Electronic Supplementary Information

Energetic derivatives of 4,4',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole (TNBP): synthesis, characterization and promising properties

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1 Crystal Structure Data

Table S1. Crystal data and structure refinement for **3**.

Identification code	**3**
CCDC number	1811781
Empirical formula	$C_7HN_{11}O_{14}$
Formula weight	463.19
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 17.130(3) Å, α = 90° b = 6.8390(11) Å, β = 93.850(6)° c = 27.832(5) Å, γ = 90°
Volume	3253.1(9) $Å^3$
Z	8
Density (20°C)	1.891 Mg/m^3
Absorption coefficient	1.670 mm^{-1}
F(000)	1856
Crystal size	0.247 × 0.086 × 0.020 mm^3
Theta range for data collection	3.183 to 68.233°.
Index ranges	-16<=h<=20, -7<=k<=8, -28<=l<=33
Reflections collected	8864
Independent reflections	2818 [R_{int} = 0.0325]
Completeness to theta = 67.679°	94.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.6057
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2818 / 6 / 309
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R_1 = 0.0514, wR_2 = 0.1283
R indices (all data)	R_1 = 0.0590, wR_2 = 0.1321
Extinction coefficient	0.0070(3)
Largest diff. peak and hole	0.318 and -0.345 e.$Å^{-3}$

Table S2. Crystal data and structure refinement for **5**

Identification code	**5**
CCDC number	1811782
Empirical formula	$C_6H_3KN_8O_9$
Formula weight	370.26
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 7.3543(3) Å, α = 105.6180(10)° b = 9.0468(3) Å, β = 94.5290(10)° c = 10.7236(4) Å, γ = 108.8990(10)°
Volume	639.18(4) $Å^3$
Z	2
Density (20°C)	1.924 Mg/m^3
Absorption coefficient	0.491 mm^{-1}
F(000)	372
Crystal size	0.231 × 0.198 × 0.080 mm^3
Theta range for data collection	3.273 to 30.000°.
Index ranges	-10<=h<=9, -12<=k<=12, -14<=l<=15
Reflections collected	9186
Independent reflections	3519 [R_{int} = 0.0183]
Completeness to theta = 25.242°	99.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.6963
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3519 / 3 / 223
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R_1 = 0.0338, wR_2 = 0.0814
R indices (all data)	R_1 = 0.0454, wR_2 = 0.0885
Largest diff. peak and hole	0.307 and -0.270 $e.Å^{-3}$

Table S3. Crystal data and structure refinement for **8**.

Identification code	**8**
CCDC number	1811783
Empirical formula	$C_6H_{12}N_{12}O_9$
Formula weight	396.28
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 24.534(7) Å, α = 90° b = 3.7499(9) Å, β = 122.434(6)° c = 18.811(5) Å, γ = 90°
Volume	1460.7(7) $Å^3$
Z	4
Density (20°C)	1.802 Mg/m^3
Absorption coefficient	0.165 mm^{-1}
F(000)	816
Crystal size	0.062 × 0.023 × 0.020 mm^3
Theta range for data collection	3.936 to 28.314°.
Index ranges	-32<=h<=32, -4<=k<=4, -25<=l<=20
Reflections collected	6763
Independent reflections	1784 [R_{int} = 0.0764]
Completeness to theta = 25.242°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.4858
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1784 / 38 / 183
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R_1 = 0.0665, wR_2 = 0.1527
R indices (all data)	R_1 = 0.1332, wR_2 = 0.1835
Largest diff. peak and hole	0.393 and -0.350 $e.Å^{-3}$

Table S4. Crystal data and structure refinement for **10**.

Identification code	**10**
CCDC number	1811784
Empirical formula	$C_8H_{14}N_{16}O_8$
Formula weight	462.35
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2/n
Unit cell dimensions	a = 6.7723(10) Å, α = 90° b = 10.2479(15) Å, β = 103.860(5)° c = 13.471(2) Å, γ = 90°
Volume	907.7(2) $Å^3$
Z	2
Density (20°C)	1.692 Mg/m^3
Absorption coefficient	0.149 mm^{-1}
F(000)	476
Crystal size	0.198 × 0.185 × 0.030 mm^3
Theta range for data collection	3.115 to 30.010°.
Index ranges	-8<=h<=9, -14<=k<=14, -18<=l<=18
Reflections collected	10605
Independent reflections	2582 [R_{int} = 0.0322]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7460 and 0.7035
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2582 / 3 / 151
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R_1 = 0.0413, wR_2 = 0.1110
R indices (all data)	R_1 = 0.0702, wR_2 = 0.1273
Largest diff. peak and hole	0.273 and -0.250 $e.Å^{-3}$

Table S5. Hydrogen bonds for **3** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(31)-H(31)...O(29)#1	0.86	2.15	2.905(3)	146.7

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

Table S6. Hydrogen bonds for **5** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(22)-H(22)...N(10)#1	0.86	2.04	2.8154(16)	150.2
O(24)-H(24A)...O(20)#2	0.811(10)	2.345(15)	3.0661(17)	149(2)

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

Table S7. Hydrogen bonds for **8** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(12)-H(12A)...O(8A)	0.89	2.16	2.794(4)	127.5
N(12)-H(12A)...N(10A)#1	0.89	2.19	2.928(4)	139.8
N(12)-H(12B)...O(14)	0.89	1.95	2.802(4)	158.9
N(13A)-H(13A)...O(7A)#3	0.910(10)	2.25(3)	3.007(5)	140(4)
N(12B)-H(12E)...O(7B)#4	0.89	1.87	2.58(5)	135.6
N(13B)-H(13C)...N(10B)#2	0.908(11)	2.16(4)	3.05(3)	163(4)
N(13B)-H(13D)...O(1B)#5	0.908(10)	2.18(7)	2.93(5)	140(6)
N(13B)-H(13D)...O(14)	0.908(10)	2.30(5)	2.90(2)	123(5)
O(14)-H(14)...N(11A)#1	0.829(10)	2.034(17)	2.801(3)	154(3)

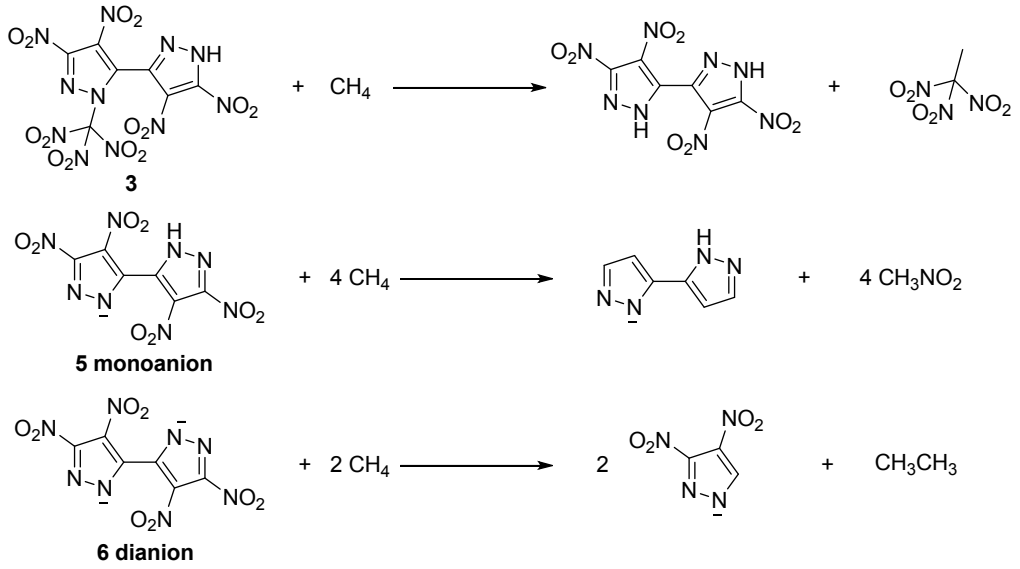
Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,-y+1/2,-z+1 #2 -x+3/2,-y+3/2,-z+1
#3 -x+3/2,y+1/2,-z+1/2 #4 -x+3/2,y-1/2,-z+1/2
#5 x-1/2,-y+1/2,z-1/2

Table S8. Hydrogen bonds for **10** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(13)-H(13)...N(9)#1	0.86	2.19	2.9814(17)	152.9
N(16)-H(16B)...O(7)	0.86	2.34	3.0938(18)	146.4
N(16)-H(16B)...O(1)	0.86	2.38	3.1019(19)	141.6
N(15)-H(15B)...O(1)	0.86	2.17	2.9432(18)	149.3
N(12)-H(12A)...N(10)#2	0.905(9)	2.387(14)	3.1795(19)	146.3(18)
N(12)-H(12B)...O(7)#3	0.905(9)	2.450(18)	3.1357(19)	132.8(18)

Symmetry transformations used to generate equivalent atoms:
#2 x,y-1,z #5 -x+1/2,y-1,-z+1/2
#6 -x,-y+1,-z+1

2 Theoretical Calculation



Scheme S1. Isodesmic reactions

3 NMR Spectra

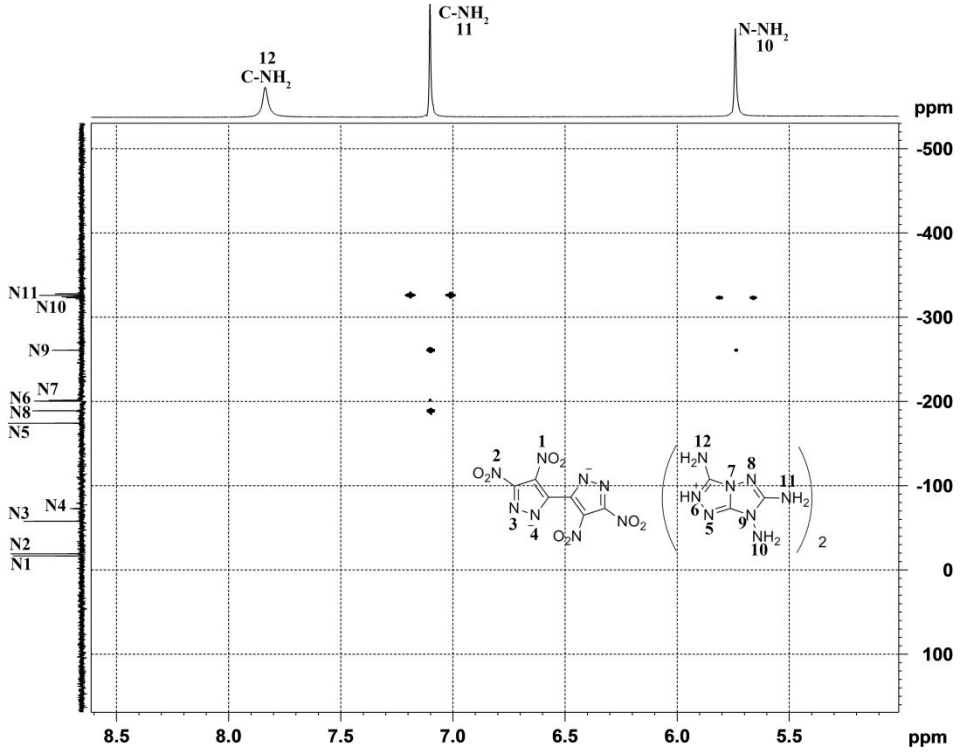


Figure S1. ^{1}H-^{15}N HMBC spectrum of **14**

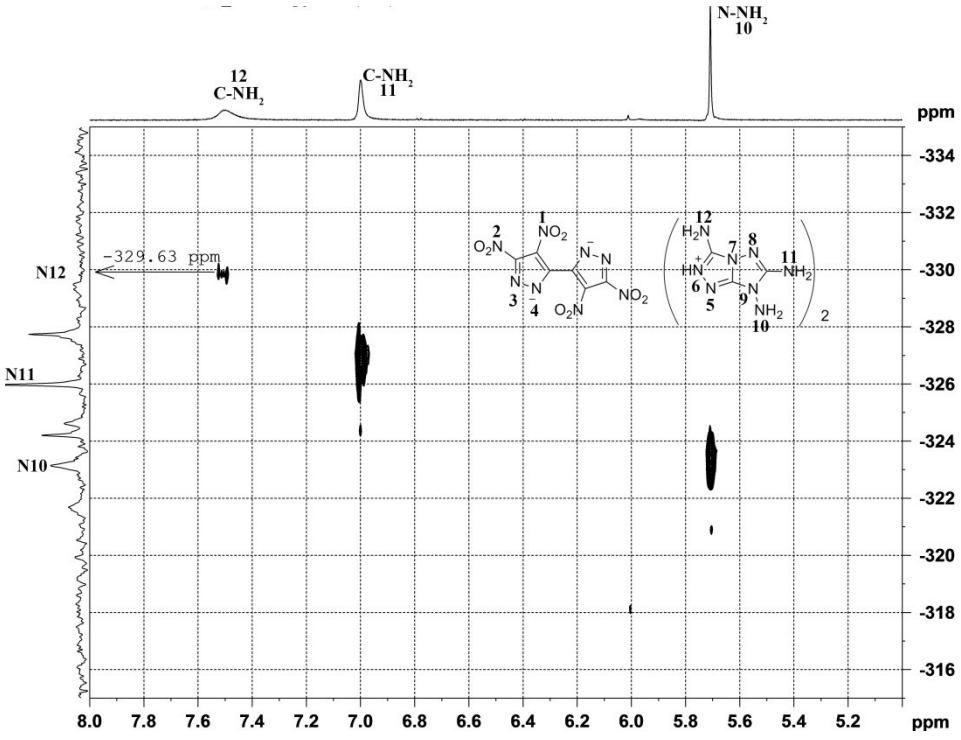


Figure S2. ^{1}H-^{15}N HSQC spectrum of **14**