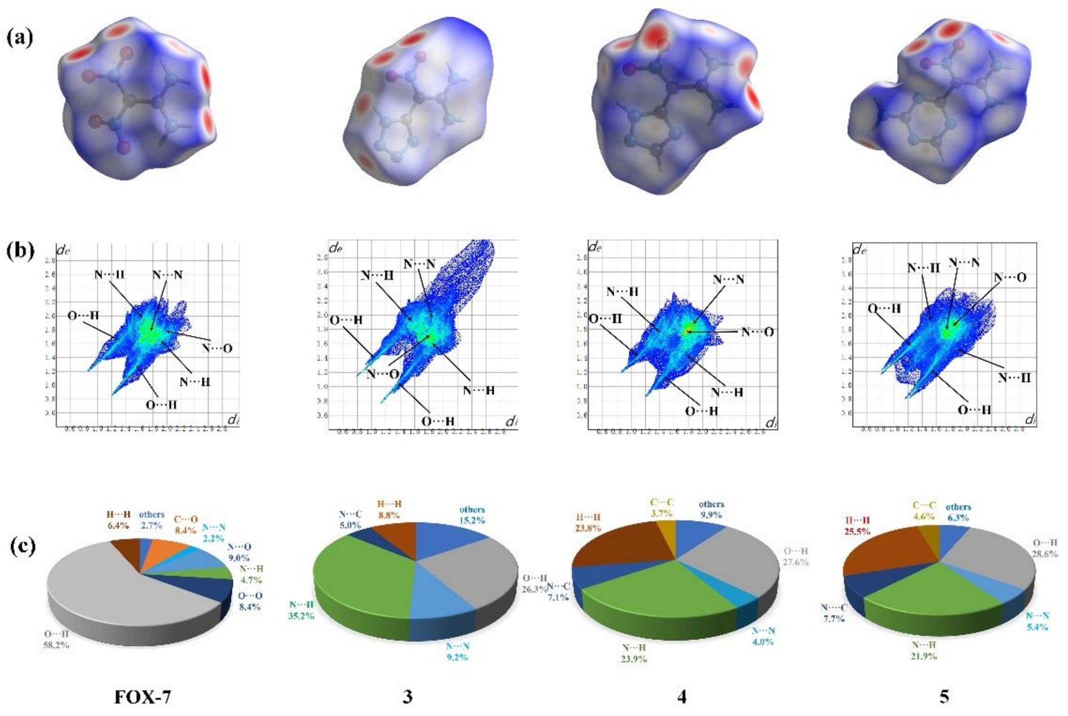


Figure 9. Crystal structures of FOX-7 and **3**-**5**



FOX-7 **3** **4** **5**

Figure 10. Hirshfeld surface (a), fingerprint plot (b) and individual atomic contact percentage contribution to the Hirshfeld surface (c) for FOX-7 and **3**-**5**.

To gain understanding of molecular stability and sensitivity between FOX-7 and FOX-7-like compounds (**3**-**5**), 2D-fingerprint and the Hirshfeld surfaces of single crystals were used to study their intermolecular interactions (Figure 10). In Hirshfeld surface analysis, the red and blue areas on the surfaces represent high and low close contact populations, respectively.[18] As can be seen (Figure 10a and Figure 10b), the remarkable spikes are concentrated on the oxygen and nitrogen atoms, demonstrating strong O···H and N···H hydrogen bonding interactions. The O···H interactions in FOX-7 plays a dominant role with the amount of 58.2% of the total weak interactions, while the O···H interactions in **3**-**5** decreases to ~ 27% (Figure 10c). Meanwhile, compounds **3**-**5** show a much higher percentage of N···H interactions (**3**: 35.3%; **4**: 23.9%; **5**: 21.9%) than that in FOX-7 (4.7%). Thus, the introduction of nitrogen-rich heterocyclic rings supplies greater intramolecular N···H interaction, which can lead to high thermal stability and low sensitivity.

In summary, three FOX-7-like compounds (**3**-**5**) were synthesized based on the newly developed direct ring cleavage reactions of amino-nitro-substituted pyrimidines. In addition, the chemical reactivity of **3** was studied and the crystal structures of **3**-**5**, **9**, **10** and **12** were obtained. Compounds **3** and **8** with high nitrogen content show promising properties as secondary explosives and gas generators. Compounds **3** and **4** exhibit high thermal stabilities and insensitivities as a result mainly of fully π-conjugated electronic structures that arise from their planar geometry. Thus, this work demonstrates that the enforced planarization of the FOX-7 structure is an exciting, viable new strategy for enhancing thermal stabilities and improving sensitivities. While the routes to balance performance and safety are full of challenges in the field of energetic materials, advances in enforced planar frameworks may be a new direction in the foreseeable future.

Caution! The compounds in this work are energetic materials that could potentially explode under certain conditions (e.g., impact, friction or electric discharge). Appropriate safety precautions, such as the use of shields in a fume hood and personal protection equipment (safety glasses, face shields, ear plugs, as well as gloves) should be taken at all times when handling these materials.

General

All reagents were purchased from AKSci or Alfa Aesar in analytical grade and were used as supplied. ^{1}H, and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer. ^{15}N NMR spectra were recorded on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra are given with respect to external $(CH_3)_4Si$ (^{1}H and ^{13}C). [D_6]DMSO was used as a locking solvent unless otherwise stated. IR spectra were recorded using KBr pellets with a FT-IR spectrometer (Thermo Nicolet AVATAR 370). Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Decomposition temperatures (onset) were recorded using a dry nitrogen gas purge and a heating rate of 5 ^{o}C min^{-1} on a differential scanning calorimeter (DSC, TA Instruments Q2000). Elemental analyses (C, H, N) were performed with a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester.

Computational Methods

The gas phase enthalpies of formation were calculated based on G2 method. The solid-state heats of formation (for **3**-**5** and **10**) were calculated based on Trouton's rule according to equation (1) (T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).[19]

$$\Delta H_{sub} = 188 / Jmol^{-1}K^{-1} \times T \qquad (1)$$

For energetic salts (**7**-**9**), the solid-phase enthalpy of formation is obtained using a Born−Haber energy cycle.[20] For **7**·H_2O, the solid-phase enthalpy of formation is obtained by adding the gas phase heat of formation of the anhydrous compound to that of water (-241.8 kJ mol^{-1}).[21]

Crystal Structure Analysis

A clear colorless block crystal (**3**) of dimensions 0.134 × 0.049 × 0.040 mm^3, a clear colorless needle crystal (**4**) of dimensions 0.389 × 0.020 × 0.020 mm^3, or a clear colorless plate crystal (**10**) of dimensions 0.301 × 0.120 × 0.023 mm^3 was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a PHOTON 100 CMOS detector. The crystals were irradiated using a 1μs microfocus CuK$_\alpha$ source (λ = 1.54178 Å) with Helios optics. Data were collected at room temperature (20 °C).

A clear colorless plate crystal (**5**) of dimensions 0.205 × 0.107 × 0.030 mm^3, a clear colorless needles crystal (**9**) of dimensions 0.418 × 0.093 × 0.028 mm^3, or a clear colorless plate crystal (**12**) of dimensions 0.261 × 0.183 × 0.020 mm^3 was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK$_\alpha$ radiation (λ = 0.71073 Å). Data were collected at room temperature (20 °C).

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].[22] Data reduction was performed using *SAINT* [v8.34A],[23] and *XPREP* [v2014/2][24]. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].[25] The structure was solved and refined with the aid of the program SHELXL-2014/7.[26] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were located from the difference electron-density maps and added using a riding model.

For **3**, severely disordered water molecules in a void running parallel to the *a*-axis were treated using the SQUEEZE procedure in PLATON. SQUEEZE calculated that the void contained 44 electrons per unit cell which is proposed to correspond to four water molecules per unit cell or two water molecules per asymmetric unit.

Synthesis

Synthesis of **2a·H_2O**

A mixture of compound **2**[27] (3.49 g, 20.0 mmol) and sodium azide (1.97 g, 30.0 mmol) were suspended in acetone/water (25 mL/25 mL). The reaction mixture was stirred at room temperature for 24 h, the white solid which was formed was collected by filtration and washed with water (15 mL) and acetone (15 mL). After drying in air, the product **2a** (2.99 g, 75%) was obtained.

2a·H_2O: White solid. $T_{d\ (onset)}$: 257 °C. ^{1}H NMR (d_6-DMSO): 10.36 (s, 2H), 8.79 (s, 1H) ppm. ^{13}C NMR (d_6-DMSO): δ 165.1, 154.0, 148.9, 102.1 ppm. IR (KBr): $\tilde{\nu}$ = 3318, 3209, 2945, 1698, 1643, 1540, 1412, 1398, 1364, 1303, 1273, 1216, 1181, 1136, 1099, 1051, 997, 970, 845, 748, 689, 587 cm^{-1}. $C_4H_5N_7O_3$ (199.13): Calcd: C 24.13, H 2.53, N 49.24 %. Found: C 24.16, H 2.64, N 49.50 %.

Synthesis of **3**

Gaseous HCl (4.8 g) was bubbled into methanol (50 mL) and then compound **2a** (2.0 g, 10.0 mmol) was added. The suspension was stirred at room temperature for 36 h. The product **3** (1.37 g, 80%) was isolated by filtration and washed with methanol (10 mL) and diethyl ether (10 mL).

3: White solid. $T_{d\ (onset)}$: 275 °C. ^{1}H NMR (d_6-DMSO): 15.02 (br), 9.31 (s, 2H), 7.92 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 158.1, 150.1, 101.5 ppm. ^{15}N NMR (d_6-DMSO): δ -19.9, -288.1 ppm.IR (KBr): $\tilde{\nu}$ = 3342, 1649, 1557, 1517, 1409, 1329, 1210, 1143, 1094, 1044, 1028, 987, 787, 762, 689, 630, 565 cm^{-1}. $C_3H_5N_7O_2$ (171.12): Calcd: C 21.06, H 2.95, N 57.30 %. Found: C 21.33, H 3.22, N 55.75 %.

Synthesis of **4**

A mixture of **2b** (0.51 g, 3.0 mmol) and formic acid was heated at 100 °C, with stirring for 2 h. After removing the insoluble solids by filtration, the filtrate was concentrated and the residue was recrystallized from hot water to give **4**.

4: White solid. $T_{d\ (onset)}$: 267 °C. ^{1}H NMR (d_6-DMSO): 13.69 (s, 1H), 9.88 (s, 2H), 7.98 (s, 1H), 7.79 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 158.6, 149.5, 148.4, 104.1 ppm. IR (KBr): $\tilde{\nu}$ = 3392, 3390, 1640, 1617, 1522, 1499, 1387, 1315, 1277, 1211, 1196, 1104, 1056, 977, 959, 907, 757, 693, 627 cm^{-1}. $C_4H_6N_6O_2$ (170.13): Calcd: C 28.24, H 3.55, N 49.40 %. Found: C 27.91, H 3.69, N 48.89 %.

Synthesis of **5**

A mixture of **2c** (0.59 g, 3.0 mmol) and formic acid was heated at 100 °C, with stirring for 2 h. After removing the insoluble solids by filtration, the filtrate was concentrated and the residue was recrystallized from hot water to give **5**.

5: White solid. $T_{d\ (onset)}$: 276 °C. ^{1}H NMR (d_6-DMSO): 8.41 (s, 1H), 7.86 (br), 7.40 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 168.8, 165.7, 165.4, 157.8, 110.5 ppm. IR (KBr): $\tilde{\nu}$ = 3454, 3392, 3321, 3165, 1635, 1569, 1534, 1404, 1361, 1303, 1258, 1088, 1028, 986, 917, 819, 797, 721, 687, 630, 607 cm^{-1}. $C_5H_7N_7O_2$ (197.15): Calcd: C 30.46, H 3.58, N 49.73 %. Found: C 30.11, H 3.78, N 49.45 %.

General procedure for the syntheses of 7-9

Compound **3** (0.34 g, 2.0) was suspended in water (10 mL), and two equivalents of base (aqueous ammonia, hydrazine monohydrate, or 50% hydroxylamine solution) were added. The reaction mixture was stirred at room temperature for 2 h, and the solvent was removed by air. The crude product was purified by recrystallization in ethanol and water.

7·H_2O: White solid. T_m: 142 °C. $T_{d\ (onset)}$: 286 °C. ^{1}H NMR (d_6-DMSO): 9.07 (br), 7.95 (br), 6.63 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 158.2, 151.1, 102.0 ppm. ^{15}N NMR (d_6-DMSO): δ -4.8, -20.8, -96.2, -282.2, -288.9 ppm. IR (KBr): $\tilde{\nu}$ = 3482, 3361, 3298, 3224, 3121, 2995, 1670, 1633, 1552, 1518, 1442, 1390, 1353, 1326, 1242, 1142, 1075, 1003, 805, 763, 668, 599 cm^{-1}. $C_3H_{10}N_8O_4$ (222.16): Calcd: C 16.22, H 4.54, N 50.44 %. Found: C 16.38, H 4.47, N 50.81 %.

8: White solid. $T_{d\,(onset)}$: 275 °C. ^{1}H NMR (d_6-DMSO): 8.54 (br), 6.37 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 159.0, 155.0, 104.2 ppm. IR (KBr): $\tilde{\nu}$ = 3313, 1615, 1541, 1390, 1337, 1293, 1138, 1096, 1065, 1001, 961, 763, 620 cm^{-1}. $C_3H_9N_9O_2$ (203.16): Calcd: C 17.74, H 4.47, N 62.05 %. Found: C 17.61, H 4.55, N 61.33 %.

9: White solid. T_m: 242 °C, $T_{d\,(onset)}$: 289 °C. ^{1}H NMR (d_6-DMSO): 8.35 (br), 7.47 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 158.8, 154.6, 103.9 ppm. IR (KBr): $\tilde{\nu}$ = 3431, 3264, 1689, 1658, 1605, 1544, 1459, 1384, 1279, 1117, 1055, 1001, 784, 753, 725, 694, 604, 508 cm^{-1}. $C_3H_8N_8O_2$ (188.15): Calcd: C 19.15, H 4.29, N 59.56 %. Found: C 18.97, H 4.34, N 58.60 %.

Synthesis of **10**

Compound **3** (0.43 g, 2.5 mmol) was added slowly to 100% nitric acid (3 mL) at -5 0 °C. The reaction mixture was stirred at 0 °C for 1 h. The solution was concentrated by air to give a white solid, which was washed with acetone (5 mL) and dried in air to give **10**.

10: White solid. $T_{d\,(onset)}$: 120 °C. ^{1}H NMR (d_6-DMSO): 10.28 (br) ppm. ^{13}C NMR (d_6-DMSO): δ 156.0, 151.3, 113.0 ppm. ^{15}N NMR (d_6-DMSO): δ 18.3, -21.2, -53.7, -261.1 ppm. IR (KBr): $\tilde{\nu}$ = 3254, 3123, 2987, 2809, 1717, 1617, 1577, 1490, 1433, 1392, 1337, 1308, 1183, 1161, 1146, 1111, 1025, 988, 864, 830, 735, 716, 684 cm^{-1}. $C_3H_4N_8O_4$ (216.12): Calcd: C 16.67, H 1.87, N 51.85 %. Found: C 16.89, H 2.08, N 51.79 %.

ASSOCIATED CONTENT

Supporting Information. Crystal structure analysis of compounds **3, 4, 5, 9, 10** and **12** and covalent bonding interactions are given in the Supporting Information. 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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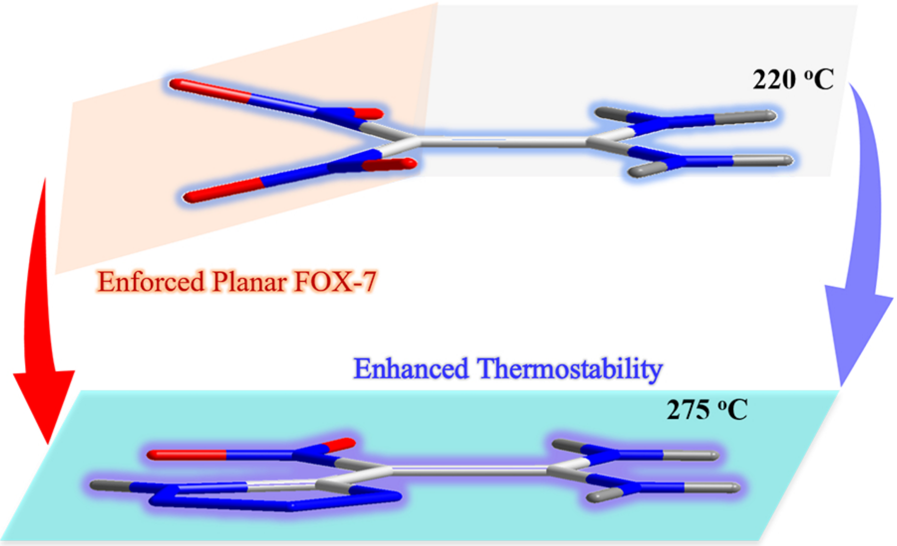

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