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Three classes of nitrogen-rich energetic compounds **7-9** (combination of tetrazolyl, dinitromethyl and furoxan), **12-17** (combination of tetrazolyl, (1,2,4-oxadiazol-5-yl)nitroamino and furoxan) and **20-22** (combination of dinitromethyl, (1,2,4-oxadiazol-5-yl)nitroamino) and furoxan) were obtained by selected reactions with 3,4-dicyano-furoxan. All the new compounds were thoroughly characterized by IR, NMR [^{1}H, ^{13}C{^{1}H}], elemental analysis, and differential scanning calorimetry (DSC). Compounds **7**, **13**, **20** and **22** were also further characterized with single-crystal X-ray diffraction studies. Heats of formation and detonation performances for nine compounds were determined using Gaussian 03 and EXPLO5 v6.01 programs, showing that **15** as a secondary explosive is superior to 1,3,5-trinitrotriazacyclohexane (RDX) and **20** is a promising green primary explosive.

Introduction

Nitrogen-rich energetic compounds are a fascinating class of high-energy density materials (HEDMs), which can be used as propellants, explosives and pyrotechnics.[1] Over many years, considerable effort has been expended in the field of energetic materials in search for new nitrogen-rich energetic compounds with high density, high detonation performance including detonation pressure and velocity, good thermal stability, low sensitivity and favorable oxygen balance (OB).[2] However, it is usually difficult to obtain energetic materials with improved comprehensive properties because the parameters that impact each property are often contradictory.[3]

A good strategy for the synthesis of nitrogen-rich energetic compounds is the combination of highly endothermic heterocycles with energetic units. High enthalpies are demonstrated by nitrogen-rich heterocycles including pentazoles, tetrazoles, triazoles, and diazoles.[4] Enthalpies of formation decrease as a function of the number of catenated nitrogen atoms. Unfortunately, pentazole and alkylated pentazoles have not been used routinely because of thermal instability or sensitivity to external stimuli.[5] One of the best ways to obtain good detonation performance and concomitant safety is by introducing tetrazole into the target molecule. Energetic units include nitro, nitroamino, dinitromethyl, and/or trinitromethyl groups. Earlier work has shown that the dinitromethyl group not only enhances oxygen balance and density, but also the planarity of the dinitromethyl group results in a more stabilizing influence than that of the trinitromethyl group –C(NO$_2$)$_3$.[6] Some compounds that contain a (1,2,4-oxadiazol-5-yl)nitroamino group show good density and detonation performance and also exhibit an acceptable sensitivity.[7] As a result, dinitromethyl- or (1,2,4-oxadiazol-5-yl)nitroamino-containing azole-based energetic materials have been studied extensively in the past few years.

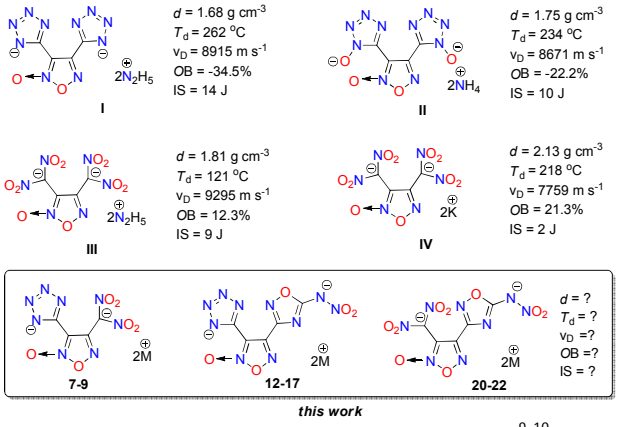

Figure 1 Nitrogen-rich energetic salts in previous studies[9, 10] and this study.

Furoxan as a "hidden" nitro group possesses the highest oxygen content (37.2%) among N-heterocycles. When a furoxan ring replaces a nitro group in a compound, the density and detonation velocity increase by about 0.06–0.08 g cm^{-3} and 300 m s^{-1},

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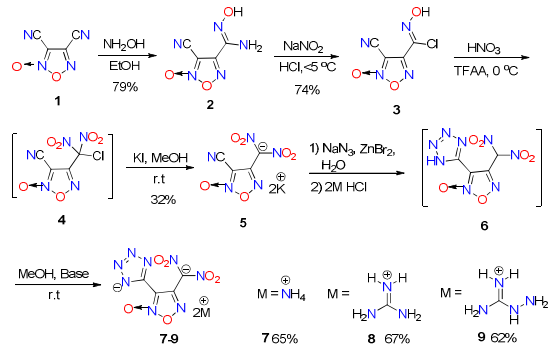
respectively.[8] Furoxan-based energetic compounds with the same substituent group at C3 and C4 have been well studied as primary or secondary explosives. For example, two salts resulting from the combination of two tetrazolyl or hydroxytetrazolyl with a furoxan ring show excellent thermal stabilities, high calculated detonation performance and acceptable sensitivities, e.g., Ⅰ : T_d = 262 °C, u_D = 8915 m s^{-1}, IS = 14 J; Ⅱ: T_d = 234 °C, u_D = 8671 m s^{-1}, IS =10 J, but their oxygen balances are negative, i.e., Ⅰ : OB = -34.5%, Ⅱ : OB = -22.2% (Fig. 1).[9] In contrast, by incorporating 4,5-bis(dinitromethyl)furoxanate-containing compounds, Ⅲ and Ⅳ possess good oxygen balances, Ⅲ: OB = 12.3%, Ⅳ: OB = 21.3%, but the thermal stability and impact sensitivity of Ⅲ are marginal, viz., T_d = 121 °C, IS = 9 J.[10] In order to pursue an optimum balance between energy and safety with furoxan coumpounds,[11] we now report the synthesis, characterization, and calculated detonation properties of nitrogen-rich energetic compounds **7-9**, **12-17** and **20-22** resulting from the combination of tetrazolyl, dinitromethyl and (1,2,4-oxadiazol-5-yl)nitroamino groups with furoxan.

Results and discussion

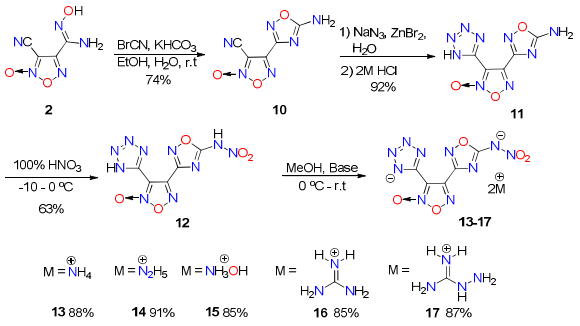
Synthesis

The synthetic pathway to the new energetic salts **7-9** is shown in Scheme 1. Hydroximoylamine **2** was readily synthesized through the selective reaction of a cyano group of compound **1**[12] with an equivalent amount of aqueous hydroxylamine. The hydroximoyl chloride **3** was prepared by diazotization in 50% HCl. This was nitrated with a mixture of trifluoroacetic acid anhydride (TFAA) and 100% HNO_3, and treated immediately with KI in methanol to give the potassium salt **5** as a yellow solid. Subsequently, via a 1,3-dipolar cycloaddition with sodium azide and acidification with 2 M HCl, 4-(dinitromethyl)-3-(1H-tetrazol-5-yl)-1,2,5-oxadiazole 2-oxide (**6**) was obtained as a yellow oil which decomposes slowly upon standing. Therefore, **6** was treated immediately with a nitrogen-containing base in methanol, which leads to energetic salts **7-9**. The structure of **7** was confirmed by single crystal X-ray diffraction analysis.

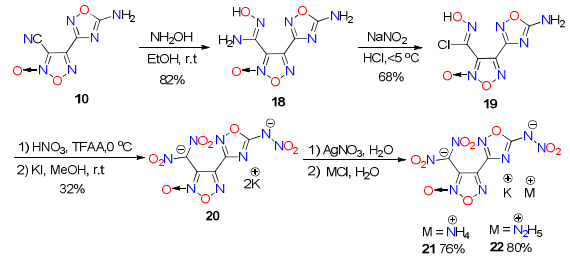
Analogous (1,2,4-oxadiazol-5-yl)nitroamino-containing energetic compounds, **12-17**, were synthesized via four steps (Scheme 2). Compound **2** was reacted with cyanogen bromide in H_2O/ethanol potassium bicarbonate solution to form 4-(5-amino-1,2,4-oxadiazol-3-yl)-3-cyano-1,2,5-oxadiazole 2-oxide (**10**). Then, the 4-(5-amino-1,2,4-oxadiazol-3-yl)-3-(1H-tetrazol- 5-yl)-1,2,5-oxadiazole 2-oxide



Scheme 1 Synthesis of energetic compounds **7-9**.



Scheme 2 Synthesis of energetic compound **12-17**.



Scheme 3 Synthesis of energetic compounds **20-22.**

(**11**) resulted from a click reaction. Subsequently, the neutral nitroamine compound (**12**) was successfully collected as a white solid with nitration by 100% nitric acid. The solid was washed with trifluoroacetic acid, and dried under vacuum. Salts of **13-17** could be readily prepared in high yield (85%-91%) by the addition of a base or the corresponding carbonates to aqueous solutions of **12**. The structure of **13** was confirmed by single crystal X-ray diffraction analysis (Figure 4). It should be noted that the compound **16** is a single salt due to the weak alkalinity of nitrogen atoms in guanidine.

Energetic potassium salts are considered to be "green" candidates for the replacement of lead-based primary explosives. To date, several furazan-based or furoxan-based primary explosives have been synthesized.[10a,13] In our continuing efforts seeking green primary explosives, a class of potential primary explosives exemplified by potassium (3-(3-(dinitromethideyl)-2-oxido-1,2,5-oxadiazol-4-yl)-1,2,4-oxadiazol-5-yl)(nitro) amide (**20-22**) was synthesized via addition of hydroxyamime, followed by diazotization and nitrification (Scheme 3). Treatment of **20** with excess silver nitrate gave a yellow solid, which was reacted with ammonium chloride or hydrazinium hydrochloride resulting in the corresponding compounds, **21** or **22.** The potassium ion from **20** remains. When the reaction was carried out by using ultrasound, but the anticipated two nitrogen base-containing ions did not form. The structures of **20** and **22** were confirmed by single crystal X-ray diffraction analysis (Figures 5 and 6).

Spectral studies of compounds

All new compounds were fully characterized by ^{1}H and ^{13}C{^{1}H} NMR and IR spectral analysis as well as elemental analysis. In the ^{13}C{^{1}H} NMR spectra of three classes compounds, two signals were observed in the range of 107.0-110.8 ppm for C3 and 149.4-159.9 ppm for C4 corresponding to the different types of carbon atoms in the furoxan rings. The carbon signals for the tetrazole rings in **7-9** and **12-17** were observed in the range of 147.1-149.6 ppm and the carbon resonance of the dinitromethyl group in **7-9** and **20-22** were detected at 118.7–124.6 ppm. Two signals are observed for the

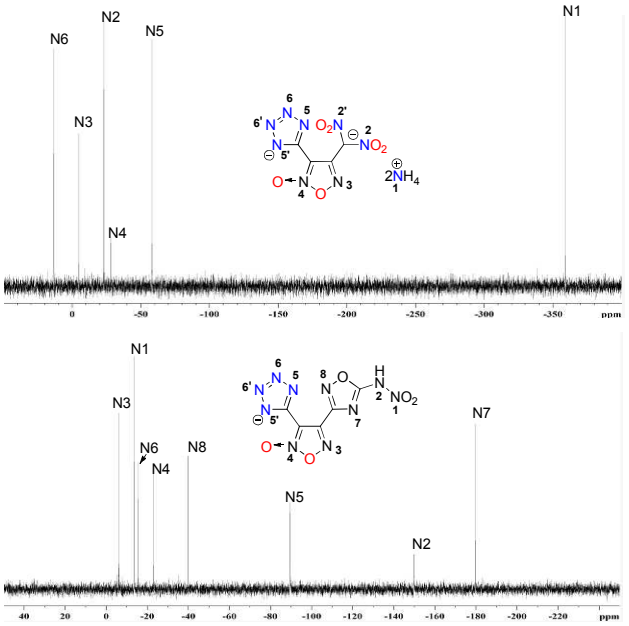


Figure 2 ^{15}N NMR spectra of **7** and **12**.

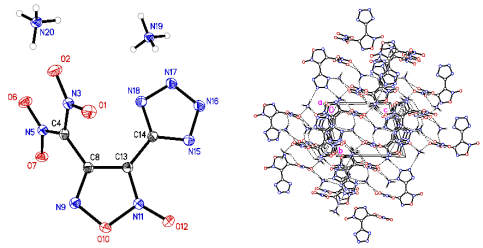
carbon of 1,2,4-oxadiazole rings in **12-17** and **20-22**, which correspond to the C3 (145.4-148.8 ppm) and the C5 (159.4–176.7 ppm) .

The ^{15}NNMR spectra were recorded for **7** and **12** in[D_6]DMSO (Figure 2). They were assigned based on GIAO NMR calculations by using the Gaussian 03 program[14] and the literature values of resonance peaks in similar compounds.[15,7a] Six signals were assigned to the compound **7** due to their symmetric tetrazole and dinitromethyl group. Whereas for **12**, three are 8 signals. The N7 signals of the 1,2,4-oxadiazole were observed at the highest field (δ = -179.8) as expected.

Single crystal X-ray diffraction studies

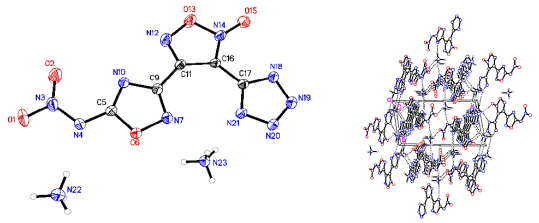
Single-crystals suitable for X-ray diffraction studies were obtained by slow evaporation at room temperature of an ethyl alcohol solution (**7** and **13**) or water (**20** and **22**). Their crystal structures are given in Figures 3 - 6. The detailed crystallographic refinement parameters and structural data for these compounds can be found in the ESI.† Compounds **7**, **13** and **20** crystallize in the triclinic space group P-1, whereas **22** crystalizes in the monoclinic space group $P2_1/c$. In the crystal structures of **7** and **13**, the furoxan and tetrazole rings are approximately coplanar, which is shown by a dihedral angle C(13)-C(14)-N(15)-N(16) = 177.65(18)° in **7** and a dihedral angle N(14)-C(16)-C(17)-N(21) = 178.95(18)° in **13**. Due to the hydrogen bonds in **13** and ligand bonds in **20** and **22**, the furoxan and 1,2,4-oxodiozole rings are distorted. The torsion of N(10)-C(9)-C(11)-N(12) in **13**, C(8)-C(13)-C(14)-N(15) in **20** and C(8)-C(13)-C(14)-N(15) in **22** were -8.2(3)°, 14.1(3)° and -6.5(2)°, respectively.

In the crystal packing of **7**, there are many strong intramolecular hydrogen bonds [between O(6) of the nitro group and proton on N(20), 2.07 Å; between N(17) of tetrazole and proton on N(19), 2.03 Å] and intermolecular hydrogen bonding [between proton on N(20) and O(7), 2.28 Å; between proton on N(20) and N(15), 2.01 Å; between proton on N(19) and O(6), 2.23 Å; and between proton on



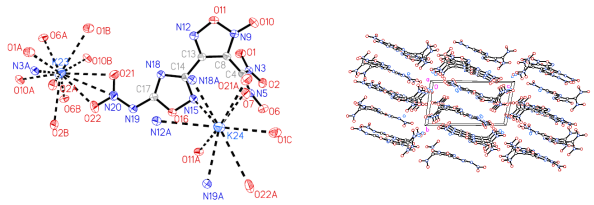
(a) (b)

Figure 3 (a) Molecular structure of **7**. (b) The packing diagram of **7.**



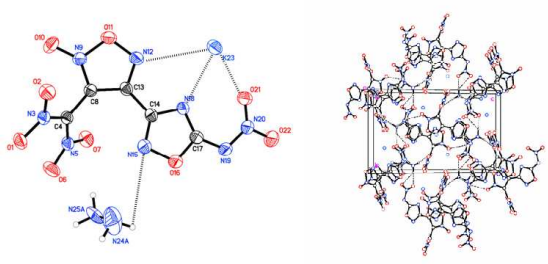
(a) (b)

Figure 4 (a) Molecular structure of **13**. (b) The packing diagram of **13**.



(a) (b)

Figure 5 (a) Molecular structure of **20**. (b) The packing diagram of **20**.



(a) (b)

Figure 6 (a) Molecular structure of **22**. (b) The packing diagram of **22**.

N(19) and N(16), 2.10 Å] (Figure 3). Energetic salt **13** also has many intramolecular hydrogen bonds between the cationic NH_4 moieties, nitroamine groups and nitrogen atoms of the tetrazole moiety of the dianion (Figure 4). In the crystal packing of **20**, the K(23) ion is chelated by N(20), O(21) and O(22) atoms of nitroamine and the bond distances are 3.36Å, 3.09Å and 2.83Å, respectively. The K(24)

ion is coordinated with the N(5) atom of 1,2,4-oxadiozole and O(7) atom of dinitromethyl group and the bond lengths are 3.44Å and 2.67Å. In addition, strong intermolecular coordinate bonds between K(23) or K(24) with N or O atoms are also observed. In comparison with salt **20**, the K(23) ion in **22** which coordinates with more atoms (N(12), N(18) and O(21)) is intramolecular. The bond distance 2.80 Å between K(23) and O(21) is shorter than in **20**. These data indicate that there is a stronger interaction between these two ions which may account for this potassium ion not being replaced by a silver ion.

Table 1 Energetic properties of compounds **7-9, 12-15, 17** and **20.**

Comp.	p^a (g cm^{-3})	Dv^b (m s^{-1})	p^c (GPa)	$\triangle H_f{}^d$ (kJ mol^{-1})	$T_m{}^e$ (^{o}C)	$T_{dec}{}^f$ (^{o}C)	IS^g (J)	FS^h (N)	OB^i (%)
7	1.74	8538	29.9	216.1	-	207.1	40	120	-11.0
8	1.73	8282	26.0	242.8	-	196.1	>55	>360	-25.5
9	1.65	8225	25.1	514.9	-	152.9	>55	>360	-27.6
12	1.86	8639	31.8	441.3	-	121.2	11	160	-5.7
13	1.75	8373	27.5	369.1	-	234.0	32	>360	-20.2
14	1.74	8713	29.7	702.9	-	204.8	15	280	-23.1
15	1.84	8977	35.3	475.8	-	179.2	13	>360	-9.2
17	1.66	8131	24.2	650.7	192.4	196.6	>50	>360	-33.5
20	2.14	8076	29.8	-376.9	-	186.4	3.0	60	12.2
TNT	1.65	7303	21.3	-59.4	81	295	15	>353	-24.7
RDX	1.80	8795	34.9	70.3	-	204	7.4	120	0
$Pb(N_3)_2$	4.80	5877	33.4	450.1	-	315	2.5-4.0	0.1-1.0	0

[a] Density measured by a gas pycnometer at 25 ℃. [b] Calculated detonation velocity. [c] Calculated detonation pressure. [d] Calculated molar enthalpy of formation in solid state. [e] Melting point. [f] Temperature of decomposition (onset). [g] Impact sensitivity. [h] Friction sensitivity. [i] Oxygen balance (based on CO).

Physicochemical and energetic properties

Thermal behavior of compounds **7-9**, **12-17** and **20-22** were determined using differential scanning calorimetric (DSC) measurements with a heating rate of 5 ℃ min^{-1} (Table 1). While the aminoguanidinum salt (**16**) melted at 150 ℃, the other salts decomposed without melting. Except for the neutral compound **12**, all salts showed better thermal stabilities than compound Ⅲ (Figure 1) with decomposition temperatures ranging from 152 ℃ to 234 ℃.

Density is one of the most important factors in determining the performance of energetic compounds. The experimentally determined densities of potassium salt **20** was 2.14 g.cm^{-3}, the values of other salts ranged between 1.65 and 1.86 g.cm^{-3}. The density of compounds **12** (1.86 g.cm^{-3}) and **15** (1.84 g.cm^{-3}) are higher than the currently used explosive RDX (1.80 g.cm^{-3}). Heats of formation of these compounds were calculated with Gaussian 03 software[14] based on isodesmic reactions (ESI). All nitrogen rich compounds (except **20**) have relatively high positive heats of formation. Based on the measured densities and calculated heats of formation, detonation performances were calculated using EXPLO5 (v 6.01).[16] Compound **15** possesses the highest calculated detonation velocity (8977 m s^{-1}) and calculated detonation pressure (35.3 GPa) and exceed those of RDX (Table 1), Ⅰ and Ⅱ (Figure 1). Compared to the commonly used primary explosive lead azide[16] (Dv: 5877 m s^{-1}, P: 33.4 GPa), the potassium salt **20** shows better calculated detonation velocity (Dv: 8076 m s^{-1}) and reasonable calculated detonation pressure (29.8 GPa). The other energetic compounds also exhibit good calculated detonation velocities (8131 m s^{-1} to 8713 m s^{-1}) and calculated detonation pressures (26.0 GPa to 31.8 GPa). These values fall in range of well-known explosives such as RDX and TNT. Sensitivities toward impact and friction were obtained using BAM technology.[17] Compounds **8**, **9** and **17** can be classified as insensitive compounds since the impact and friction sensitivities are greater than 40 J, 360 N, respectively. The potassium salt **20** is a sensitive energetic compound with an impact sensitivity of 3 J. The others are less sensitive than RDX (IS: 7.4 J, 120 N) and compound Ⅲ (Figure 1). In addition, the oxygen balance (OB) values for **12**, **15** and **20** (-5.7%, -9.2% and 12.2, respectively) are higher than the values of Ⅰ and Ⅱ (Figure 1).

Conclusions

In conclusion, three classes of asymmetric nitrogen-rich energetic materials resulting from the combination of tetrazolyl, dinitromethyl and (1,2,4-oxadiazol-5-yl)nitroamino groups with furoxan were effectively synthesized. The majority of promising energetic compounds were fully characterized with multinuclear NMR, infrared spectra and elemental analysis. Four compounds were further confirmed by X-ray diffraction. Some representative compounds, especially **15**, exhibit high densities and excellent calculated detonation velocities and pressures, which in theory outperform the current secondary-explosive benchmark RDX. The potassium salt **20** is very sensitive mechanically but exhibits

excellent density, good thermal stability and detonation, which makes it a competitive candidate as a green primary explosive.

Experimental section

Caution!

Although no explosions were observed in syntheses and handing of these compounds in this study, all manipulations must be carried out in a hood and behind a safety shield. Mechanical actions of these energetic materials, involving scratching or scraping, must be avoided. Eye protection and leather gloves must be worn. All of the energetic compounds must be synthesized only on a small scale.

General methods

All reagents were purchased from AKSci, VWR or Alfa Aesar in analytical grade and were used as supplied. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer or 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts for ^{1}H, and ^{13}C NMR spectra are reported relative to $(CH_3)_4Si$. [D_6]DMSO was used as a locking solvent unless otherwise stated. Infrared (IR) spectra were recorded on an FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Melting and decomposition (onset) points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q2000) at a scan rate of 5 ℃ min^{-1}. Elemental analyses (C, H, N) were performed on 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 isodesmic reactions (Scheme S1, ESI†). The enthalpy of reaction is obtained by combining the MP2/6-311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid state heat of formation of **20** was calculated with Trouton's rule according to eqn (1) (T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).[18]

$$\triangle H_{sub} = 188/\text{J mol}^{-1}\,\text{K}^{-1} \times T \quad (1)$$

For energetic salts **7-9**, **12-15, 17** and **20**, the solid-phase enthalpy of formation is obtained using a Born–Haber energy cycle.[19]

X-ray crystallography data

A clear colorless block crystal (**7**) of dimensions 0.189 x 0.154 x 0.091 mm^{-3}, a clear colorless block crystal (**13**) of dimensions 0.210 x 0.107 x 0.030 mm^{-3}, a clear yellow chunk crystal (**20**) of dimensions 0.315 x 0.246 x 0.086 mm^{-3}, or a clear yellow block crystal (**22**) of dimensions 0.208 x 0.119 x 0.082 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 **7** and **22** were irradiated using a 1µs microfocus CuK_a source (l = 1.54178) with Helios optics, while the crystals **13** and **22** were irradiated using graphite monochromated MoK_α radiation (λ= 0.71073). Data of **7** were collected at 150(2) K and the data of **13**, **20** and **22** were collected at room temperature (20 °C).

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].[20] Data Reduction was performed using *SAINT* [v8.34A][21] and *XPREP* [v2014/2].[22] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].[23] The structure was solved and refined with the aid of the program SHELXL-2014/7.[24] 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.

3-Cyano-4-(N'-hydroxycarbamimidoyl)-1,2,5-oxadiazole 2-oxide (2). Compound **1** [**(**5.2 g (43.3 mmol)] was dissolved in ethanol (25 mL) and added over 20 min to 50% hydroxylamine solution [3.14 g (47.6 mmol)] which was diluted with ethanol (30 mL). The solvent was removed under reduced pressure over 2 h. Upon filtering, **2** **[**5.7 g (79%)] was obtained as a yellowish solid. $T_{d(onset)}$: 124 °C; ^{1}H NMR (d_6-DMSO) δ 11.00 (s, 1H), 6.34(s, 2H) ppm. ^{13}C NMR (d_6-DMSO) δ 149.9, 141.2, 108.4, 96.6 ppm. IR (KBr): $\tilde{\nu}$ 3298, 3021, 2266, 1617, 1417, 1171, 1023, 913, 831, 753, 585, 516 cm^{-1}; Elemental analysis (%) for $C_4H_3N_5O_3$ (169.02): calcd C 28.41, H 1.79, N 41.42%. Found: C 28.27, H 1.65, N 40.97%.

4-(Chloro(hydroxyimino)methyl)-3-cyano-1,2,5-oxadiazole 2-oxide (3). Compound **2** **[**6.0 g (35.5 mmol)] was dissolved in HCl (70 mL of 6 N). A solution of sodium nitrite [6.1 g (88.8 mmol)] in water (24 mL) was added dropwise while maintaining the temperature below 0 °C and stirred for 0.5 hour; then the flask was allowed to remain at ambient temperature for 3h. Upon filtering, **3** [4.9 g (74%)] was obtained as a white solid. Tm: 173 °C. $T_{d(onset)}$: 176 °C; ^{1}H NMR (d_6-DMSO) δ 14.08 (s, 1H) ppm. ^{13}C NMR (d_6-DMSO) δ 151.8, 125.8, 108.0, 98.7 ppm. IR (KBr): $\tilde{\nu}$ 3298, 3021, 2266, 1617, 1417, 1171, 1023, 913, 831, 753, 585, 516 cm^{-1}; Elemental analysis (%) for $C_4HClN_4O_3$ (187.97): calcd C 25.48, H 0.53, N 29.72%. Found: C 25.56, H 0.75, N 29.78%.

4-Cyano-3-(dinitromethyl)-1,2,5-oxadiazole 2-oxide, potassium salt (5). Compound **3** (1.88 g, 10 mmol) in $CHCl_3$ (15 mL) was added dropwise to a stirred mixture of trifluoroacetic anhydride (10 mL) and 100% HNO_3 (6 mL), while maintaining the reaction temperature between -5 and 0 °C. After the addition was complete, the ice bath was removed, and the mixture was allowed to warm slowly to room temperature. It was stirred for another 2 h, and then poured into ice water (50 mL) and extracted with $CHCl_3$ (3×15 mL). The organic phases were combined, washed with water and brine, dried over sodium sulfate, and then concentrated under vacuum to provide the intermediate as a colorless oil, **4**. Compound **4** was dissolved in methanol (15 mL), potassium iodide (2 g, 12 mmol) in methanol (15 mL) was added dropwise, and the mixture was stirred overnight at room temperature. The precipitate was collected by filtration and washed with cold water (3 mL), then methanol (3 mL) and ethyl ether (10 mL) to give **5** (0.8 g, 31.6%) as a yellow solid. $T_{d(onset)}$: 137 °C; ^{13}C NMR (d_6-DMSO) δ149.7, 116.1, 106.4, 98.3 ppm. IR (KBr): $\tilde{\nu}$ 3069, 3024, 2987, 2803, 2260, 1618, 1469, 1399, 1274, 1157, 1030, 983, 812, 745, 600, 443 cm^{-1}; Elemental analysis (%) for $C_4HKN_5O_6$ (253.95): calcd C 18.90, H 0.40, N 27.55%. Found: C 18.94, H 0.23, N 27.01%.

General procedures for salts 7-9: Compound **5** (0.25g, 1.0 mmol) was dissolved in water (12 mL) and sodium azide (0.16 g, 2 mmol), and zinc bromide (0.27 g, 1.2 mmol) were added. The clear solution

was heated under reflux for 7 h. After several minutes, a colorless precipitate was formed. The solution was cooled to ambient temperature and 2 N HCl (8 mL) was added. The mixture was extracted with ethyl acetate (3×15 mL). The organic phases were combined, washed with water and brine, dried over sodium sulfate, and concentrated under vacuum to provide the intermediate as a yellow oil (250 mg). The imtermediate was dissolved in ethanol (5 mL). Then 28% aqueous ammonium hydroxide (0.23g, 2 mmol), guanidinium carbonate (0.18 g, 1 mmol), or aminoguanidinium carbonate (0.14 g, 0.5 mmol) was added. After stirring 2 h at room temperature, the product was obtained by filtration to give **7**, **8** or **9**.

Ammonium 5-(3-(dinitromethideyl)-2-oxido-1,2,5-oxadiazol-4-yl)tetrazol-1-ide (7). Yellow solid (65%). $T_{d(onset)}$: 207 °C; ^{1}H NMR (d_6-DMSO) δ 7.15 (s, 8H) ppm. ^{13}C NMR (d_6-DMSO) δ 150.9, 147.2, 123.3, 109.0 ppm. IR (KBr): $\tilde{\nu}$ 3436, 3287, 2365, 1629, 1536, 1404, 1236, 1138, 992, 794, 735 cm^{-1}; Elemental analysis (%) for $C_4H_8N_{10}O_6$ (292.06): calcd C 16.44, H 2.76, N 47.94%. Found: C 16.42, H 2.80, N 48.29%.

Diaminomethaniminium 5-(3-(dinitromethideyl)-2-oxido-1,2,5-oxadiazol-4-yl)tetrazol-1-ide (8). Yellow solid (67%). $T_{d(onset)}$: 196 °C; ^{1}H NMR (d_6-DMSO) δ 6.95 (s, 12H) ppm. ^{13}C NMR (d_6-DMSO) δ 159.3, 152.1, 150.6, 148.6, 124.5, 110.1 ppm. IR (KBr): $\tilde{\nu}$ 3453, 3177, 1662, 1542, 1469, 1247, 1136, 998, 963, 796, 751, 579 cm^{-1}; Elemental analysis (%) for $C_6H_{12}N_{14}O_6$ (376.11): calcd C 19.15, H 3.21, N 52.12%. Found: C 19.62, H 3.26, N 53.82%.

Amino(hydrazinyl)methaniminium 5-(3-(dinitromethideyl)-2-oxido-1,2,5-oxadiazol-4-yl) tetrazol-1-ide (9). Yellow solid (62%). $T_{d(onset)}$: 153 °C; ^{1}H NMR (d_6-DMSO) δ 8.62 (s, 1H), 7.24 (s, 2H), 6.85 (s, 2H), 4.77 (s, 2H). ^{13}C NMR (d_6-DMSO) δ 160.2, 152.2, 148.6, 124.6, 110.1 ppm. IR (KBr): $\tilde{\nu}$ 3343, 3238, 2364, 1685, 1623, 1540 1472, 1332, 1234, 1131, 964, 789, 639, 576 cm^{-1}; Elemental analysis (%) for $C_6H_{12}N_{14}O_6$ (376.11): calcd C 17.74, H 3.47, N 55.16%. Found: C 17.97, H 3.63, N 54.10%.

3-(5-Amino-1,2,4-oxadiazol-3-yl)-4-cyano-1,2,5-oxadiazole 2-oxide (10). A solution of potassium hydrogen carbonate [3.6 g (36 mmol)] in water (40 mL) was added to a suspension of **2** [5.07 g (30 mmol)] in alcohol (30 mL), and cyanogen bromide [3.8 g (36 mmol)] was added in portions. The mixture was stirred for 24 h at 20 °C. The precipitate formed was collected by filtration and washed with water to give **10** (4.3 g, 74%) as a white solid. T_m: 202 °C. $T_{d(onset)}$: 239 °C; ^{1}H NMR (d_6-DMSO) δ 8.55 (s, 1H) ppm. ^{13}C NMR (d_6-DMSO) δ 174.2, 159.1, 147.6, 107.5, 98.9 ppm. IR (KBr): $\tilde{\nu}$ 3447, 3263, 3193, 2245, 1664, 1605, 1518, 1464, 1378, 1355, 1273, 1104, 1034, 962, 829, 768, 660, 532, 465 cm^{-1}; Elemental analysis (%) for $C_5H_2N_6O_3$ (194.02): calcd C 30.94, H 1.04, N 43.30%. Found: C 31.10, H 1.23, N 43.24%.

3-(5-Amino-1,2,4-oxadiazol-3-yl)-4-(1H-tetrazol-5-yl)-1,2,5-oxadiazole 2-oxide (11). Compound **10** (2.32g, 12.0 mmol) was dissolved in water (60 mL) and sodium azide (1.56 g, 24.0 mmol) and zinc bromide (3.24 g, 14.4 mmol) were added. The clear solution was heated under reflux for 7 h. The solution was then cooled to ambient temperature and 2 N HCl (30 mL) was added. After several minutes, a colorless precipitate was formed. The precipitate (**11**) was filtered. $T_{d(onset)}$: 251 °C; ^{1}H NMR (d_6-DMSO) δ 12.85 (s, 1H), 8.38 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO) δ 174.0, 15°C 9.7, 148.0, 146.3, 107.3 ppm. IR (KBr): $\tilde{\nu}$ 3412, 3288, 3211, 3057, 3012, 1785, 1677, 1629, 1522, 1371, 1287, 1220, 1109, 1056, 993, 830, 541 cm^{-1}; Elemental analysis (%) for $C_5H_3N_9O_3$ (237.04): calcd C 25.32, H 1.28, N 53.16%. Found: C 25.30, H 1.41, N 52.72%.

3-(5-(Nitroamino)-1,2,4-oxadiazol-3-yl)-4-(1H-tetrazol-5-yl)-1,2,5-oxadiazole 2-oxide (12). Compound **11** (1.1 g, 5.0 mmol) was added in portions to a mixture of HNO_3 (100%; 12.5 mL) with stirring and cooling at 0 °C. The mixture was stirred for 2 h at -10 - 0 °C and afterward the solvent was removed by blowing air. Then CF_3COOH (5 mL) was added to the flask. The precipitate formed was collected by filtration and washed with CF_3COOH to give **12** (0.9 g, 63%) as a white solid. $T_{d(onset)}$: 121 °C; ^{1}H NMR (d_6-DMSO) δ 13.64 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO) δ 176.7, 158.8, 148.0, 145.8, 107.0 ppm. IR (KBr): $\tilde{\nu}$ 3154, 3056, 2962, 1642, 1511, 1401, 1270, 1107, 1058, 986, 843, 745 cm^{-1}; Elemental analysis (%) for $C_5H_2N_{10}O_5$ (282.02): calcd C 21.29, H 0.71, N 49.65%. Found: C 21.28, H 0.97, N 49.26%.

General procedures for salts 13-17: Compound **12** (0.28 g, 1 mmol) was dissolved in ethanol (3 mL). Then 28% aqueous ammonium hydroxide (0.23g, 2 mmol), hydrazine monohydrate (0.20 g, 2 mmol), 50% aqueous hydroxyamine (0.13g, 2 mmol), guanidinium carbonate (0.21 g, 1 mmol), or aminoguanidine bicarbonate (0.27 g, 2 mmol) was added. After stirring 2 h at room temperature, the product was obtained by filtration to give **13**-**17**.

Diammonium mono(nitro(3-(2-oxido-4-(1H-tetrazol-5-yl)-1,2,5-oxadiazol-3-yl)-1,2,4- oxadiazol -5-yl)amide) (13). White solid (88%). $T_{d(onset)}$: 234 °C; ^{1}H NMR (d_6-DMSO) δ 7.14 (s, 8H) ppm. ^{13}C NMR (d_6-DMSO) δ 176.7, 159.9, 149.6, 147.2, 110.8 ppm. IR (KBr): $\tilde{\nu}$ = 3530, 3220, 3065, 2831, 2750, 1606, 1552, 1433, 1289, 1091, 1002, 948, 836, 500 cm^{-1}; Elemental analysis (%) for $C_5H_8N_{12}O_5$ (316.07): calcd C 18.99, H 2.55, N 53.16%. Found: C 18.57, H 2.97, N 52.46%.

Dihydrazinium mono(nitro(3-(2-oxido-4-(1H-tetrazol-5-yl)-1,2,5-oxadiazol-3-yl)- 1,2,4-oxadiazol-5-yl)amide) (14). White solid (85%). $T_{d(onset)}$: 205 ℃; 1H NMR (d6-DMSO)δ7.05 (s, 10H) ppm. ^{13}C NMR (d_6-DMSO) δ 176.7, 159.9, 149.6, 147.3, 110.8 ppm. IR (KBr): $\tilde{\nu}$ 3345, 3184, 3166, 3089, 3067, 2980, 2938, 1620, 1548, 1434, 1389, 1299, 1266, 1107, 993, 953, 833, 765, 495 cm^{-1}; Elemental analysis (%) for $C_5H_{10}N_{14}O_5$ (346.10): calcd C 17.35, H 2.91, N 56.64%. Found: C 17.59, H3.07, N 57.59%.

Dihydroxylammonium mono(nitro(3-(2-oxido-4-(1H-tetrazol-5-yl)-1,2,5-oxadiazol-3-yl)-1,2,4-oxadiazol-5 -yl)amide) (15). White solid (85%). Td(onset): 179 ℃; 1H NMR (d6-DMSO) δ 8.53 (s, 8H) ppm. 13C NMR (d_6-DMSO) δ 176.7, 159.8, 149.5, 147.2, 110.7 ppm. IR (KBr): $\tilde{\nu}$ 3404, 3376, 3228, 3133, 3039, 3012, 2984, 2720, 2676, 1554, 1450, 1383, 1292, 1094, 1006, 950, 838, 753, 505 cm^{-1}; Elemental analysis (%) for $C_5H_8N_{12}O_7$ (348.06): calcd C 17.25, H 2.32, N 48.27%. Found: C 17.15, H 2.40, N 47 .25%.

Bis(diaminomethaniminium) mono(nitro(3-(2-oxido-4-(1H-tetrazol-5-yl)-1,2,5- oxadiazol-3-yl) -1,2,4-oxadiazol-5-yl)amide) (16). White solid (85%). $T_{d(onset)}$: 221 °C; ^{1}H NMR (d_6-DMSO) δ 6.90 (s, 6H) ppm. ^{13}C NMR (d_6-DMSO) δ 176.8, 159.2, 158.9, 148.1, 145.9, 107.2 ppm. IR (KBr): $\tilde{\nu}$ 3453, 3367, 3190, 3113, 1360, 3243, 1683, 1614, 1558, 1524, 1448, 1414, 1330, 1254, 1223, 1092, 953, 833, 742, 554 cm^{-1}; Elemental analysis (%) for $C_6H_7N_{13}O_5$ (400.12): calcd C 21.12, H 2.07, N 53.37%. Found: C 21.48, H 2.32, N 53.62%.

Diaminomethaniminium 5-(3-(5-(nitroamino)-1,2,4-oxadiazol-3-yl)-2-oxido-1,2,5-oxadiazol- 4-yl)tetrazol-1-ide (17). White solid (87%). T_m: 192 °C. $T_{d(onset)}$: 197 °C; ^{1}H NMR (d_6-DMSO) δ 8.57 (s, 2H),

7.23 (s, 4H), 6.80 (s, 4H), 4.71 (s, 4H) ppm. ^{13}C NMR (d_6-DMSO) δ176.7, 160.1, 159.9, 149.6, 147.2, 110.7 ppm. IR (KBr): $\tilde{\nu}$ = 3375, 3138, 2961, 2610, 1708, 1585, 1169, 1095, 959, 908, 821, 752, 532 cm^{-1}; Elemental analysis (%) for $C_6H_7N_{13}O_5$ (341.07): calcd C 19.54, H 3.28, N 58.59%. Found: C 19.82, H 3.31, N 58.71%.

3-(5-amino-1,2,4-oxadiazol-3-yl)-4-(N'-hydroxycarbamimidoyl)-1,2,5-oxadiazole 2-oxide (18). Compound **10** [0.97 g (5.0 mmol)] was dissolved in ethanol (5 mL) and added over 10 min to 50% hydroxylamine solution [0.46 g (7.0 mmol)] which was diluted with ethanol (2.0 mL). The solvent was removed under reduced pressure after 3 h. Upon filtering **18** [0.93 g (82%)] was obtained as a white solid. $T_{d(onset)}$: 185 °C; ^{1}H NMR (d_6-DMSO) δ 10.24 (s, 1H), 8.34 (s, 2H), 6.13 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO) δ 173.9, 160.0, 139.6, 111.0 ppm. IR (KBr): $\tilde{\nu}$ 3392, 3208, 3114, 3089, 3065, 3045, 2984, 2940, 1663, 1283, 1104, 957, 863, 772 cm^{-1}; Elemental analysis (%) for $C_5H_5N_7O_4$ (227.04): calcd C 26.44, H 2.22, N 43.17%. Found: C 26.57, H 2.41, N 42.29%.

3-(5-Amino-1,2,4-oxadiazol-3-yl)-4-(chloro(hydroxyimino)methyl)-1,2,5-oxadiazole 2-oxide (19). Compound **18** [2.35 g (10.3 mmol)] was dissolved in 6 N HCl (22 mL). A solution of sodium nitrite [5.69 g (82.4 mmol)] in water (5.5 mL) was added dropwise while maintaining the temperature below 0 °C and was stirred for 0.5 hour; then the flask was allowed to remain at ambient temperature for 8 h. Upon filtering, **19** [1.72 g (68%)] was obtained as a white solid. T_m: 145 °C. $T_{d(onset)}$: 150 °C; ^{1}H NMR (d_6-DMSO) δ 13.60 (s, 1H), 8.43 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO) δ 174.1, 159.6, 147.5, 120.6, 111.5 ppm. IR (KBr): $\tilde{\nu}$ 3335, 3155, 3045, 2953, 2840, 2408, 2334, 1624, 1505, 1265, 1096, 1015, 812, 644, 548 cm^{-1}; Elemental analysis (%) for $C_5H_3ClN_6O_4$ (245.99): calcd C 24.36, H 1.23, N 34.08%. Found: C 24.37, H 1.39, N 33.85%.

Dipotassium (3-(3-(dinitromethyl)-2-oxido-1,2,5-oxadiazol-4-yl)-1,2,4-oxadiazol-5-yl)(nitro) amide (20). Compound **19** (3.69 g, 15 mmol) in $CHCl_3$ (25 mL) was added dropwise to a stirred mixture of trifluoroacetic acid anhydride (15 mL) and 100% HNO_3 (10 mL), while maintaining the reaction temperature between -5 and 0 °C. After the addition was complete, the ice bath was removed, and the mixture was allowed to warm slowly to room temperature. It was stirred for another 2 h. The solvent was removed by blowing air. Then CF_3COOH (8 mL) was added to the flask and the yellow precipitate was collected by filtration. The solid was dissolved in methanol (18 mL), potassium iodide (5.0 g, 30 mmol) in methanol (35 mL) was added dropwise, and the mixture was stirred overnight at room temperature. The precipitate formed was collected by filtration and washed with cold water (5 mL) and then methanol (5 mL) and ethyl ether (10 mL) to give **20** (1.90 g, 32.0%) as a yellow solid. $T_{d(onset)}$: 164 °C; ^{13}C NMR (d_6-DMSO) δ 159.4, 149.1, 145.5, 118.7, 109.1 ppm. IR (KBr): $\tilde{\nu}$ 3373, 3006, 1685, 1528, 995, 947, 860, 765, 516 cm^{-1}; Elemental analysis (%) for $C_5K_2N_8O_9$ (393.91): calcd C 15.23, H 0, N 28.42%. Found: C 15.02, H 0.28, N 27.70%.

General procedures for salts 21 and 22: Silver nitrate (0.34 g, 2 mmol) was dissolved in water (5 mL) and carefully added to a solution of **20** (0.394 g, 1.0 mmol) in water (5 mL). The mixture was stirred for 2 h. After filtration, the product was obtained as a yellow solid (0.44 g). This solid was added to the methanol solution (10 mL) of ammonium chloride (0.11 mg, 2 mmol) or hydrazinium chloride (0.137 g, 2 mmol). After stirring for 2 h at room temperature, silver chloride was removed by filtration and washed with a small amount of methanol. The filtrate was concentrated under reduced pressure and dried in vacuum to yield **21** or **22**.

Potassium ammonium (3-(3-(dinitromethyl)-2-oxido-1,2,5-oxadiazol-4-yl)-1,2,4-oxadiazol-5- yl)(nitro)amide (21). Yellow solid (76%). $T_{d(onset)}$: 217 °C; ^{1}H NMR (d_6-DMSO) δ 7.13 (s, 4H) ppm. ^{13}C NMR (d_6-DMSO) δ 175.5, 158.4, 148.8, 119.4, 110.4 ppm. IR (KBr): $\tilde{\nu}$ 3466, 3180, 3108, 2945, 1634, 1455, 935, 884, 786, 590, 522 cm^{-1}; Elemental analysis (%) for $C_5H_4KN_9O_9$ (372.98): calcd C 16.09, H 1.08, N 33.77%. Found: C 15.68, H 1.51, N 33.82%.

Potassium hydrazinium (3-(3-(dinitromethyl)-2-oxido-1,2,5-oxadiazol-4-yl)-1,2,4-oxadiazol -5-yl) (nitro)amide (22). Yellow solid (80%). $T_{d(onset)}$: 217 ℃; ^{1}H NMR (d6-DMSO) δ7.04 (s, 5H) ppm. ^{13}C NMR (d_6-DMSO) δ 175.4, 158.5, 148.9, 119.6, 110.4 ppm. IR (KBr): $\tilde{\nu}$ 3475, 3190, 3109, 3090, 3033, 2936, 1628, 1442, 946, 853, 791, 570, 506 cm^{-1}; Elemental analysis (%) for $C_5H_5KN_{10}O_9$ (387.98): calcd C 15.47, H 1.30, N 36.08%. Found: C 15.35, H 1.37, N 36.18%.

Conflicts of interest

There are no conflicts to declare.

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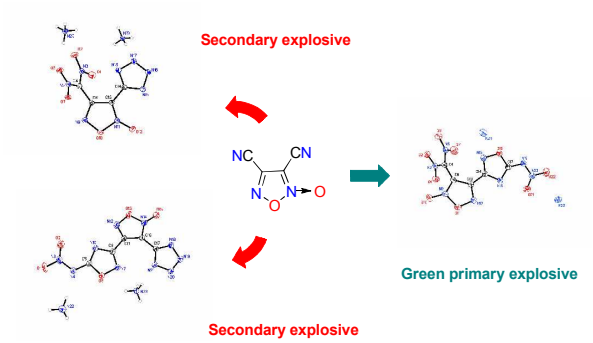

Three classes of nitrogen-rich energetic compounds were obtained from 3,4-dicyano-furoxan.