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An interesting ring cleavage of 1,2,4-oxadiazole ring

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Table of Contents

1 Experimental Section

Caution! Although none of the compounds described herein has exploded or detonated in the course of this research, these materials should be handled with care using the best safety practices.

General: The reagents were purchased from commercial sources, and were of analytical grade. ^{1}H, and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometers operating at 300.13 and 75.48 MHz, respectively. Chemical shifts in ^{1}H and ^{13}C NMR spectra are reported in ppm relative to Me_4Si for the ^{1}H NMR and ^{13}C NMR spectra which were recorded using d_6-acetone and d_6-DMSO as the locking solvent. The decomposition points were obtained on a differential scanning calorimeter (DSC, TA Instruments Company, model Q 10) at a scan rate of 5 $^{o}C\ min^{-1}$ in a dynamic nitrogen atmosphere (flow rate = 30 mL min^{-1}). IR spectra were recorded by using attenuated total reflection mode for solids on Thermo Scientific Nicolet Is 10 spectrometer. Elemental analysis was performed with a Vario EL III instrument. The sensitivity towards impact (IS) were determined according to BAM standards, with a 2 kg drop hammer. Densities of the compounds were determined at room temperature by employing a gas pycnometer.

X-ray Crystallography: The X-ray diffraction measurements for **1-3** were performed with a Brukerthree-circle platform diffractometer equipped with a PHOTON 100 CMOS detector. A Kryo-Flex II low-temperature device was used to keep the crystals at a constant 173 K during the data collection. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0).[1] Data Reduction was performed by using SAINT (v7.68A)[2] and XPREP (v2008/2).[3] Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1).[4] The structure plots were carried out with the SHELXTL program.[5] The hydrogen atoms were located and refined. Please see the CIF files. Relevant data are given in Tables S3-S30.

Synthesis of 3-trinitroethylamino-5-amino-1,2,4-oxadiazole (1): 3,5-diamino-1,2,4-oxadiazole (0.300 g, 3.0 mmol) was dissolved in 20 mL water at ambient temperature. 2,2,2-Trinitroethanol (0.905 g, 5.0 mmol) was subsequently added into the reaction solution. The reaction mixture was stirred for 3 hours. The white precipitate was washed with water and dried to give pure compound **1**

0.710 g (yield 90.0%). T_d *(oneset)*, 155 °C, T_d *(peak)*, 163 °C; ^{1}H NMR (300 MHz, d_6- acetone): δ=7.06 (s, 2H, -NH_2), 6.68 (t, *J* = 9.0 Hz, 1H, -NH-), 5.16 (d, *J* = 9.0 Hz, 2H, -CH_2-) ppm; ^{13}C NMR (75 MHz, d_6-acetone): δ= 170.72, 167.71, 125.76, 46.89 ppm; IR: ῡ= 3491, 3288, 3194, 1664, 1570, 1541, 1406, 1308, 1101, 1007, 911, 881, 855, 805, 772, 708, 640 cm^{-1}; elemental analysis calcd. (%) for $C_4H_5N_7O_7$ (263.13): calcd. C 18.26, H 1.92, N 37.26; found: C 17.68, H 1.36, N 36.57.

Synthesis of bis(2,2,2-trinitroethyl)urea (2): 1 (0.526 g, 2 mmol) and 2,2,2-trinitroethanol (0.5435 g, 3.0 mmol) were dissolved in 0.1M dilute hydrochloric acid solution (30 mL) at ambient temperature. The reaction mixture was heated to 30 °C and stirred for 2 hour. The reaction mixture was cooled to room temperature. The white precipitate was collected by filtration, washed with water, and dried in air to yield pure product **2** (0.628 g, 81.3 %). T_d *(oneset)*, 142 °C, T_d *(peak)*, 188 °C; ^{1}H NMR (300 MHz, d_3-acetonitrile): δ= 6.13 (t, *J* = 6.0 Hz, 1H, -NH-), 4.19 (d, *J* = 6.0 Hz, 2H, -CH_2-) ppm; ^{13}C NMR (75 MHz, d_3-acetonitrile): δ= 156.92, 126.99, 44.77 ppm; IR: ῡ= 3438, 1713, 1587, 1524, 1420, 1308, 1272, 1225, 1113, 857, 804, 782, 664, 640 cm^{-1}; elemental analysis calcd. (%) for $C_5H_6N_8O_{13}$ (386.15): calcd. C 15.55, H 1.57, N 29.02; found: C 16.14, H 1.02, N 28.79.

Synthesis of 3-(2,2,2-trinitroethyl)-4-(nitrocarbamoyl) urea (3): Nitric acid (100%, 20 mL) was placed in a 50 mL two-necked round bottom flask and cooled to -5 °C. **1** (0.526 g, 2 mmol) was slowly added to the cooled nitric acid while maintaining the reaction temperature below -5 °C. After the reaction mixture was stirred for 1 hour at -0 °C. The reaction mixture was poured into ice water (80 mL). The precipitate was filtered, washed with cold water and dried in air. Compound **3** (0.518 g, 83.2%) was obtained. T_d *(oneset)*, 114 °C, T_d *(peak)*, 134 °C; ^{1}H NMR (300 MHz, d_6-DMSO): δ= 9.89 (s, 1H,-NH-), 8.64 (t, *J* = 6.0 Hz, 1H, -NH-), 7.94 (br, 1H,-NH-NO_2), 5.23 (d, *J* = 6.0 Hz, 2H, -CH_2-) ppm; ^{13}C NMR (75 MHz, d_6-DMSO): δ= 151.95, 148.33, 125.68, 42.85 ppm; IR: ῡ= 3312, 3068, 2980, 2794, 1713, 1609, 1588, 1522, 1493, 1421, 1406, 1335, 1299, 1232, 1177, 1069, 995, 935, 869, 805, 759, 730, 644 cm^{-1}; elemental analysis calcd. (%) for $C_4H_5N_7O_{10}$ (311.12): calcd. C 15.44, H 1.62, N 31.51; found: C 14.98, H 1.42, N 30.88.

2. Thermogravimetric analysis (TG) and differential thermal gravity (DTG) curves of compounds 1-3

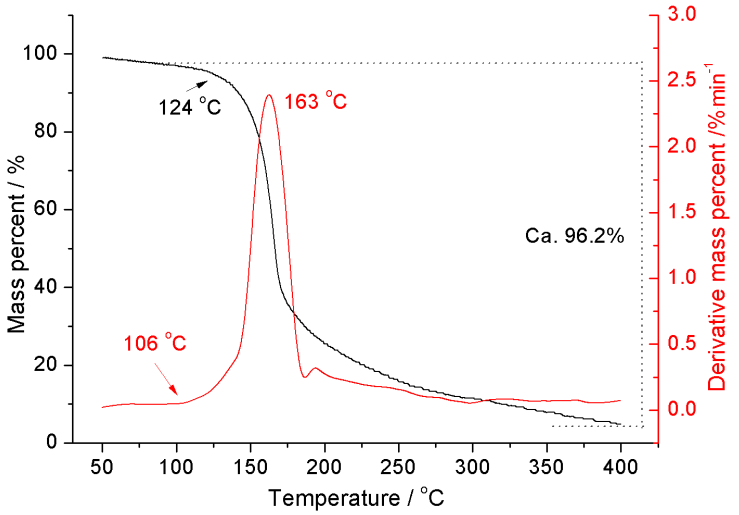


Fig. S1 TG and DTG curves of **1** under nitrogen with a heating rate of 5 °C min^{-1}.

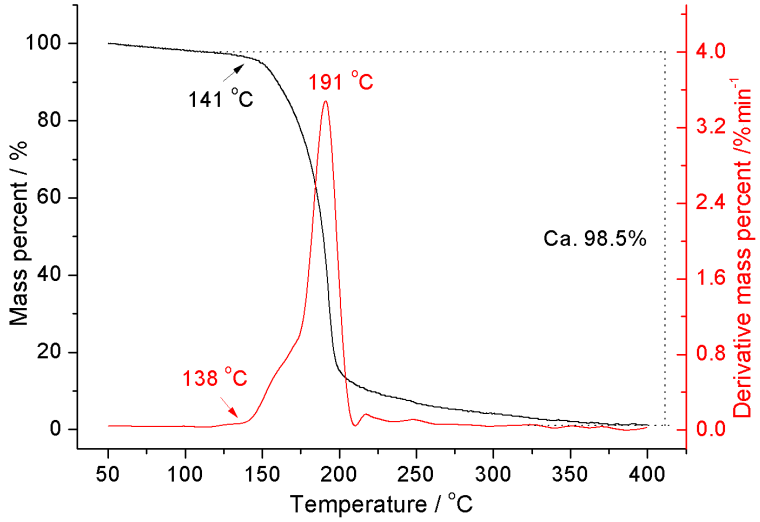


Fig. S2 TG and DTG curves of **2** under nitrogen with a heating rate of 5 °C min^{-1}.

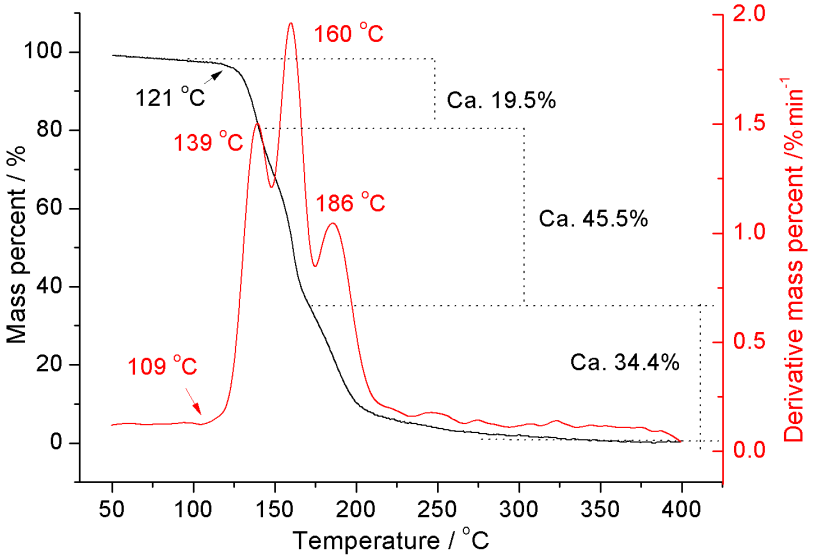
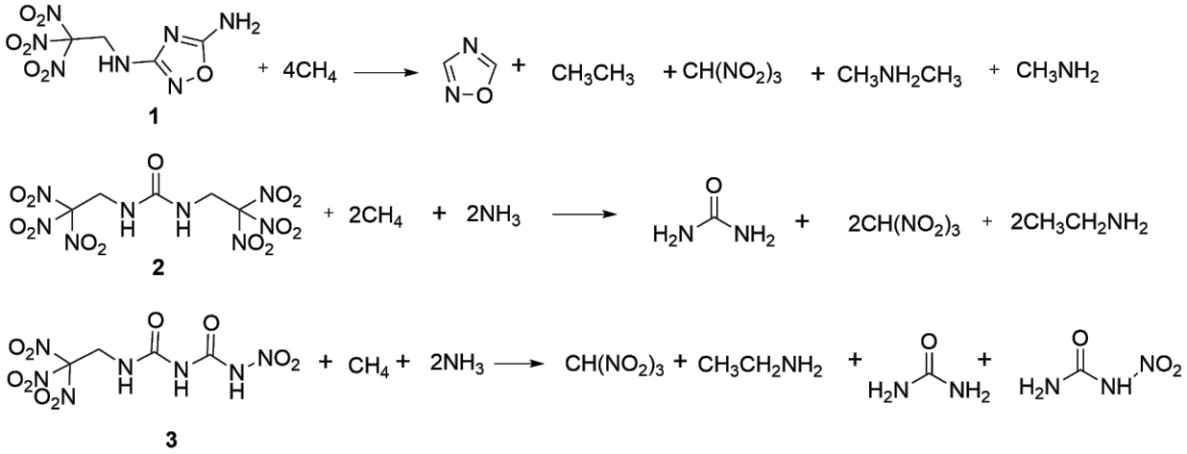


Fig. S3 TG and DTG curves of **3** under nitrogen with a heating rate of 5 °C min^{-1}.

3. Computational data

Computations were performed by using the Gaussian09 suite of programs.[6] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)[7] functional with the 6-311+G** basis set.[8] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.[9] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The lattice energy of the trinitroethyl derivatives were predicted by using the formula suggested by Jenkins et al.[10]



Scheme S1. Isodesmic and tautomeric reactions to compute the HOF.

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of compounds **1-3**, are shown in Scheme S1. The heats of formation of the furazan and tetrazine ring used in the isodesmic reaction are 215.72 and 487.03 kJ mol^{-1}, respectively. The change of enthalpy for the reactions at 298 K can be expressed as Equation (1).

$$\Delta H_{298} = \Sigma \Delta_f H_P - \Sigma \Delta_f H_R \quad (1)$$

$\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression, see Equation (2).

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (2)$$

ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T is the thermal correction from 0 to 298 K. The Δ(*PV*) value in Equation [(2)] is the *PV* work term. It equals Δ*nRT* for the reactions of an ideal gas. For the isodesmic reactions, Δ*n* = 0, so Δ(*PV*) = 0. On the left side of Equation [(1)], apart from target compound, all the others are called reference compounds. The HOF of reference compounds are available either from experiments[11] or from the high-level computing such as CBS-4M.

The detonation velocity (*D*) and detonation pressure (*P*) were evaluated by the semi-empirical Kamlet-Jacobs (K-J) equations[12] as shown in Equations (6), (7), (8).

$$P = 1.558\,\rho^2\Phi \quad (6)$$

$$D = 1.01\Phi^{1/2}(1 + 1.30\rho_0) \quad (7)$$

$$\Phi = 0.4889N(MQ)^{1/2} \quad (8)$$

D is the predicted detonation velocity (km s^{-1}), *P* is the detonation pressure (GPa), and ρ is the compound density (g cm^{-3}). Φ, *N*, *M* and *Q* are characteristic parameters of an explosive; *Q* is the chemical energy of detonation (kJ g^{-1}). The measured densities and the calculated heats of formation were used to compute the *D* and *P* values.

Table S1 *Ab initio* computational values compounds **1**-**3**.

Compound	E_0[a]	ZPE[b]	H_T[c]	HOF[d]
1	-1065.184057	361.85	46.57	134.22
2	-1609.8611488	478.22	69.43	-72.39
3	-1290.9115982	392.07	56.12	-303.86
CH_4	-40.5339263	112.26	10.04	-74.60[e]
$CH(NO_2)_3$	-654.163836	136.82	26.41	-13.40 [e]
CH_3NHCH_3	-135.2095645	231.80	14.35	-18.80 [e]
CH_3CH_3	-79.8565413	187.31	11.79	-84.00 [e]
CH_3NH_2	-95.8938402	160.78	11.64	-22.50 [e]
NH_3	-56.5826356	86.27	10.05	-45.90 [e]

NH_2NO_2	-261.1248168	98.79	12.39	-3.90 [e]
NH_2CONH_2	-225.3482312	161.38	12.97	-245.80 [e]
$CH_3CH_2NH_2$	-135.2214437	232.74	14.38	-47.50[f]
$NH_2CONHNO_2$	-429.8726272	165.37	20.56	-143.84 [f]
	-262.1529348	116.90	11.67	99.39 [f]

[a] Total energy calculated by B3LYP/6-31+G** method (a.u.); [b] zero-point correction (kJ mol^{-1}); [c] thermal correction to enthalpy (kJ mol^{-1}); [d] heat of formation (kJ mol^{-1}); [e] D. R. Lide, CRC Handbook of Chemistry and Physics, 84th Edition (2003-2004), CRC Press/Taylor and Francis, Boca Raton, FL; [f] calculated by CBS-4 Enthalpy.

4. Single-crystal X-ray diffraction analysis of compound 1-3

Table S2. Crystallographic data for compounds **1-3**.

Compound	**1**	**2**	**3**
CCDC number	1042138	1042137	1042139
Formula	$C_4H_5N_7O_7$	$C_5H_6N_8O_{13}$	$C_4H_5N_7O_{10}$
Formula weight [g·mol^{-1}]	263.15	386.18	311.15
Temperature [K]	173 (2)	173	173
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/c$	$Pnn2$	$P2_1$
Crystal size [mm]	0.09 x 0.13 x 0.18	0.13 x 0.16 x 0.21	0.15 x0.16 x0.18
a [Å]	8.8179(15)	12.142(2)	7.1401(11)
b [Å]	9.2863(16)	18.658(4)	7.8040(13)
c [Å]	11.802(2)	9.923(2)	10.6428(19)
α [°]	90.00	90	90
β [°]	101.562(4)	112.089(8)	109.113(3)
γ [°]	90.00	90	90
Cell volume [Å^{-3}]	946.8(3)	678.3(2)	560.34(16)
Formula Z	4	2	2
Calc. density [g cm^{-3}]	1.846	1.891	1.844
μ [mm^{-1}]	0.175	0.189	0.183
F (000)	536	392	316
θ for data collection range [°]	2.4-26.3	2.7-26.5	2.0-25.8
index ranges	$-8 \le h \le 10$ $-11 \le k \le 11$ $-12 \le l \le 14$	$-13 \le h \le 9$ $-13 \le k \le 9$ $-5 \le l \le 7$	$-8 \le h \le 5$ $-9 \le k \le 9$ $-9 \le l \le 12$
reflns collected	4659	2265	3211
indep ref/ R_{int}	1895 / 0.067	756 / 0.047	1106 / 0.040
Goodness-of-fit on F^2	1.025	1.046	1.024
R_1(F) ($I > 2\sigma(I)$) [a]	0.0505	0.0389	0.0371
wR_2 [all date][b]	0.0911	0.0852	0.0841
largest diff. peak / hole [e Å^3]	-0.37 / 0.27	-0.23 / 0.22	-0.24 / 0.29

[a] $R_1 = \Sigma| F_0 | - | Fc | / \Sigma| F_0|$. [b] $wR_2 = \{\Sigma[w (F_0^2 - F_c^2)^2] / \Sigma[w (F_0^2)^2]\}^{1/2}$

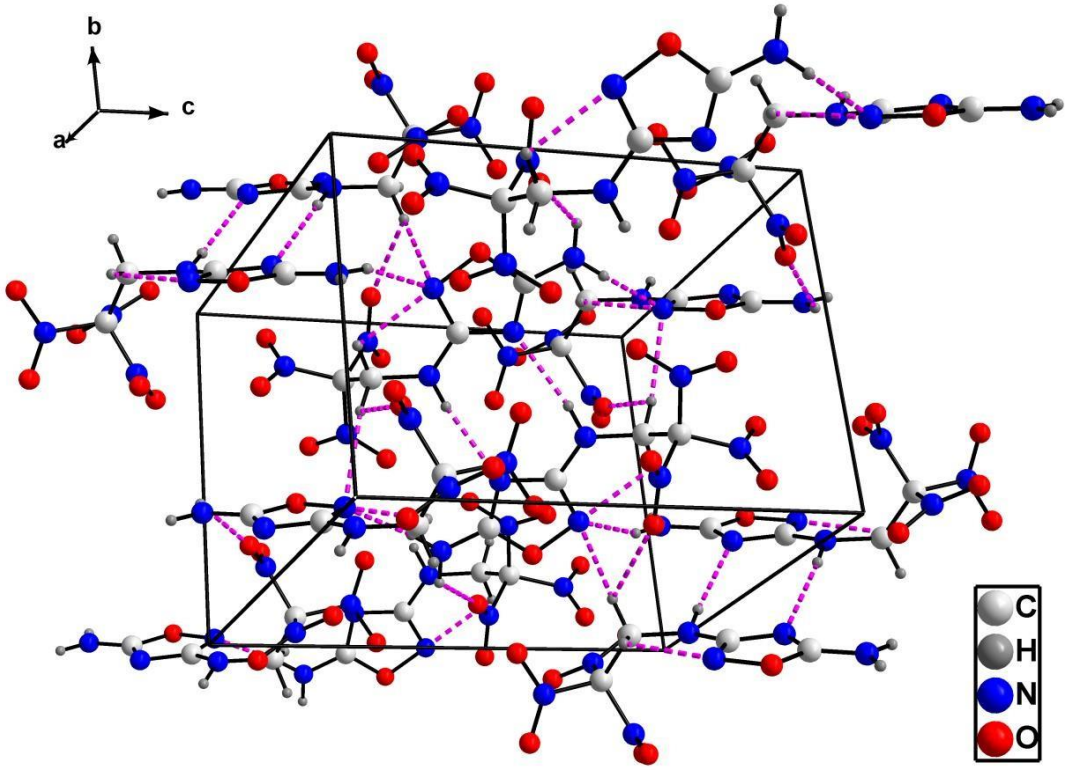


Fig. S4 Ball and stick packing diagram of **1** viewed along the *a* axis. Hydrogen bonds are indicated as dotted lines.

Table S3 Selected bond lengths [Å] for **1**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N1	1.450(3)	N3-C3	1.437(4)
O1-C2	1.346(4)	N4-C4	1.527(4)
O2-N4	1.210(4)	N5-C4	1.514(4)
O3-N4	1.224(3)	N6-C4	1.514(4)
O4-N5	1.224(3)	N7-C2	1.324(4)
O5-N5	1.214(3)	C3-C4	1.529(4)
O6-N6	1.211(4)	N2-C1	1.365(4)
O7-N6	1.227(4)	N2-C2	1.319(4)
N1-C1	1.317(4)	N3-C1	1.365(4)

Table S4 Selected bond angles [º] for **1**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N1-O1-C2	105.6(2)	N2-C2-N7	128.2(3)
O1-N1-C1	101.8(2)	N3-C3-C4	112.7(3)
C1-N2-C2	101.5(3)	C3-N3-H3	116.0(16)
C1-N3-C3	120.1(3)	C1-N3-H3	115.4(18)
O2-N4-O3	127.7(3)	N4-C4-N6	106.4(2)
O2-N4-C4	115.7(2)	N4-C4-C3	113.5(2)
O3-N4-C4	116.7(2)	N5-C4-C3	112.3(2)

O4-N5-O5	126.7(3)	N6-C4-C3	111.2(3)
O4-N5-C4	118.5(2)	N5-C4-N6	106.7(2)
O5-N5-C4	114.9(2)	N4-C4-N5	106.3(2)
O6-N6-O7	127.3(3)	N1-C1-N3	122.3(3)
O6-N6-C4	118.9(2)	N2-C1-N3	120.8(3)
O7-N6-C4	113.8(3)	O1-C2-N2	114.3(3)
N1-C1-N2	116.9(3)	O1-C2-N7	117.5(2)

Symmetry codes: [i] 2-x,2-y,2-z

Table S5 Selected torsion angles [°] for **1**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C2-O1-N1-C1	-0.7(3)	O6-N6-C4-C3	-138.1(3)
N1-O1-C2-N7	-178.3(2)	O7-N6-C4-C3	41.8(3)
N1-O1-C2-N2	1.7(3)	N3-C3-C4-N4	-76.8(3)
O1-N1-C1-N3	176.1(3)	N3-C3-C4-N5	43.8(3)
O1-N1-C1-N2	-0.5(3)	N3-C3-C4-N6	163.2(2)
C2-N2-C1-N1	1.5(4)	O5-N5-C4-C3	51.7(3)
C1-N2-C2-O1	-1.9(3)	O4-N5-C4-N6	109.7(3)
C2-N2-C1-N3	-175.2(3)	O5-N5-C4-N6	-70.4(3)
C1-N2-C2-N7	178.1(3)	O5-N5-C4-N4	176.4(2)
C3-N3-C1-N1	8.5(4)	O4-N5-C4-C3	-128.2(3)
C3-N3-C1-N2	-175.1(3)	O7-N6-C4-N4	-82.3(3)
C1-N3-C3-C4	-120.8(3)	O6-N6-C4-N5	-15.4(4)
O2-N4-C4-C3	34.2(4)	O6-N6-C4-N4	97.8(3)
O3-N4-C4-C3	-145.3(3)	O7-N6-C4-N5	164.5(3)
O2-N4-C4-N6	156.9(3)	O3-N4-C4-N6	-22.7(3)
O2-N4-C4-N5	-89.7(3)	O4-N5-C4-N4	-3.6(3)
O3-N4-C4-N5	90.8(3)		

Table S6 Hydrogen bonds for **1** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N3-H3…N2	0.87(2)	2.29(2)	3.137(4)	166(2)
N7-H7A…N1	0.8800	2.1700	3.010(3)	159.00
N7-H7B…O4	0.8800	2.4600	3.067(3)	127.00
C3-H3A…O5	0.9900	2.4600	2.941(3)	109.00
C3-H3A…N1	0.9900	2.4200	3.382(4)	163.00
C3-H3B…N1	0.9900	2.3300	2.798(4)	108.00

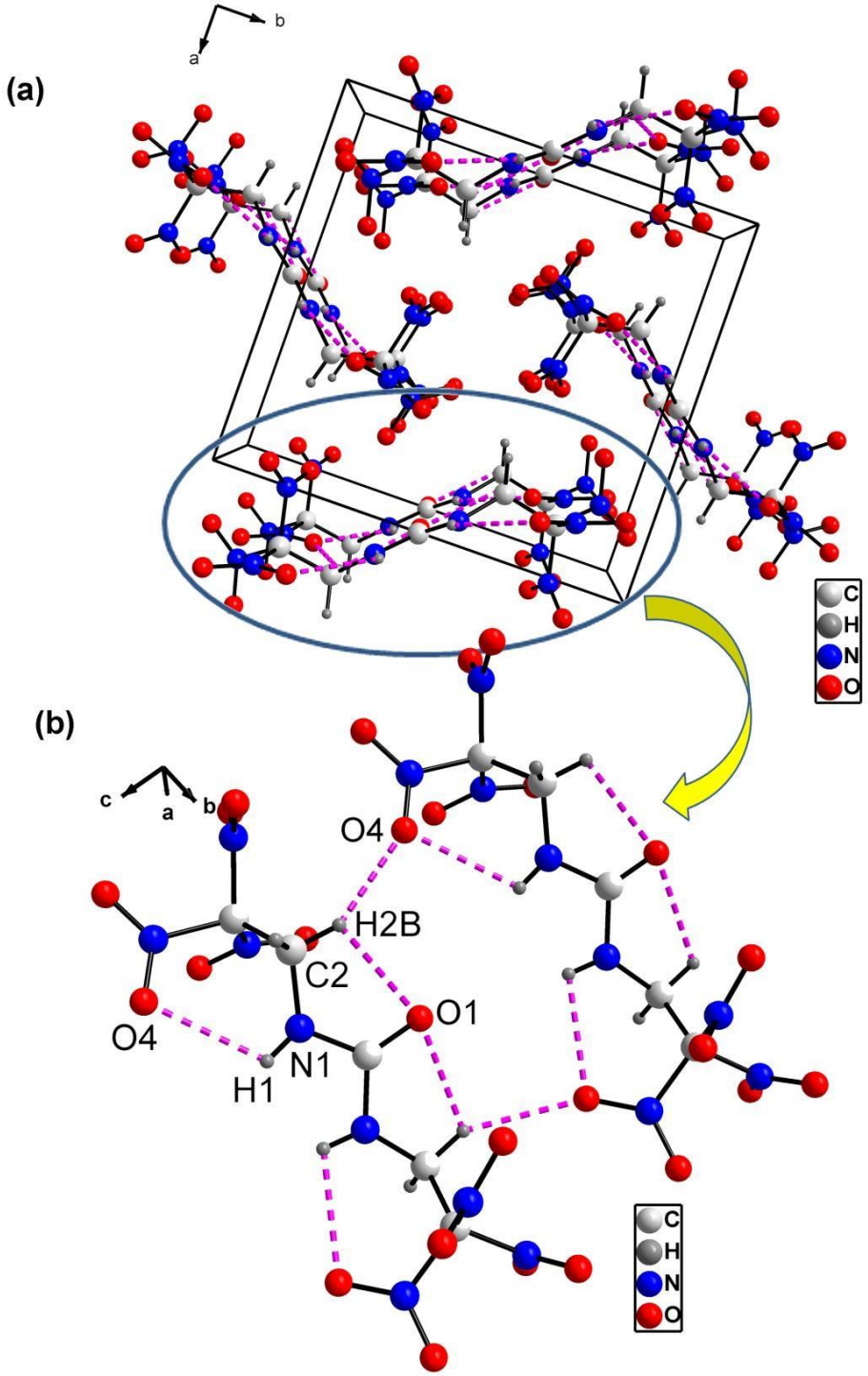


Fig. S5 (a) Ball and stick packing diagram of **2** view along the *c* axis. (b) Unit-cell view along the *a* axis. Hydrogen bonds are indicated as dotted lines.

Table S7 Selected bond lengths [Å] for **2**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-C1	1.211(8)	N1-C2	1.444(5)
O2-N2	1.211(4)	N2-C3	1.512(5)
O3-N2	1.231(4)	N3-C3	1.534(5)

O4-N3	1.216(5)	N4-C3	1.513(4)
O5-N3	1.211(5)	C2-C3	1.519(5)
O6-N4	1.207(5)	N1-C1	1.379(5)
O7-N4	1.217(5)		

Table S8 Selected bond angles [°] for **2**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
C1-N1-C2	119.9(4)	N1-C2-C3	110.7(3)
O2-N2-O3	127.1(3)	N2-C3-N4	107.2(3)
O2-N2-C3	118.7(3)	N2-C3-C2	113.0(3)
O3-N2-C3	114.2(3)	N3-C3-C2	113.2(3)
O4-N3-O5	127.0(4)	N4-C3-C2	111.9(3)
O4-N3-C3	115.4(3)	N3-C3-N4	106.7(3)
O5-N3-C3	117.6(3)	N2-C3-N3	104.4(3)
O6-N4-O7	127.4(3)	O1-C1-N1^{i}	124.7(3)
O6-N4-C3	118.4(4)	N1-C1-N1^{i}	110.6(5)
O7-N4-C3	114.2(3)	O1-C1-N1	124.7(3)

Symmetry codes: ^{i} -x,1-y,z

Table S9 Selected torsion angles [°] for **2**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C2-N1-C1-O1	6.4(4)	O5-N3-C3-N2	-21.3(4)
C2-N1-C1-N1^{i}	-173.6(3)	O4-N3-C3-C2	35.6(4)
C1-N1-C2-C3	-123.3(3)	O7-N4-C3-N2	-75.3(4)
O2-N2-C3-C2	-136.5(4)	O6-N4-C3-N3	-5.9(4)
O3-N2-C3-C2	44.6(4)	O6-N4-C3-N2	105.5(4)
O2-N2-C3-N4	-12.8(5)	O7-N4-C3-N3	173.3(3)
O2-N2-C3-N3	100.2(4)	O6-N4-C3-C2	-130.1(4)
O3-N2-C3-N3	-78.8(4)	O7-N4-C3-C2	49.1(5)
O3-N2-C3-N4	168.3(3)	N1-C2-C3-N2	168.3(3)
O4-N3-C3-N2	158.9(3)	N1-C2-C3-N3	-73.3(4)
O5-N3-C3-C2	-144.6(3)	N1-C2-C3-N4	47.2(5)
O4-N3-C3-N4	-87.8(4)	O5-N3-C3-N4	92.0(4)

Symmetry codes: ^{i} -x,1-y,z

Table S10 Hydrogen bonds for **2** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N1-H1…O4	0.85(2)	2.43(4)	2.814(5)	108(3)
C2-H2B…O1	0.9900	2.3700	2.802(4)	105.00
C2-H2B…O4	0.9900	2.4200	3.311(5)	149.00

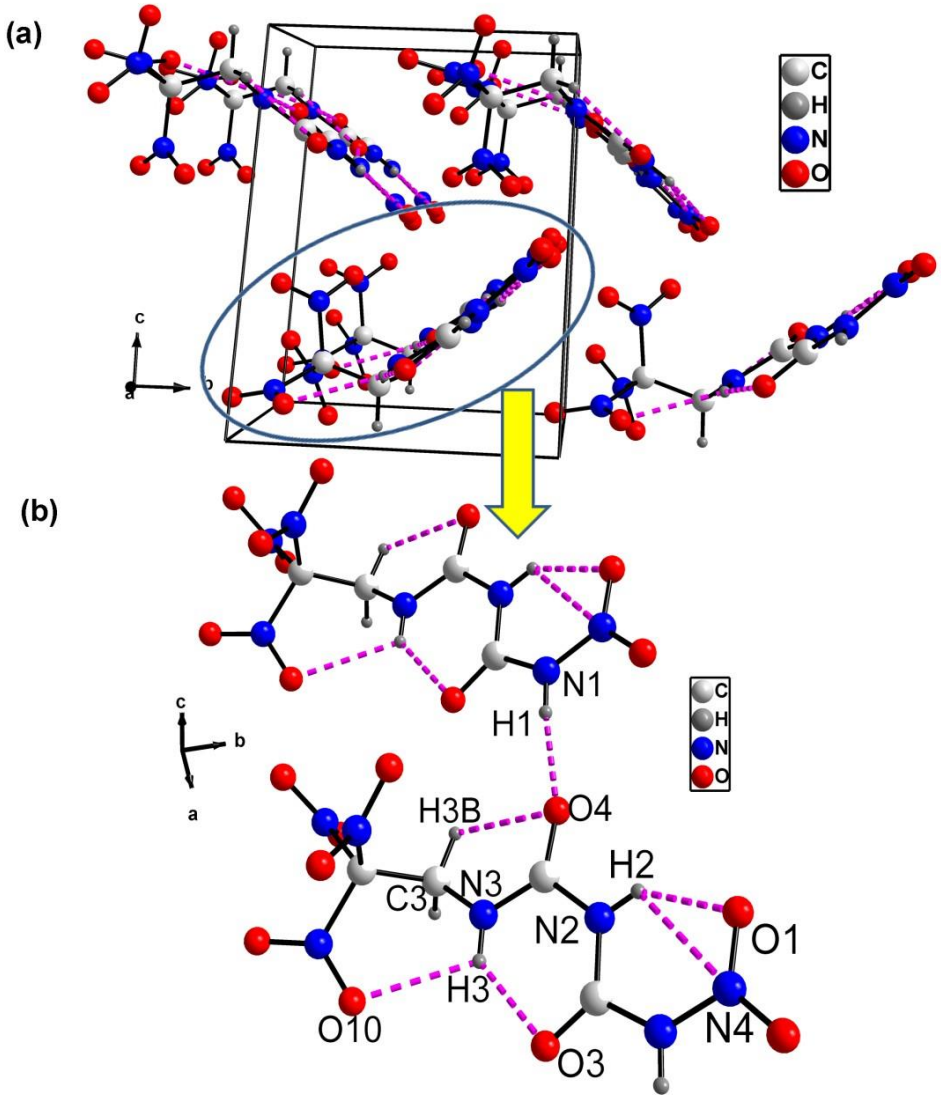


Fig. S6 (a) Ball and stick packing diagram of **3** view along the *a* axis. (b) Unit-cell view along the *c* axis. Hydrogen bonds are indicated as dotted lines.

Table S11 Selected bond lengths [Å] for **3**.

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O1-N4	1.223(5)	N2-C2	1.398(6)
O2-N4	1.222(5)	N3-C2	1.341(5)
O3-C1	1.213(5)	N3-C3	1.443(6)
O4-C2	1.214(5)	N5-C4	1.510(6)
O5-N5	1.221(5)	N6-C4	1.516(6)
O6-N5	1.211(5)	N7-C4	1.532(6)
O7-N6	1.212(5)	O10-N7	1.215(5)
O8-N6	1.208(5)	N1-N4	1.365(5)
O9-N7	1.203(5)	N1-C1	1.392(5)
N2-C1	1.362(6)		

Table S12 Selected bond angles [°] for **3**.

Parameter	Bond angle (°)	Parameter	Bond angle (°)
N4-N1-C1	129.1(4)	N2-C2-N3	117.5(4)
C1-N2-C2	126.6(3)	O4-C2-N2	117.6(4)
C2-N3-C3	120.1(4)	O4-C2-N3	124.9(4)
O1-N4-O2	124.8(4)	N3-C3-C4	112.1(3)
O1-N4-N1	119.6(4)	N7-C4-C3	112.9(3)
O2-N4-N1	115.5(4)	N5-C4-N6	108.2(3)
O5-N5-O6	127.7(4)	N5-C4-N7	107.4(3)
O5-N5-C4	117.8(4)	N5-C4-C3	112.4(4)
O6-N5-C4	114.5(4)	N6-C4-N7	105.8(3)
O7-N6-O8	126.2(4)	N6-C4-C3	109.8(3)
O7-N6-C4	118.2(4)	O3-C1-N1	117.1(4)
O8-N6-C4	115.7(4)	O3-C1-N2	125.8(4)
O9-N7-O10	127.3(4)	N1-C1-N2	117.1(3)
O9-N7-C4	117.8(4)	O10-N7-C4	114.9(4)

Table S13 Selected torsion angles [°] for **3**.

Parameter	Torsion angle (°)	Parameter	Torsion angle (°)
C1-N1-N4-O1	-6.7(6)	O10 -N7-C4-C3	35.5(5)
C1-N1-N4-O2	175.3(4)	N3-C3-C4-N5	47.0(5)
N4-N1-C1-O3	-177.0(4)	N3-C3-C4-N6	167.4(3)
N4-N1-C1-N2	3.7(6)	N3-C3-C4-N7	-74.8(4)
C2-N2-C1-O3	8.2(6)	O7-N6-C4-N7	95.2(4)
C2-N2-C1-N1	-172.6(3)	O8-N6-C4-N7	-83.4(4)
C1-N2-C2-O4	178.7(4)	O8-N6-C4-N5	161.8(3)
C1-N2-C2-N3	-1.4(6)	O7-N6-C4-C3	-142.7(4)
C3-N3-C2-O4	8.4(6)	O10 -N7-C4-N5	-89.0(5)
C3-N3-C2-N2	-171.6(3)	O9-N7-C4-N6	-24.6(5)
C2-N3-C3-C4	-119.8(4)	O9-N7-C4-N5	90.8(4)
O5-N5-C4-C3	-122.7(4)	O10 -N7-C4-N6	155.6(4)
O6-N5-C4-C3	56.1(5)	O9-N7-C4-C3	-144.7(4)
O5-N5-C4-N7	2.1(5)	O6-N5-C4-N7	-179.1(4)
O5-N5-C4-N6	115.9(4)	O7-N6-C4-N5	-19.7(5)
O6-N5-C4-N6	-65.3(5)	O8-N6-C4-C3	38.8(5)

Table S14 Hydrogen bonds for **3** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N1-H1…O4	0.82(4)	1.90(4)	2.714(5)	173(4)
N2-H2…O1	0.83(4)	1.98(4)	2.626(4)	134(4)

N2-H2…N4	0.83(4)	2.54(4)	2.877(5)	106(4)
N3-H3…O3	0.83(4)	2.04(4)	2.691(5)	136(4)
N3-H3…O10	0.83(4)	2.45(5)	2.841(5)	110(4)
C3-H3B…O4	0.9900	2.3500	2.774(5)	105.00

10. ^{1}H NMR and ^{13}C NMR spectra of compounds 1-3

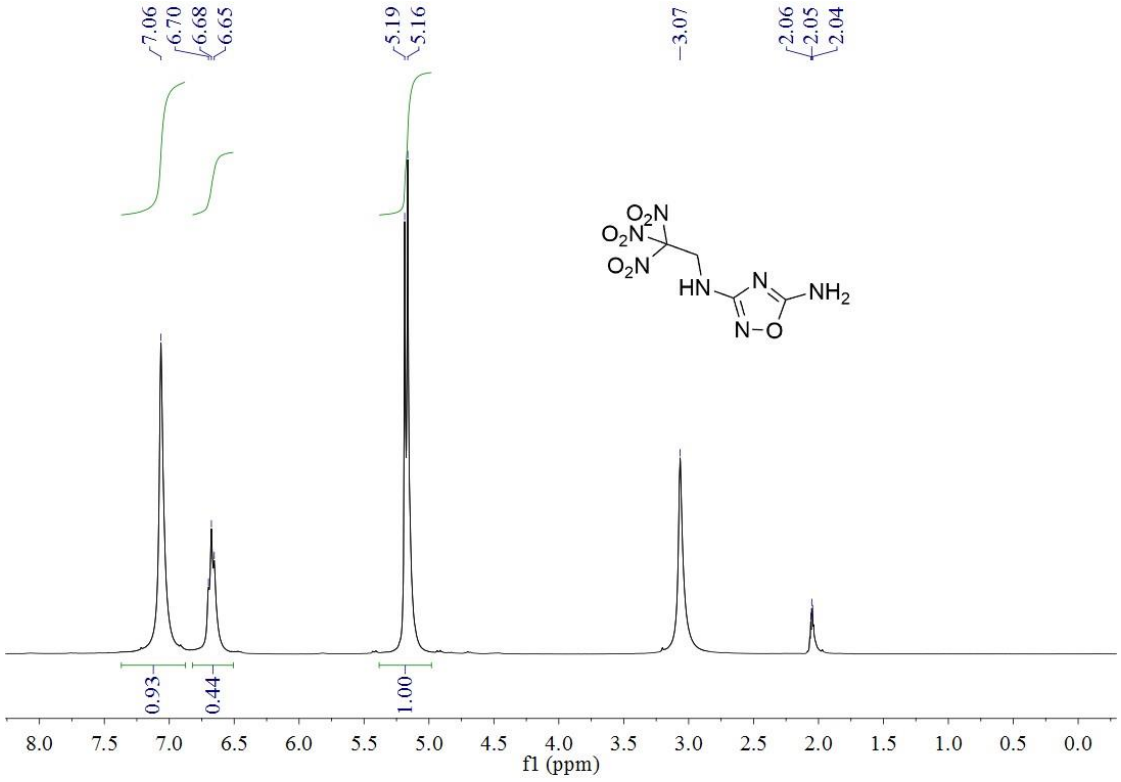


Fig. S7 ^{1}H-NMR spectrum of **1** in d_6-acetone.

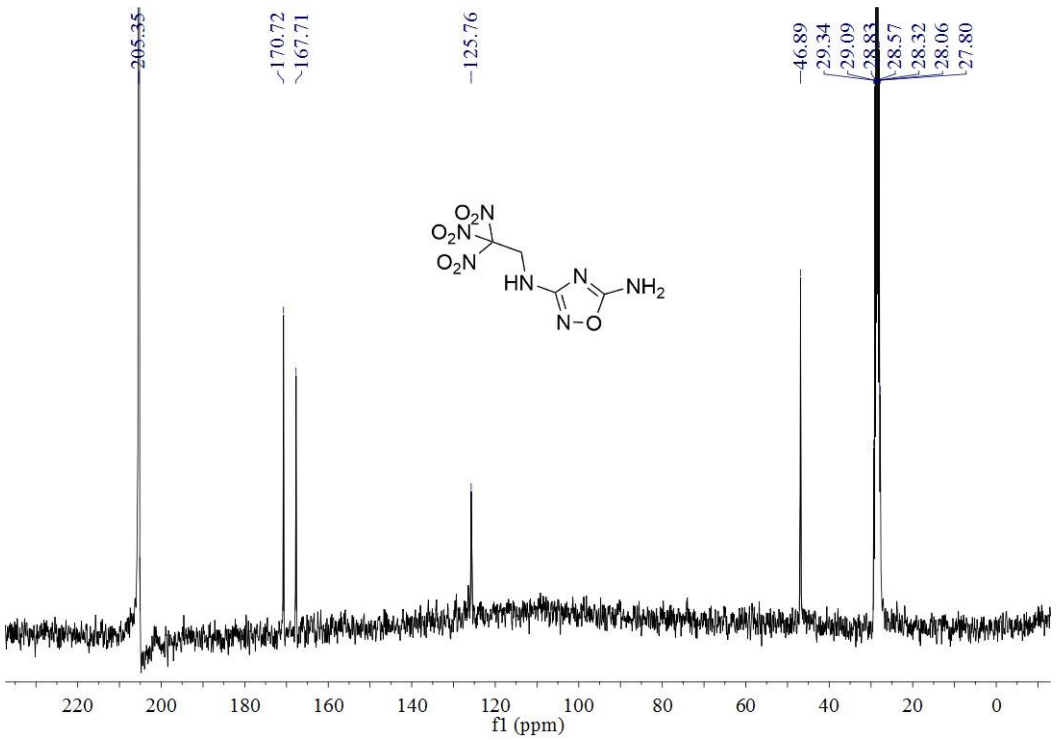


Fig. S8 ^{13}C-NMR spectrum of **1** in d_6-acetone.

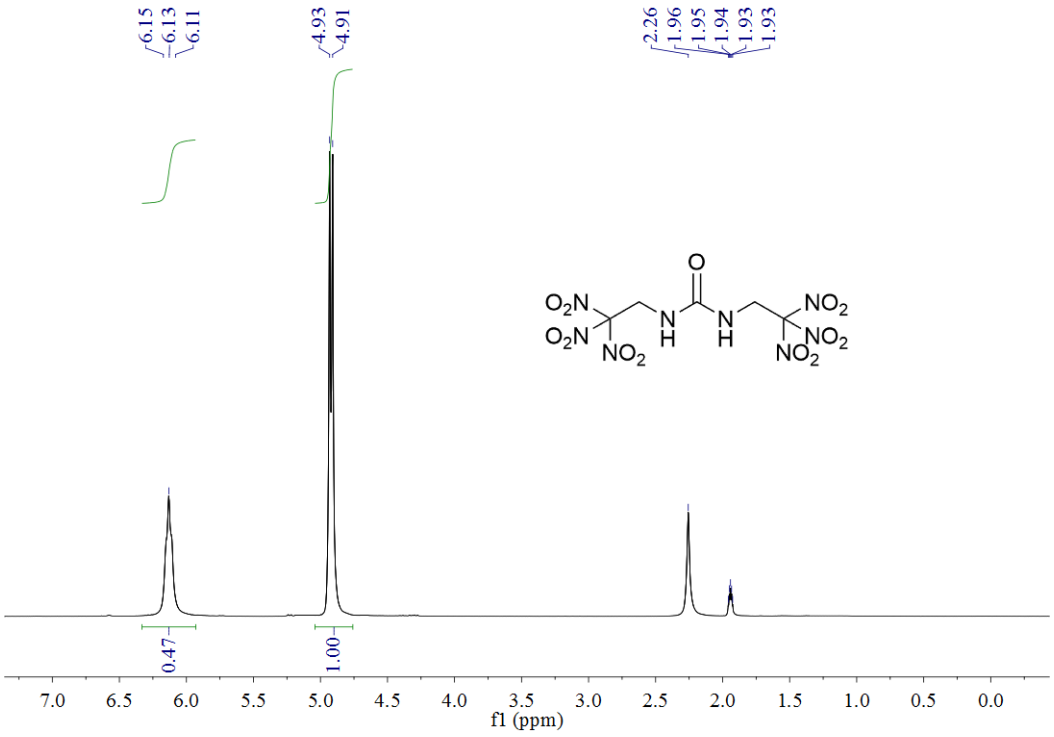


Fig. S9 ^{1}H-NMR spectrum of **2** in d_3-acetonitrile.

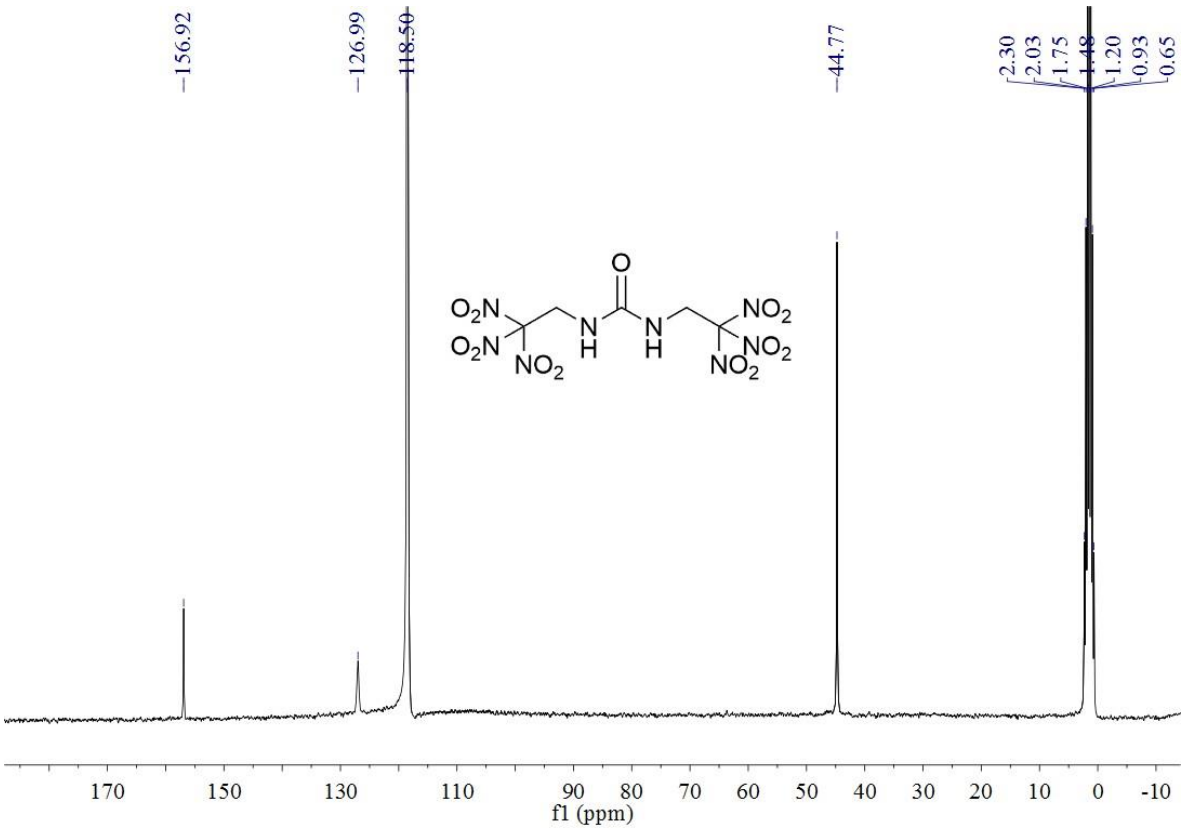


Fig. S10 ^{13}C-NMR spectrum of **2** in d_3-acetonitrile.

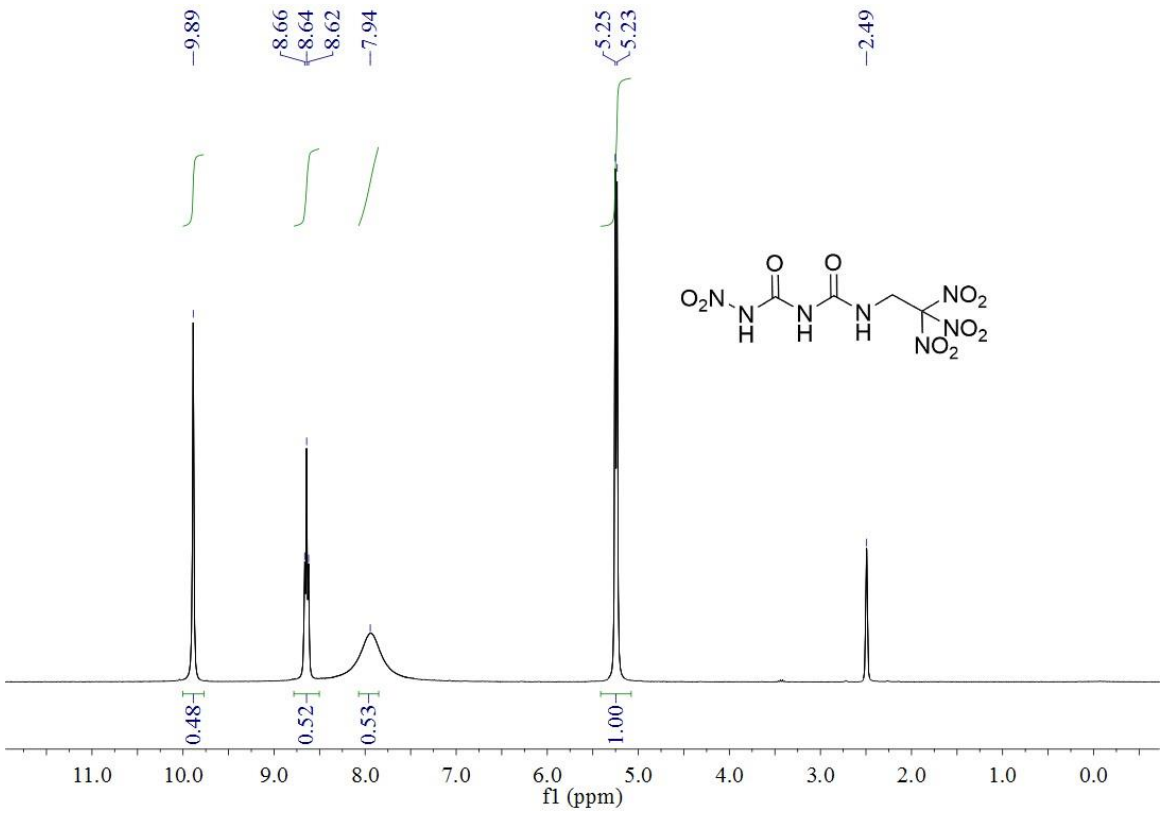


Fig. S11 ^{1}H-NMR spectrum of **3** in d_6-DMSO.

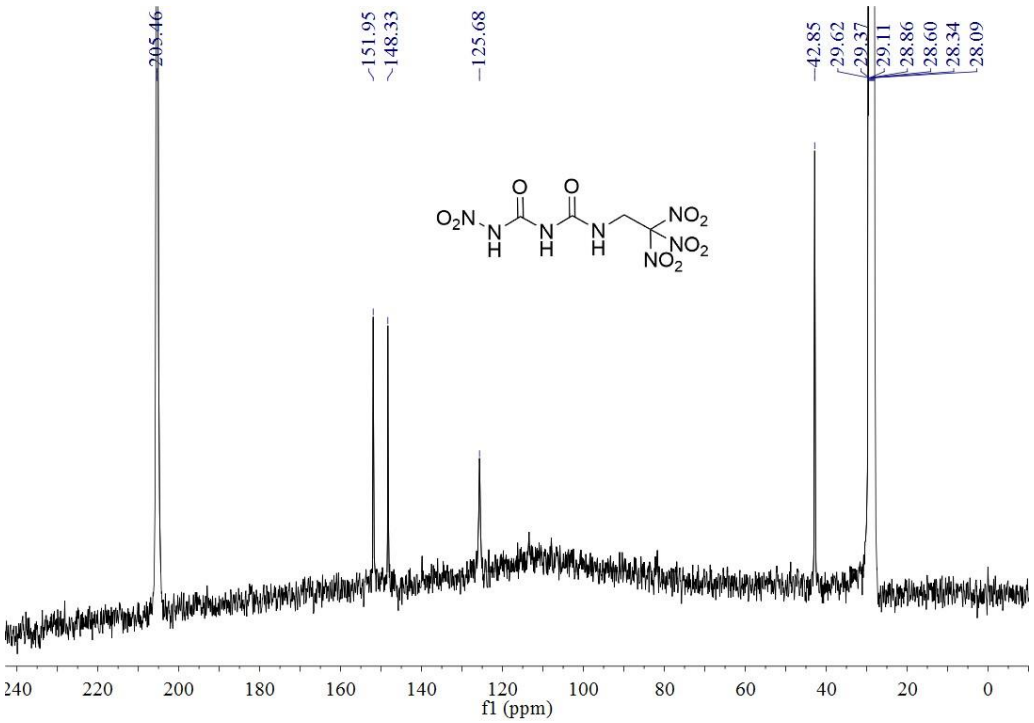


Fig. S12 ^{13}C-NMR spectrum of **3** in d_6-Acetone.

References

1 APEX2, v. 2010.3-0, Bruker AXS Inc. Madison, 2010.

2 Bruker, SAINT v7.68A, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.

3 Bruker, XPREP v2008/2, Bruker AXS Inc., Madison, Wisconsin, USA, 2008.

4 Bruker, SADABS v2008/1, Bruker AXS Inc., Madison, Wisconsin, USA, 2008.

5 Bruker, SHELXTL v2008/4, Bruker AXS Inc., Madison, Wisconsin, USA, 2008.

6 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C.

Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 09, revision A. 01; Gaussian, Inc.: Wallingford, CT, 2009.

7 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.

8 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta.*, 1973, **28**, 213-222.

9 J. W. Ochterski, G. A. Petersson and J. A. Montgomery, *J. Chem. Phys.*, 1996, **104**, 2598.

10 H. D. B. Jenkins, D. Tudeal and L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364-2367.

11 D. R. Lide, *CRC Handbook of Chemistry and Physics*, 88th ed. (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, 2007-2008.

12 M. J. Kamlet and S. J. Jacobs, *J. Chem. Phys.*, 1968, **48**, 3685-3692.