# Supporting information

Regulation of Stability and Density of Energetic Materials via Isomerism

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## 1 Isodesmic Reactions and Calculation Methods

The heat of formation for compound 3 was obtained using the isodesmic reaction method. The calculations were performed using Gaussian 09 suite of programmes. The geometric optimisation and frequency analyses of the structure were calculated at the B3LYP/6-31+G\*\* level, and the single-point energies were calculated at the MP2/6-

311+G\*\* level. The heats of formation for the cations were obtained via an atomisation approach using the G2 ab initio method.



The gas phase enthalpy of formation and heat of sublimation of 3a are 256.63 kJ mol<sup>-1</sup> and 66.35 kJ mol<sup>-1</sup>, respectively. 3b are 265.67 kJ mol<sup>-1</sup> and 71.1 kJ mol<sup>-1</sup>.

The solid-phase enthalpy of formation is obtained using a Born–Haber energy cycle and the relevant calculation formulas are shown below.



Table S1 Lattice energy for heat of formation.						
Compound	$\Delta H_{f}(cation)$	$\Delta H_{f}(anion)$	$\Delta H_L$	$\Delta \mathrm{H_{f}}$		
	kJ/mol	kJ/mol	kJ/mol	kJ/mol		
4a	23.27	669.54	492.16	200.65		
4b	20.92	669.54	495.30	195.16		

Packing coefficients were calculated using equation (1), wherein Vm and Vc represent the molecular and crystal volumes, respectively. Notably, a volume enclosed through a surface with an assigned electronic density was considered Vm. In this study, the electronic density was calculated at the theory level of B3LYP/6-311+G(d, p) and a density of 0.003 au was used for Vm calculations<sup>1</sup>.

$$PC = \Sigma V_{mol} V_{cell}^{-1}$$
 (1)

### 2 Experimental Sections

#### General Methods

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectra were recorded using a 400-MHz nuclear magnetic spectrometer (Bruker). The melting point and decomposition temperature were obtained using a differential scanning calorimeter (Mettler Toledo DSC823e) at a rate of 10°C/min under a nitrogen flow rate of 50 ml/min. Infrared spectra were recorded using KBr pellets for solid samples on a Bruker Tensor 27 instrument. Elemental analyses were performed using a Vario EL Analyser.

Caution!

Although no explosions or hazards were observed during the preparation and handling of these compounds, all are potentially explosive materials. Mechanical actions involving scratching or scraping must be avoided. Moreover, all compounds must be synthesised on a small scale. Manipulations must be performed in a hood behind a safety shield. Eye protection should be exercised and leather gloves must be worn at all times.

2-acetonyl-4-nitro-1,2,3-triazole 2a and 2b 1-acetonyl-4-nitro-1,2,3-triazole

Compound 1, 4-nitro-1,2,3-triazole<sup>2</sup> (1.14g 10mmol14 g, 10 mmol) was dissolved in an aqueous NaOH (400 mg, 10 mL) aqueous solution. Subsequently, bromoacetone (1.37g 10mmol) in10 mL of acetone was added to the obtained solution at room temperature. The reaction mixture was stirred for 16 h at room temperature. The solvent was removed under reduced pressure, and the resulting mixture was then purified via silica column chromatography to obtain 739mg 2a (43.5%) and 800mg 2b (47%). 2a: <sup>1</sup>H NMR (D6-DMSO): δ=2.28 (S,3H) δ=5.81 (S,2H) δ=8.78 (S,1H). <sup>13</sup>C NMR (D6-DMSO): δ=200.20, 154.04, 132.28, 64.78, 27.25. IR (KBr pellet) υ 3532, 3454, 3227, 3017, 2975, 2891, 1737, 1653, 1620, 1541, 1520, 1480, 1413, 1395, 1336, 1312, 1204, 1176, 1085, 1045, 844, 808, 768, 685, 499 cm<sup>-1</sup>. Elemental analysis (%) C6H7N3O3 (170) calcd C, 35.30 H,3.55 N, 32.93; found C, 35.26 H, 3.73, N, 33.46. 2b: <sup>1</sup>H NMR (D6-DMSO):  $\delta$ =2.30 (S,3H)  $\delta$ =5.67 (S,2H)  $\delta$ =9.15 (S,1H). <sup>13</sup>C NMR (D6-DMSO): δ=200.05, 153.32, 126.59, 59.57, 27.49. IR (KBr pellet) υ 3416, 3120, 2987, 2950, 1731, 1537, 1511, 1471, 1394, 1322, 1302, 1204, 1253, 1176, 1114, 1038, 882, 831, 758, 576, 544 cm<sup>-1</sup>. Elemental analysis (%) C6H7N3O3 (170) calcd C, 35.30 H,3.55 N, 32.93; found C, 35.31 H, 3.51, N, 33.04.

2-Dinitromethyl-4-Nitro-1,2,3-Triazole 3a and 1-Dinitromethyl-4-Nitro-1,2,3-Triazole 3b

HNO<sub>3</sub> (100%, 5 mL) was dropwise added to an ice-cold suspension of 2a (739 mg, 4.4 mmol) or 2b (739 mg, 4.4 mmol) in 6 mL of 98% H<sub>2</sub>SO<sub>4</sub>. After 1 h, the reaction mixture was heated to room temperature and stirred for 2 h, following which the separated product was filtered off, washed with CF<sub>3</sub>COOH (3 mL), and dried in air to obtain 3a in 63% (610 mg) yield. 3a: <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$ =8.01 (S,1H)  $\delta$ =8.59 (S,1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ =161.43, 154.04, 125.84. IR (KBr pellet) v 3417, 3253, 3157, 3021, 2908, 1593, 1393, 1325, 1265, 1230, 1031, 926, 882, 808, 749, 657, 578 cm<sup>-1</sup>. Elemental analysis (%) C3H2N6O6 (218) calcd C, 16.52 H,0.92 N, 38.54; found C, 16.59 H, 0.91, N, 38.48. 3b (545mg 56%): <sup>1</sup>H NMR (CD<sub>3</sub>CN):  $\delta$ =8.74 (S,1H)  $\delta$ =9.30 (S,1H). <sup>13</sup>C NMR (CD<sub>3</sub>CN):  $\delta$ =154.04, 126.65, 105.85. IR (KBr pellet) v 3310, 3001, 2781, 1744,

1624, 1565, 1522, 1458, 1394, 1228, 1093, 1037, 830, 756, 689, 578, 454 cm<sup>-1</sup>. Elemental analysis (%) C3H2N6O6 (218) calcd C, 16.52 H,0.92 N, 38.54; found C, 16.73 H, 0.97, N, 38.29.

General method for preparing compound 4a-4b

Compound 3 (0.43 g, 2 mmol) was dissolved in methanol (8 mL); subsequently, 50% hydroxylamine (0.66 g, 10 mmol) in methanol (5 mL) was added dropwise to the obtained solution. After stirring for 30 min at room temperature, the precipitate was collected via filtration and then dried to obtain 4a (0.443g 88%) and 4b (0.467g 93%).

Hydroxylammonium 2-Dinitromethyl-4-Nitro-1,2,3-Triazole 4a

<sup>1</sup>H NMR (D6-DMSO):  $\delta$ =10.09 (S,4H)  $\delta$ =8.92 (S,1H). <sup>13</sup>C NMR (D6-DMSO):  $\delta$ =154.72, 134.95, 133.41. IR (KBr pellet)  $\upsilon$  3204, 2709, 1549, 1507, 1486, 1429, 1351, 1253, 1156, 1075, 1019, 953, 875, 836, 740, 681, 613, 584 cm<sup>-1</sup>. Elemental analysis (%) C3H5N7O7 (251) calcd C, 14.35 H,2.01 N, 39.05; found C, 14.42 H, 2.05, N, 38.96.

Hydroxylammonium 1-Dinitromethyl-4-Nitro-1,2,3-Triazole 4b

<sup>1</sup>H NMR (D6-DMSO):  $\delta$ =9.67 (S,1H)  $\delta$ =9.93 (S,4H). <sup>13</sup>C NMR (D6-DMSO):  $\delta$ =154.11, 130.26, 127.50. IR (KBr pellet)  $\upsilon$  3417, 3143, 3000, 2699, 1614, 1565, 1460, 1384, 1352, 1317, 1222, 1146, 1035, 976, 899, 828, 747, 616, 473 cm<sup>-1</sup>. Elemental analysis (%) C3H5N7O7 (251) calcd C, 14.35 H,2.01 N, 39.05; found C, 14.36 H, 2.09, N, 38.94.

3 X-ray Crystallographic Data

Empirical formula	C <sub>3</sub> H <sub>2</sub> N <sub>6</sub> O <sub>6</sub> (3a)	$C_{3}H_{2}N_{6}O_{6}$ (3b)	C <sub>3</sub> H <sub>7</sub> N <sub>7</sub> O <sub>8</sub> (4a)	$C_{3}H_{5}N_{7}O_{7}$ (4b)
CCDC	2224685	2224691	2224689	2224692
Formula weight	218.11	218.11	269.16	251.14
Temperature	296 K	296 K	170 K	170 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	Сс	P21/n	P21/c	$P_l/n_l$
a /Å	9.5399 (11)	7.0555 (7)	6.4647 (7)	4.8820 (5)
b /Å	8.8744 (11)	12.4013 (14)	15.866 (2)	10.0306 (10)
c /Å	10.5124 (14)	9.011 (10)	10.0270 (11)	8.9963 (9)
α (°)	90	90	90	90
β (°)	116.970 (5)	102.052 (3)	96.745 (4)	95.203 (4)
γ (°)	90	90	90	90
$V/Å^3$	793.20 (17)	771.06 (14)	1021.3 (2)	438.73 (8)
Z	4	4	4	2
pcalc g/cm3 (296K)	1.826	1.879	1.750 (170 K)	1.901 (170 K)
Mu(mm-1)	0.176	0.181	0.171	0.183
F000	440	440	552.0	256.0
h, k, lmx	12,11,13	18,14,10	8,19,12	6,13,11
Nref	1140	1363	2097	1686
Tmin, Tmax	0.864,0.864	0.864,0.864	0.661,0.745	0.671,0.746
R (reflections)	0.03	0.04	0.055	0.039

Table S2 Crystal data and structure refinement for 3a-4a and 3b-4b.



Fig S1 OPTEP diagram for compound 3a with 50% probability ellipsoids (296 K)



Fig S2 OPTEP diagram for compound 4a with 50% probability ellipsoids (170 K)







Fig S4 OPTEP diagram for compound 4b with 50% probability ellipsoids (170 K)

4 NMR



Fig S5 <sup>1</sup>H NMR of compound 2a



Fig S8 <sup>13</sup>C NMR of compound 2b











Fig S11 <sup>1</sup>H NMR of compound 3b







Fig S13 <sup>1</sup>H NMR of compound 4a



Fig S14 <sup>13</sup>C NMR of compound 4a







Fig S16 <sup>13</sup>C NMR of compound 4b

5 DSC



Fig S17 DSC of compound 3a



### 5 References and Notes

(1) Xiong, J.; Cai, J.; Lai, Q.; Yin, P.; Pang, S., Asymmetric assembly of pyrazole and 1,2,3-triazole with a methylene bridge: regioisomerism and energetic properties. *Chem Commun (Camb)* **2022**.

(2) Lai, Q.; Fei, T.; Yin, P.; Shreeve, J. n. M., 1,2,3-Triazole with linear and branched catenated nitrogen chains – The role of regiochemistry in energetic materials. *Chemical Engineering Journal* **2021**, *410*.