Electronic Supporting Information

Ring Closure of Polynitroazoles via an N,N'-Alkylene Bridge: Towards High Thermally Stable Energetic Compounds

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1 Crystal Structure Data

Table S1. Crystal data and structure refinement for **2**.

Identification code	**2**	
Empirical formula	$C_9H_{5.5}N_{8.5}O_8$	
CCDC number	1818128	
Formula weight	360.72	
Temperature	293(2) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	$P3_221$	
Unit cell dimensions	a = 8.443(2) Å	α = 90.00(3)°.
	b = 8.443(2) Å	β = 90.00(3)°.
	c = 33.962(7) Å	γ = 120.00(3)°.
Volume	2096.8(11) $Å^3$	
Z	6	
Density (20°C)	1.714 Mg/m^3	
Absorption coefficient	1.349 mm^{-1}	
F(000)	1098	
Crystal size	0.124 × 0.120 × 0.026 mm^3	
Theta range for data collection	3.905 to 68.302°.	
Index ranges	-10<=h<=8, -9<=k<=9, -40<=l<=38	
Reflections collected	11485	
Independent reflections	2529 [R_{int} = 0.0375]	
Completeness to theta = 67.684°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7531 and 0.6711	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2529 / 8 / 242	
Goodness-of-fit on F^2	1.114	
Final R indices [I>2sigma(I)]	R_1 = 0.0404, wR_2 = 0.0805	
R indices (all data)	R_1 = 0.0502, wR_2 = 0.0853	
Absolute structure parameter	-0.03(14)	
Extinction coefficient	0.0024(2)	
Largest diff. peak and hole	0.191 and -0.148 e.$Å^{-3}$	

Table S2. Crystal data and structure refinement for **3**.

Identification code	**3**	
CCDC number	1818129	
Empirical formula	$C_9H_6N_8O_8$	
Formula weight	354.22	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.4365(10) Å	α = 90°.
	b = 11.5612(12) Å	β = 92.305(3)°.
	c = 12.9442(14) Å	γ = 90°.
Volume	1411.0(3) $Å^3$	
Z	4	
Density (20°C)	1.667 Mg/m^3	
Absorption coefficient	0.149 mm^{-1}	
F(000)	720	
Crystal size	0.231 × 0.180 × 0.020 mm^3	
Theta range for data collection	2.622 to 25.348°.	
Index ranges	-11<=h<=11, -13<=k<=13, -15<=l<=15	
Reflections collected	11903	
Independent reflections	2574 [R_{int} = 0.0370]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.6766	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2574 / 56 / 254	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R_1 = 0.0481, wR_2 = 0.1149	
R indices (all data)	R_1 = 0.0789, wR_2 = 0.1321	
Largest diff. peak and hole	0.336 and -0.293 $e.Å^{-3}$	

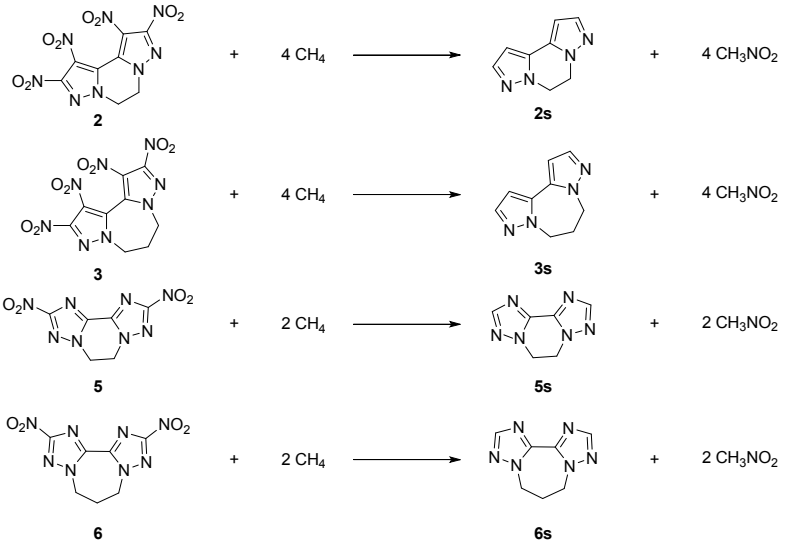
Table S3. Crystal data and structure refinement for **5**.

Identification code	**5**
CCDC number	1818130
Empirical formula	$C_6H_4N_8O_4$
Formula weight	252.17
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 12.326(5) Å, α = 90°. b = 6.678(3) Å, β = 104.517(11)°. c = 12.126(5) Å, γ = 90°.
Volume	966.3(6) $Å^3$
Z	4
Density (20°C)	1.733 Mg/m^3
Absorption coefficient	0.148 mm^{-1}
F(000)	512
Crystal size	0.260 × 0.159 × 0.033 mm^3
Theta range for data collection	3.415 to 29.977°.
Index ranges	-17<=h<=17, -9<=k<=9, -14<=l<=16
Reflections collected	5479
Independent reflections	1376 [R_{int} = 0.0256]
Completeness to theta = 25.242°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.6432
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1376 / 1 / 92
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R_1 = 0.0456, wR_2 = 0.1289
R indices (all data)	R_1 = 0.0753, wR_2 = 0.1485
Largest diff. peak and hole	0.214 and -0.159 $e.Å^{-3}$

Table S4. Crystal data and structure refinement for **6**.

Identification code	**6**
CCDC number	1818132
Empirical formula	$C_7H_6N_8O_4$
Formula weight	266.20
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.6012(4) Å, α = 90°. b = 11.5875(5) Å, β = 96.837(2)°. c = 9.7940(4) Å, γ = 90°.
Volume	1081.87(8) $Å^3$
Z	4
Density (20°C)	1.634 Mg/m^3
Absorption coefficient	0.137 mm^{-1}
F(000)	544
Crystal size	0.249 × 0.143 × 0.041 mm^3
Theta range for data collection	2.767 to 30.213°.
Index ranges	-12<=h<=13, -14<=k<=15, -13<=l<=13
Reflections collected	12676
Independent reflections	3091 [R_{int} = 0.0309]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.6894
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3091 / 0 / 172
Goodness-of-fit on F^2	1.012
Final R indices [I>2sigma(I)]	R_1 = 0.0426, wR_2 = 0.1049
R indices (all data)	R_1 = 0.0722, wR_2 = 0.1211
Largest diff. peak and hole	0.187 and -0.218 $e.Å^{-3}$

2 Theoretical Calculations



Scheme S1. Isodesmic reactions

Table S7. 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})
2	0.167943	0.187959	-1343.66435	-1343.48311	421.70
3	0.19687	0.218173	-1382.866683	-1382.65639	383.72
5	0.140036	0.1543	-967.5448133	-967.39611	453.77
6	0.168843	0.18438	-1006.745416	-1006.56779	419.60
2s	0.159147	0.168374	-527.2866574	-527.12465	389.9 [a]
3s	0.187929	0.198403	-566.4817731	-566.29089	370.4 [a]
5s	0.136234	0.145108	-559.360645	-559.22099	427.1 [a]
6s	0.165034	0.175136	-598.5588092	-598.39027	399.2 [a]
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.].

3 ^{1}H-^{15}N HMBC **NMR Spectra**

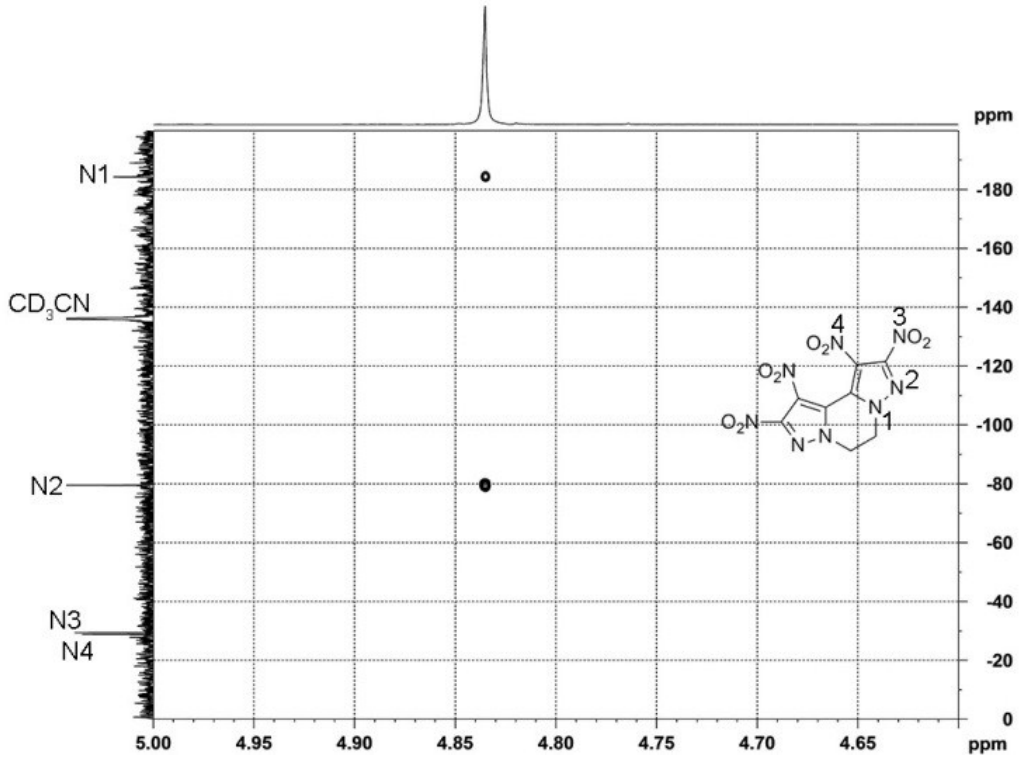


Figure S1. ^{1}H-^{15}N HMBC spectrum of **2**

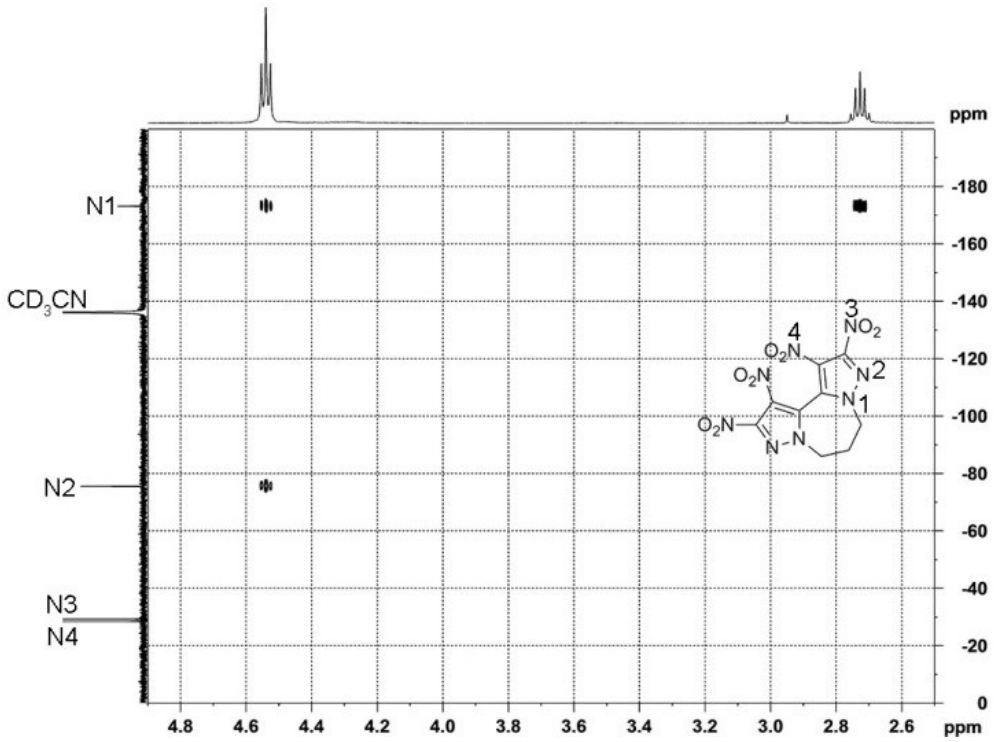


Figure S2. ^{1}H-^{15}N HMBC spectrum of **3**

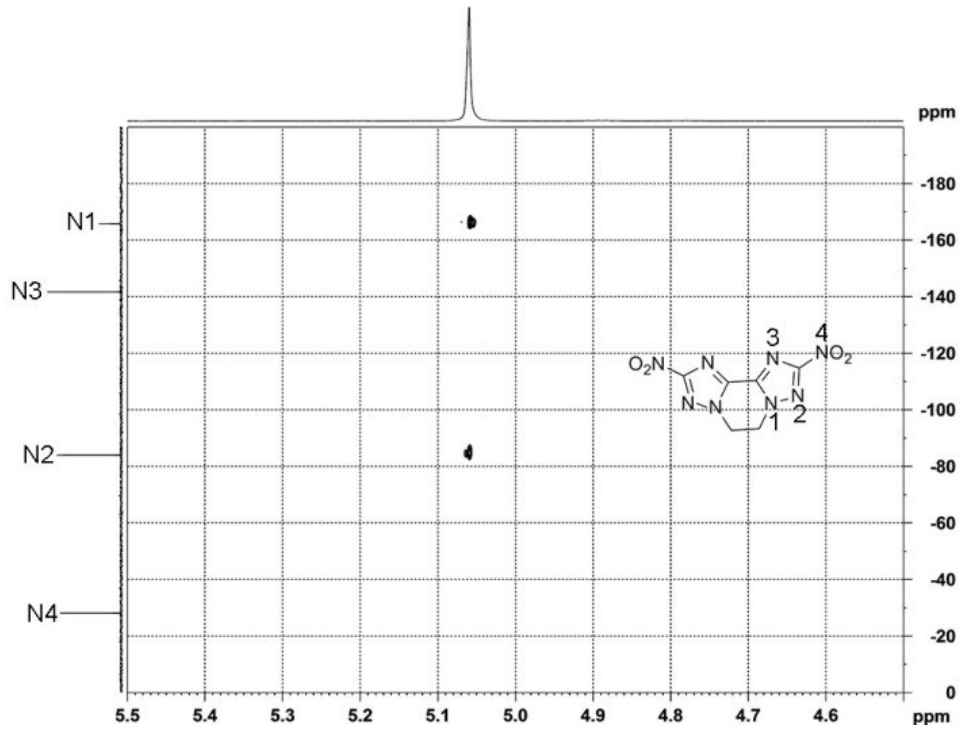


Figure S3. ^{1}H-^{15}N HMBC spectrum of **5**

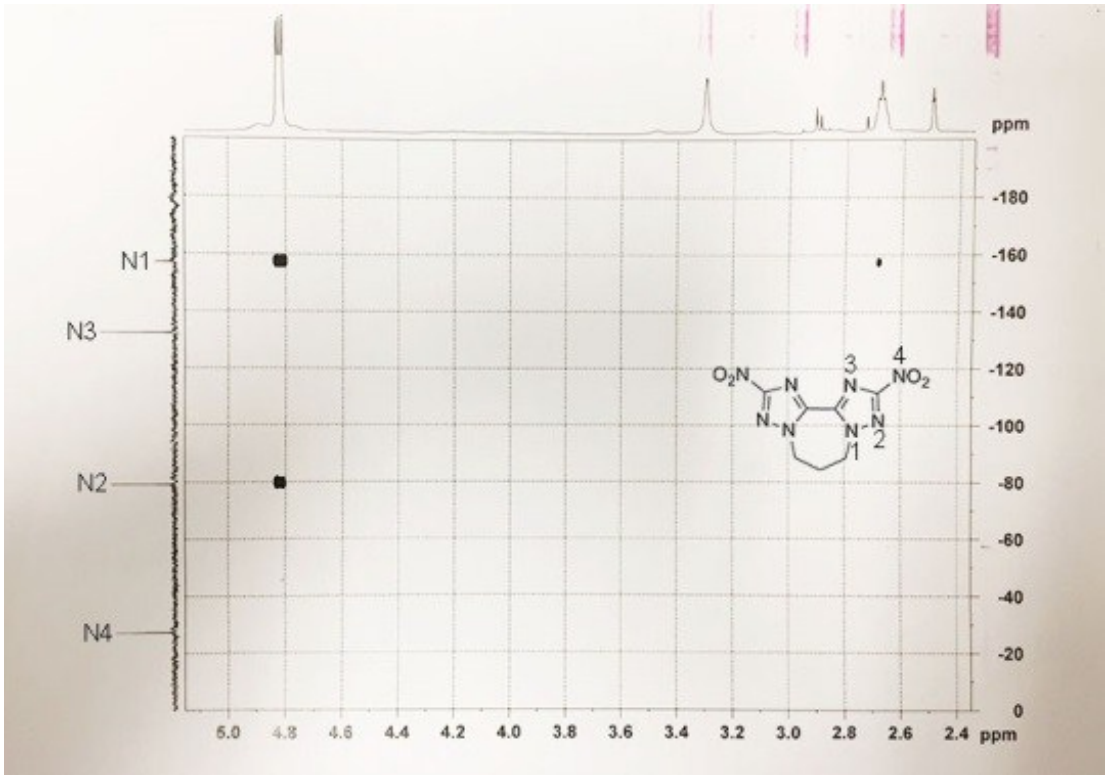


Figure S4. ^{1}H-^{15}N HMBC spectrum of **6**