



**Energetic salts of 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furazan: Powerful alliance towards good thermal stability and high performance**

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## Energetic salts of 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furanan: Powerful alliance towards good thermal stability and high performance

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Two different methods were developed to synthesize 4-amino-3-(5-acetic acid methyl ester-1,2,4-oxadiazolyl)-furanan (**1**), the precursor to prepare 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furananate, in scalable good yields. In four steps, three energetic salts were obtained with an overall yield of ~50% and show promising characteristics of typical secondary explosives. The structure of the diammonium salt (**2a**) was confirmed by X-ray single crystal diffraction. It has a high crystal density of 1.840 g cm<sup>-3</sup> at 150 K and a measured density of 1.804 g cm<sup>-3</sup> at room temperature. All of the compounds were fully characterized by infrared spectroscopy (IR), <sup>1</sup>H NMR, and <sup>13</sup>C NMR spectroscopy as well as elemental analysis. Compound **2b** and **2c** exhibit better sensitivities and comparable detonation properties relative to HMX, showing great promise as replacements.

Design and synthesis of new high-energy-density materials (HEDMs) have attracted increasing interest around the world during the last decade. Most of the motivation is the preparation of replacements for hexogen (RDX), octogen (HMX) or hexanitrohexaazaisowurtzitane (CL-20).<sup>1-6</sup> The "hot" strategies to achieve powerful materials with good density and appropriate oxygen balance involve combination of varying heterocyclic rings, which would profit from the positive aspects of each of the components.<sup>7-14</sup> Recently, Zhang's group used a materials genomic approach to discover a promising insensitive high explosive molecule (ICM-102), which efficiently solved the contradictory relationship between high energy and low mechanical sensitivity in most energetic materials.<sup>15</sup>

The introduction of the nitramino group into energetic molecules is a well-established method to improve the oxygen balance and density of an energetic molecule; many nitramino

energetic compounds were designed and synthesized during the last few years.<sup>6,13,16-21</sup> However, more nitramino groups in the compound usually lead to higher sensitivity due to the low bond dissociation energy (BDE) of the N–NO<sub>2</sub> bond.<sup>20,22</sup> Compared to the nitramino group, the dinitromethyl group [–C(NO<sub>2</sub>)<sub>2</sub>] possesses more nitro groups and thus a higher oxygen content. Additionally, the planarity of dinitromethyl and higher C–NO<sub>2</sub> BDE are expected to give rise to a better density, and oxygen balance as well as sensitivity.

Only a few dinitromethyl-containing energetic compounds were investigated due to the small number of known dinitromethyl precursors.<sup>3,23-25</sup> Among the reported dinitromethyl energetics, compounds with single heterocyclic ring backbones tend to show poor thermal stability likely because of the strong electron withdrawing effect of the dinitromethyl group which makes the ring easy to open upon heating. The alliance of 1,2,5-oxadiazole (furanan) and 1,2,4-oxadiazole was studied to give compounds with good thermal stability as well as high energy performance.<sup>13</sup> In our continuing interest in finding energetic materials with high density, good thermal stability, low sensitivity and high detonation performance, a new series of energetic salts based on 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furananate were designed and synthesized (Figure 1).

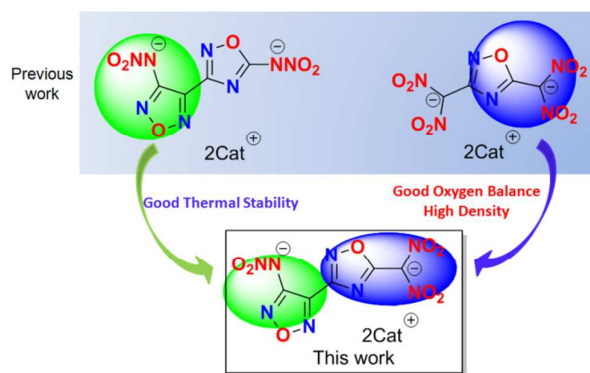


Figure 1. The design of new energetic compounds

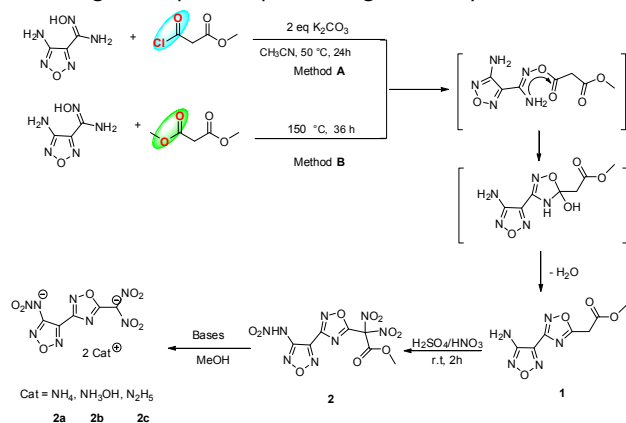
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The starting material 3-amino-4-aminooximinofurazan was readily prepared by using a scalable procedure in high yield according to literature.<sup>26</sup> Our first attempt to prepare 4-amino-3-(5-acetic acid methyl ester-1,2,4-oxadiazolyl)-furazan (**1**) was by reacting 3-amino-4-aminooximinofurazan with methyl malonyl chloride in acetonitrile in the presence of potassium carbonate. After heating at 50 °C for 24h, compound **1** was isolated in a yield of 72.4%. In order to seek a broader prospective for practical applications, a more economical method to synthesize **1** was developed by replacing the expensive methyl malonyl chloride with dimethyl malonate, which after heating at 150 °C for 36h, gave **1** in a slightly lower yield of 67.8%. The nitration of **1** using mixed acids gives **2** as a white solid with a yield of 87.5%. Three nitrogen-rich salts, the diammonium (**2a**), dihydroxylammonium (**2b**), and dihydrazinium (**2c**), were synthesized in excellent yields by reacting **2** with the free bases in methanol solution as shown in Scheme 1. All of the salts were precipitated from the methanol solution and were collected by filtration, and air dried to give the product pure enough for analyses.



Scheme 1 Synthetic routes for compound **1**, **2** and **2a-2c**.

All the compounds were fully characterized by IR, and <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy as well as elemental analysis. The <sup>15</sup>N NMR spectrum of **2c** was recorded in [D<sub>6</sub>]DMSO at room temperature as shown in Figure 2. The signal for N6 in the 1,2,4-oxadiazole ring at -153.06 ppm was observed farther downfield compared to the other nitrogen atom in the oxadiazole ring. The assignments of <sup>15</sup>N signals are based on the literature values of similar compounds.<sup>13,27</sup>

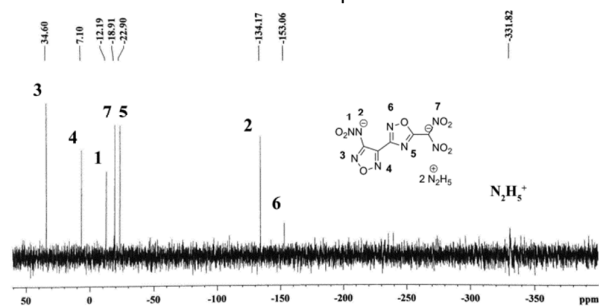


Figure 2. <sup>15</sup>N spectrum of **2c**.

Crystals of **2a** suitable for single-crystal X-ray diffraction were obtained by dissolving the compound in a minimum amount of water and the solvent evaporated slowly. The unit cell of **2a**, which crystallizes in the monoclinic space group *C2/c*, contains eight formula moieties, with a good crystal density of 1.840 g cm<sup>-3</sup> at 150 K, (detailed crystallographic data in the Electronic Supplementary Information). As shown in Figure 3, extensive hydrogen bonding (dotted lines) and layer by layer stacking were observed in the packing diagram (Figure 3b). The angle of the hydrogen bonds N(22)-H(22A)...O(17) #1, N(22)-H(22C)...N(11), N(23)-H(23B)...O(1) and N(23)-H(23C)...N(14)#6 [symmetry code: #1 -x+3/2, y-1/2, -z+3/2; #6 x, y, 1, z] ranges between 170.7° to 177.8° (Table S7), indicating very strong hydrogen bond interactions. In the packing diagram, the distances between 1,2,5-oxadiazole and 1,2,4-oxadiazole centroids is 3.479 Å and the distance between the two planes is 3.138 Å, much shorter compared to typical geometrical parameters of aromatic π-π interactions (3.65–4.00 Å),<sup>28</sup> suggesting strong π-π interactions together with hydrogen bonds resulting in closer packing.

In order to obtain a better understanding of intermolecular interactions in the crystal structure of **2a**, the two-dimensional (2D)-fingerprint of crystals and the associated Hirshfeld surfaces<sup>29</sup> were employed by using the suite of tools in CrystalExplorer17<sup>30</sup> as shown in Figure 3d-f. The red and blue area on the Hirshfeld surface (Figure 3d) represent high and low close contact populations, respectively. Most of the strong interactions are located between O...H and N...H according the red area on the Hirshfeld surface. The combination of the distances from the Hirshfeld surface to the nearest nucleus inside the surface (*d<sub>i</sub>*) and outside the surface (*d<sub>e</sub>*) forms a 2D fingerprint plot.

In the fingerprint plots (Figure 3e), two remarkable spikes at the bottom left of the plot, demonstrating strong O...H and H...O hydrogen bonding interactions. The percentage of contribution for each type of interaction to the total weak interactions is summarized in Figure 3f; the O...H interaction in **2a** plays a dominant role with the amount of 44.0% of the total

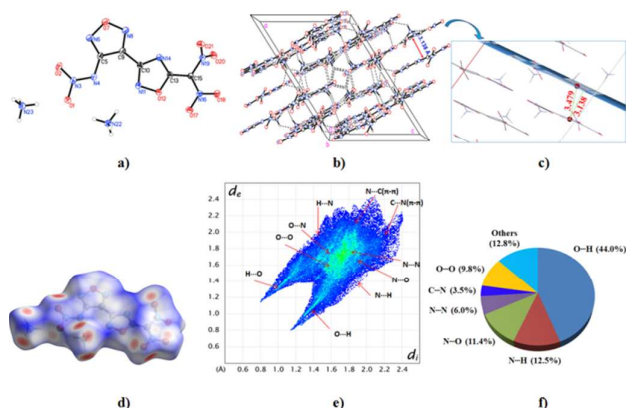


Figure 3. a) X-ray crystal structure of **2a**; b) Packing diagram of **2a** (dotted lines represent hydrogen bonds); c) Distances of π-π interactions; d) Hirshfeld surface for **2a**; e) Fingerprint plot for **2a**; f) Individual atomic contact percentage contribution to the Hirshfeld surface.

weak interactions and the N...H interaction makes up 12.5% of total weak interactions, indicating extensive hydrogen bonding interactions.

The densities of the new salts were measured by using a gas pycnometer (25 °C) and fall in the range between 1.804 (**2a**) and 1.862 g cm<sup>-3</sup> (**2b**). Their high densities are attributed to existence of extensive hydrogen bonds and to  $\pi$ - $\pi$  interactions. Furthermore, those interactions also result in good thermal stability for the new energetic salts which have onset decomposition temperatures over the range of 161.0 to 209.7 °C. The presence of the dinitromethyl group in **2a** – **2c** brings the improved oxygen balance close to zero. In comparison with the bis-nitramino analogues,<sup>13</sup> both density and oxygen balance are enhanced when one nitramino group is replaced by a dinitromethyl group while good thermal stabilities are maintained.

The heats of formation for **2a** – **2c** were calculated by Gaussian 03 (Revision E.01) suite of programs<sup>31</sup> using the isodesmic reactions shown in the Electronic Supplementary Information. The hydrazinium salt **2c** has the highest heat of formation of 466.9 kJ mol<sup>-1</sup>, followed by hydroxylammonium salt **2b** (259.9 kJ mol<sup>-1</sup>) and ammonium salt **2a** (145.0 kJ mol<sup>-1</sup>). The detonation properties **2a** – **2c** were evaluated by using the EXPLO5 V6.01 code.<sup>32</sup> The physiochemical properties of compound **2a** – **2c** compared with traditional explosives RDX and HMX are summarized in Table 1. The calculated detonation velocity and pressure of **2a** are 8652 ms<sup>-1</sup> and 32.8 GPa, which are comparable to RDX. The detonation properties of **2b** ( $D_v$ : 9028 m s<sup>-1</sup>,  $P$ : 38.0 GPa) and **2c** ( $D_v$ : 9064 m s<sup>-1</sup>,  $P$ : 36.0 GPa), which approaches that of HMX (9144 ms<sup>-1</sup> and 39.2 GPa, respectively). For safety purposes, the sensitivities toward friction and impact were measured by using standard BAM methods. All of the compounds were determined to be insensitive to friction (>360N), and the impact sensitivities of **2a**–**2c** are 23 J, 22 J and 19 J, respectively. The more insensitive properties of **2a**–**2c**, relative to RDX and HMX, together with their good thermal stability, oxygen balance and comparable detonation properties highlight their application potential.

## Conclusions

A new series of 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furazanate energetic salts was designed, synthesized and fully characterized. They were prepared in four steps by starting from malononitrile in an overall yield of 47% ~ 51%. A more economical route was developed to prepare the intermediate **1** which makes it more attractive for practical applications. The structure of the ammonium salt, **2a**, was determined by single crystal X-ray diffraction. Remarkable inter- and intramolecular hydrogen bonds and strong  $\pi$ - $\pi$  interactions were observed in the structure, which contribute to their high densities, and good thermal stability. Additionally, **2a**–**2c** are less sensitive towards impact and friction compared to currently used explosives such as RDX, HMX and CL-20. Compounds **2b** and **2c** show detonation properties comparable to HMX, have good oxygen balance and are simple and inexpensive to prepare from commonly available

chemicals in good overall yield, which allows them to compete as a replacement for HMX. This strategy can also be utilized to synthesize other acetic acid methyl ester-1,2,4-oxadiazole or dinitromethyl-1,2,4-oxadiazole analogues, the preparation of more derivatives based on dinitromethyl-1,2,4-oxadiazolate is still in progress.

## Experimental Section

**Caution:** All the nitrogen-rich compounds used are energetic materials and may explode under certain conditions. Appropriate safety precautions should be taken when preparing and/or handling.

**General methods:** <sup>1</sup>H, and <sup>13</sup>C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively, and a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz for <sup>15</sup>N spectra. Chemical shifts in <sup>13</sup>C and <sup>15</sup>N NMR spectra are reported relative to Me<sub>4</sub>Si and MeNO<sub>2</sub>, respectively. The melting and decomposition points were obtained on a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of 5 °C/min. IR spectra were recorded using KBr pellets for solids on a Thermo Nicolet AVATAR 370 FTIR. Densities were determined at 25 °C by employing a Micromeritics AccuPyc 1340 II gas pycnometer. Elemental analyses were carried out using an Exeter CE-440 or Elementar vario MICRO cube elemental analyzer. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester, respectively.

**4-Amino-3-(5-acetic acid methyl ester-1,2,4-oxadiazolyl)-furazan (1): Method A:** To a suspension of 4-amino-1,2,5-oxadiazole-3-carboxamidoxime (1.43 g, 10 mmol) in 20 mL of acetonitrile was added methyl malonyl chloride (1.37 g, 10 mmol). The mixture was stirred at room temperature, the suspension turned into a clear solution and then a solid precipitated in a few minutes. After stirring 10 minutes, potassium carbonate (2.76 g, 20 mmol) was added in one portion. The reaction mixture was heated to 50 °C and maintained at this temperature for 24 h. After the mixture was cooled to room temperature, the solvent was removed under vacuum. The solid residue was added to 80 g of ice water, the precipitate was collected by filtration and air dried to obtain **1**, yield 1.63g, 72.4%. **Method B:** A mixture of 4-amino-1,2,5-oxadiazole-3-carboxamidoxime (4.29 g, 30 mmol) with dimethyl malonate (19.8 g, 150 mmol) was heated at 150 °C. A Dean–Stark apparatus was used to collect the H<sub>2</sub>O and MeOH which formed. After heating 24 h, the reaction mixture was cooled to room temperature and the excess dimethyl malonate was removed by blowing air. Water (50 mL) was then added to the solid residue. After stirring for 1 h, the solid was collected by filtration to give **1**, yield 4.58g, 67.8%. The product has the same <sup>1</sup>H and <sup>13</sup>C NMR characteristics as the product obtained by method A. *M.p.*: 73.4; *T*<sub>dec</sub>: 270.9 °C; IR (cm<sup>-1</sup>)  $\tilde{\nu}$  = 3429, 3335, 2989, 2958, 1735, 1697, 1637, 1608, 1590, 1555, 1463, 1437, 1408, 1391, 1350, 1291, 1207, 1184, 1164, 1149, 1014, 993, 969, 944, 902, 865, 810, 766, 734, 703,

Table 1 Physicochemical properties of compound **2a** – **2c**.

Compd	$T_d^{[a]}$ [°C]	$d^{[b]}$ [g/cm <sup>3</sup> ]	$\Delta H_f^{[c]}$ [kJ/mol (kJ/g)]	$D^{[d]}$ [m/s]	$P^{[e]}$ [Gpa]	$IS^{[f]}$ (J)	$FS^{[g]}$ (N)	$OB^{[h]}$ [%]
<b>2a</b>	161.0	1.804	145.0 (0.43)	8652	32.8	23	>360	-4.8
<b>2b</b>	190.2	1.862	259.9 (0.71)	9028	38.0	22	>360	+4.3
<b>2c</b>	209.7	1.829	466.9 (1.27)	9064	36.0	19	>360	-8.7
RDX	204	1.80	70.3 (0.32)	8795	34.9	7.5 <sup>i</sup>	120	0
HMX	287	1.91	74.8 (0.25)	9144	39.2	7.4	120	0

[a] Decomposition temperature (onset temperature at heating rate of 5 °C min<sup>-1</sup>). [b] Density, measured - gas pycnometer (25 °C). [c] Calculated heat of formation [d] Calculated detonation velocity - EXPLO5 V6.01. [e] Calculated detonation pressure - EXPLO5 V6.01. [f] Impact sensitivity. [g] Friction sensitivity. [h] Oxygen balances for CaHbOcNd, 1600 (c-a-b/2)/Mw; Mw = molecular weight – based on CO formation. [i] Idaho expt<sup>l</sup> value.

648, 575, 524; <sup>1</sup>H NMR (CD<sub>3</sub>CN): 5.46 (2H, s, NH<sub>2</sub>); 4.21 (2H, s, CH<sub>2</sub>); 3.75 (3H, s, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR(CD<sub>3</sub>CN):  $\delta$  175.97, 167.32, 161.00, 156.54, 138.20, 53.72, 33.65. EA (C<sub>7</sub>H<sub>7</sub>N<sub>5</sub>O<sub>4</sub>, 225.16): Calcd, C, 37.34; H, 3.13; N, 31.10; Found, C: 37.31; H: 3.08; N: 31.07.

**4-Nitramino-3-(5-(2,2'-dinitro)-acetic acid methyl ester-1,2,4-oxadiazolyl)-furazan (2):** Compound **1** (0.6 g, 2.7 mmol) was suspended in 6 mL of concentrated H<sub>2</sub>SO<sub>4</sub> at -5 °C. 100% HNO<sub>3</sub> (2.3 mL) was added dropwise, the reaction mixture was stirred at 0 °C for 30 min, then the reaction mixture was slowly warmed to room temperature and stirred for another 2h. The white solid was collected by filtration, washed with trifluoroacetic acid (3×2 mL), and air dried to give compound **2**, 0.84 g, yield 87.5%.  $T_{dec}$ : 88.2 °C; IR (cm<sup>-1</sup>)  $\tilde{\nu}$  = 3273, 2971, 2924, 1776, 1622, 1594, 1471, 1438, 1317, 1303, 1260, 1167, 1082, 1044, 1029, 972, 960, 920, 842, 807, 750, 720, 622, 611, 509. <sup>1</sup>H NMR (CD<sub>3</sub>CN): 11.76 (1H, br, NH); 4.16 (3H, s, CH<sub>3</sub>); <sup>13</sup>C{<sup>1</sup>H} NMR(CD<sub>3</sub>CN):  $\delta$  166.73, 160.34, 155.68, 149.33, 142.64, 110.76, 58.68. EA (C<sub>7</sub>H<sub>4</sub>N<sub>8</sub>O<sub>10</sub>, 360.15): C, 23.34; H, 1.12; N, 31.11; Found, C: 23.16; H: 1.12; N: 28.45.

**General method for preparing compound 2a – 2c:** Compound **2** (0.36 g, 1 mmol) was dissolved in methanol (8 mL) and the free base (conc. aqueous ammonia, 0.7 mL), 10 mmol; 50% hydroxylamine, 0.66g, 10 mmol; hydrazine hydrate, 0.5g, 10 mmol) in methanol (5 mL) added dropwise. After stirring 2 hours at room temperature, the precipitate was collected by filtration, air dried to give **2a** – **2c** (**2a**, 0.32g, yield 95.2%; **2b**, 0.35 g, yield 95.1%, **2c**, 0.36 g, yield 98.4%), respectively.

**Diammonium 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furazanate (2a):**  $T_{dec}$ : 161.0 °C; IR (cm<sup>-1</sup>)  $\tilde{\nu}$  = 3230, 1587, 1551, 1505, 1483, 1424, 1300, 1248, 1169, 1149, 1087, 1009, 982, 972, 922, 871, 822, 778, 766, 746 563 445. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 7.06 (8H, s, NH<sub>4</sub><sup>+</sup>); <sup>13</sup>C{<sup>1</sup>H} NMR(DMSO-d<sub>6</sub>):  $\delta$  171.39, 159.80, 158.05, 142.32, 122.14; EA (C<sub>5</sub>H<sub>8</sub>N<sub>10</sub>O<sub>8</sub>, 336.18): Calcd, C, 17.86; H, 2.40; N, 41.66; Found, C: 17.84; H: 2.24; N: 40.33.

**Dihydroxylammonium 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furazanate (2b):**  $T_{dec}$ : 190.2 °C; IR (cm<sup>-1</sup>)  $\tilde{\nu}$  = 3056, 1595 1552, 1508, 1480, 1431, 1412, 1385, 1313, 1231, 1183, 1143, 1091, 1015, 1006, 973, 923, 882, 836, 770, 748, 594, 567, 453. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 8.39 (8H, br, NH<sub>3</sub>OH<sup>+</sup>); <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>):  $\delta$  171.31, 159.76, 158.11, 142.32, 122.01; EA (C<sub>5</sub>H<sub>8</sub>N<sub>10</sub>O<sub>10</sub>, 368.18): Calcd, C, 16.31; H, 2.19; N, 38.04; Found, C: 16.46; H: 2.08; N: 37.52.

**Dihydrazinium 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furazanate (2c):**  $T_{dec}$ : 209.7 °C; IR (cm<sup>-1</sup>)  $\tilde{\nu}$  = 3327, 3194, 3012, 1567, 1502, 1485, 1430, 1373, 1310, 1273, 1177, 1108, 1084, 1010, 974, 921, 874, 824, 766, 743. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 5.56 (10H, br, N<sub>2</sub>H<sub>5</sub><sup>+</sup>); <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>):  $\delta$  171.37, 159.84, 158.27, 142.39, 122.07; EA (C<sub>5</sub>H<sub>10</sub>N<sub>12</sub>O<sub>8</sub>, 366.21): Calcd, C, 16.40; H, 2.75; N, 45.90; Found, C: 16.00; H: 2.66; N: 43.68.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

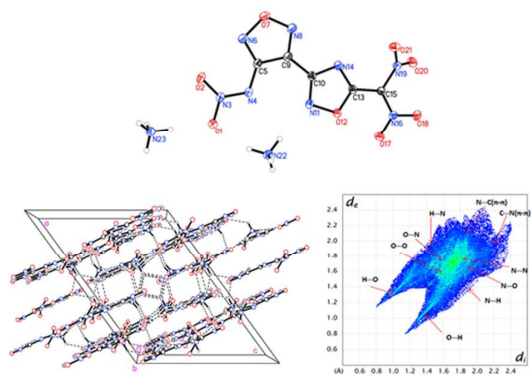
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## TOC



A new series of 4-nitramino-3-(5-dinitromethyl-1,2,4-oxadiazolyl)-furan-based energetic compounds which are competitive with HMX was synthesized in four steps with an overall yield of ~50% by using a straightforward method.