**N,N'-Methylenebis(N-(1,2,5-oxadiazol-3-yl)nitramide) Derivatives as Metal-free Green Primary Explosives**

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A series of new energetic salts based on N,N'-methylenebis(N-(4-(dinitromethyl)-1,2,5-oxadiazol-3-yl)nitramide) was synthesized and fully characterized by NMR and IR spectroscopy, and elemental analysis. Their excellent performance and priming ability of potassium-based primary explosives (Fig. 1), such as nitramine and dinitromethyl. However, the initiation towards impact and friction derived from explosophore groups can enhance the oxygen balance values and density of the resulting compounds which improve their detonation velocities and pressures. Therefore, we synthesized a series of energetic salts where furazan rings were chosen as the backbone and dinitromethyl and nitramide groups were chosen as the explosive sources. These salts have high densities, and high heats of formation coupled with the acceptable heats of formation and comparable low sensitivities suggest these high nitrogen materials as attractive candidates for metal-free primary explosives.

3-Amino-4-chloroximinofurazan (ACOF) was synthesized in two steps using a known procedure starting from the commercially available malononitrile. 9 (3Z,3’Z)-4,4’- (Methylenebis(azanediyl)) bis(N-hydroxy-1,2,5-oxadiazole-3-carboximidoyl chloride) (1) was easily obtained by the reaction of...
formaldehyde and ACOF in 1M hydrochloric acid. Compound 1 was treated with a mixture of 100% nitric acid and trifluoroacetic anhydride (TFAA) at 0 °C to form 2 (Scheme 1). Compound 2 was extracted from the reaction mixture using dichloromethane. The nitration reaction process of sulfuric acid. Compound was obtained as a white solid which became a liquid when exposed to moist air since it is hygroscopic. The silver salt (5) was synthesized by the metathesis reaction of 4 and silver nitrate. The corresponding energetic salts 6–8 were realized by reactions of 5 and hydrochloric salts in methanol. Salts 9 and 10 were synthesized by acid-base neutralization reactions in which 4 reacted with 1,5-diaminotetrazole or gaseous ammonia. Compound 11 was obtained by fluorination of 10 using Selectfluor in anhydrous acetonitrile in moderate yields (59%).

In this work, all of the newly prepared compounds were fully characterized by using IR, 1H and 13C NMR spectra, and elemental analyses. Compound 11 was further characterized by 19F NMR spectra. The 15N NMR spectra were recorded for 6–10 in [D6]DMSO (Fig. 2). They were assigned based on the literature values of resonance peaks in similar compounds10 and GIAO NMR calculations by using the Gaussian 03 program.11 There are five nitrogen signals associated with the anion. Interestingly, the hydroxylammonium and ammonium cations did not give 15N signals.

A suitable crystal of 6 was obtained by slow evaporation of its saturated solution in methanol. The crystal structure of 6 is given in Fig. 4. Crystallographic data and data collection parameters, bond lengths, and bond angles are in the Supporting Information. The unit cell of 6, which crystallizes in the monoclinic space group P21/n, contains four formula moieties. The crystal density is 1.917 g cm–3 at 170 K (1.886 g cm–3 at 20 °C). The furazan ring of the anion of 6 is planar which is supported by the torsion angles: O10-N11-C12-C8, 1.36(14); C8-N9-O10-N11, 0.33(14); C12-C8-N9-O10, 0.49(14); N9-C8-C12-N11, -1.21(15); N9-O10-N11-C12, -1.08(14); N23-O24-N25-C26, 0.91(14); C22-N23-O24-N25, -1.09(14); N23-C22-C26-N25, -0.32(16); O24-N25-C26-C22, -0.36(14); and C26-C22-N23-O24, 0.84(15). However, the dinitromethyl group is
twisted out of the plane of the furazan ring which is indicated by a dihedral angle of 41.383(34). Hydrogen bonding interactions occur between the nitrogen atom of the hydroxylammonium cation and the nitro groups and the furazan ring of the anion.

The thermal stabilities of these new energetic salts were determined by differential scanning calorimetric (DSC) measurements at a heating rate of 5 °C min⁻¹. All compounds decomposed between 119 and 141 °C (onset temperature) without melting (Table 1). The heats of formation of 11 and the anion of compounds 6–10 were calculated by using the isodesmic reaction approach with the Gaussian 03 (Revision E.01) suite of programs (Supporting Information). The solid-phase heats of formation of energetic salts were calculated on the basis of the Born-Haber energy cycle. 11 Compounds 8, 9 and 11 have positive heats of formation which range from 0.05 kJ g⁻¹ to 0.83 kJ g⁻¹.

With the values of the heats of formation and measured densities (gas pycnometer), detonation properties were calculated by using EXPLO5 (version 6.01). 13 The neutral compound 11 has the highest detonation velocity (8885 m s⁻¹) and detonation pressure (37.8 GPa), which is superior to RDX (8748 m s⁻¹, 34.9 GPa) (Table 1). Of all the energetic salts, the hydroxylammonium salt 6·H₂O has superior detonation properties (8606 m s⁻¹, 32.2 GPa). The sp values range from 205 to 268 s, which are higher than that of ADN.

Impact and friction sensitivities of 11 and the energetic salts were measured using a BAM drop hammer apparatus and a BAM friction tester, respectively. 14 All the compounds are sensitive towards impact and friction, thereby highlighting their potential for application as primary explosives. Compound 6·H₂O is the most sensitive with an impact sensitivity of 1 J and a friction sensitivity of 60 N.

### Conclusions

In summary, a new family of energetic compounds of N,N'-methylenebis(N-1,2,5-oxadiazol-3-yl)nitramide featuring the dinitromethyl and fluorodinitromethyl groups were designed, synthesized, and characterized. The potassium salt 3 has a density of 2.03 g cm⁻³, positive oxygen balance and detonation properties (D, 7955 km s⁻¹; P, 28.1 GPa), which indicates that it might be useful as a green primary explosive. Of all the energetic salts, the hydroxylammonium salt 6·H₂O exhibits the highest density of 1.84 g cm⁻³ and best detonation properties (D, 8606 km s⁻¹; P, 32.2 GPa). The calculated detonation parameters of other salts are in the range of TNT and RDX, respectively. The high sensitivities and remarkable detonation performance of these energetic salts as well as the green detonation products make them competitive candidates as metal-free green primary explosives.

### Experimental section

**Caution!!!** Although we have encountered no difficulties in preparing these new compounds (3, 6·H₂O–11) herein, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be worn. Mechanical actions of these energetic materials involving scratching or scraping must be avoided.

**General methods:** Reagents were purchased from Aldrich and Acros Organics and were used as received. ¹H and ¹³C spectra were recorded on a 300 MHz (Bruker AVANCE 300) NMR spectrometer operating at 300.13 and 75.48 MHz, respectively. [D₆]DMSO and CDCl₃ were used as solvent and locking solvent. Chemical shifts in the ¹H and ¹³C NMR spectra are reported relative to Me₄Si. ¹⁵N spectra were obtained on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz. The melting and decomposition (onset temperature) points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a heating rate of 5 °C min⁻¹. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities were determined at 25 °C by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made by using a standard BAM Fall hammer and a BAM friction tester.

**Computational methods:** The gas-phase enthalpies of formation were calculated using the G2 method. For energetic salts, the solid-phase enthalpies of formation were obtained.
by using a Born-Haber energy cycle. The details are given in the Supporting Information.

**X-ray crystallography of 6-H$_2$O:** A yellow needle (0.330 x 0.145 x 0.117 mm$^3$) for 6-H$_2$O was mounted on a MiteGen MicroMesh by 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 by using graphite monochromatized MoKα radiation (λ = 0.71073) for a constant 150(2) K during data collection. Data collection was performed and the unit cell was initially refined by using APEX2 [v2014.3-0]. Data reduction was performed using SINT [v7.68A] and XPREP [v2014/2]. Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS [v2008/1]. The structure was solved and refined with the aid of the programs SHELXL-2014/7 within WinGX. The full matrix least-squares refinement on F$^2$ included atomic coordinates and anisotropic thermal parameters for all non-H atoms.

**(3Z,3’Z)-4,4’-(methylenedisazanediyl)bis(N-hydroxy-1,2,5-oxadiazole-3-carbimidoyl chloride) (1):** 25 °C, 1.63 g (10 mmol) 3-amino-4-chloroximinofurazan (ACOF) [9] (0.07 g, 2 mmol) was added to a solution of 1M HCl (30 mL) and 0.41 g (5 mmol) 37% formaldehyde was dropped in. Then the mixture was stirred for 3 h. The precipitate was filtered, washed with water, and dried in air to yield 1 (0.07 g) as a white solid, yield 91.1%. $T_{\text{decomp; onset}}$ = 156 °C. $^1$H NMR: δ = 4.86 (t, 2H), 6.64 (t, 2H), 13.47 (s, 2H) ppm; $^{13}$C NMR: δ = 153.5, 141.8, 126.5, 53.7 ppm; IR (KBr pellet): $\tilde{\nu}$ = 3441, 1588, 1562, 1514, 1485, 1414, 1385, 133, 1268, 1156, 1128, 1101, 1028, 1004, 965, 916, 902, 821, 806, 771, 746, 735, 723, 670, 593, 462 cm$^{-1}$; elemental analysis (%) calcd for C$_7$H$_6$Cl$_2$N$_2$O$_3$ (337.08): C 24.94, H 1.79, N 33.24; found: C 25.06, H 1.84, N 33.63.

**Disilver N,N’-dinitro-N,N’-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine (5):** Concentrated sulfuric acid (1 mL) was added dropwise into a stirred mixture of 3 (0.56 g, 1 mmol) and H$_2$O (0.5 mL). After the addition was complete, the mixture was stirred for another 30 minutes, and then extracted with CH$_2$Cl$_2$ (6 x 5 mL). The combined extracts were concentrated under vacuum to provide white solid 4 (0.33 g), yield 68.8%. The solid 4 should be stored under vacuum.

**Compounds (6-8):** Compound 5 (0.69 g, 1 mmol) was added to a methanol solution (10 mL) of hydroxyaluminium chloride (0.140 g, 2 mmol), hydrazinium chloride (0.137 g, 2 mmol) or trimanguanidinium chloride (0.281 g, 2 mmol). After stirring for 2 h at room temperature, the 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 6-8.

**Dihydroxyaluminium N,N’-dinitro-N,N’-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine hydrate (6-H$_2$O):** yellow solid, 82% yield. $T_{\text{decomp; onset}}$ = 133.2 °C. $^1$H NMR: δ = 6.27 (s, 2H), 9.87 (s, 2H), 10.06 (s, 6H) ppm; $^{13}$C NMR: δ = 151.1, 146.4, 120.7, 64.5 ppm; IR (KBr pellet): $\tilde{\nu}$ = 3416, 3057, 2696, 1610, 1593, 1563, 1526, 1483, 1340, 1346, 1326, 1292, 1242, 1144, 1087, 1029, 999, 895, 820, 779, 747, 731, 674, 651, 624, 603, 537 cm$^{-1}$; elemental analysis (%) calcd for C$_7$H$_6$N$_2$O$_3$·H$_2$O (564.25): C 14.90, H 2.14, N 34.75; found: C 14.65, H 2.27, N 34.08.

**Dihydrazinium N,N’-dinitro-N,N’-bis[3-dinitromethyl-furazanate-4-yl] methylenediamine hydrate (7-H$_2$O):** yellow solid, 80% yield. $T_{\text{decomp; onset}}$ = 133.2 °C. $^1$H NMR: δ = 6.27 (s, 2H), 9.87 (s, 2H), 10.06 (s, 6H) ppm; $^{13}$C NMR: δ = 151.1, 146.4, 120.7, 64.5 ppm; IR (KBr pellet): $\tilde{\nu}$ = 3416, 3150, 1596, 1523, 1475, 1384, 1285, 1233, 1141, 1088, 1025, 996, 962, 903, 820, 750, 650, 596, 464 cm$^{-1}$; elemental analysis (%) calcd for...
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Di(triaminoquinodimine) N,N'-ditrio-N,N'-bis[3-dinitromethyl-furazanate-4-yl] methylendiamine (8): yellow solid, 88% yield. \( T_{\text{deg}} = 120.1 \degree C \). \( ^1H \) NMR: \( \delta = 4.48 \) (s, 12H), 6.27 (s, 2H), 8.58 (s, 6H) ppm; \( ^13C \) NMR: \( \delta = 159.0, 151.0, 146.3, 120.6, 64.4 \) ppm; IR (KBr pellet): \( \bar{\nu} = 3354, 3320, 3213, 3044, 1686, 1588, 1527, 149, 1393, 1360, 128, 1247, 1136, 1091, 1026, 996, 953, 907, 821, 800, 751, 23, 652, 605 cm\(^{-1}\)); elemental analysis (% calcd for \( C_{16}H_{32}N_2O_8 \) (688.41): \( C = 15.70, H 2.93, N 48.83 \); found: C 15.91, H 3.00, N 49.39.

Di(1,5-diaminotetrazolium) N,N'-ditrio-N,N'-bis[3-dinitromethyl-furazanate -4-yl] methylendiamine (9): Compound 4 (0.48 g, 1 mmol) was dissolved in 5 mL acetonitrile, and 1,5-diaminotetrazole (0.2 g, 2 mmol) was added. The precipitate was filtered, washed with acetonitrile, and dried in air, giving 9 (0.54 g) as a yellow solid, yield 79%. \( T_{\text{deg}} = 118.7 \degree C \). \( ^1H \) NMR: \( \delta = 6.28 \) (s, 2H) ppm; \( ^13C \) NMR: \( \delta = 153.2, 151.2, 146.4, 120.7, 64.5 \) ppm; IR (KBr pellet): \( \bar{\nu} = 3355, 3264, 1718, 1718, 1596, 152, 145, 1401, 1283, 1233, 1141, 1091, 1024, 995, 900, 818, 776, 750, 647, 600, 480 \) cm\(^{-1}\)); elemental analysis (% calcd for \( C_{14}H_{20}N_4O_8 \) (562.29): C 14.95, H 2.51, N 39.86; found: C 14.89, H 2.50, N 40.49.

There are no conflicts to declare.

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Notes and references


13 M. Sućeska, Brodarski Institute, Zagreb, Croatia, EXPLOS, Version 6.01, 2013.

14 (a) Tests were conducted according to the UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria, 5th rev. ed., United Nations Publication, New York, 2009; (b) 13.4.2 Test 3 (a) (ii) BAM Fallhammer, 2009, pp. 75–82; c) 13.5.1 Test 3 (b) (i): BAM friction apparatus, 2009, pp. 104–107.


Metal-free green primary explosives with excellent detonation properties and acceptable sensitivities were synthesized and fully characterized.