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SUPPORTING INFORMATION

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1. The crystallographic data

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Chemical formula	$C_4H_4N_7O_8CI$	$C_4H_5N_6O_6CI$	C ₄ H ₄ N ₇ O ₇ Cl	$C_4H_5N_7O_8$
Formula mass	313.59	268.59	297.59	279.15
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
a/Å	11.4945(17)	8.582(5)	8.1381(17)	18.913(11)
b/Å	11.5752(18)	11.470(7)	11.242(2)	5.827(3)
c/Å	16.011(2)	10.482(6)	11.677(2)	18.914(10)
α/°	90	90	90	90
β / °	90	110.736(11)	106.132(5)	102.724(13)
γ / °	90	90	90	90
Volume/Å ³	2130.3(6)	965.0(10)	1026.2(4)	2033.3(18)
Temperature/K	173	173	173	173
Space group	Pbca	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /n
Z	8	4	4	8
Radiation type	Мо-Ка	Мо-Ка	Мо-Ка	Мо-Ка
µ/mm⁻¹	0.422	0.431	0.425	0.176
Density _{calcd} /g cm ⁻³	1.955	1.849	1.926	1.824
F(000)	1264.0	544.0	600.0	1136.0
20 range for data	5.088 to 54.892	5.076 to	5.13 to	3.448 to
collection/°		55.344	54.886	52.656
Index ranges	-14/14;-14/14;	-11/11;-14/14;	-10/10;-13/14;	-23/22;-7/5;
index ranges	-20/20	-13/13	-13/15	-23/23
Reflections collected	14757	5282	8999	13792
Independent reflections	2432	2206	2341	4094
R _{int}	0.0347	0.0428	0.0385	0.0784
Data/restraints/ parameters	1544/0/181	2206/0/154	2341/0/172	4094/0/343
R_1 / w R_2 [all data]	0.0358/0.0811	0.0533/0.1392	0.0581/0.1262	0.0964/0.1499
$R_1 / wR_2 [I > 2\sigma(I)]$	0.0299/0.0772	0.0428/0.1207	0.0464/0.1201	0.0531/0.1262
Goodness-of-fit on F ²	1.061	1.102	1.055	0.979
CCDC number	1846305	1846307	1846310	1846311

Table S1. X-ray data and parameters of 2, 3, 4, 5, 7 and 9.

Table S1 (Continued)

	7	9 (α polymorph)	9 (β polymorph)
Chemical formula	$C_4H_5N_7O_8$	$C_4H_6N_6O_6$	$C_4H_6N_6O_6$
Formula mass	279.15	234.15	234.15
Crystal system	triclinic	orthorhombic	orthorhombic
a/Å	5.886(3)	8.8210(19)	7.1223(15)
b/Å	8.134(4)	9.509(2)	10.448(2)
c/Å	20.460(9)	19.681(4)	11.389(3)
α/ °	99.275(11)	90	90
β / °	90.656(10)	90	90
γ/°	93.353(10)	90	90
Volume/Å ³	964.9(8)	1650.7(6)	847.5(3)
Temperature/K	173	173	173
Space group	<i>P</i> -1	Pbca	Pnma
Z	4	8	4
Radiation type	Мо-Ка	Мо-Ка	Мо-Ка
µ/mm⁻¹	0.185	0.176	0.171
Density _{calcd} /g cm ⁻³	1.922	1.884	1.835
F(000)	568.0	960.0	480.0
20 range for data	2.018 to	4.14 to	5.29 to
collection/°	55.036	55.044	54.966
Index ranges	-	-11/11;-12/12; - 25/23	-9/9;-13/13; -12/14
Reflections collected	4393	8074	5543
Independent reflections	4393	1900	1013
R _{int}	-	0.0728	0.0600
Data/restraints/ parameters	4393/0/343	1900/0/145	1013/12/101
R_1 / w R_2 [all data]	0.0995/0.2391	0.1109/0.1883	0.0851/0.1956
$R_1 / wR_2 [I > 2\sigma(I)]$	0.0670/0.2077	0.0632/0.1608	0.0526/0.1521
Goodness-of-fit on F ²	1.014	1.028	1.109
CCDC number	1846421	1846590	1846317

2. Theoretical study

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.¹ Based on the method of isodesmic reactions (Scheme S1), gas-phase heats of formation of the neutral compounds were computed. The gas-phase

enthalpies of the building-block molecules were obtained by using the atomization method with the G2 ab initio calculations. Then the remaining task is to determine the solid-state heats of formation for the synthesized compounds.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation.

 $\Delta H_{\rm f} = \Delta H_{\rm f}(g) - \Delta H_{\rm sub} \quad (1)$

On the basis of the literature,² the heat of sublimation can be estimated with Trouton's rule according to eq 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

 $\Delta H_{\rm sub} = 188/\text{J mol}^{-1}\text{K}^{-1} \times \text{T}$ (2)

The detailed principle can be consulted from literatures¹⁻⁴.



Scheme S1. Isodesmic reactions

3. Experimental Section

Safety precautions. Although no explosion or detanation happened during the synthesis, characterization and handling of the compounds described in this work, all manipulations must be carried out by using appropriate standard safety precautions like face shield, leather coat and leather gloves. Mechanical actions involving scratching or scraping must be avoided.

Hexahydro-1-tert-butyl-4-dinitromethylene-1,3,5-triazine(1).

To a suspension of FOX-7 (1.48 g, 10 mmol) in 15mL water with the pH of 8^{-10} , 37% formaldehyde (3.2mL) was added, and the mixture was stirring for 30min at room temperature. To above suspension tert-butylamine (1.06mL, 10 mmol) was added at one portion and the reaction was stirred for an additional 3 h at room temperature. The precipitate was filtered, washed with water and dried in the air to give **1** as yellow powder (2.26g, 92.3%). The product was identical in all respects to that previously reported.⁵

6-(chlorodinitromethyl)-1,3-dinitro-1,2,3,4-tetrahydro-1,3,5-triazine (2). To 5mL acetic anhydride, 2.5 mL of 100% nitric acid was added at 0°C. After 15 min, **1** (0.245 g, 1mmol) was added portionwise over a 10 min period, followed by one portion addition of additives (3 mmol). The resulting suspension was stirring at 0 °C for 3h. The reaction was quenched by dumping into ice water. A white solid formed was filtrated, washed with water and dried in air to give **2** (NH₄Cl, 64.31%; ZnCl₂, 65.17%; PCl₅, 67.78%; POCl₃, 18.25%; CH₃COCl, 61.52%).¹H NMR (600 MHz, CD₃CN) : $\delta_{\rm H}$ = 5.92 (2H, s), 6.10 (2H, s) ppm; ¹³C NMR (151MHz, CD₃CN): $\delta_{\rm C}$ = 59.48, 65.29, 140.79 ppm; IR (KBr): v = 3063, 3004, 2978, 2936, 2908, 1662, 1606, 1591, 1562, 1441, 1418, 1376, 1308, 1265, 1255, 1162, 1107, 1034, 1002, 957, 927, 905, 862, 824, 803, 785, 755, 742, 707, 676, 632, 606, 575, 546, 473, 450, 424 cm⁻¹; elemental analysis calcd (%) for C₄H₄N₇O₈Cl (313.57): C 15.32, H 1.29, N 31.27, found: C 15.25, H 1.33, N 31.25.

6-(chlorodinitromethyl)-3-nitro-1,2,3,4-tetrahydro-1,3,5-triazine (3). To 2 mL of fuming nitric acid at 0°C, **1** (0.245 g, 1 mmol) was added portionwise over a 10 min period, followed by one portion addition of NH₄Cl (0.156 g, 3 mmol). The reaction was stirring at 0 °C for 3h. The reaction was quenched by dumping into ice water. A white solid formed was filtrated, washed with water and dried in air to give **3** (0.139 g, 51.7%). ¹H NMR (600 MHz, CD₃COCD₃): $\delta_{\rm H}$ = 5.42 (2H, s), 5.61 (2H, s), 7.94 (1H, s) ppm; ¹³C NMR (151MHz, CD₃COCD₃): $\delta_{\rm C}$ = 57.34, 64.15, 120.44, 147.18 ppm; IR (KBr): v = 3248, 3058, 2989, 1651, 1615, 1596, 1560, 1505, 1469, 1436, 1389, 1349, 1295, 1156, 1096, 1033, 968, 948, 924, 840, 823, 784, 765, 691, 644, 621, 523, 437 cm⁻¹; elemental analysis calcd (%) for C₄H₅N₆O₆Cl (268.59): C 17.89, H 1.88, N 31.29, found: C 17.83, H 1.89, N 31.24.

6-(chlorodinitromethyl)-3-nitro-1-nitroso-1,2,3,4-tetrahydro-1,3,5-triazine (4).

To 2 mL of freshly 100% nitric acid at 10°C, **1** (0.245 g, 1 mmol) was added portionwise over a 10 min period, followed by one portion addition of NH₄Cl (0.156 g, 3 mmol). The reaction was stirring at 0 °C for 3h. The reaction was quenched by dumping into ice water. A white solid formed was filtrated, washed with water and dried in air to give **4** (0.176 g, 59.2%). ¹H NMR (600 MHz, CD₃CN) : δ_{H} = 5.34 (2H, s), 5.78(2H, d) ppm; ¹³C NMR (151MHz, CD₃CN): δ_{C} = 55.01, 65.39, 147.15 ppm; IR (KBr): v = 3039, 2957, 2904, 2852, 1655, 1615, 1605, 1579, 1527, 1453, 1428, 1387, 1355, 1337, 1294, 1281, 1254, 1192, 1158, 1110, 1030, 1004, 956, 920, 905, 879, 819, 792, 777, 768, 701, 655, 632, 614, 568, 534, 466, 444

cm⁻¹; elemental analysis calcd (%) for C₄H₄N₇O₇Cl (297.59): C 16.15, H 1.35, N 32.95, found: C 16.04, H 1.39, N 32.78.

6-(trinitromethyl)-3-nitro-1,2,3,4-tetrahydro-1,3,5-triazine (5).

To 2.5 mL of 100% nitric acid, **1** (0.245 g, 1mmol) was added portionwise at 0°C over a 10 min period. The reaction was stirring at 0 °C for 3h. The reaction was quenched by dumping into ice water. A white solid formed was filtrated, washed with water and dried in air to give **5** (0.034 g, 12.3 %). ¹H NMR (400 MHz, CD₃CN) : δ_{H} = 5.22 (2H, s), 5.57 (2H, s), 7.08 (1H, s) ppm; ¹³C NMR (100MHz, CD₃CN): δ_{C} = 56.78, 64.00, 123.14, 143.14 ppm; IR (KBr): v = 3429, 3053, 3006, 2894, 1670, 1616, 1608, 1593, 1553, 1470, 1457, 1434, 1386, 1342, 1285, 1263, 1237, 1160, 1105, 1040, 975, 940, 913, 850, 827, 802, 762, 669, 648, 614, 596, 516, 502, 425 cm⁻¹; elemental analysis calcd (%) for C₄H₅N₇O₈ (279.15): C 17.21, H 1.81, N 35.13, found: C 17.15, H 1.83, N 35.08.

6-(dinitromethyl)-1,3-dinitro-1,2,3,4-tetrahydro-1,3,5-triazine (7). 2 (1mmol) was dissolved in methanol (3 mL), potassium iodide (0.2 g, 1.2 mmol) in methanol (1 mL) was added dropwise, and the mixture was stirring for 12 h at room temperature. The precipitate formed was collected by filtration, washed with ethanol and dried in the air to give potassium salt as a yellow solid. Potassium salt was dissolved in water (3 mL), then concentrated hydrochloride acid (0.5 mL) was added dropwise in room temperature. The white solid formed was collected by filtration, washed with water and dried in air to give **7** (0.251 g, 89.86%). ¹H NMR (600 MHz, DMSO-d₆) : $\delta_{\rm H}$ = 5.71 (2H, s), 6.09 (2H, s) ppm; ¹³C NMR (151MHz, DMSO-d₆): $\delta_{\rm C}$ = 59.58, 63.96, 128.65, 141.33 ppm; IR (KBr): v = 3062, 3044, 2999, 2957, 2913, 2815, 1665, 1598, 1560, 1447, 1421, 1381, 1359, 1328, 1299, 1264, 1240, 1163, 1083, 1028, 1003, 954, 940, 912, 868, 860, 818, 804, 771, 759, 741, 700, 678, 638, 611, 590, 577, 460, 439, 416 cm⁻¹; elemental analysis calcd (%) for C₄H₅N₇O₈ (279.15): C 17.21, H 1.81, N 35.13, found: C 17.11, H 1.85, N 35.02.

4-(dinitromethylene)-1-nitro-1,3,5-triazinane (**9**, polymorph α). **3** (0.269 g, 1 mmol) was dissolved in methanol (3 mL), potassium iodide (0.2 g, 1.2 mmol) in methanol (2 mL) was added dropwise, and the mixture was stirred for 12 h at room temperature. The precipitate formed was collected by filtration, washed with water and dried in the air to give the polymorph α of **9** (0.194 g, 83%). ¹H NMR (600 MHz, DMSO-d₆) : δ_{H} = 5.30 (2H, s), 6.03 (2H, s), 10.56 (1H, s), 10.99 (1H, s) ppm; ¹³C NMR (151MHz, DMSO-d₆): δ_{C} = 48.12, 57.30, 126.30, 153.77 ppm; IR (KBr): v = 3249, 3030, 1582, 1510, 1469, 1452, 1365, 1319, 1270, 1181, 1126, 1038, 1018, 981, 851, 819, 781, 745, 709, 676, 578, 542 cm⁻¹; elemental analysis calcd (%) for C₄H₆N₆O₆ (234.15): C 20.52, H 2.58, N 35.90, found: C 20.48, H 2.61, N 35.85.

4-(dinitromethylene)-1-nitro-1,3,5-triazinane (**9**, polymorph β). **4** (0.298 g, 1 mmol) was dissolved in methanol (3 mL), potassium iodide (0.2 g, 1.2 mmol) in methanol (2 mL) was added dropwise, and the mixture was stirred for 12 h at room temperature. The precipitate formed was collected by filtration, washed with ethanol and dried in the air to give the polymorph β of **9** (0.189 g, 80.62%). ¹H NMR (600 MHz, DMSO-d₆) : δ_{H} = 5.58 (4H, s), 10.87 (2H, s) ppm; ¹³C NMR (151MHz, DMSO-d₆): δ_{C} = 57.02, 126.13, 153.91 ppm; IR (KBr): v = 3220, 3040, 2966, 2857, 1599, 1504, 1458, 1441, 1395, 1353, 1315, 1293, 1263, 1127, 979, 906, 856, 821, 784, 754, 657, 623, 542, 431 cm⁻¹; elemental analysis calcd (%) for C₄H₆N₆O₆ (234.15): C 20.52, H 2.58, N 35.90, found: C 20.47, H 2.61, N 35.82.

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