

## Electronic Supplementary Information

### Selecting suitable substituents for energetic materials

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#### 1. Experimental Section

Caution: Although we have not experienced any difficulties in preparing and handling these new energetic materials, proper protective precautions must be used. All compounds should be handled with care using the best safety practices.

#### General Methods

All reagents were obtained from Alfa Aesar or AK Scientific and were used as supplied. A Bruker AVANCE 300 nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz was used to collect <sup>1</sup>H and <sup>13</sup>C spectra, respectively. DMSO-d<sub>6</sub> was employed as solvent and locking solvent. Chemical shifts are given relative to Me<sub>4</sub>Si for <sup>1</sup>H and <sup>13</sup>C spectra. Thermal decomposition (onset) points were measured by a differential scanning calorimeter (TA Instruments Co., model Q2000) at a scan rate of 5 °C min<sup>-1</sup>. Densities were determined at room temperature by a Micromeritics AccuPyc 1340 gas pycnometer. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. The impact and friction sensitivities were obtained by using a standard BAM Fallhammer and a BAM friction tester. The crystal structures, Hirshfeld surfaces and 2D fingerprint plots for **5** was generated by CrystalExplorer 3.1.<sup>1</sup> Elemental analyses (C, H, N) were performed on a Vario Micro cube Elementar Analyser.

The starting material **3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide nitrite** was prepared according to the literature.<sup>2</sup>

**3, 6-Nitramino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (1).**

To nitric acid (100 %, 10 mL) was added 3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide nitrite (0.3 g, 1.3 mmol) in small portions with stirring at 10-15 °C. After complete addition, the reaction mixture was stirred at this temperature for 1 h. The mixture was concentrated by removing a large portion of the HNO<sub>3</sub> by blowing air. Then, trifluoroacetic acid (20 mL) was added and the mixture was stirred for 20 min. The red precipitate was filtered, air dried to give an orange solid **1** [0.16 g (47.7%)]. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ 142.7, 144.7, 149.4 ppm; IR (KBr pellet): ν 3345, 3228, 1662, 1621, 1590, 157, 1484, 1438, 1314, 1270, 1233, 1201, 1090, 974, 775, 707 cm<sup>-1</sup>; elemental analysis (C<sub>3</sub>H<sub>2</sub>N<sub>10</sub>O<sub>5</sub>, 258.02): calcd: C 13.96, H 0.78, N 54.27; found: C 13.86 H 1.06, N 53.44.

**Disilver 3, 6-nitramino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (2).**

To nitric acid (100%, 10 mL) was added 3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide nitrite (0.3 g, 1.3 mmol) in small portions with stirring at 10-15 °C. After complete addition, the reaction mixture was stirred for 1h at this temperature. The mixture was poured into ice (20 g). AgNO<sub>3</sub> (13 mmol in 5mL water) was added dropwise and the mixture was stirred for 30 min. The solid was filtered, and air dried to give red solid **2** [0.47 g (76.7%)]. <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ 144.8, 148.2, 148.4 ppm; IR (KBr pellet): ν 3460, 1636, 1576, 1500, 1448, 1404, 1334, 1271, 771, 708, 552 cm<sup>-1</sup>; elemental analysis (C<sub>3</sub>N<sub>10</sub>O<sub>5</sub>, 471.84): calcd: C 7.64, H 0.0, N 29.69; found: C 7.59, H 0.28, N 29.95.

Compounds **3**, **4** and **5** were obtained from the respective hydrochloride salts by reacting with silver salt (**2**). Compound **2** (1 mmol) was suspended in water, and respective bases (2 mmol) were added as hydrochlorides. The solution was stirred for 1 h at room temperature and filtered. The liquid phase was concentrated by air-drying. Acetonitrile (2 mL) was added to give a precipitate of **3**, **4** and **5**. Crystalline **5** was obtained during concentration of the solution by air. These solids were filtered and dried to give pure compounds.

**Diammonium 3, 6-nitramino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (3).**

Orange solid, yield 0.22 g (75%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ 7.12 (s, 4H); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ 144.9, 147.6, 149.5 ppm; IR (KBr pellet): ν 3570, 3447, 3167, 1619, 1566, 1501, 1439, 1400, 1327, 1267, 1245, 1224, 1159, 1011, 870, 712 cm<sup>-1</sup>; elemental analysis (C<sub>3</sub>H<sub>8</sub>N<sub>12</sub>O<sub>5</sub>, 292.18): calcd: C 12.33, H 2.76, N 57.53; found: C 12.27, H 3.08, N 56.58;

**Ditriaminoguanidinium 3, 6-nitramino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (4).**

Brown solid, yield 0.34 g (72%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ 4.48 (s, 4H), 8.57 (s, 2H); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ 144.9, 147.5, 149.6, 159.0 ppm; IR (KBr pellet): ν 3432, 3322, 3210, 1685, 1618, 1492, 1438, 1328, 1132, 962, 639, 617 cm<sup>-1</sup>; elemental analysis (C<sub>5</sub>H<sub>18</sub>N<sub>22</sub>O<sub>5</sub>, 466.35): calcd: C 12.88, H 3.89, N 66.08; found: C 12.92, H 4.16, N 65.33;

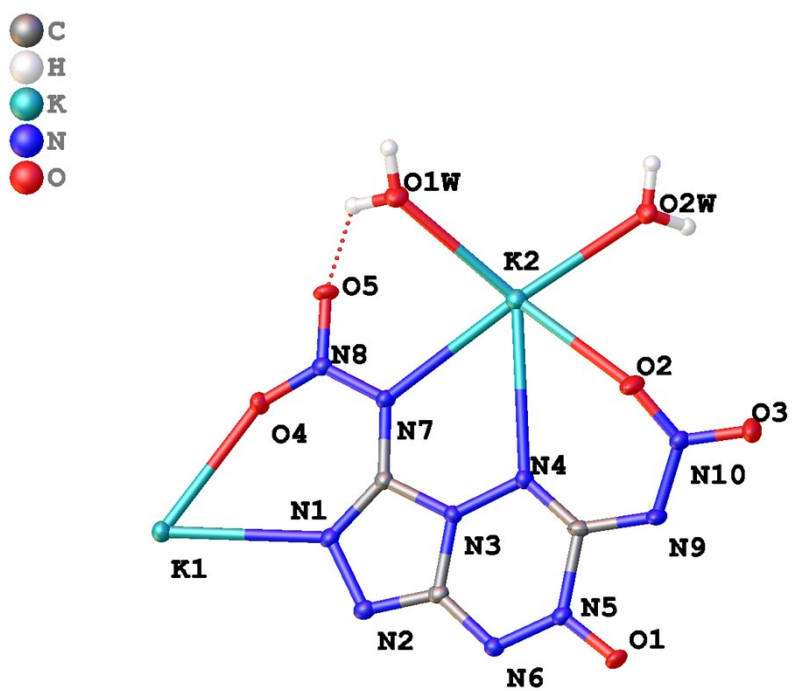
**Dipotassium 3, 6-nitramino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (5).**

Red crystal, yield 0.22 g (65%).  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ): 145.0, 147.6, 149.7 ppm; IR (KBr pellet):  $\nu$  3449, 1571, 1500, 1438, 1412, 1327, 1294, 1265, 1247, 1221, 1158, 1038, 1004, 869, 773, 711  $\text{cm}^{-1}$ ; elemental analysis ( $\text{C}_3\text{K}_2\text{N}_{10}\text{O}_5$ , 334.3): calcd: C 10.78, H 0, N 41.90; found: C 10.71, H 0.29, N 41.66;

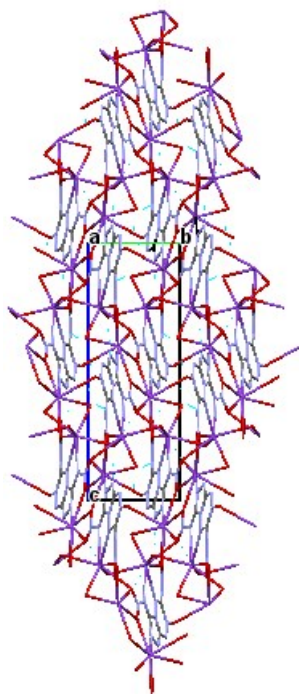
## 2. X-ray Crystallography of 5

**Table S1.** Crystal data and structure refinement for crystals

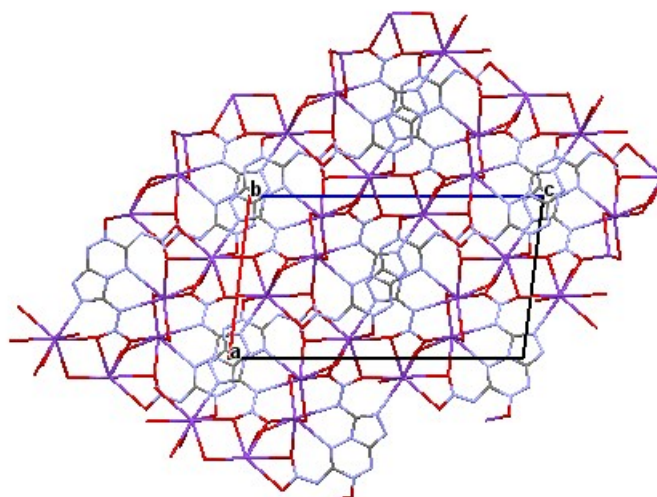
<b>Compound</b>	<b>5</b>
CCDC number	2009369
Formula	C <sub>3</sub> H <sub>4</sub> K <sub>2</sub> N <sub>10</sub> O
	7
$D_{calc.}/\text{g cm}^{-3}$	2.043
$m/\text{mm}^{-1}$	7.616
Formula Weight	370.36
Colour	red
Shape	needle
Size/ $\text{mm}^3$	0.16×0.06×0.05
$T/\text{K}$	99.99(10)
Crystal System	monoclinic
Space Group	$P2_1/n$
$\alpha/\text{\AA}$	10.2264(4)
$\beta/\text{\AA}$	6.4609(3)
$\gamma/\text{\AA}$	18.3714(7)
$\alpha^\circ$	90
$\beta^\circ$	97.157(4)
$\gamma^\circ$	90
$V/\text{\AA}^3$	1204.37(9)
$Z$	4
$Z'$	1
Wavelength/ $\text{\AA}$	1.54184
Radiation type	Cu K $\alpha$
$Q_{min}^\circ$	4.716
$Q_{max}^\circ$	71.098
Measured Refl's.	5029
Ind't Refl's	2209
Refl's with $I > 2(I)$	2006
$R_{int}$	0.0289
Parameters	215
Restraints	6
Largest Peak	0.302
Deepest Hole	-0.390
GooF	1.074
$wR_2$ (all data)	0.0868
$wR_2$	0.0839
$R_1$ (all data)	0.0341
$R_1$	0.0313



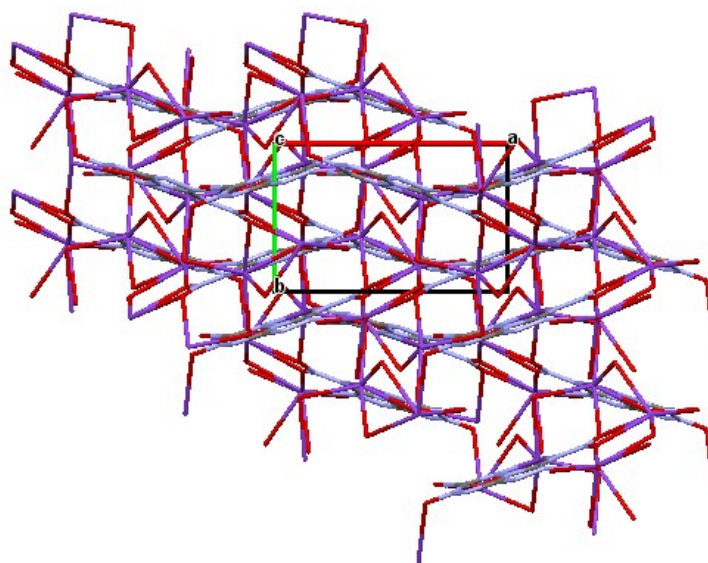
**Figure S1.** Single-crystal X-ray structures of **5** with numbering.



**Figure S2.** Unit cell view for **5** along a axis; hydrogen bonds are marked as dotted lines.



**Figure S3.** Unit cell view for **5** along b axis; hydrogen bonds are marked as dotted lines



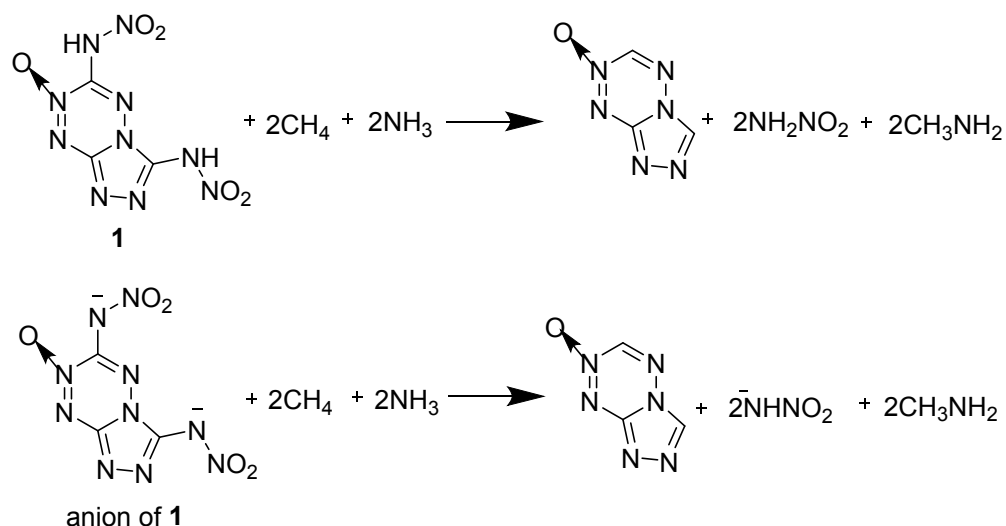
**Figure S4.** Unit cell view for **5** along c axis; hydrogen bonds are marked as dotted lines.

**Table S2.** Hydrogen bonds for **5** [Å and °]

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/deg
O1W	H1WB	O5	0.86(2)	2.21(3)	2.852(2)	131(3)

### 3. Theoretical calculations

The calculations of the heats of formation were carried out using Gaussian 03 (Revision D.01) suite of programs. All the compounds were determined using isodesmic reactions (Scheme S1). The geometric optimization and frequency analyses of the structures were calculated using B3LYP/6-31+G\*\* level. The gas phase enthalpy of formation was calculated, and the enthalpy of reaction was 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.



**Scheme 1S. Isodesmic reactions for 1 and the anion of 1.**

### 4. References

1. S. K. Wolff, D. J. Grimwood, J. J. McKinnon, M. J. Turner, D. Jayatilaka, M. A. Spackman, CrystalExplorer (Version 3.1), University of Western Australia, 2012.
2. L. Hu, P. Yin, G. H. Imler, D. A. Parrish, H. Gao and J. M. Shreeve, *Chem. Commun.*, 2019, **55**, 8979-8982.