Electronic Supplementary Information

From FOX-7 to H-FOX to Insensitive Energetic Materials with Hypergolic Properties

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1. EXPERIMENTAL SECTION

Safety Precautions

***Caution*:** While we have experienced no difficulties in syntheses and characterization of these materials, proper protective measures should be used. Manipulations must be carried out in a hood behind a safety shield. Face shield and leather gloves must be worn. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials. *Special precautions should be utilized with H-FOX since it is known to detonate on standing without warning. It should be synthesized only in small amounts, utilized immediately upon synthesis and not be stored.* Mechanical actions involving scratching or scraping (especially with metal devices) must be avoided for all the compounds.

GENERAL METHODS

All reagents were purchased from Alfa Aesar, Merck **o**r AK Scientific in analytical grade and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300 and 75 MHz, respectively. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported relative to $(CH_3)_4Si$. DMSO-d_6 was used as solvent for NMR unless otherwise stated. Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer. Melting and decomposition (onset) points were recorded on a differential scanning calorimeter ((TA Instruments Co., model Q10) at a scan rate of 5 °C min^{-1}. Densities were determined at room temperature by employing a Micrometrics AccuPyc 1330 gas pycnometer. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester, respectively. IR spectra were recorded using KBr pellets with a Bio-Rad model 3000 FTS spectrometer.

X-RAY CRYSTALLOGRAPHY

Crystals **4** and **9** were mounted on 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 Mo Kα radiation (λ = 0.71073). Data collection was performed, and the unit

cell was initially refined using APEX2 [v2010.3-0].[1] Data reduction was performed using SAINT [v7.68A][2] and XPREP [v2008/2].[3] An Oxford Cobra room temperature device was used to keep crystals **4** and **9** at a constant 296K for data collection. Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2008/1].[4] Structures were solved and refined with the aid of the programs in the SHELXTL-SHELXL-2014/7 within WingX.[5] The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

CCDC numbers for **4** and **9** are 1435626 and 1435627, respectively, and contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

SYNTHETIC PROCEDURES:

2,2-Dinitroethene-1,1-diamine[6] **(1) and 1-hydrazinyl-2,2-dinitroethenamine**[7] **(2)** were synthesized according to the literature.

(1*Z*,1'*Z*,*N*',*N*''*E*,*N*',*N*''*E*)-*N*',*N*''-(ethane-1,2-diylidene)bis(2,2-dinitroacetohydrazonamide) (3)[7]. To a suspension of **2** (1 g, 6.13 mmol) in water (10 mL), an aqueous solution of glyoxal (2 mL) was added and the solution was acidified with dilute HCl to pH 2. The resulting mixture was stirred 5 h at room temperature and remained overnight. The solid was filtered off, and washed with water and dried in air to give **3** as a yellow solid. Yield (1.6 g, 75%). T_{dec} (onset): 225.6 °C. IR (KBr): ν 3494, 3404, 3298, 3210, 1623, 1531, 1419, 1359, 1323, 1231, 1143, 1057, 937, 864, 739, 704, 589, 459, 420 $cm^{-1.}$ ^{1}H NMR: δ 10.25 (s, 2H), 10.02 (s, 4H), 8.06(s, 2H); ^{13}C NMR: δ 154.5, 149.5, 125.5 ppm. Elemental analysis for $C_6H_6N_{10}O_8$ (346.03): calculated C, 20.82; H, 1.75; N, 40.46%. Found: C, 20.81; H, 1.83; N, 38.82%. IS: 30 J. FS: 340 N.

1,1,2,2-Tetrachloro-1,2-bis((*Z*)-((*E*)-2-chloro-1-(chloroimino)-2,2-dinitroethyl)diazenyl)-ethane (4). To a solution of **3** (0.6 g, 1.724 mmol) in commercial bleach (NaOCl 8.25%, 60 mL), AcOH (30 mL) was added drop wise at room temperature and stirred for an additional 30 min. The precipitate was filtered, washed with water (3 × 50 mL) and dried in air to give **4**

as an orange solid. Yield (0.9 g, 83.6%). T_{dec} (onset): 132.5 °C. IR (KBr): ν 3448, 3177, 1616, 1400, 1338, 1290, 1207, 1025, 950, 896, 854, 823, 793, 731, 663, 611, 419 cm^{-1}. ^{13}C NMR: δ 161.6, 150.1, 138.3 ppm. Elemental analysis for $C_6Cl_8N_{10}O_8$ (619.74): calculated C, 11.55; H, 0.00; N, 22.46%. Found: C, 11.82; H, 0.12; N, 21.68%. IS: 25 J. FS: 340 N.

4,6-Dihydroxy-5,5-dinitro-2-(dinitromethylene)-2,5-dihydropyrimidine (5) [8] and **1-tert-butyl-4-(dinitromethylene)-1,3,5-triazinane (6)**[8,9] were synthesized based on the literature.

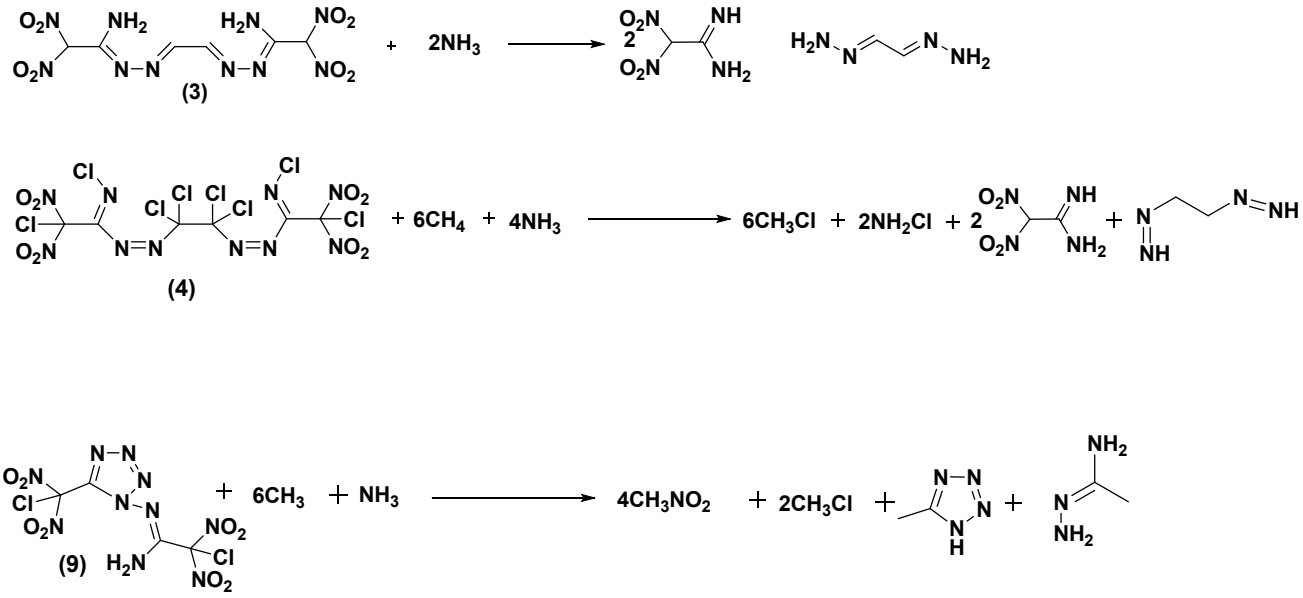
(*E*)-1-((*E*)-2-Chloro-1-(chloroimino)-2,2-dinitroethyl)-2-((*Z*)-2-chloro-1-(chloroimino)-2,2-dinitroethyl)diazene (8).[9,10] 4,6-Dihydroxy-5,5-dinitro-2-(dinitromethylene) 2,5-dihydropyrimidine (5) (6.53 mmol, 2 g) was dissolved in AcOH (30 mL), commercial bleach (NaOCl 8.25%, 60 mL) was added drop wise at room temperature, and the solution was stirred for 1h. The clear solution was extracted with $CHCl_3$ (20 mL × 3) and washed with water (20 mL x 3). The combined organic phase was dried over Na_2SO_4. The solvent was removed under vacuum to give **8** as a purple solid. Yield (1.6 g, 57 %). T_{dec} (onset): 139.0 °C. IR (KBr): ν 2889, 2618, 1603, 1336, 1294, 1207, 1020, 941, 888, 831, 799, 723, 695, 655, 611 cm^{-1}. Elemental analysis for $C_4Cl_8N_8O_8$ (427.85): calculated C, 11.18; H, 0.0; N, 26.06%. Found: C, 11.14; H, 0.08; N, 24.66%. IS: 3.5 J. FS: 40 N.

(*E*)-2-Chloro-*N*'-(5-(chlorodinitromethyl)-1*H*-tetrazol-1-yl)-2,2-dinitroacetimidamide (9). To a suspension of **8** (0.6 g, 1.4 mmol) in methanol (20 mL), sodium azide (0.18 g, 2.8 mmol) was added, and the mixture was stirred at room temperature for 12 h. The purple solid changed to light yellow. The solvent was evaporated under high vacuum and the residue was washed with water. The compound dried in air to give a yellow solid (**9).** Yield (0.390 g, 71.8 %). T_{dec} (onset): 121.9 °C. IR (KBr): ν 3450, 3321, 3154, 1681, 1603, 1445, 1394, 1337, 1300, 1105, 1055, 959, 923, 821, 783, 707, 657, 560, 468 cm^{-1}. ^{1}H NMR: δ 9.6 (s, 2H) ppm. ^{13}C NMR: δ 151.5, 146.5, 125.4, 107.6 ppm. Elemental analysis for $C_4H_2Cl_2N_{10}O_8$ (387.94): calculated C, 12.35; H, 0.52; N, 36.00%. Found: C, 12.82; H, 0.63; N, 35.04%. IS: 8 J. FS: 240 N.

(1*Z*,*N*'*Z*)-*N*'-(1-amino-2-chloro-2,2-dinitroethylidene)-2-chloro-2,2-dinitroacetohydrazonamide (**10**).[9] To a solution of **8** **(**0.5 g, 1.16 mmol) in $CHCl_3$ (150 mL), Me_2S (2 mL), and Me_2SO_4 (1 mL) were added drop wise at room temperature. After stirring for 6 h, the solid was filtered and washed with a small amount of $CHCl_3$ and dried in high

vacuum to give a pale yellow solid (**10**). Yield (0.230 g, 48 %). T_{dec} (onset): 139.6 °C. IR (KBr): ν 3475, 3370, 3124, 3898, 1636, 1593, 1373, 1340, 1311, 1166, 1094, 1052, 953, 833, 788, 731, 660, 625, 542, 442, 413cm^{-1}. ^{1}H NMR: δ 7.1 (s, 2H) ppm. ^{13}C NMR: δ 150.3, 122.7 ppm. Elemental analysis for $C_4H_4Cl_2N_8O_8$ (361.95): calculated C, 13.23; H, 1.10; N, 29.82%. Found: C, 13.57; H, 1.14; N, 28.57%. IS: 5 J. FS: 240 N.

2. Isodesmic reactions



Scheme 1. Isodesmic reactions for calculating heats of formation.

3. Single Crystal X-ray structures of 4 and 9

Table S1: Crystallographic data for **4** and **9**

Compound	4	9
Formula	$C_6Cl_8N_{10}O_8$	$C_4H_2Cl_2N_{10}O_8$
CCDC number	1435626	1435627
M_w	623.76	389.06
Crystal size [mm3]	0.269 x 0.237 x 0.046	0.221 x 0.110 x 0.085
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a [Å]	a = 6.1067(2)	10.3037(3)
b [Å]	b = 13.7465(4)	9.6323(3)
c [Å]	c = 12.4167(3)	14.3934(4)
α[°]	90	90
β [°]	96.0240(10)°	107.9270(10)
γ [°]	90	90
V [Å3]	1036.57(5)	1359.17
Z	2	4
T [K]	296(2)	296(2)
ρ_{calcd} [Mg m-3]	1.998	1.901
μ [mm-1]	1.148	0.547
F(000)	612	776
ϑ[°]	3.300 to 27.621	2.077 to 26.486
Index ranges	-7<=h<=7, -17<=k<=17, -16<=l<=16	-12<=h<=12, -12<=k<=12, -18<=l<=18
Reflections collected	3.300	12853
Independent reflections (R_{int})	2376 [R_{int} = 0.0184]	2796 [R_{int} = 0.0315]
Data/restraints/parameters	2376 / 0 / 146	2796 / 0 / 223
GOF on *F*2	1.023	1.013
R_1 (I > 2δ(I))a	0.0274	0.0329
wR_2 (*I* > 2δ (*I*))*b*	0.0757	0.0966
R_1 (all data)	0.0328	0.0451
wR_2 (all data)	0.0804	0.1058
Largest diff. peak and hole [e.Å-3]	0.533 and -0.342	0.511 and -0.280

a $R_1 = \sum||F_0| - |F_c|| \,/\, \sum|F_0|$ b $R_2 = [\sum w(F_0^2 - F_c^2)^2 \,/\, \sum w(F_0^2)^2]^{1/2}$

Single-crystal X-ray diffraction analysis of 4

An orange plate crystal of dimensions 0.269 x 0.237 x 0.046 mm^3 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 (λ= 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 296(2) K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX2* [v2014.3-0].[11] Data reduction was performed using *SAINT* [v7.68A][12] and *XPREP* [v2014/2].[13] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].[14] The structure was solved and refined with the aid of the programs SHELXL-2014/7 within WingX.[15,16] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

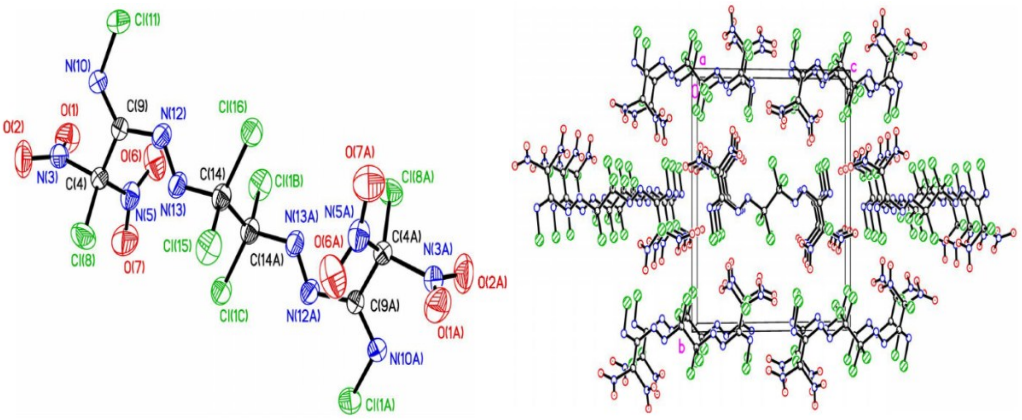


Figure S1. (a) Thermal ellipsoids shown at 50% **4**. (b) Unit cell view along b axis; Packing diagram of **4** along x axis.

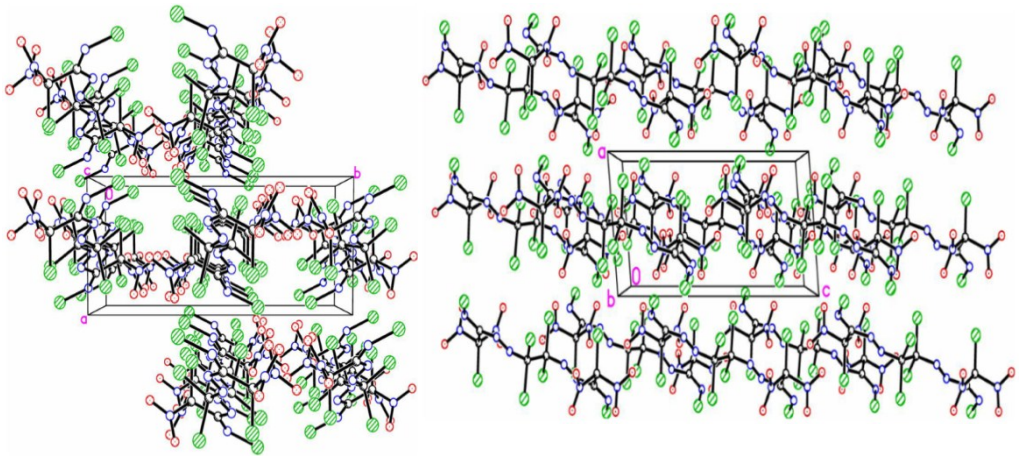


Figure S2. Ball and stick packing diagrams of **4**.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	8600(3)	3095(1)	799(1)	57(1)
O(2)	5864(3)	3766(1)	-168(1)	65(1)
N(3)	6907(3)	3555(1)	669(1)	39(1)
C(4)	6001(3)	3929(1)	1729(1)	30(1)
N(5)	6847(3)	3167(1)	2586(1)	42(1)
O(6)	8585(3)	3362(1)	3095(1)	60(1)
O(7)	5759(3)	2442(1)	2637(1)	71(1)
Cl(8)	3181(1)	3949(1)	1532(1)	53(1)
C(9)	7031(3)	4914(1)	2018(1)	30(1)
N(10)	8218(2)	5265(1)	1338(1)	37(1)
Cl(11)	9310(1)	6385(1)	1596(1)	53(1)
N(12)	6595(2)	5406(1)	2990(1)	36(1)
N(13)	5477(3)	4910(1)	3549(1)	37(1)
C(14)	4900(3)	5394(1)	4547(1)	35(1)
Cl(15)	2097(1)	5730(1)	4284(1)	50(1)
Cl(16)	6542(1)	6413(1)	4946(1)	46(1)

Table S3. Bond lengths [Å] and angles [°] for **4**

O(1)-N(3)	1.208(2)
O(2)-N(3)	1.196(2)
N(3)-C(4)	1.567(2)
C(4)-C(9)	1.520(2)
C(4)-N(5)	1.544(2)
C(4)-Cl(8)	1.7135(17)
N(5)-O(7)	1.203(2)
N(5)-O(6)	1.207(2)
C(9)-N(10)	1.265(2)
C(9)-N(12)	1.4326(19)
N(10)-Cl(11)	1.6948(15)
N(12)-N(13)	1.2293(19)
N(13)-C(14)	1.482(2)
C(14)-C(14)#1	1.557(3)
C(14)-Cl(16)	1.7632(17)
C(14)-Cl(15)	1.7698(18)
O(2)-N(3)-O(1)	127.77(16)
O(2)-N(3)-C(4)	116.57(15)
O(1)-N(3)-C(4)	115.65(14)
C(9)-C(4)-N(5)	109.94(12)
C(9)-C(4)-N(3)	108.50(12)
N(5)-C(4)-N(3)	103.53(12)
C(9)-C(4)-Cl(8)	113.88(11)
N(5)-C(4)-Cl(8)	111.57(11)
N(3)-C(4)-Cl(8)	108.86(11)

O(7)-N(5)-O(6)	128.06(17)
O(7)-N(5)-C(4)	116.86(16)
O(6)-N(5)-C(4)	115.00(14)
N(10)-C(9)-N(12)	123.57(14)
N(10)-C(9)-C(4)	115.71(14)
N(12)-C(9)-C(4)	120.70(13)
C(9)-N(10)-Cl(11)	117.53(12)
N(13)-N(12)-C(9)	112.17(13)
N(12)-N(13)-C(14)	114.72(13)
N(13)-C(14)-C(14)#1	106.50(16)
N(13)-C(14)-Cl(16)	114.41(11)
C(14)#1-C(14)-Cl(16)	110.57(15)
N(13)-C(14)-Cl(15)	105.83(11)
C(14)#1-C(14)-Cl(15)	108.41(15)
Cl(16)-C(14)-Cl(15)	110.80(9)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	52(1)	60(1)	62(1)	-10(1)	22(1)	8(1)
O(2)	72(1)	91(1)	29(1)	-9(1)	-1(1)	1(1)
N(3)	42(1)	41(1)	35(1)	-9(1)	10(1)	-8(1)
C(4)	29(1)	33(1)	29(1)	-1(1)	5(1)	-1(1)
N(5)	59(1)	33(1)	36(1)	2(1)	8(1)	3(1)
O(6)	68(1)	52(1)	55(1)	1(1)	-18(1)	15(1)
O(7)	102(1)	43(1)	70(1)	14(1)	14(1)	-18(1)
Cl(8)	28(1)	69(1)	60(1)	-12(1)	4(1)	-6(1)
C(9)	31(1)	32(1)	26(1)	1(1)	4(1)	-1(1)
N(10)	38(1)	42(1)	31(1)	0(1)	6(1)	-10(1)
Cl(11)	64(1)	51(1)	45(1)	3(1)	11(1)	-27(1)
N(12)	45(1)	32(1)	32(1)	-1(1)	12(1)	-3(1)
N(13)	49(1)	34(1)	29(1)	-2(1)	11(1)	-4(1)
C(14)	42(1)	32(1)	32(1)	0(1)	8(1)	2(1)
Cl(15)	43(1)	58(1)	49(1)	8(1)	5(1)	18(1)
Cl(16)	66(1)	32(1)	41(1)	-6(1)	14(1)	-11(1)

Table S5. Torsion angles [°] for **4**

O(2)-N(3)-C(4)-C(9)	-91.18(18)
O(1)-N(3)-C(4)-C(9)	87.96(17)
O(2)-N(3)-C(4)-N(5)	152.05(16)
O(1)-N(3)-C(4)-N(5)	-28.80(18)
O(2)-N(3)-C(4)-Cl(8)	33.26(19)
O(1)-N(3)-C(4)-Cl(8)	-147.60(13)
C(9)-C(4)-N(5)-O(7)	160.04(15)
N(3)-C(4)-N(5)-O(7)	-84.21(18)
Cl(8)-C(4)-N(5)-O(7)	32.71(19)
C(9)-C(4)-N(5)-O(6)	-22.82(19)
N(3)-C(4)-N(5)-O(6)	92.93(16)
Cl(8)-C(4)-N(5)-O(6)	-150.15(13)
N(5)-C(4)-C(9)-N(10)	117.99(15)
N(3)-C(4)-C(9)-N(10)	5.43(19)
Cl(8)-C(4)-C(9)-N(10)	-115.98(15)
N(5)-C(4)-C(9)-N(12)	-63.83(18)
N(3)-C(4)-C(9)-N(12)	-176.40(13)
Cl(8)-C(4)-C(9)-N(12)	62.20(17)
N(12)-C(9)-N(10)-Cl(11)	-0.9(2)
C(4)-C(9)-N(10)-Cl(11)	177.27(11)
N(10)-C(9)-N(12)-N(13)	-177.18(16)
C(4)-C(9)-N(12)-N(13)	4.8(2)
C(9)-N(12)-N(13)-C(14)	-177.83(13)
N(12)-N(13)-C(14)-C(14)#1	-140.14(18)
N(12)-N(13)-C(14)-Cl(16)	-17.66(19)
N(12)-N(13)-C(14)-Cl(15)	104.62(15)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1

Single-crystal X-ray Diffraction Analysis of 9

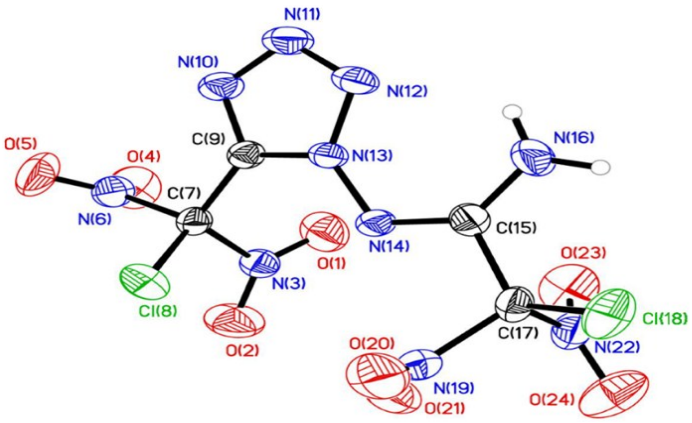


Figure S3. Thermal ellipsoid plot (50%) and labelling scheme for **9.**

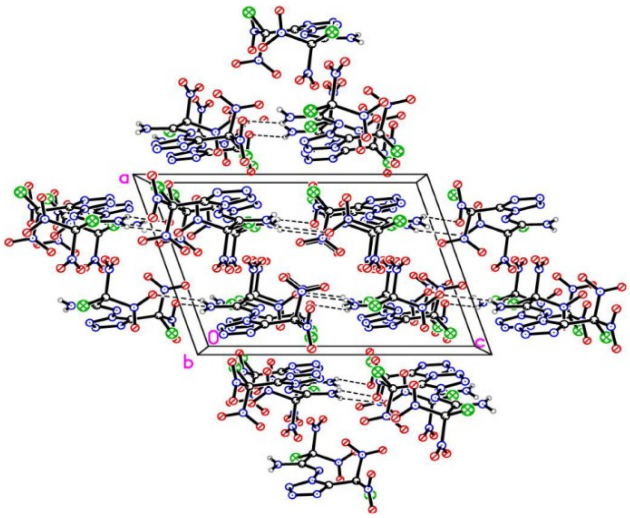


Figure S4. Ball and stick packing diagrams of **9**.

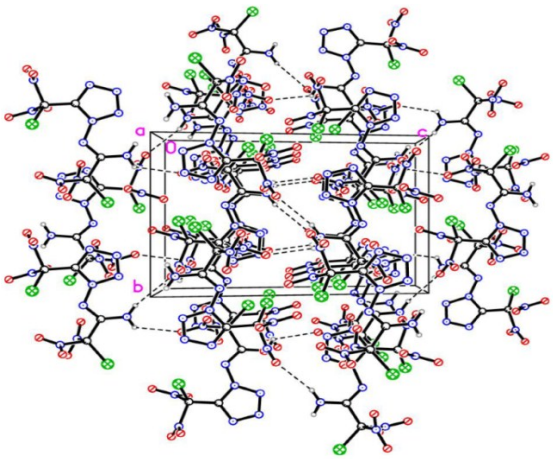


Figure S5. Ball and stick packing diagram of **9** with hydrogen bonding (Dashed lines indicate hydrogen bonding)

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4293(2)	3362(2)	8874(1)	59(1)
O(2)	3764(2)	4006(2)	10141(1)	67(1)
N(3)	3521(2)	3616(2)	9321(1)	33(1)
O(4)	2644(2)	1121(2)	9406(1)	60(1)
O(5)	496(2)	1617(2)	8986(1)	61(1)
N(6)	1674(2)	1872(2)	9095(1)	40(1)
C(7)	1982(2)	3344(2)	8756(1)	28(1)
Cl(8)	979(1)	4580(1)	9072(1)	43(1)
C(9)	1750(2)	3236(2)	7687(1)	27(1)
N(10)	1340(2)	2122(2)	7161(1)	36(1)
N(11)	1228(2)	2501(2)	6231(1)	42(1)
N(12)	1562(2)	3793(2)	6188(1)	37(1)
N(13)	1902(2)	4279(2)	7115(1)	28(1)
N(14)	2336(2)	5584(2)	7462(1)	29(1)
C(15)	2651(2)	6459(2)	6887(1)	29(1)
N(16)	2625(2)	6350(2)	5969(1)	45(1)
C(17)	3140(2)	7833(2)	7405(2)	31(1)
Cl(18)	2695(1)	9255(1)	6646(1)	48(1)
N(19)	2564(2)	7990(2)	8276(1)	38(1)
O(20)	1440(2)	8473(2)	8091(2)	62(1)
O(21)	3289(2)	7592(2)	9062(1)	59(1)
N(22)	4723(2)	7815(2)	7875(1)	39(1)
O(23)	5281(2)	6801(2)	7787(2)	61(1)
O(24)	5201(2)	8897(2)	8255(2)	72(1)

Table S7. Bond lengths [Å] and angles [°] for **9**

O(1)-N(3)	1.191(2)	O(2)-N(3)	1.190(2)
N(3)-C(7)	1.565(3)	O(4)-N(6)	1.203(3)
O(5)-N(6)	1.200(3)	N(6)-C(7)	1.564(2)
C(7)-C(9)	1.486(3)	C(7)-Cl(8)	1.727(2)
C(9)-N(10)	1.306(2)	C(9)-N(13)	1.339(2)
N(10)-N(11)	1.358(2)	N(11)-N(12)	1.298(3)
N(12)-N(13)	1.354(2)	N(13)-N(14)	1.375(2)
N(14)-C(15)	1.291(2)	C(15)-N(16)	1.318(3)
C(15)-C(17)	1.526(3)	N(16)-H(16A)	0.81(3)
N(16)-H(16B)	0.86(3)	C(17)-N(19)	1.550(3)
C(17)-N(22)	1.562(3)	C(17)-Cl(18)	1.724(2)
N(19)-O(20)	1.200(3)	N(19)-O(21)	1.210(3)
N(22)-O(23)	1.160(2)	N(22)-O(24)	1.209(3)
O(2)-N(3)-O(1)	128.90(19)	O(2)-N(3)-C(7)	115.98(17)

O(1)-N(3)-C(7)	115.08(16)	O(5)-N(6)-O(4)	128.1(2)
O(5)-N(6)-C(7)	116.00(19)	O(4)-N(6)-C(7)	115.85(18)
C(9)-C(7)-N(6)	106.00(14)	C(9)-C(7)-N(3)	111.32(15)
N(6)-C(7)-N(3)	105.07(15)	C(9)-C(7)-Cl(8)	113.74(13)
N(6)-C(7)-Cl(8)	110.35(13)	N(3)-C(7)-Cl(8)	109.93(13)
N(10)-C(9)-N(13)	109.79(16)	N(10)-C(9)-C(7)	125.30(17)
N(13)-C(9)-C(7)	124.89(16)	C(9)-N(10)-N(11)	105.34(16)
N(12)-N(11)-N(10)	111.21(15)	N(11)-N(12)-N(13)	106.05(15)
C(9)-N(13)-N(12)	107.60(15)	C(9)-N(13)-N(14)	123.28(15)
N(12)-N(13)-N(14)	129.12(15)	C(15)-N(14)-N(13)	118.78(16)
N(14)-C(15)-N(16)	131.27(19)	N(14)-C(15)-C(17)	111.36(16)
N(16)-C(15)-C(17)	117.37(18)	C(15)-N(16)-H(16A)	121(2)
C(15)-N(16)-H(16B)	117.2(18)	H(16A)-N(16)-H(16B)	122(3)
C(15)-C(17)-N(19)	109.17(15)	C(15)-C(17)-N(22)	110.24(15)
N(19)-C(17)-N(22)	105.03(16)	C(15)-C(17)-Cl(18)	113.36(14)
N(19)-C(17)-Cl(18)	109.95(13)	N(22)-C(17)-Cl(18)	108.77(13)
O(20)-N(19)-O(21)	127.3(2)	O(20)-N(19)-C(17)	116.24(19)
O(21)-N(19)-C(17)	116.46(19)	O(23)-N(22)-O(24)	129.0(2)
O(23)-N(22)-C(17)	116.64(18)	O(24)-N(22)-C(17)	114.33(18)

Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9** The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	38(1)	86(1)	52(1)	-5(1)	14(1)	-2(1)
O(2)	56(1)	95(2)	42(1)	-23(1)	3(1)	-7(1)
N(3)	35(1)	36(1)	28(1)	0(1)	7(1)	-2(1)
O(4)	77(1)	37(1)	65(1)	17(1)	22(1)	10(1)
O(5)	60(1)	66(1)	55(1)	10(1)	14(1)	-32(1)
N(6)	57(1)	35(1)	29(1)	4(1)	13(1)	-11(1)
C(7)	33(1)	26(1)	27(1)	1(1)	10(1)	-5(1)
Cl(8)	48(1)	47(1)	40(1)	-3(1)	21(1)	7(1)
C(9)	30(1)	23(1)	28(1)	-1(1)	9(1)	-1(1)
N(10)	47(1)	26(1)	35(1)	-5(1)	13(1)	-4(1)
N(11)	58(1)	35(1)	33(1)	-11(1)	14(1)	-7(1)
N(12)	51(1)	38(1)	24(1)	-6(1)	13(1)	-5(1)
N(13)	37(1)	25(1)	21(1)	-2(1)	9(1)	-3(1)
N(14)	40(1)	22(1)	25(1)	-2(1)	11(1)	-5(1)
C(15)	33(1)	26(1)	31(1)	2(1)	13(1)	3(1)
N(16)	74(1)	34(1)	35(1)	2(1)	28(1)	-7(1)
C(17)	32(1)	25(1)	39(1)	4(1)	16(1)	-1(1)
Cl(18)	51(1)	27(1)	65(1)	15(1)	16(1)	3(1)
N(19)	44(1)	30(1)	46(1)	-12(1)	22(1)	-8(1)
O(20)	44(1)	72(1)	80(1)	-21(1)	32(1)	-1(1)
O(21)	76(1)	67(1)	40(1)	-5(1)	25(1)	1(1)
N(22)	36(1)	37(1)	46(1)	1(1)	16(1)	-7(1)

O(23)	43(1)	58(1)	81(1)	6(1)	15(1)	14(1)
O(24)	47(1)	57(1)	102(2)	-14(1)	6(1)	-14(1)

Table S9. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **9**

	x	y	z	U(eq)
H(16A)	2370(30)	5640(30)	5660(20)	54
H(16B)	2950(30)	7030(30)	5727(19)	54

Table S10. Torsion angles [°] for **9**

O(5)-N(6)-C(7)-C(9)	-83.1(2)	O(4)-N(6)-C(7)-C(9)	94.9(2)
O(5)-N(6)-C(7)-N(3)	158.97(18)	O(4)-N(6)-C(7)-N(3)	-23.1(2)
O(5)-N(6)-C(7)-Cl(8)	40.5(2)	O(4)-N(6)-C(7)-Cl(8)	-141.57(17)
O(2)-N(3)-C(7)-C(9)	164.68(19)	O(1)-N(3)-C(7)-C(9)	-17.4(2)
O(2)-N(3)-C(7)-N(6)	-81.0(2)	O(1)-N(3)-C(7)-N(6)	96.9(2)
O(2)-N(3)-C(7)-Cl(8)	37.7(2)	O(1)-N(3)-C(7)-Cl(8)	-144.33(17)
N(6)-C(7)-C(9)-N(10)	1.4(3)	N(3)-C(7)-C(9)-N(10)	115.2(2)
Cl(8)-C(7)-C(9)-N(10)	-119.99(19)	N(6)-C(7)-C(9)-N(13)	179.87(18)
N(3)-C(7)-C(9)-N(13)	-66.4(2)	Cl(8)-C(7)-C(9)-N(13)	58.4(2)
N(13)-C(9)-N(10)-N(11)	-0.4(2)	C(7)-C(9)-N(10)-N(11)	178.21(18)
C(9)-N(10)-N(11)-N(12)	0.3(2)	N(10)-N(11)-N(12)-N(13)	-0.1(2)
N(10)-C(9)-N(13)-N(12)	0.4(2)	C(7)-C(9)-N(13)-N(12)	-178.24(17)
N(10)-C(9)-N(13)-N(14)	-179.39(17)	C(7)-C(9)-N(13)-N(14)	2.0(3)
N(11)-N(12)-N(13)-C(9)	-0.2(2)	N(11)-N(12)-N(13)-N(14)	179.58(19)
C(9)-N(13)-N(14)-C(15)	169.57(18)	N(12)-N(13)-N(14)-C(15)	-10.2(3)
N(13)-N(14)-C(15)-N(16)	0.8(3)	N(13)-N(14)-C(15)-C(17)	-178.65(16)
N(14)-C(15)-C(17)-N(19)	-23.3(2)	N(16)-C(15)-C(17)-N(19)	157.19(19)
N(14)-C(15)-C(17)-N(22)	91.60(19)	N(16)-C(15)-C(17)-N(22)	-87.9(2)
N(14)-C(15)-C(17)-Cl(18)	-146.21(15)	N(16)-C(15)-C(17)-Cl(18)	34.3(2)
C(15)-C(17)-N(19)-O(20)	-85.4(2)	N(22)-C(17)-N(19)-O(20)	156.45(18)
Cl(18)-C(17)-N(19)-O(20)	39.6(2)	C(15)-C(17)-N(19)-O(21)	93.4(2)
N(22)-C(17)-N(19)-O(21)	-24.8(2)	Cl(18)-C(17)-N(19)-O(21)	-141.62(17)
C(15)-C(17)-N(22)-O(23)	-1.4(2)	N(19)-C(17)-N(22)-O(23)	116.1(2)
Cl(18)-C(17)-N(22)-O(23)	-126.25(19)	C(15)-C(17)-N(22)-O(24)	176.20(19)
N(19)-C(17)-N(22)-O(24)	-66.3(2)	Cl(18)-C(17)-N(22)-O(24)	51.3(2)

Table S11. Hydrogen bonds for **9** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(16)-H(16A)...O(4)#1	0.81(3)	2.56(3)	3.280(3)	148(3)
N(16)-H(16A)...N(12)	0.81(3)	2.19(3)	2.753(3)	126(2)
N(16)-H(16B)...O(21)#2	0.86(3)	2.55(3)	3.194(2)	132(2)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z-1/2 #2 x,-y+3/2,z-1/2

4. ^{1}H, ^{13}C and DSC data

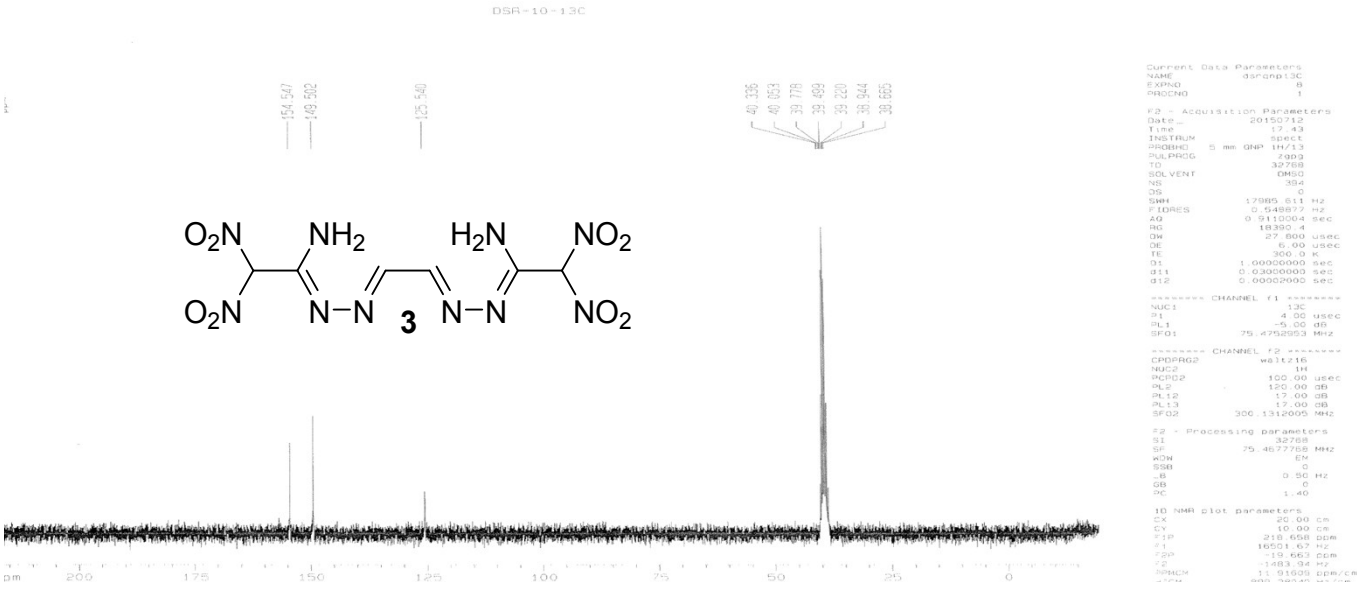


Figure S6. ^{13}C NMR spectra of **3** in DMSO-d_6

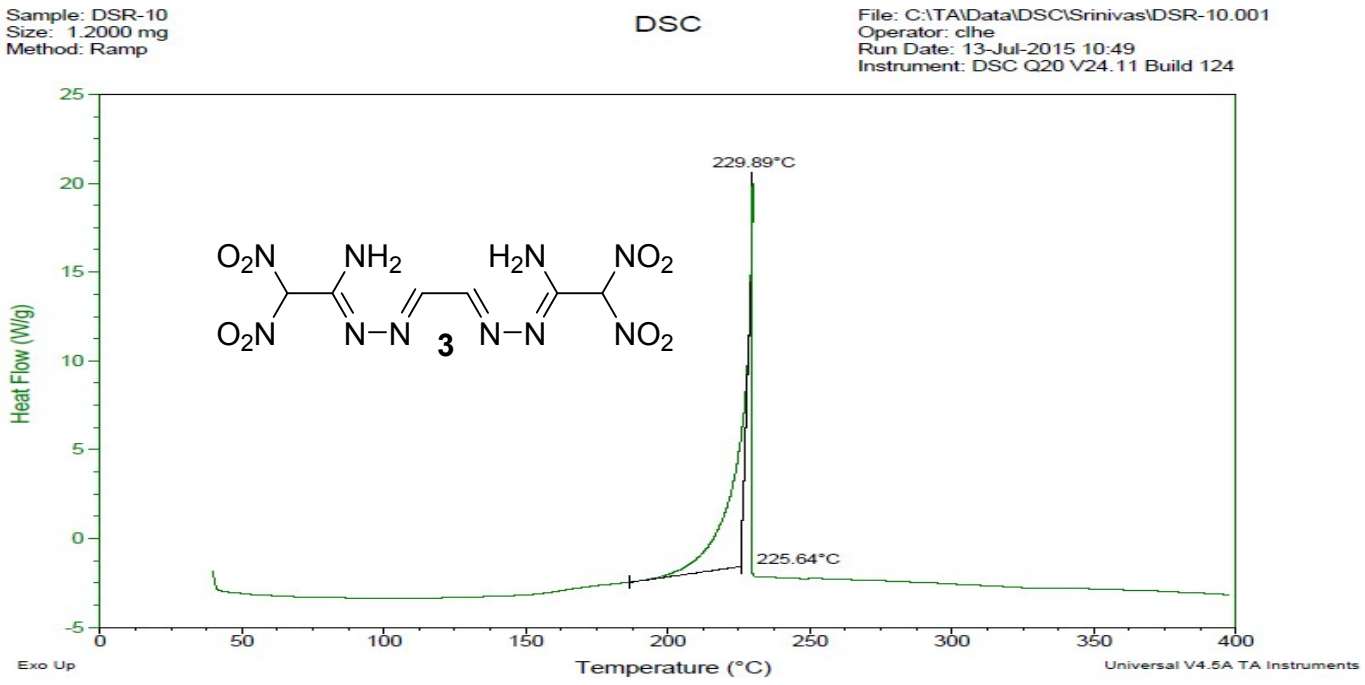


Figure S7. DSC curve of **3**

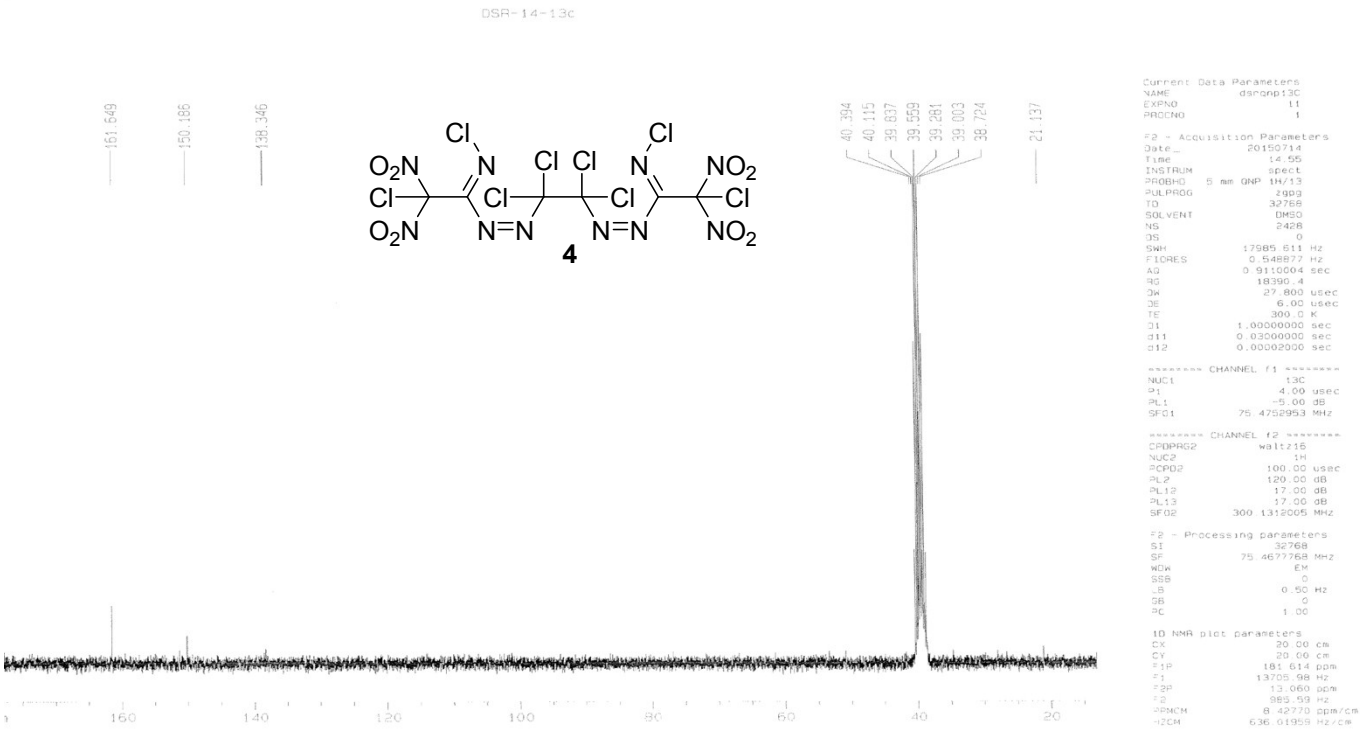


Figure S8. ^{13}C NMR spectra of **4** in DMSO-d_6

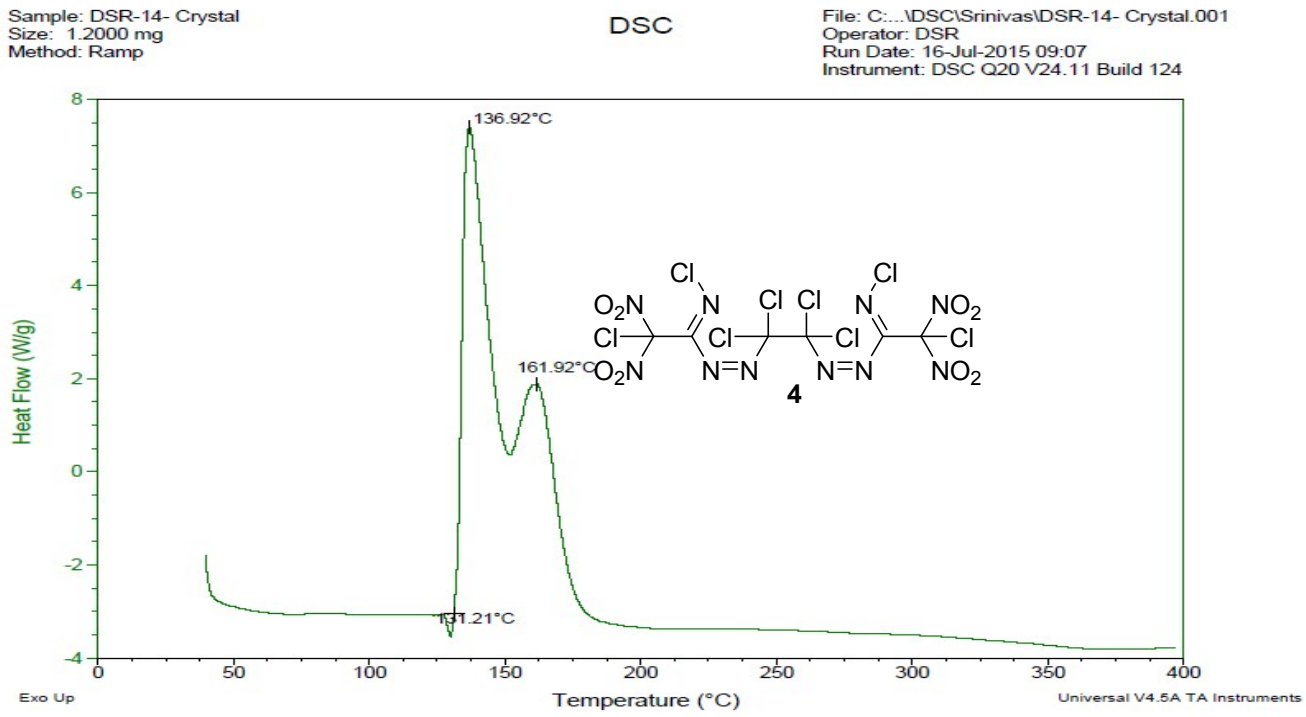


Figure S9. DSC curve of **4**

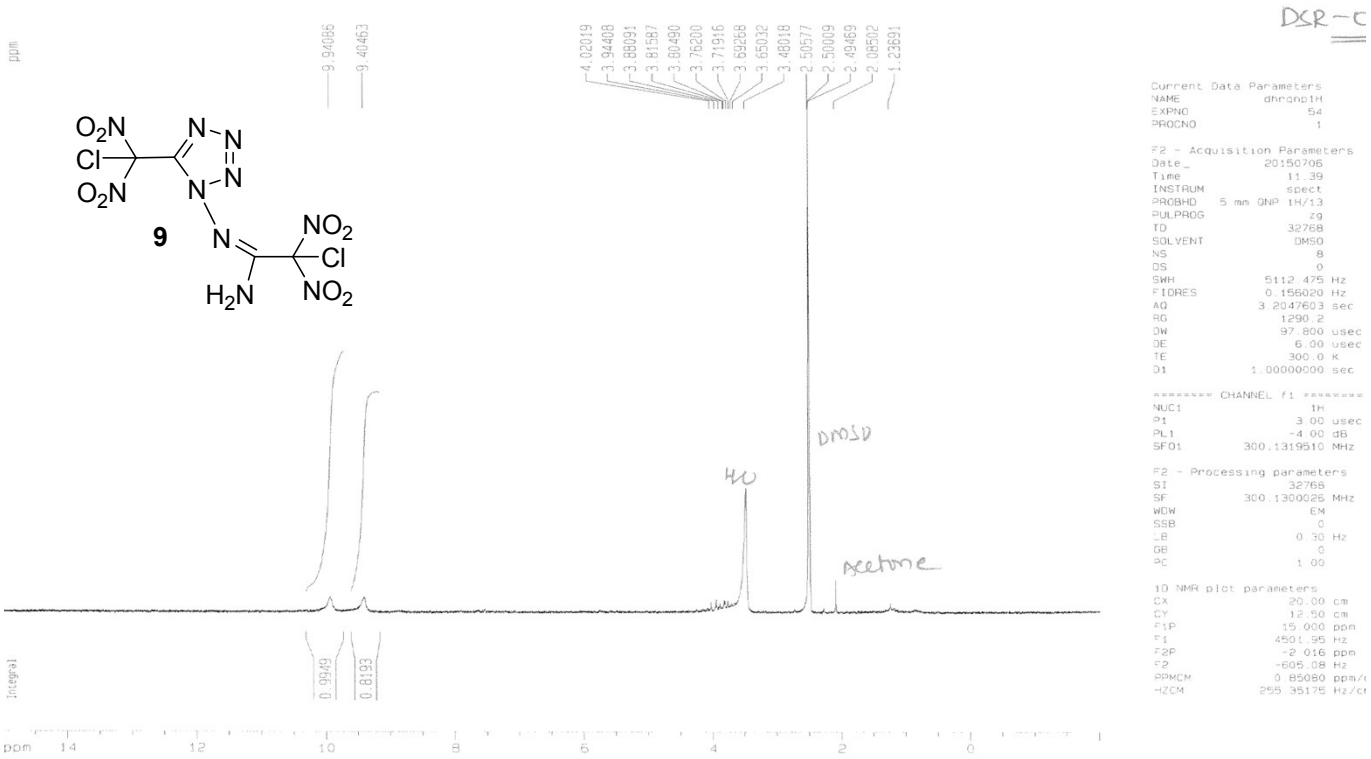


Figure S10. ^{1}H NMR spectra of **9** in DMSO-d_6

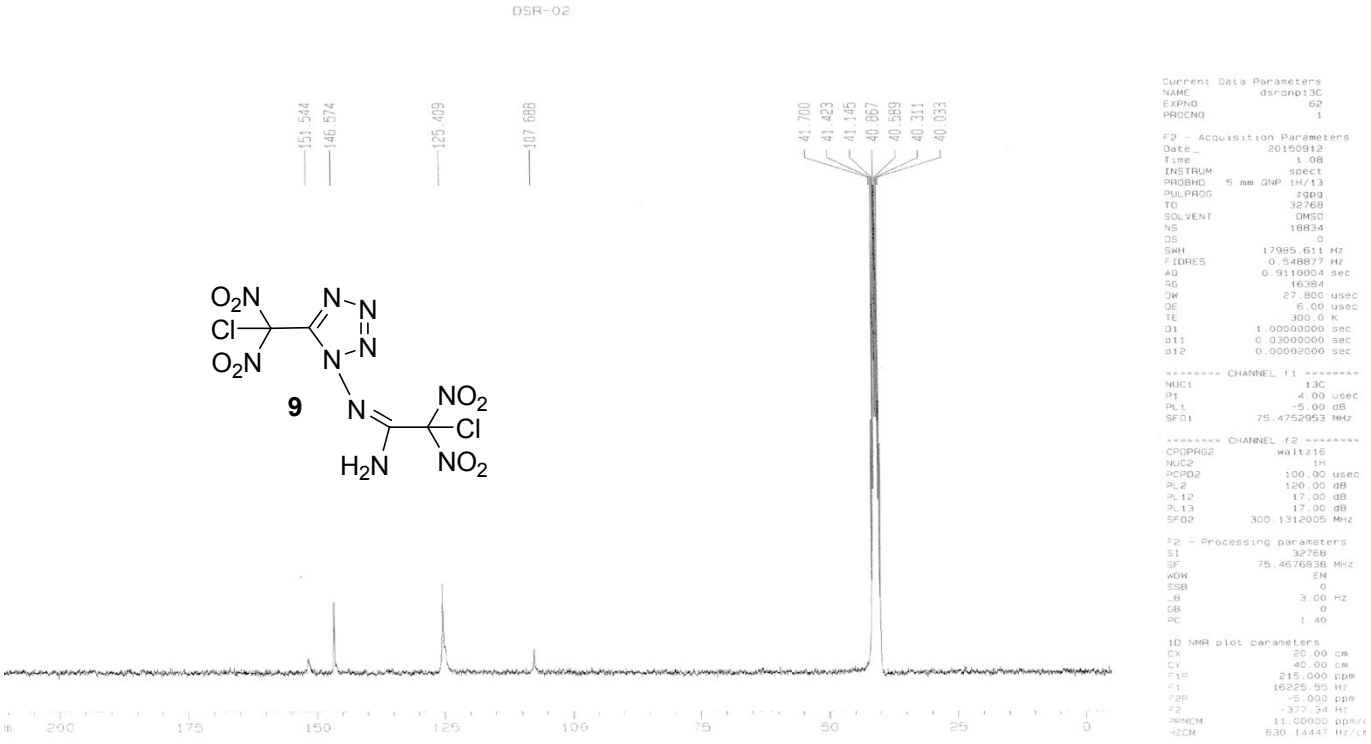


Figure S11. ^{13}C NMR spectra of **9** in DMSO-d_6

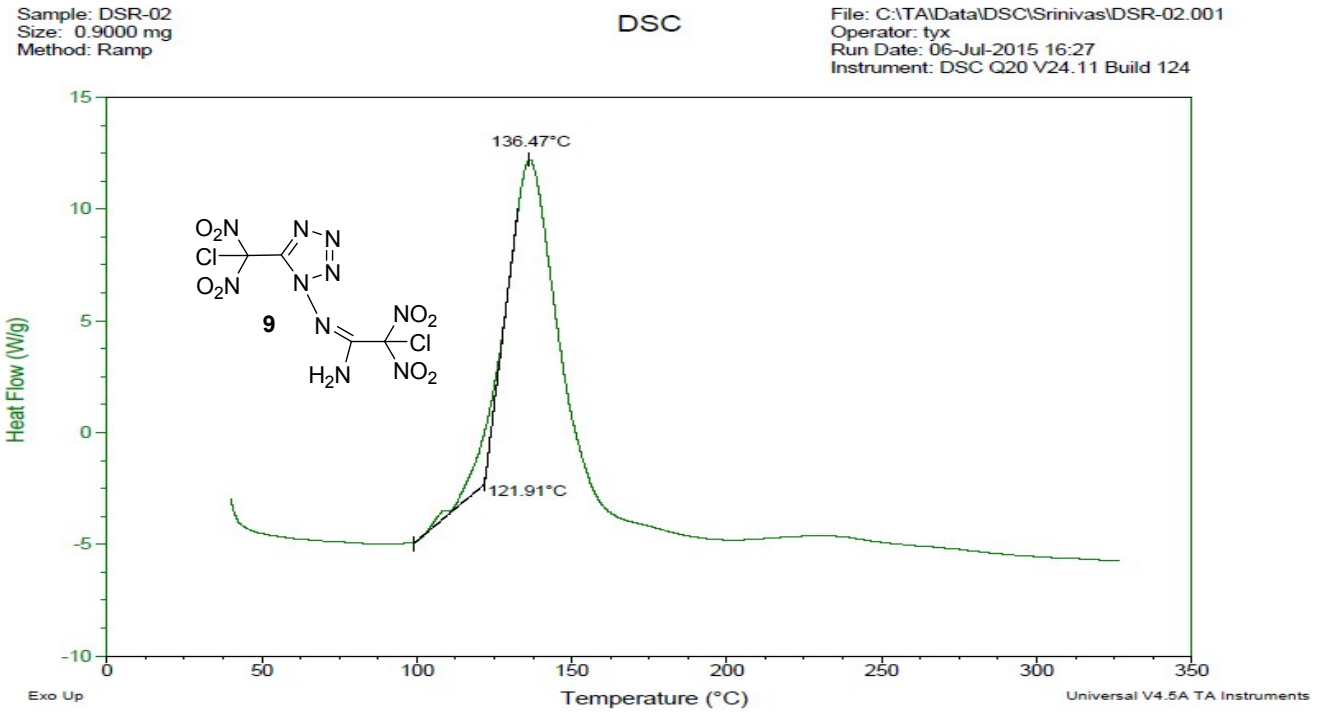


Figure S12. DSC curve of **9**

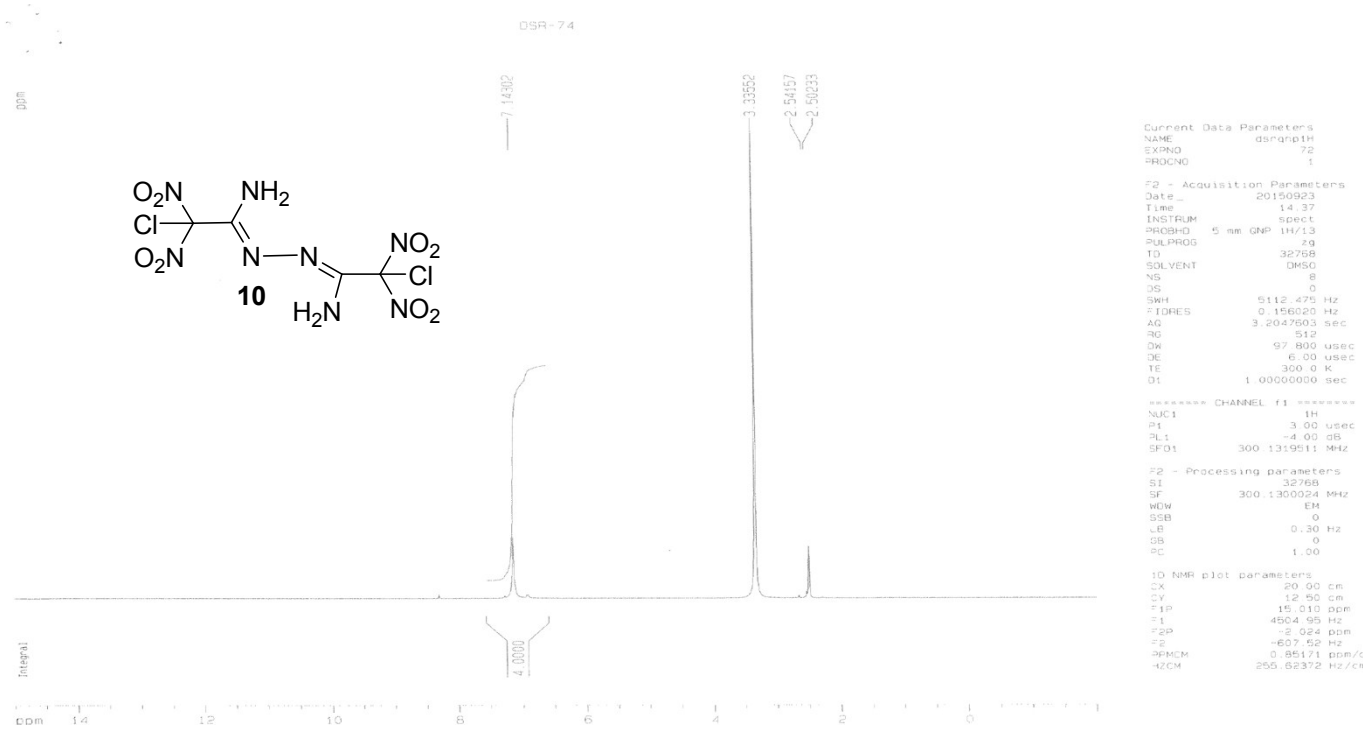


Figure S13. ^{1}H NMR spectra of **10** in DMSO-d_6

Figure S14. ^{13}C NMR spectra of **10** in DMSO-d_6

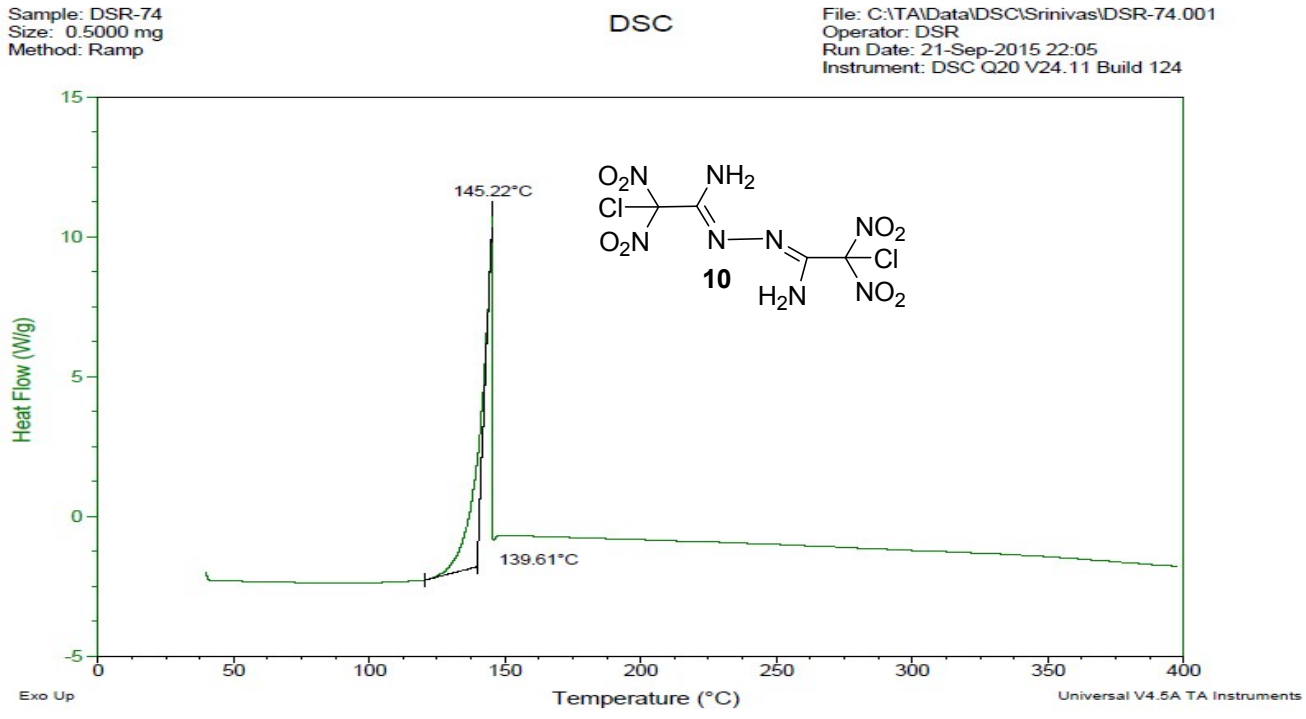


Figure S15. DSC curve of **10**

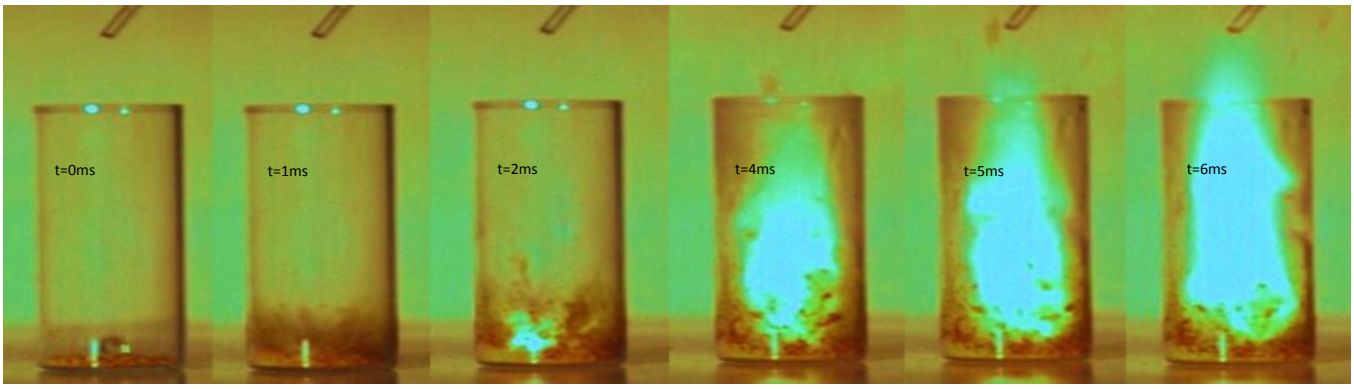
5. Hypergolic test of 4 and 8, Table S12 and Figure S16

Table S12. Ignition Delay Times for **4** and **8**.

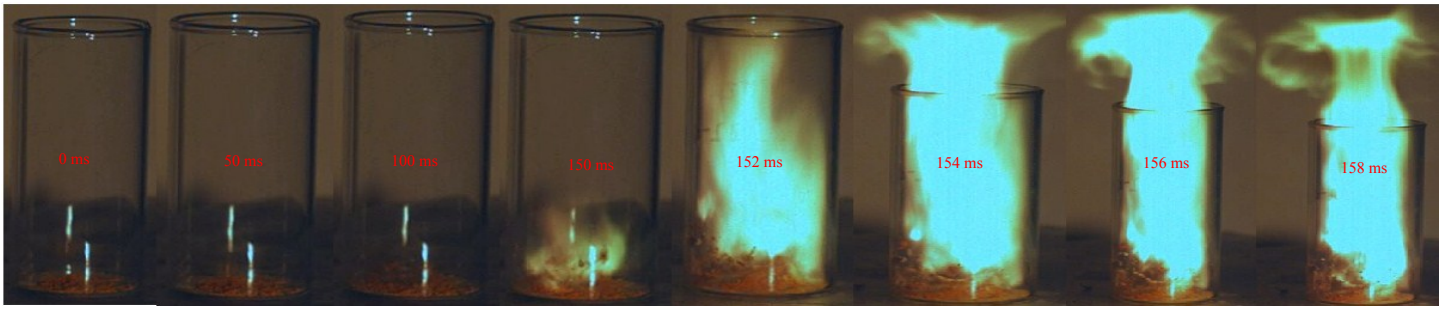
Compound	MMH (ms)	HH (ms)	EN (ms)	DAP (ms)	AB[a] (ms)
4	**2.5**	**5**	**10**	**10**	**150**
8[b]	**4.6**[b]	**13.3**[b]	**14.7**[b]	**14.7**[b]	**162**

[a] Ammonia borane in 1-allyl-3-methyl imidazolium dicyanamide (1:1 molar ratio). Compound **4** and **8** do not inflame with the ionic liquid. [b] Ref. [10]

Figure S16



Hypergolic test of **4** with MMH



Hypergolic test of compound **4** with ammonia borane as a fuel solubilized in a green ionic Liquid, 1-allyl-3-methyl imidazolium dicyanamide, (1:1 molar ratio)

Table S13. Specific Impulses (ISp) of mixtures of compound **4** and MMH

S. No	Compound 4 (%)	MMH (%)	ISp xc(s)
1	100	0	186.9
2	90	10	217.2
3	80	20	211.8
4	70	30	209.4
5	60	40	208.8
6	50	50	208.9
7	40	60	210.2
8	30	70	210.8
9	20	80	211.3
10	10	90	211.0
11	0	100	209.6

6. References

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