

Electronic Supplementary Information

Fused rings with N-oxide and -NH₂: good combination for high density and low sensitive energetic material

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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 received. A Bruker AVANCE 300 nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz were used to collect ^1H and ^{13}C spectra. ($[\text{D}_6]\text{DMSO}$) was employed as solvent and locking solvent. Chemical shifts are given relative to Me_4Si for ^1H and ^{13}C spectra. Melting and decomposition (onset) points were measured by a differential scanning calorimeter (TA Instruments Co., Model Q2000) at a scan rate of $5\text{ }^\circ\text{C min}^{-1}$. Infrared (IR) spectra were recorded on an FT-IR spectrometer (Thermo Nicolet AVATAR 370) using KBr pellets. Densities were determined at room temperature by a Micromeritics AccuPyc 1340 gas pycnometer. Elemental analyses (C, H, N) were performed on a Vario Micro cube Elementar Analyser. The impact and friction sensitivity measurements were made by using a standard BAM Fallhammer and a BAM friction tester. Hirshfeld surfaces and 2D fingerprint plots for **1** and **2** were generated by CrystalExplorer 3.1.2.

3,6-Diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine was prepared according to the literature.¹

3-Nitro-6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (1)

To a mixture of hydrogen peroxide (50 %, 4 mL) and concentrated sulfuric acid (7.7 mL) was added 3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine (2 mmol) slowly at $0\text{ }^\circ\text{C}$. This mixture was allowed to warm slowly to room temperature and held overnight. The mixture was poured into ice-water (100 g). The solution was extracted with ethyl acetate (4 x 100 mL). The organic phase was washed with water and dried over anhydrous magnesium sulfate, and the solvent was concentrated. The residue was separated by column chromatography (EtOAc/n-hexane 1:3) to give of **1** [41 mg (10%)] as a light yellow crystal. ^1H NMR ($[\text{D}_6]\text{DMSO}$): 9.08 (s, 2H); ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): 145.7, 147.5, 149.2 ppm; IR (KBr pellet): 3465, 3353, 1662, 1552, 1519, 1489, 1464, 1422, 1389, 1356, 1327, 1288, 1275, 1245, 1082, 859, 814, 742, 719, 650, 633, 538, cm^{-1} ; elemental analysis (%) for $\text{C}_3\text{H}_2\text{N}_8\text{O}_3$, (198.10): calcd: C 18.19, H 1.02, N 56.56; found: C 18.03, H 1.31, N 56.79;

3,6-Diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (2) and its NO_3^- salt (3)

To a mixture of 50 % hydrogen peroxide (2 mL) in methylene chloride (20 mL) was added trifluoroacetic anhydride (6 mL) slowly while maintaining the temperature $< 10\text{ }^\circ\text{C}$. After warming to room temperature, 3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine (2 mmol) was added, and stirring continued for 24 h. A yellow solid precipitated. Most of the solvent was blown off by air, and the remaining liquid/solid was filtered to give a mixture of **2** and **3**. The product is a mixture of **2** and **3**, with the nitrate salt **2** as the main product. To the mixed solid in methylene chloride was added several drops of fuming HNO_3 . It was stirred for 30 mins, then filtered to give pure compound **2** (nitrate salt). It was dried to give 0.253 g (55%) of **2** as a yellow solid. ^1H NMR ($[\text{D}_6]\text{DMSO}$): δ 8.39 (s, 2H); ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): 142.8, 145.1, 147.3 ppm; IR (KBr pellet): 3441, 3401, 3281, 3117, 2680, 1705, 1680, 1499, 1384, 1325, 1271, 1083, 722, 605, 520, 455 cm^{-1} ; elemental analysis ($\text{C}_3\text{H}_5\text{N}_9\text{O}_4$, 231.13): calcd: C 15.59, H 2.18, N 54.54; found: C 15.62, H 2.27, N 54.71;

To compound **3** in methanol was added NaOH (2 mmol) in methanol. The solution was stirred for 30 mins, then filtered to give compound **3**. It was dried to give 0.17 g (50.6%) of **2** as a red solid. ¹H NMR ([D₆]DMSO): δ 6.40 (s, 2H), 7.94 (s, 2H); ¹³C NMR ([D₆]DMSO): 143.3, 146.3, 148.3 ppm; IR (KBr pellet): 3413, 3323, 3248, 3112, 1731, 1665, 1626, 1597, 1450, 1395, 1349, 1311, 1240, 1172, 1124, 1104, 1030, 1004, 932, 858, 685 cm⁻¹; elemental analysis (C₃H₄N₈O₁, 182.03): calcd: C 21.43, H 2.4, N 66.65; found: C 21.34, H 2.45, N 65.77;

6,6'-Diamino-3,3'-azo-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7, 7'-N-oxide (4•H₂O)

To a suspension of **2** (1 mmol) in concentrated hydrochloric acid (10 mL) combined with water (10 mL), solid potassium permanganate (6 mmol) was added slowly and the mixture was stirred at room temperature for 5 h. The orange precipitate was filtered, washed with water (3 mL) and dried to give pure **4•H₂O** (92 mg, 52.6%). ¹H NMR ([D₆]DMSO): 8.80 (s, 4H); ¹³C NMR ([D₆]DMSO): 148.4, 149.1, 152.3 ppm; IR (KBr pellet): 3252, 3182, 1666, 1544, 1488, 1451, 1433, 1374, 1333, 1274, 1237, 1072, 573 cm⁻¹; elemental analysis (C₆H₄N₁₆O₂•H₂O, 350.22): calcd: C 20.58, H 1.73, N 63.99; found: C 20.95, H 1.94, N 64.4;

^1H , ^{13}C NMR spectra S1-S6

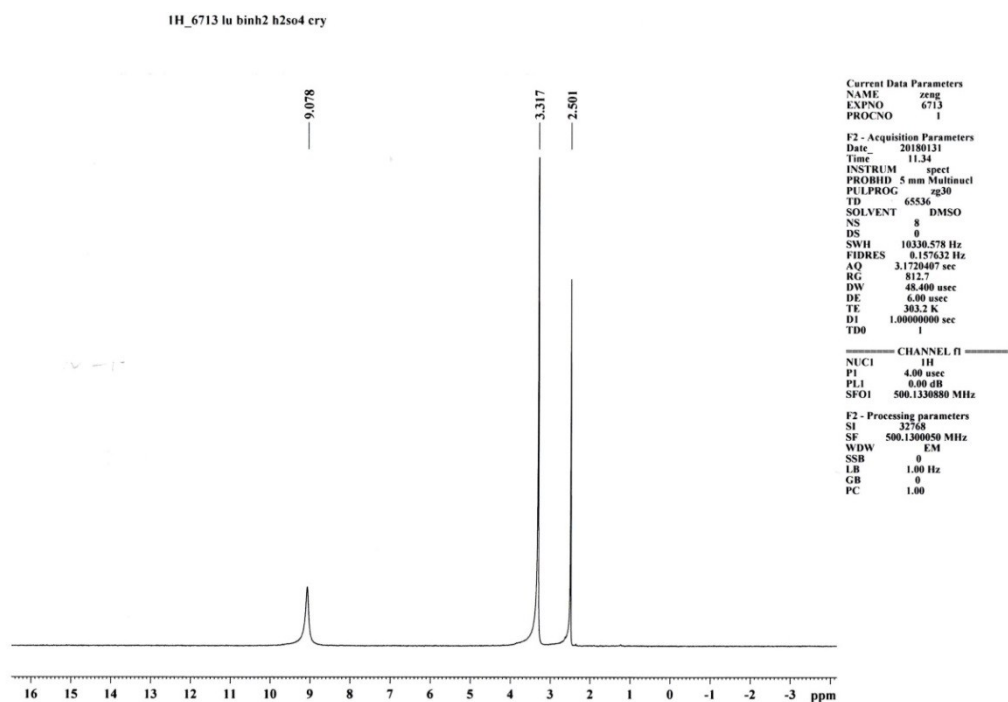


Figure S1 ^1H NMR of **1**.

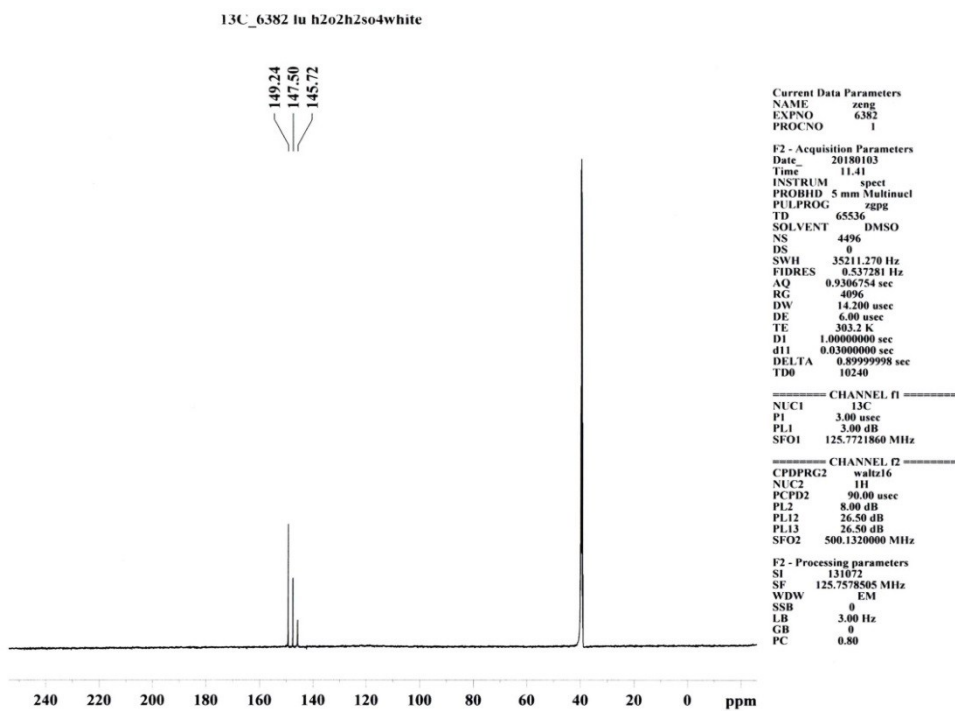


Figure S2 ¹³C NMR of 1.

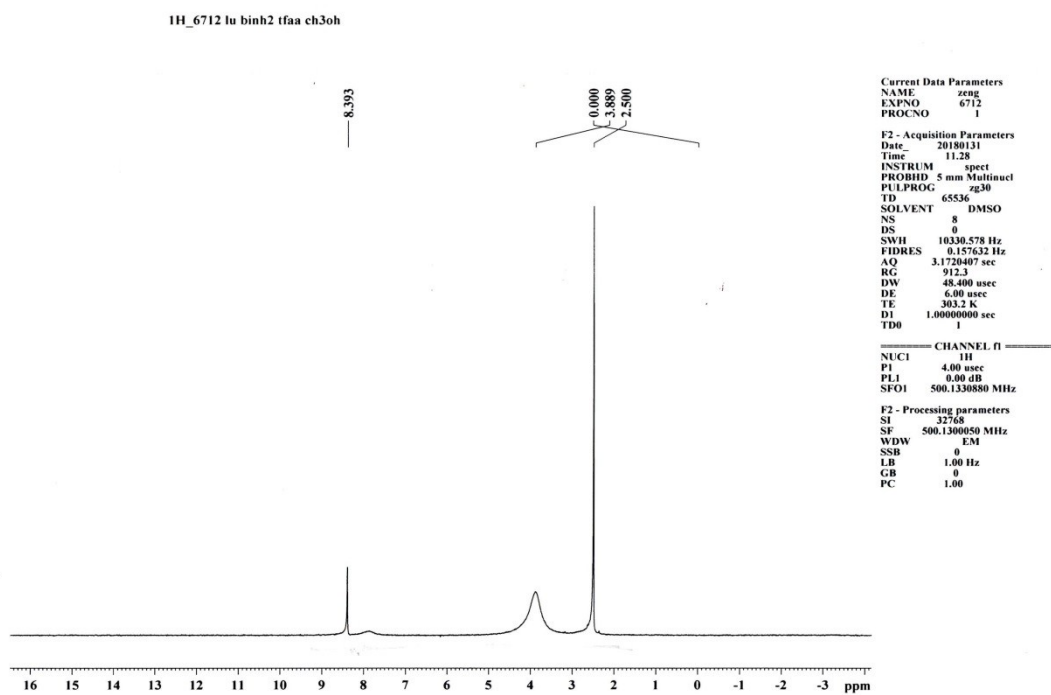


Figure S3 ¹H NMR of 2.

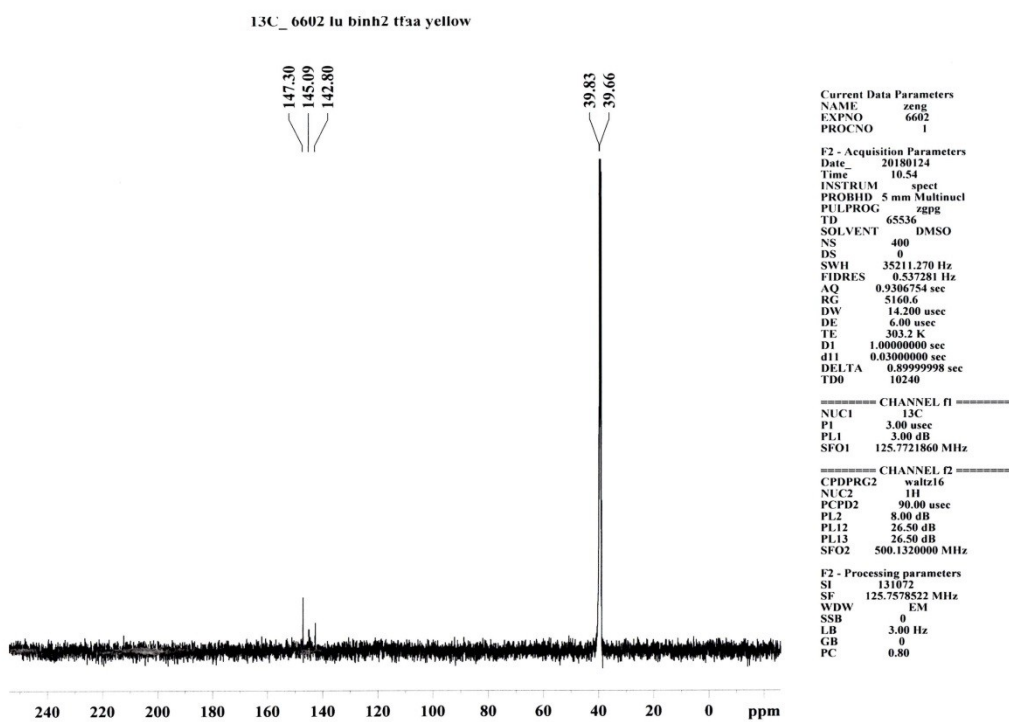


Figure S4 ¹³C NMR of 2.

1H_6759 lu binh21faa not desolve

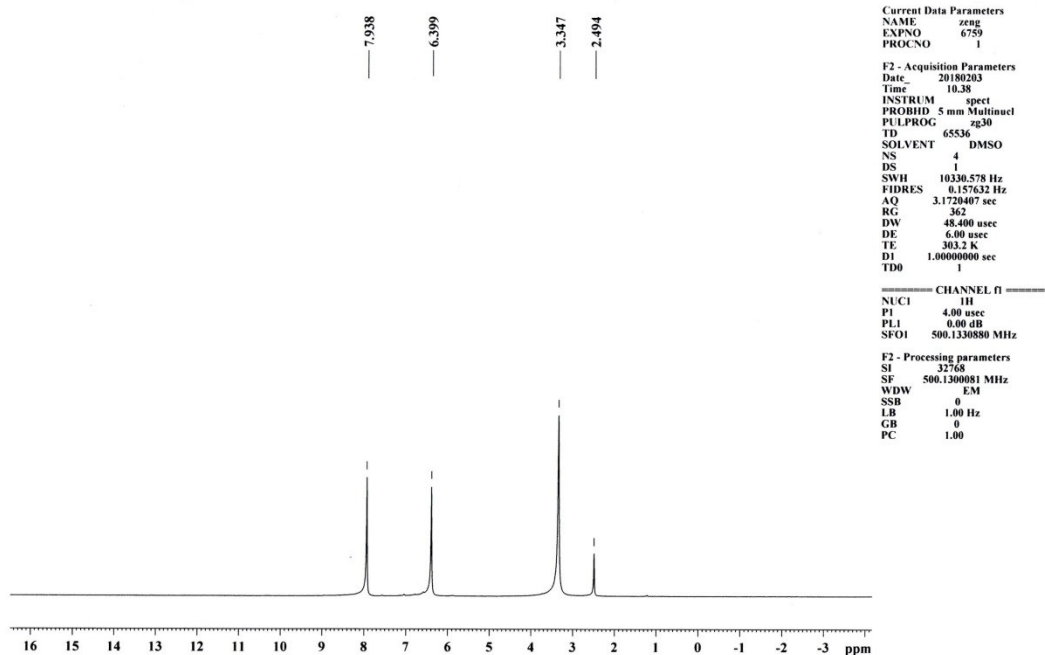


Figure S5 ¹H NMR of 3.

1H 6770 lu binh2 not desolve

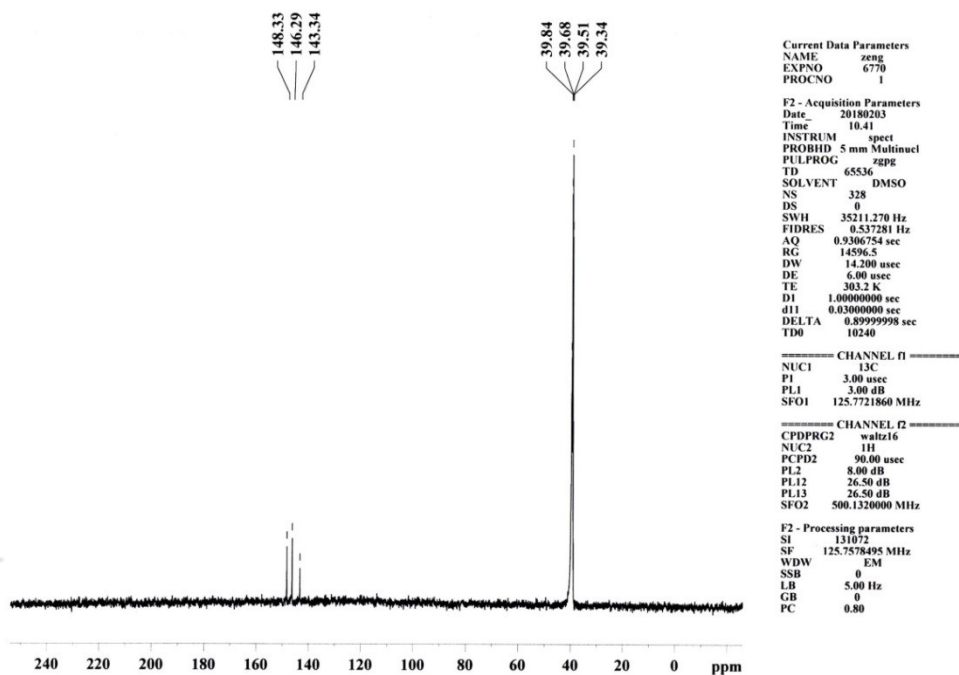


Figure S6 ¹³C NMR of 3.

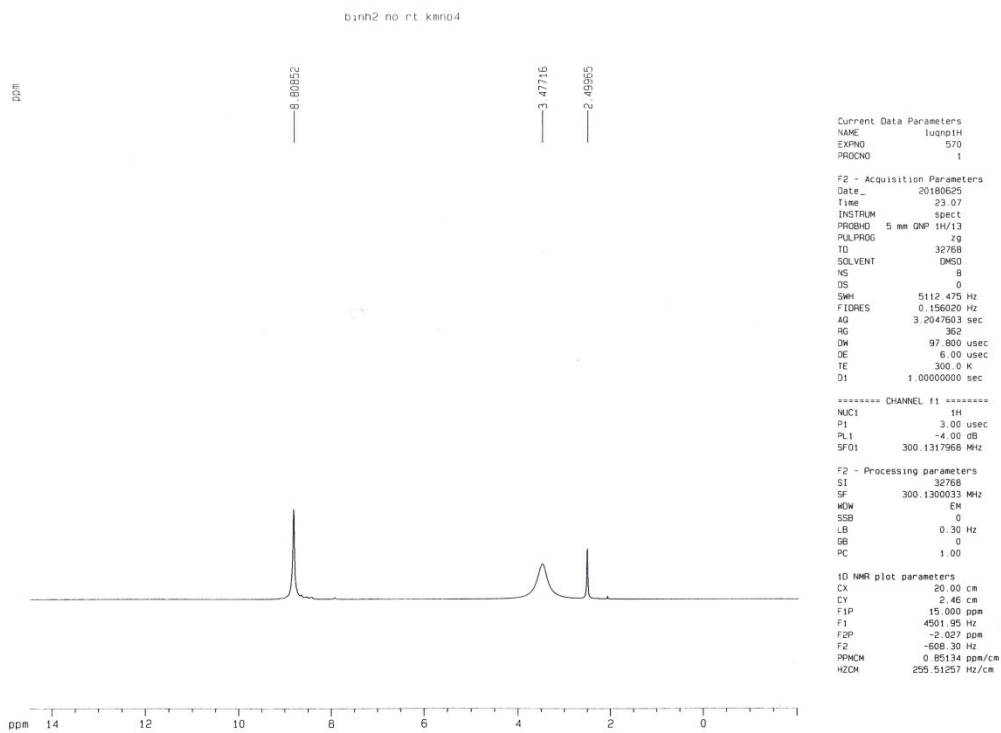


Figure S7 ¹H NMR of **4**.

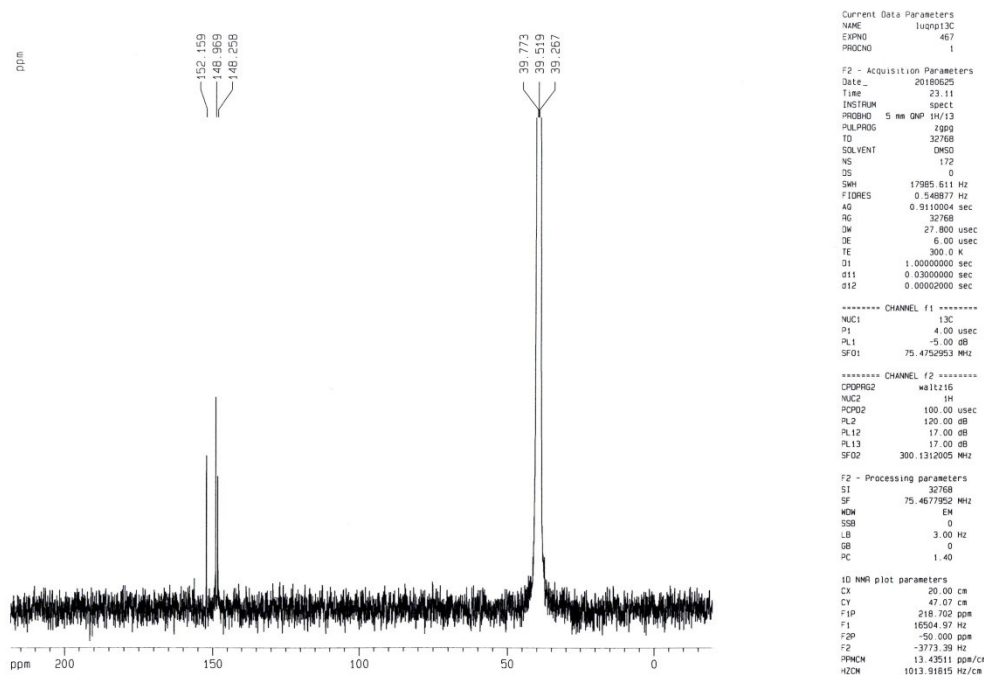


Figure S8 ^{13}C NMR of 4.

X-ray Crystallography of 1 and 2 (Table S1 and Figure S9-S16)

Single-crystal X-ray diffraction analysis of 1.

A clear colorless block crystal of dimensions 0.179 x 0.136 x 0.049 mm was mounted on a MiteGen MicroMesh 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 using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$). Data was collected at room temperature (20 °C).

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].² Data Reduction was performed using *SAINTE* [v8.34A]³ and *XPREF* [v2014/2]⁴. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].⁵ The structure was solved and refined with the aid of the program *SHELXL-2014/7*.⁶ The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were located from the difference electron-density maps and added using a riding model.

Single-crystal X-ray diffraction analysis of 2.

A clear yellow needle crystal of dimensions 0.557 x 0.024 x 0.024 mm was mounted on a MiteGen MicroMesh 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 using graphite monochromated MoK α radiation ($\lambda = 0.71073$). Data was collected at room temperature (20 °C).

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].² Data Reduction was performed using *SAINT* [v8.34A]³ and *XPREP* [v2014/2]⁴. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].⁵ The structure was solved and refined with the aid of the program *SHELXL-2014/7*.⁶ The full-matrix least-squares refinement on F² included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were located from the difference electron-density maps and added using a riding model.

Table S1. Crystal data and structure refinement for Crystals

Compound	1	2
CCDC No.	1906614	1906615
Empirical formula	C ₃ H ₂ N ₈ O ₃	C ₃ H ₅ N ₉ O ₄
Formula weight	198.13	215.16
Temperature	150(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Monoclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ /c
a/Å	6.6953(9)	5.4287(3)
b/Å	6.8192(9)	9.3438(5)
c/Å	15.5018(19)	16.7314(8)
α /°	90°	90°
β /°	90°	90°
γ /°	90°	90°
Volume	707.76(16) Å ³	848.70(8) Å ³
Z	4.00	4.00
Density (20°C)	1.859 Mg/m ³	1.809 Mg/m ³

μ/mm^{-1}	0.164 mm^{-1}	0.162 mm^{-1}
F(000)	400.00	472.00
Crystal size mm^3	0.179 x 0.136 x 0.049 mm^3	0.557 x 0.024 x 0.024 mm^3
Theta range for data collection/ $^\circ$	3.616 to 29.954	2.936 to 29.923
Index ranges	-14 \leq h \leq 14, -8 \leq k \leq 8, -15 \leq l \leq 15	-9 \leq h \leq 8, -19 \leq k \leq 18, -11 \leq l \leq 11
Reflections collected	7883.00	9187.00
Independent reflections	1972 [$R_{\text{int}} = 0.0187$]	2197 [$R_{\text{int}} = 0.0276$]
Data / restraints / parameters	1972 / 0 / 118	2197 / 0 / 140
Goodness-of-fit on F2	1.02	1.06
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0337$, $wR2 = 0.0688$	$R1 = 0.0362$, $wR2 = 0.0720$
R indices (all data)	$R1 = 0.0541$, $wR2 = 0.0757$	$R1 = 0.0651$, $wR2 = 0.0809$
Largest diff. peak	0.160 and -0.171 $\text{e.}\text{\AA}^{-3}$	0.193 and -0.169 $\text{e.}\text{\AA}^{-3}$

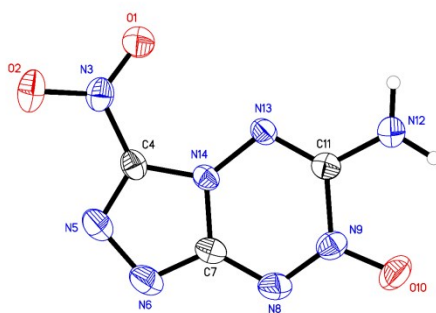


Figure S9. Single-crystal X-ray structures of **1** with numbering.

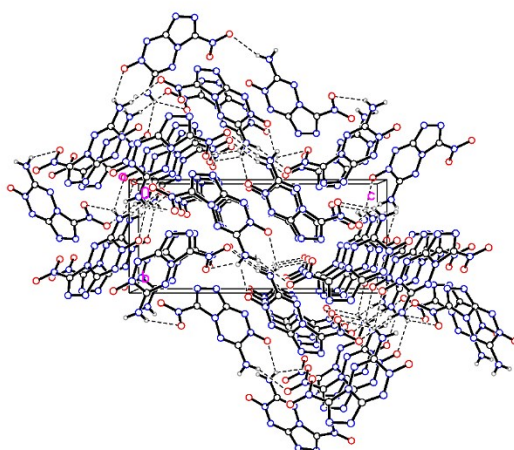


Figure S10. Unit cell view for **1** along a axis, hydrogen bonds are marked as dotted lines.

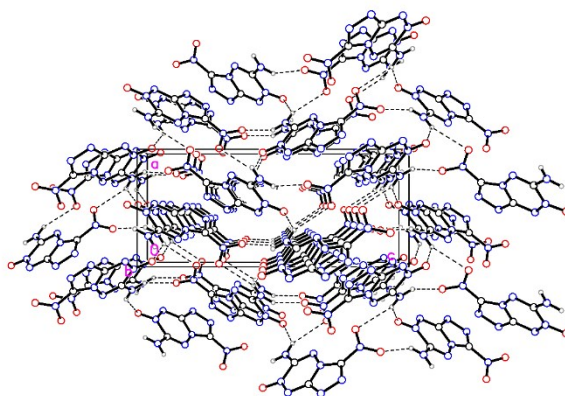


Figure S11. Unit cell view for **1** along b axis, hydrogen bonds are marked as dotted lines.

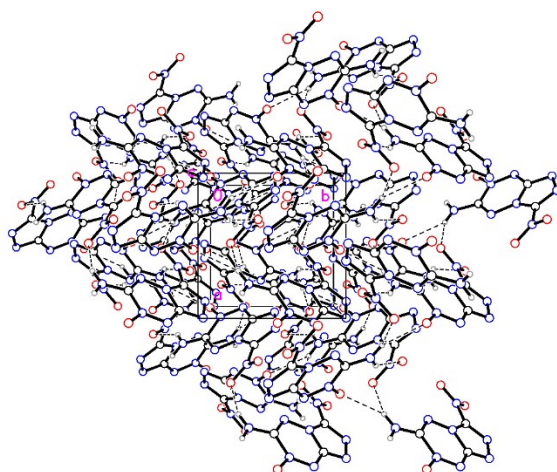


Figure S12. Unit cell view for **1** along *c* axis, hydrogen bonds are marked as dotted lines.

Table S2. Hydrogen bonds for LU-006 [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(12)-H(12A)...O(1)#1	0.88	2.42	3.194(2)	147.2
N(12)-H(12A)...O(10)#2	0.88	2.37	3.041(2)	132.7
N(12)-H(12B)...O(2)#3	0.88	2.29	3.071(2)	148.1

Symmetry transformations used to generate equivalent atoms:

#1 $-x+2, y+1/2, -z+1/2$ #2 $x+1/2, -y+3/2, -z+1$ #3 $-x+3/2, -y+1, z+1/2$

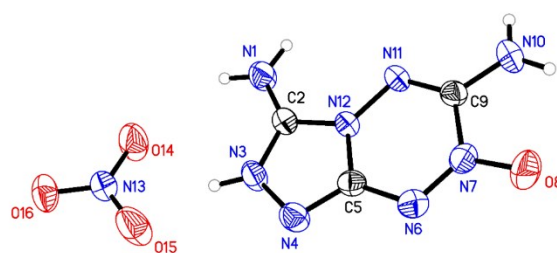


Figure S13. Single-crystal X-ray structures of **2** with numbering.

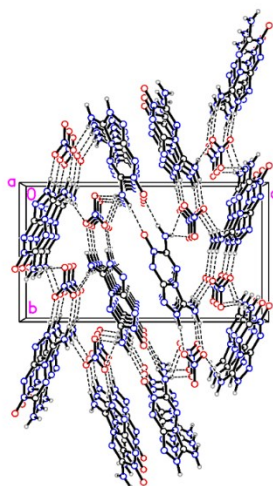


Figure S14. Unit cell view for **2** along a axis, hydrogen bonds are marked as dotted lines.

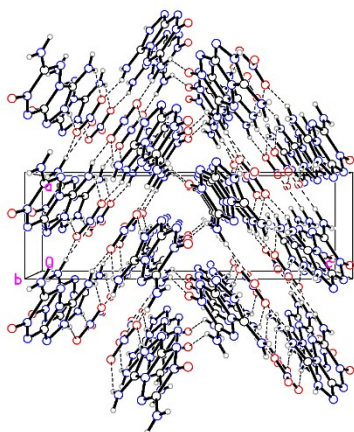


Figure S15. Unit cell view for **2** along b axis, hydrogen bonds are marked as dotted lines.

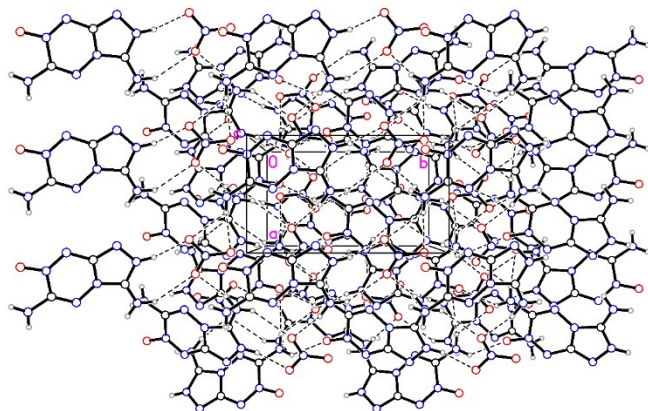


Figure S16. Unit cell view for **2** along *c* axis, hydrogen bonds are marked as dotted lines.

Table S3. Hydrogen bonds for LU-011 [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
N(1)-H(1A)...O(14)	0.86	2.39	3.135(3)	145.8
N(1)-H(1B)...O(14)#1	0.86	2.07	2.901(3)	161.4
N(3)-H(3)...O(15)	0.86	1.88	2.719(3)	166.3
N(10)-H(10A)...O(15)#2	0.86	2.35	2.995(3)	132.4
N(10)-H(10A)...O(16)#2	0.86	2.37	3.228(3)	172.0
N(10)-H(10B)...O(8)#3	0.86	2.24	2.946(3)	139.6

Symmetry transformations used to generate equivalent atoms:

#1 $-x, y+1/2, -z+1/2$ #2 $x-1, y+1, z$ #3 $x-1/2, -y+5/2, -z+1$

References

1. D. Fischer, T. M. Klapotke, J. Stierstorfer and N. Szimhardt, *Chemistry*, 2016, **22**, 4966-4970.
2. Bruker (2015). APEX3 v2015.5-2. Bruker AXS Inc., Madison, Wisconsin, USA.
3. Bruker (2013). SAINT v8.34A. Bruker AXS Inc., Madison, Wisconsin, USA.
4. Bruker (2014). XPREP v2014/2. Bruker AXS Inc., Madison, Wisconsin, USA.
5. Bruker (2014). SADABS v2014/5, Bruker AXS Inc., Madison, Wisconsin, USA.
6. Sheldrick, G. M. (2014). SHELXL-2014/7. University of Göttingen, Germany.