Electronic Supplementary Information

A C-C bonded 5,6-fused bicyclic energetic molecule: exploring an advanced energetic compound with improved performance

Yongxing Tang,[a] Chunlin He,[a] Gregory H. Imler,[b] Damon A. Parrish[b] and Jean'ne M. Shreeve*[a]

[a] Dr. Y. Tang, Dr. C. He, Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho, Moscow, Idaho, 83844-2343, USA.
Fax: (+1) 208-885-9146
E-mail: jshreeve@uidaho.edu

[b] Dr. G. H. Imler, Dr. D. A. Parrish
Naval Research Laboratory, 4555 Overlook Avenue, Washington, D.C. 20375, United States

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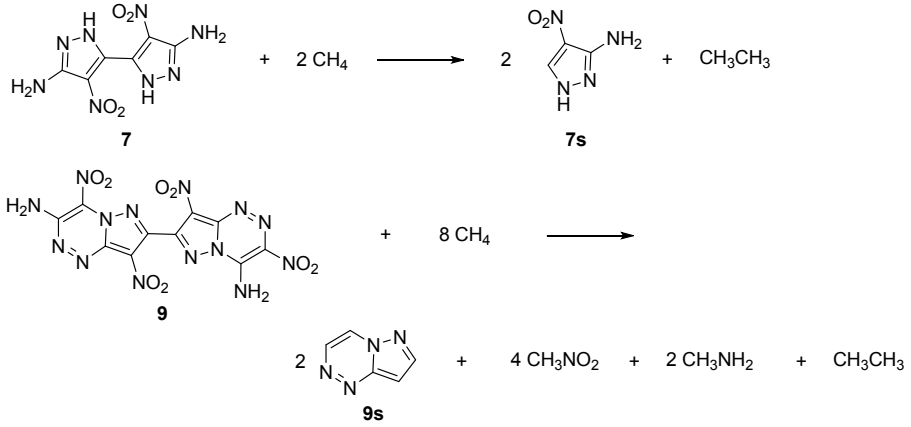
General Methods: ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, by using d_6-DMSO as solvent and locking solvent. The decomposition points were obtained on a differential scanning calorimeter (TA Instruments Company, Model: Q2000) at a scan rate of 5 °C min^{-1}, respectively. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. Densities were measured at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were determined using a Vario Micro cube Elementar Analyser. The sensitivities were carried out by using a BAM drop hammer and friction tester.

Computational Methods: The gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S1). The enthalpy of reaction is obtained by combining the MP2/6–311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid state heats of formation were calculated with Trouton's rule according to equation (1) (*T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).[1]

$$\Delta H_{sub} = 188 / Jmol^{-1}K^{-1} \times T \qquad (1)$$



Scheme S1. Isodesmic reaction for **7** and **9**

Table S1. Calculated zero point energy (*ZPE*), values of the correction (H_r), total energy (E_0) and heats of formation (*HOF*) in gas state

Species	*ZPE*	H_r	E_0	corrected E_0	*HOF*(kJ mol^{-1})
7	0.161254	0.17767	-968.7470726	-968.57585	306.1619965
9	0.208875	0.235073	-1747.379331	-1747.15261	970.6703072
7s	0.090717	0.099141	-484.95632	-484.86080	152.36 [a]
9s	0.093248	0.09993	-410.840383	-410.74418	497.4 [a]
CH_3NH_2	0.064026	0.068401	-95.5938424	-95.528000	-23 [b]
CH_4	0.044793	0.048605	-40.3796224	-40.33281	-74.6 [b]
CH_3NO_2	0.04984	0.055138	-244.4784821	-244.42534	-74.3 [b]

[a] Data obtained from G2.

[b] Data are from Ref. [D. R. Lide, ed., CRC Handbook of Chemistry and Physics, 88th Edition (Internet Version 2008), CRC Press/Taylor and Francis, Boca Raton, FL.].

DSC plot

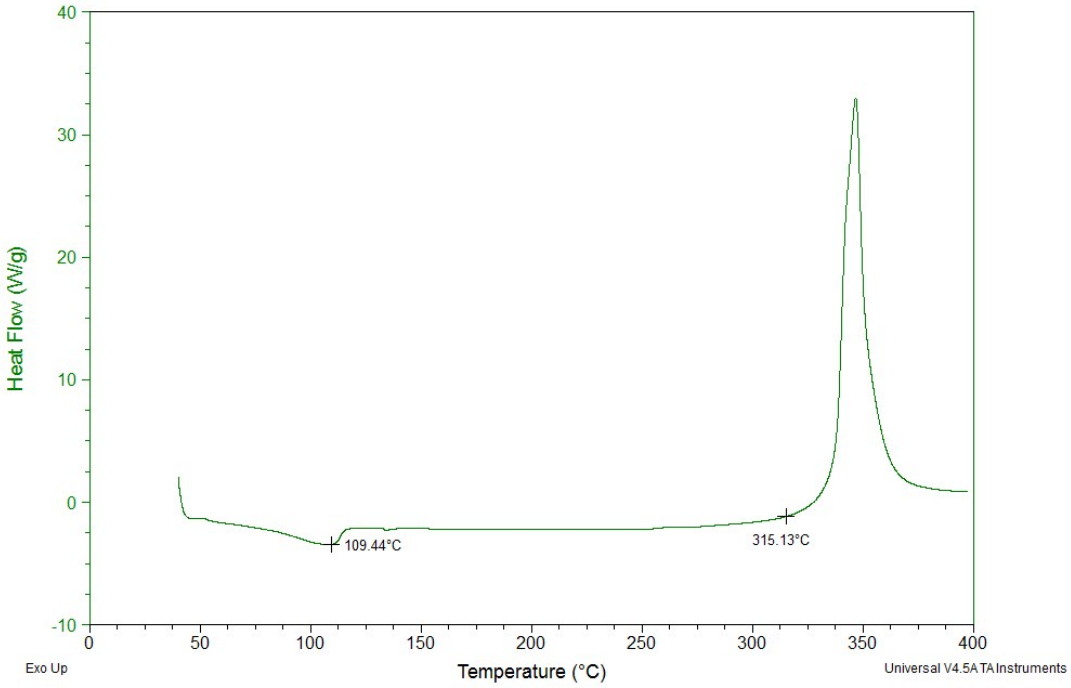


Fig. S1 The DSC plot of **9**

Crystal Structure Analysis

A clear yellow block crystal (**7**·$2H_2O$) of dimensions 0.718 × 0.214 × 0.091 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 PHOTON 100 CMOS detector. The crystals were irradiated using a 1μs microfocus CuK_α source (λ = 1.54178 Å) with Helios optics. Data was collected at room temperature (20°C).

A clear orange needle crystal of dimensions 0.173 × 0.064 × 0.020 mm^3 (**7**·CH_3CN) and a clear yellow plate crystal of dimensions 0.384 × 0.263 × 0.094 mm^3 (**9**) 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 Å). Data was collected at room temperature (20°C).

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].[1] Data Reduction was performed using *SAINT* [v8.34A][2] and *XPREP* [v2014/2][3]. Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].[4] The structure was solved and refined with the aid of the program SHELXL-2014/7.[5] 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.

In **7**·$2H_2O$, one pyrazole hydrogen displays two-component disorder and is alternately bound to N7 or N8. Hydrogen atom occupancies on both atoms have been fixed at 0.5. Water molecule atoms O19 and H19B lie on a 2-fold rotation axis and H19A is disordered around this rotation axis. A second water molecule (O20) displays two-component disorder with a 0.6:0.4 ratio between the major and minor component. In **7**·CH_3CN, one acetonitrile molecule displayed two-component disorder with a 0.74:0.26 ratio between the major and minor components. Atomic displacement parameters for major component were refined anisotropically and for minor component were refined isotropically. Bond lengths for disordered acetonitrile molecules were restrained to literature values. Enhanced rigid-bond restraints were applied to all atoms (esds = 0.004). In **9**·CH_3OH·CH_3NO_2, aniostropic displacement parameters for nitromethane were restrained using enhanced rigid-bond restraints (esds = 0.001).

Table S2. Crystal data and structure refinement for **7**·$2H_2O$.

Identification code	**7**·$2H_2O$
Empirical formula	$C_{12}H_{18}N_{16}O_{11}$
CCDC number	1848976
Formula weight	562.42
Temperature	293(2) K
Wavelength	1.54178 Å

Crystal system	Orthorhombic
Space group	Pbcn
Unit cell dimensions	a = 10.8470(3) Å, α = 90°
	b = 14.2197(5) Å, β = 90°
	c = 14.3756(4) Å, γ = 90°
Volume	2217.31(12) Å^3
Z	4
Density (20°C)	1.685 Mg/m^3
Absorption coefficient	1.299 mm^{-1}
F(000)	1160
Crystal size	0.718 × 0.214 × 0.091 mm^3
Theta range for data collection	5.128 to 74.763°.
Index ranges	-13<=h<=12, -13<=k<=17, -15<=l<=16
Reflections collected	11323
Independent reflections	2172 [R_{int} = 0.0514]
Completeness to theta = 67.679°	97.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.6373
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2172 / 8 / 182
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R_1 = 0.0525, wR_2 = 0.1328
R indices (all data)	R_1 = 0.0590, wR_2 = 0.1380
Extinction coefficient	0.0045(3)
Largest diff. peak and hole	0.303 and -0.253 e.Å^{-3}

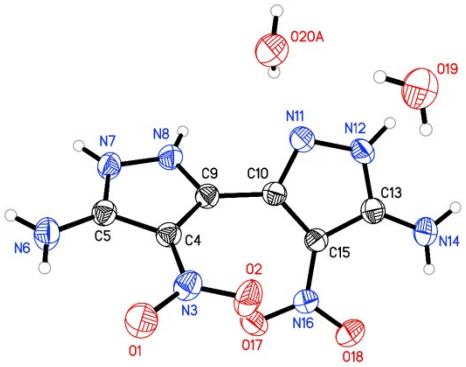


Fig. S2 The crystal structure of **7**·2H_2O

Table S3. Bond lengths [Å] for **7**·2H_2O.

O(1)-N(3)	1.246(3)	O(2)-N(3)	1.229(3)
N(3)-C(4)	1.394(3)	C(4)-C(9)	1.400(3)
C(4)-C(5)	1.419(3)	C(5)-N(6)	1.328(3)
C(5)-N(7)	1.335(3)	N(6)-H(6A)	0.8593
N(6)-H(6B)	0.8594	N(7)-N(8)	1.369(3)

N(7)-H(7)	0.8600	N(8)-C(9)	1.322(3)
N(8)-H(8)	0.8611	C(9)-C(10)	1.468(3)
C(10)-N(11)	1.311(3)	C(10)-C(15)	1.415(3)
N(11)-N(12)	1.375(3)	N(12)-C(13)	1.342(3)
N(12)-H(12)	0.8627	C(13)-N(14)	1.326(3)
C(13)-C(15)	1.411(3)	N(14)-H(14A)	0.8631
N(14)-H(14B)	0.8583	C(15)-N(16)	1.387(3)
N(16)-O(17)	1.234(3)	N(16)-O(18)	1.246(3)
O(19)-H(19A)	0.7807	O(19)-H(19B)	0.7984
O(20B)-O(20A)	0.774(6)	O(20B)-H(20A)	0.8298
O(20B)-H(20B)	0.8360	O(20A)-H(20A)	0.8477
O(20A)-H(20B)	0.8326		

Table S4. Torsion angles [°] for **7**·2H_2O.

O(2)-N(3)-C(4)-C(9)	3.2(4)
O(1)-N(3)-C(4)-C(9)	-177.1(2)
O(2)-N(3)-C(4)-C(5)	-172.3(2)
O(1)-N(3)-C(4)-C(5)	7.4(4)
N(3)-C(4)-C(5)-N(6)	-1.9(4)
C(9)-C(4)-C(5)-N(6)	-178.1(2)
N(3)-C(4)-C(5)-N(7)	176.7(2)
C(9)-C(4)-C(5)-N(7)	0.4(3)
N(6)-C(5)-N(7)-N(8)	178.3(2)
C(4)-C(5)-N(7)-N(8)	-0.3(3)
C(5)-N(7)-N(8)-C(9)	0.1(3)
N(7)-N(8)-C(9)-C(4)	0.2(3)
N(7)-N(8)-C(9)-C(10)	-177.7(2)
N(3)-C(4)-C(9)-N(8)	-176.4(2)
C(5)-C(4)-C(9)-N(8)	-0.4(3)
N(3)-C(4)-C(9)-C(10)	1.1(4)
C(5)-C(4)-C(9)-C(10)	177.2(2)
N(8)-C(9)-C(10)-N(11)	49.9(3)
C(4)-C(9)-C(10)-N(11)	-127.4(3)
N(8)-C(9)-C(10)-C(15)	-130.2(3)
C(4)-C(9)-C(10)-C(15)	52.6(4)
C(15)-C(10)-N(11)-N(12)	0.0(3)
C(9)-C(10)-N(11)-N(12)	180.0(2)
C(10)-N(11)-N(12)-C(13)	-0.6(3)
N(11)-N(12)-C(13)-N(14)	179.6(2)
N(11)-N(12)-C(13)-C(15)	0.9(3)
N(14)-C(13)-C(15)-N(16)	-0.6(4)
N(12)-C(13)-C(15)-N(16)	178.0(2)
N(14)-C(13)-C(15)-C(10)	-179.4(3)

N(12)-C(13)-C(15)-C(10)	-0.8(3)
N(11)-C(10)-C(15)-N(16)	-178.2(2)
C(9)-C(10)-C(15)-N(16)	1.8(4)
N(11)-C(10)-C(15)-C(13)	0.5(3)
C(9)-C(10)-C(15)-C(13)	-179.5(2)
C(13)-C(15)-N(16)-O(17)	-175.6(2)
C(10)-C(15)-N(16)-O(17)	2.9(4)
C(13)-C(15)-N(16)-O(18)	5.8(4)
C(10)-C(15)-N(16)-O(18)	-175.7(2)

Table S5. Hydrogen bonds for **7**·2H_2O [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...O(17)#2	0.86	2.28	3.027(3)	144.7
N(6)-H(6B)...O(1)	0.86	2.23	2.766(3)	120.8
N(8)-H(8)...N(8)#4	0.86	2.08	2.914(4)	163.3
N(12)-H(12)...O(1)#5	0.86	1.97	2.832(3)	173.3
N(14)-H(14A)...O(20B)#6	0.86	2.09	2.945(5)	171.3
N(14)-H(14A)...O(20A)#6	0.86	2.18	2.979(7)	153.2
N(14)-H(14B)...O(18)	0.86	2.27	2.795(3)	119.8
N(14)-H(14B)...O(18)#7	0.86	2.18	2.989(3)	156.7
O(19)-H(19A)...N(7)#6	0.78	2.09	2.819(3)	154.3
O(20B)-H(20B)...N(11)	0.84	2.13	2.849(4)	144.1
O(20A)-H(20B)...N(11)	0.83	2.13	2.929(6)	160.7

Symmetry transformations used to generate equivalent atoms:

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

#4 -x,y,-z+1/2 #5 -x+1/2,-y+1/2,z+1/2 #6 -x+1/2,y+1/2,z

#7 -x,-y+1,-z #8 -x+1,y,-z+1/2

Table S6. Crystal data and structure refinement for **7**·CH_3CN.

Identification code	**7**·CH_3CN
Empirical formula	$C_8H_9N_9O_4$
CCDC number	1848968
Formula weight	295.24
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 7.7715(4) Å, α = 90°
	b = 29.4724(14) Å, β = 96.9890(10)°
	c = 11.6745(6) Å, γ = 90°
Volume	2654.1(2) $Å^3$
Z	8
Density (20°C)	1.478 Mg/m^3

Absorption coefficient	0.122 mm^{-1}
F(000)	1216
Crystal size	0.173 × 0.064 × 0.020 mm^3
Theta range for data collection	3.276 to 27.482°.
Index ranges	-10<=h<=10, -38<=k<=38, -14<=l<=15
Reflections collected	27200
Independent reflections	6033 [R_{int} = 0.0434]
Completeness to theta = 25.242°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.6725
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6033 / 306 / 395
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)]	R_1 = 0.0531, wR_2 = 0.1283
R indices (all data)	R_1 = 0.0836, wR_2 = 0.1439
Largest diff. peak and hole	0.385 and -0.285 e.$Å^{-3}$

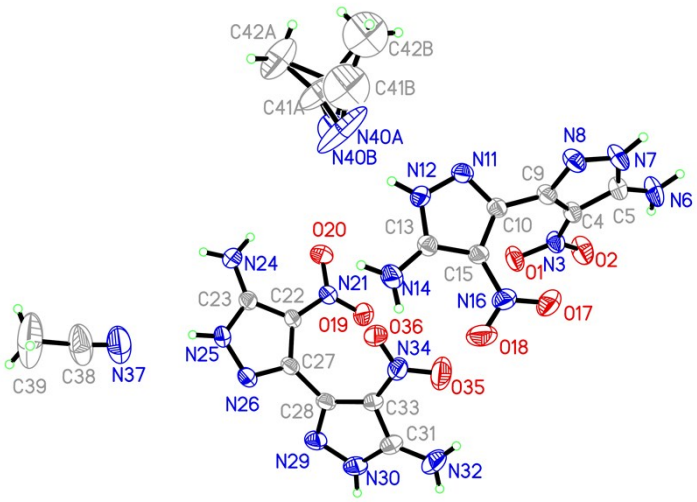


Fig. S3 The crystal structure of **7**·CH_3CN

Table S7. Bond lengths [Å] for **7**·CH_3CN.

O(1)-N(3)	1.240(2)	O(2)-N(3)	1.250(2)
N(3)-C(4)	1.376(2)	C(4)-C(5)	1.402(3)
C(4)-C(9)	1.420(3)	C(5)-N(6)	1.326(3)
C(5)-N(7)	1.344(3)	N(6)-H(6A)	0.8600
N(6)-H(6B)	0.8600	N(7)-N(8)	1.379(2)
N(7)-H(7)	0.8600	N(8)-C(9)	1.309(2)
C(9)-C(10)	1.466(3)	C(10)-N(11)	1.312(3)
C(10)-C(15)	1.421(3)	N(11)-N(12)	1.377(2)
N(12)-C(13)	1.338(3)	N(12)-H(12)	0.8600
C(13)-N(14)	1.325(2)	C(13)-C(15)	1.406(3)
N(14)-H(14A)	0.8600	N(14)-H(14B)	0.8600

C(15)-N(16)	1.383(3)	N(16)-O(17)	1.238(2)
N(16)-O(18)	1.245(2)	O(19)-N(21)	1.230(2)
O(20)-N(21)	1.240(2)	N(21)-C(22)	1.393(2)
C(22)-C(23)	1.408(3)	C(22)-C(27)	1.415(3)
C(23)-N(24)	1.329(3)	C(23)-N(25)	1.341(3)
N(24)-H(24A)	0.8600	N(24)-H(24B)	0.8600
N(25)-N(26)	1.373(2)	N(25)-H(25)	0.8600
N(26)-C(27)	1.318(2)	C(27)-C(28)	1.465(3)
C(28)-N(29)	1.319(2)	C(28)-C(33)	1.410(3)
N(29)-N(30)	1.379(3)	N(30)-C(31)	1.337(3)
N(30)-H(30)	0.8600	C(31)-N(32)	1.322(3)
C(31)-C(33)	1.405(3)	N(32)-H(32A)	0.8600
N(32)-H(32B)	0.8600	C(33)-N(34)	1.394(3)
N(34)-O(35)	1.228(3)	N(34)-O(36)	1.237(2)
N(37)-C(38)	1.119(4)	C(38)-C(39)	1.488(5)
C(39)-H(39A)	0.9600	C(39)-H(39B)	0.9600
C(39)-H(39C)	0.9600	N(40A)-C(41A)	1.171(5)
C(41A)-C(42A)	1.421(5)	C(42A)-H(42A)	0.9600
C(42A)-H(42B)	0.9600	C(42A)-H(42C)	0.9600
N(40B)-C(41B)	1.131(7)	C(41B)-C(42B)	1.449(7)
C(42B)-H(42D)	0.9600	C(42B)-H(42E)	0.9600
C(42B)-H(42F)	0.9600		

Table S8. Torsion angles [°] for **7**·CH_3CN.

O(1)-N(3)-C(4)-C(5)	-175.2(2)	O(2)-N(3)-C(4)-C(5)	3.8(3)
O(1)-N(3)-C(4)-C(9)	-2.0(3)	O(2)-N(3)-C(4)-C(9)	177.0(2)
N(3)-C(4)-C(5)-N(6)	-5.7(4)	C(9)-C(4)-C(5)-N(6)	179.8(2)
N(3)-C(4)-C(5)-N(7)	173.4(2)	C(9)-C(4)-C(5)-N(7)	-1.1(2)
N(6)-C(5)-N(7)-N(8)	-179.8(2)	C(4)-C(5)-N(7)-N(8)	0.9(3)
C(5)-N(7)-N(8)-C(9)	-0.4(3)	N(7)-N(8)-C(9)-C(4)	-0.3(2)
N(7)-N(8)-C(9)-C(10)	179.32(18)	N(3)-C(4)-C(9)-N(8)	-173.3(2)
C(5)-C(4)-C(9)-N(8)	0.9(3)	N(3)-C(4)-C(9)-C(10)	7.1(4)
C(5)-C(4)-C(9)-C(10)	-178.7(2)	N(8)-C(9)-C(10)-N(11)	60.1(3)
C(4)-C(9)-C(10)-N(11)	-120.4(2)	N(8)-C(9)-C(10)-C(15)	-114.8(2)
C(4)-C(9)-C(10)-C(15)	64.7(3)	C(15)-C(10)-N(11)-N(12)	-0.7(2)
C(9)-C(10)-N(11)-N(12)	-176.52(16)	C(10)-N(11)-N(12)-C(13)	0.7(2)
N(11)-N(12)-C(13)-N(14)	-179.82(18)	N(11)-N(12)-C(13)-C(15)	-0.3(2)
N(14)-C(13)-C(15)-N(16)	-6.6(3)	N(12)-C(13)-C(15)-N(16)	173.97(19)
N(14)-C(13)-C(15)-C(10)	179.3(2)	N(12)-C(13)-C(15)-C(10)	-0.1(2)
N(11)-C(10)-C(15)-N(16)	-173.21(19)	C(9)-C(10)-C(15)-N(16)	2.0(3)
N(11)-C(10)-C(15)-C(13)	0.5(2)	C(9)-C(10)-C(15)-C(13)	175.79(18)
C(13)-C(15)-N(16)-O(17)	-179.5(2)	C(10)-C(15)-N(16)-O(17)	-6.8(3)
C(13)-C(15)-N(16)-O(18)	-0.9(3)	C(10)-C(15)-N(16)-O(18)	171.7(2)

O(19)-N(21)-C(22)-C(23)	-173.1(2)	O(20)-N(21)-C(22)-C(23)	5.9(3)
O(19)-N(21)-C(22)-C(27)	-1.3(3)	O(20)-N(21)-C(22)-C(27)	177.7(2)
N(21)-C(22)-C(23)-N(24)	-8.9(3)	C(27)-C(22)-C(23)-N(24)	177.8(2)
N(21)-C(22)-C(23)-N(25)	172.46(18)	C(27)-C(22)-C(23)-N(25)	-0.9(2)
N(24)-C(23)-N(25)-N(26)	-178.26(18)	C(22)-C(23)-N(25)-N(26)	0.5(2)
C(23)-N(25)-N(26)-C(27)	0.1(2)	N(25)-N(26)-C(27)-C(22)	-0.7(2)
N(25)-N(26)-C(27)-C(28)	-179.32(17)	N(21)-C(22)-C(27)-N(26)	-171.9(2)
C(23)-C(22)-C(27)-N(26)	1.0(2)	N(21)-C(22)-C(27)-C(28)	6.6(4)
C(23)-C(22)-C(27)-C(28)	179.5(2)	N(26)-C(27)-C(28)-N(29)	46.7(3)
C(22)-C(27)-C(28)-N(29)	-131.7(2)	N(26)-C(27)-C(28)-C(33)	-135.6(2)
C(22)-C(27)-C(28)-C(33)	46.1(4)	C(33)-C(28)-N(29)-N(30)	0.9(2)
C(27)-C(28)-N(29)-N(30)	179.07(18)	C(28)-N(29)-N(30)-C(31)	-2.2(3)
N(29)-N(30)-C(31)-N(32)	-178.6(3)	N(29)-N(30)-C(31)-C(33)	2.5(3)
N(32)-C(31)-C(33)-N(34)	-6.8(5)	N(30)-C(31)-C(33)-N(34)	172.1(2)
N(32)-C(31)-C(33)-C(28)	179.3(3)	N(30)-C(31)-C(33)-C(28)	-1.8(3)
N(29)-C(28)-C(33)-N(34)	-173.0(2)	C(27)-C(28)-C(33)-N(34)	9.1(4)
N(29)-C(28)-C(33)-C(31)	0.6(3)	C(27)-C(28)-C(33)-C(31)	-177.3(2)
C(31)-C(33)-N(34)-O(35)	14.2(4)	C(28)-C(33)-N(34)-O(35)	-173.4(3)
C(31)-C(33)-N(34)-O(36)	-165.5(2)	C(28)-C(33)-N(34)-O(36)	7.0(4)

Table S9. Hydrogen bonds for **7**·CH_3CN.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...N(26)#1	0.86	2.28	3.018(2)	143.8
N(6)-H(6B)...O(2)	0.86	2.27	2.796(2)	119.6
N(7)-H(7)...N(29)#1	0.86	2.11	2.964(2)	169.0
N(12)-H(12)...N(40A)	0.86	1.94	2.761(5)	159.9
N(12)-H(12)...N(40B)	0.86	2.09	2.93(2)	165.8
N(14)-H(14A)...O(36)#3	0.86	2.30	3.054(2)	147.2
N(14)-H(14B)...O(18)	0.86	2.27	2.795(3)	119.3
N(14)-H(14B)...O(20)#4	0.86	2.20	2.806(2)	127.7
N(24)-H(24A)...O(1)#5	0.86	2.15	2.972(2)	159.1
N(24)-H(24B)...O(20)	0.86	2.25	2.779(2)	119.7
N(24)-H(24B)...O(36)#5	0.86	2.39	3.176(2)	152.0
N(25)-H(25)...N(37)	0.86	2.10	2.950(3)	168.1
N(30)-H(30)...O(2)#6	0.86	2.30	2.927(2)	130.1
N(32)-H(32A)...O(18)#7	0.86	2.10	2.909(3)	156.5
N(32)-H(32B)...O(35)	0.86	2.27	2.804(3)	120.2

Symmetry transformations used to generate equivalent atoms:

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

#3 -x+1,-y+1,-z+1 #4 x+1,y,z #5 -x,-y+1,-z+1

#6 -x,-y+1,-z #7 -x+1,-y+1,-z #8 x,y,z+1

Table S10. Crystal data and structure refinement for **9**·2CH_3OH·CH_3NO_2.

Identification code	**9**·2CH_3OH·CH_3NO_2
Empirical formula	$C_{13}H_{15}N_{15}O_{12}$
CCDC number	1848975
Formula weight	573.40
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 8.8353(2) Å, α = 90°
	b = 18.9345(4) Å, β = 90.0620(10)°
	c = 13.7810(3) Å, γ = 90°
Volume	2305.45(9) $Å^3$
Z	4
Density (20°C)	1.652 Mg/m^3
Absorption coefficient	1.288 mm^{-1}
F(000)	1176
Crystal size	0.384 × 0.263 × 0.094 mm^3
Theta range for data collection	4.671 to 74.578°.
Index ranges	-10<=h<=10, -23<=k<=21, -13<=l<=17
Reflections collected	7494
Independent reflections	3343 [R_{int} = 0.0257]
Completeness to theta = 67.679°	96.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.6610
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3343 / 25 / 371
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R_1 = 0.0372, wR_2 = 0.1006
R indices (all data)	R_1 = 0.0397, wR_2 = 0.1032
Absolute structure parameter	0.00(12)
Extinction coefficient	0.00162(19)
Largest diff. peak and hole	0.356 and -0.233 $e.Å^{-3}$

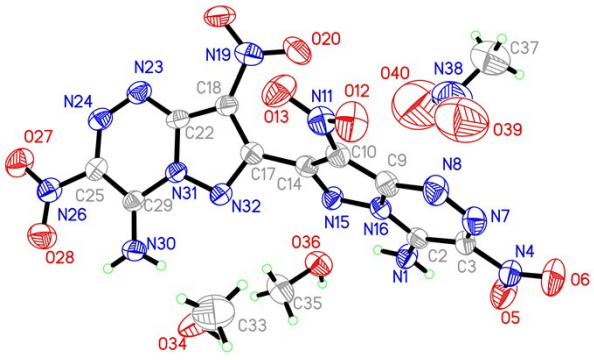


Fig. S4 The crystal structure of **9**·2CH_3OH·CH_3NO_2

Table S11. Bond lengths [Å] for **9**·2CH_3OH·CH_3NO_2.

N(1)-C(2)	1.303(5)	N(1)-H(1A)	0.8600
N(1)-H(1B)	0.8600	C(2)-N(16)	1.356(5)
C(2)-C(3)	1.413(5)	C(3)-N(7)	1.325(5)
C(3)-N(4)	1.457(5)	N(4)-O(6)	1.206(4)
N(4)-O(5)	1.223(5)	N(7)-N(8)	1.316(5)
N(8)-C(9)	1.361(5)	C(9)-N(16)	1.376(4)
C(9)-C(10)	1.386(5)	C(10)-C(14)	1.416(5)
C(10)-N(11)	1.420(5)	N(11)-O(12)	1.220(4)
N(11)-O(13)	1.226(4)	C(14)-N(15)	1.331(5)
C(14)-C(17)	1.463(5)	N(15)-N(16)	1.368(4)
C(17)-N(32)	1.328(5)	C(17)-C(18)	1.411(5)
C(18)-C(22)	1.385(5)	C(18)-N(19)	1.429(5)
N(19)-O(20)	1.223(5)	N(19)-O(21)	1.224(5)
C(22)-N(23)	1.364(5)	C(22)-N(31)	1.368(5)
N(23)-N(24)	1.309(5)	N(24)-C(25)	1.323(5)
C(25)-C(29)	1.415(5)	C(25)-N(26)	1.442(5)
N(26)-O(27)	1.225(4)	N(26)-O(28)	1.236(5)
C(29)-N(30)	1.288(5)	C(29)-N(31)	1.368(5)
N(30)-H(30A)	0.8600	N(30)-H(30B)	0.8600
N(31)-N(32)	1.364(4)	C(33)-O(34)	1.356(7)
C(33)-H(33A)	0.9600	C(33)-H(33B)	0.9600
C(33)-H(33C)	0.9600	O(34)-H(34)	0.829(13)
C(35)-O(36)	1.416(6)	C(35)-H(35A)	0.9600
C(35)-H(35B)	0.9600	C(35)-H(35C)	0.9600
O(36)-H(36)	0.818(13)	C(37)-N(38)	1.446(8)
C(37)-H(37A)	0.9600	C(37)-H(37B)	0.9600
C(37)-H(37C)	0.9600	N(38)-O(40)	1.194(5)
N(38)-O(39)	1.209(5)		

Table S12. Torsion angles [°] for **9**·2CH_3OH·CH_3NO_2.

N(1)-C(2)-C(3)-N(7)	-179.8(4)	N(16)-C(2)-C(3)-N(7)	0.5(5)
N(1)-C(2)-C(3)-N(4)	-0.2(6)	N(16)-C(2)-C(3)-N(4)	-180.0(3)
N(7)-C(3)-N(4)-O(6)	-0.8(6)	C(2)-C(3)-N(4)-O(6)	179.6(4)
N(7)-C(3)-N(4)-O(5)	-179.8(4)	C(2)-C(3)-N(4)-O(5)	0.6(6)
C(2)-C(3)-N(7)-N(8)	-0.6(6)	N(4)-C(3)-N(7)-N(8)	179.8(3)
C(3)-N(7)-N(8)-C(9)	-0.2(6)	N(7)-N(8)-C(9)-N(16)	1.1(6)
N(7)-N(8)-C(9)-C(10)	-178.4(4)	N(8)-C(9)-C(10)-C(14)	-179.7(4)
N(16)-C(9)-C(10)-C(14)	0.8(4)	N(8)-C(9)-C(10)-N(11)	-1.5(7)
N(16)-C(9)-C(10)-N(11)	178.9(4)	C(9)-C(10)-N(11)-O(12)	-10.5(6)
C(14)-C(10)-N(11)-O(12)	167.3(4)	C(9)-C(10)-N(11)-O(13)	169.7(4)
C(14)-C(10)-N(11)-O(13)	-12.5(6)	C(9)-C(10)-C(14)-N(15)	-0.1(4)
N(11)-C(10)-C(14)-N(15)	-178.3(4)	C(9)-C(10)-C(14)-C(17)	172.5(4)

N(11)-C(10)-C(14)-C(17)	-5.7(7)	C(10)-C(14)-N(15)-N(16)	-0.5(4)
C(17)-C(14)-N(15)-N(16)	-174.4(3)	N(1)-C(2)-N(16)-N(15)	0.2(5)
C(3)-C(2)-N(16)-N(15)	180.0(3)	N(1)-C(2)-N(16)-C(9)	-179.4(3)
C(3)-C(2)-N(16)-C(9)	0.4(5)	C(14)-N(15)-N(16)-C(2)	-178.5(3)
C(14)-N(15)-N(16)-C(9)	1.1(4)	N(8)-C(9)-N(16)-C(2)	-1.2(6)
C(10)-C(9)-N(16)-C(2)	178.4(3)	N(8)-C(9)-N(16)-N(15)	179.2(3)
C(10)-C(9)-N(16)-N(15)	-1.2(4)	N(15)-C(14)-C(17)-N(32)	55.1(4)
C(10)-C(14)-C(17)-N(32)	-117.2(4)	N(15)-C(14)-C(17)-C(18)	-120.8(4)
C(10)-C(14)-C(17)-C(18)	66.9(6)	N(32)-C(17)-C(18)-C(22)	-1.6(4)
C(14)-C(17)-C(18)-C(22)	174.4(3)	N(32)-C(17)-C(18)-N(19)	-175.9(3)
C(14)-C(17)-C(18)-N(19)	0.1(6)	C(22)-C(18)-N(19)-O(20)	-161.3(4)
C(17)-C(18)-N(19)-O(20)	11.9(5)	C(22)-C(18)-N(19)-O(21)	17.6(5)
C(17)-C(18)-N(19)-O(21)	-169.3(3)	C(17)-C(18)-C(22)-N(23)	-174.6(4)
N(19)-C(18)-C(22)-N(23)	-0.3(6)	C(17)-C(18)-C(22)-N(31)	1.8(3)
N(19)-C(18)-C(22)-N(31)	176.1(3)	N(31)-C(22)-N(23)-N(24)	2.6(5)
C(18)-C(22)-N(23)-N(24)	178.5(4)	C(22)-N(23)-N(24)-C(25)	3.0(5)
N(23)-N(24)-C(25)-C(29)	-4.3(5)	N(23)-N(24)-C(25)-N(26)	175.2(3)
N(24)-C(25)-N(26)-O(27)	2.0(5)	C(29)-C(25)-N(26)-O(27)	-178.5(3)
N(24)-C(25)-N(26)-O(28)	-176.4(3)	C(29)-C(25)-N(26)-O(28)	3.1(5)
N(24)-C(25)-C(29)-N(30)	-179.8(4)	N(26)-C(25)-C(29)-N(30)	0.7(6)
N(24)-C(25)-C(29)-N(31)	-0.3(5)	N(26)-C(25)-C(29)-N(31)	-179.7(3)
N(23)-C(22)-N(31)-N(32)	175.5(3)	C(18)-C(22)-N(31)-N(32)	-1.5(4)
N(23)-C(22)-N(31)-C(29)	-7.6(5)	C(18)-C(22)-N(31)-C(29)	175.4(3)
N(30)-C(29)-N(31)-N(32)	2.3(5)	C(25)-C(29)-N(31)-N(32)	-177.3(3)
N(30)-C(29)-N(31)-C(22)	-174.4(3)	C(25)-C(29)-N(31)-C(22)	6.0(4)
C(18)-C(17)-N(32)-N(31)	0.7(4)	C(14)-C(17)-N(32)-N(31)	-176.0(3)
C(22)-N(31)-N(32)-C(17)	0.5(3)	C(29)-N(31)-N(32)-C(17)	-176.5(3)

Table S13. Hydrogen bonds for **9**·2CH_3OH·CH_3NO_2.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...O(36)	0.86	2.03	2.835(4)	156.3
N(1)-H(1B)...O(5)	0.86	2.10	2.672(4)	123.0
N(30)-H(30A)...O(34)	0.86	1.92	2.725(5)	154.7
N(30)-H(30B)...O(28)	0.86	2.10	2.667(5)	123.0
N(30)-H(30B)...O(36)#2	0.86	2.31	2.951(5)	130.9
O(34)-H(34)...N(23)#4	0.829(13)	2.08(3)	2.873(5)	160(9)
O(36)-H(36)...O(12)#5	0.818(13)	2.37(3)	3.145(5)	158(6)

Symmetry transformations used to generate equivalent atoms:

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

#4 x+1,y,z #5 x+1/2,y+1/2,z

NMR spectra

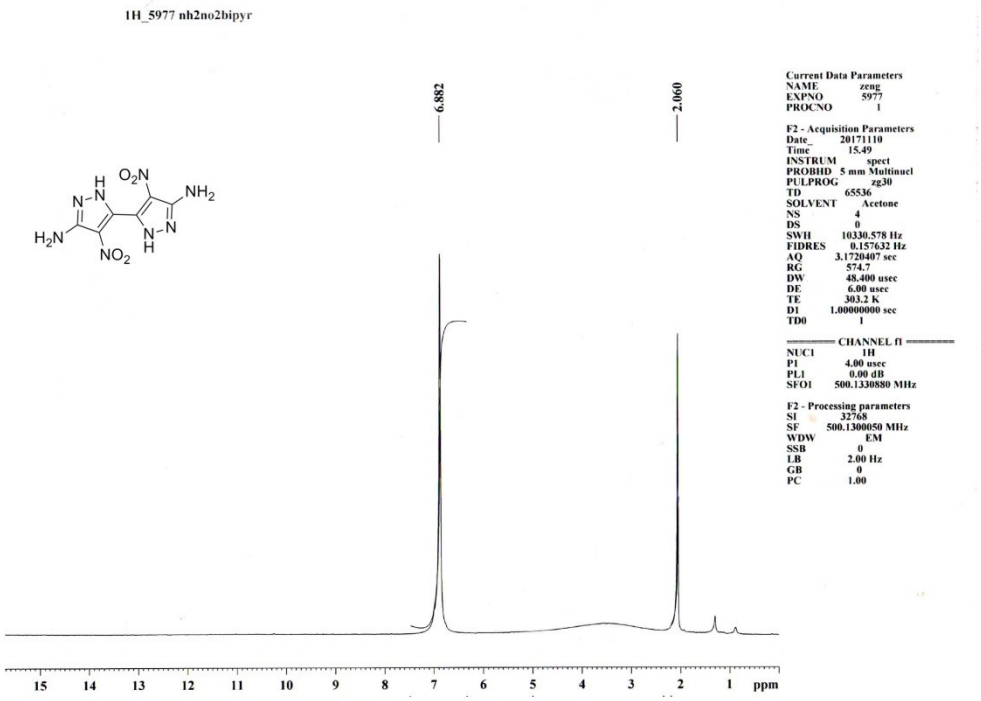


Fig. S5 ^{1}H NMR spectrum of **7**

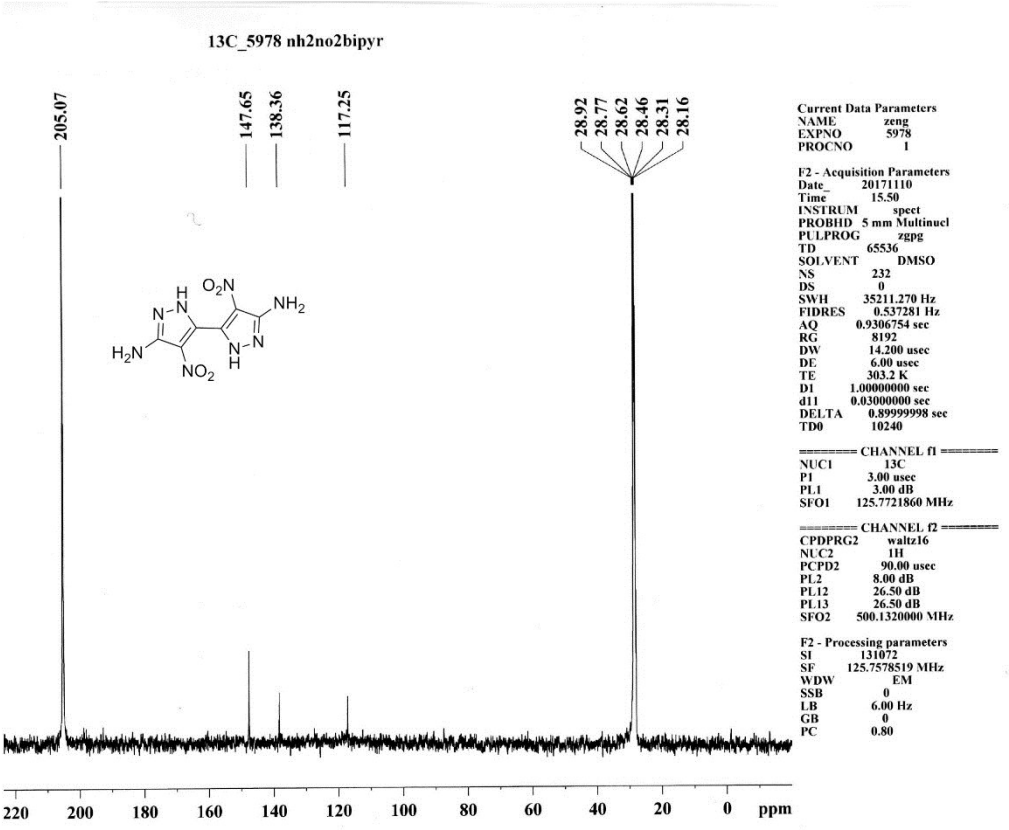


Fig. S6 ^{13}C NMR spectrum of **7**

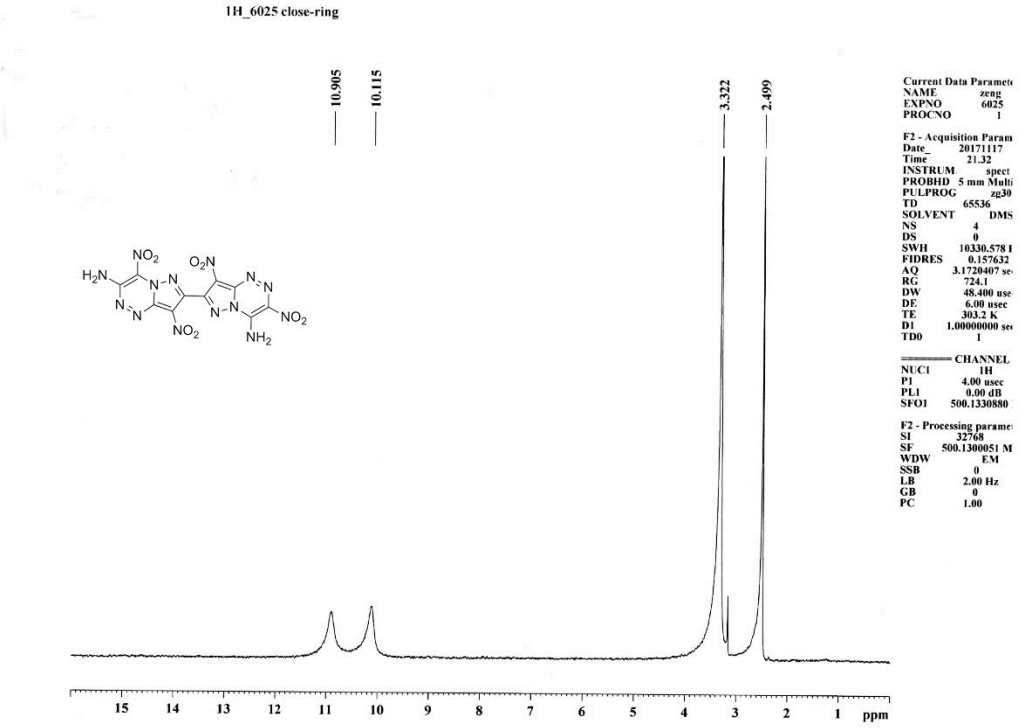


Fig. S7 ^{1}H NMR spectrum of **9**

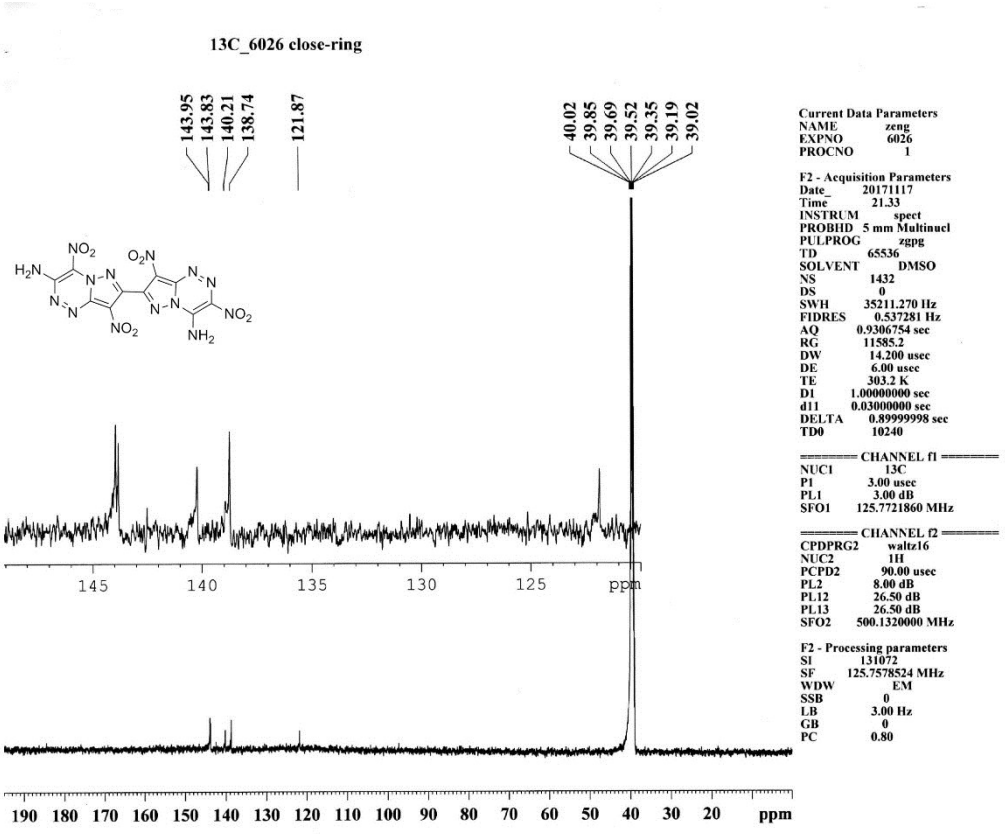


Fig. S8 ^{13}C NMR spectrum of **9**

References:

1 M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, *J. Am. Chem. Soc.* 1995, **117**, 5013.

2 Bruker, *APEX3 v2015.5-2*. Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

3 Bruker, *SAINT v8.34A*. Bruker AXS Inc., Madison, Wisconsin, USA, 2013.

4 Bruker, *XPREP v2014/2*. Bruker AXS Inc., Madison, Wisconsin, USA, 2014.

5 Bruker, *SADABS v2014/5*, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.

6 Sheldrick, G. M. *SHELXL-2014/7*, University of Göttingen, Germany, 2014.

7. Gaussian 03 (Revision E.01): M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Rabuck, K. Raghavachari, J. B. Foesman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, A. Lo. G. Liu, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc, Wallingford CT, 2004.