Electronic Supplementary Information

Versatile Functionalization of 3,5-Diamino-4-nitropyrazole for Promising Insensitive Energetic Compounds

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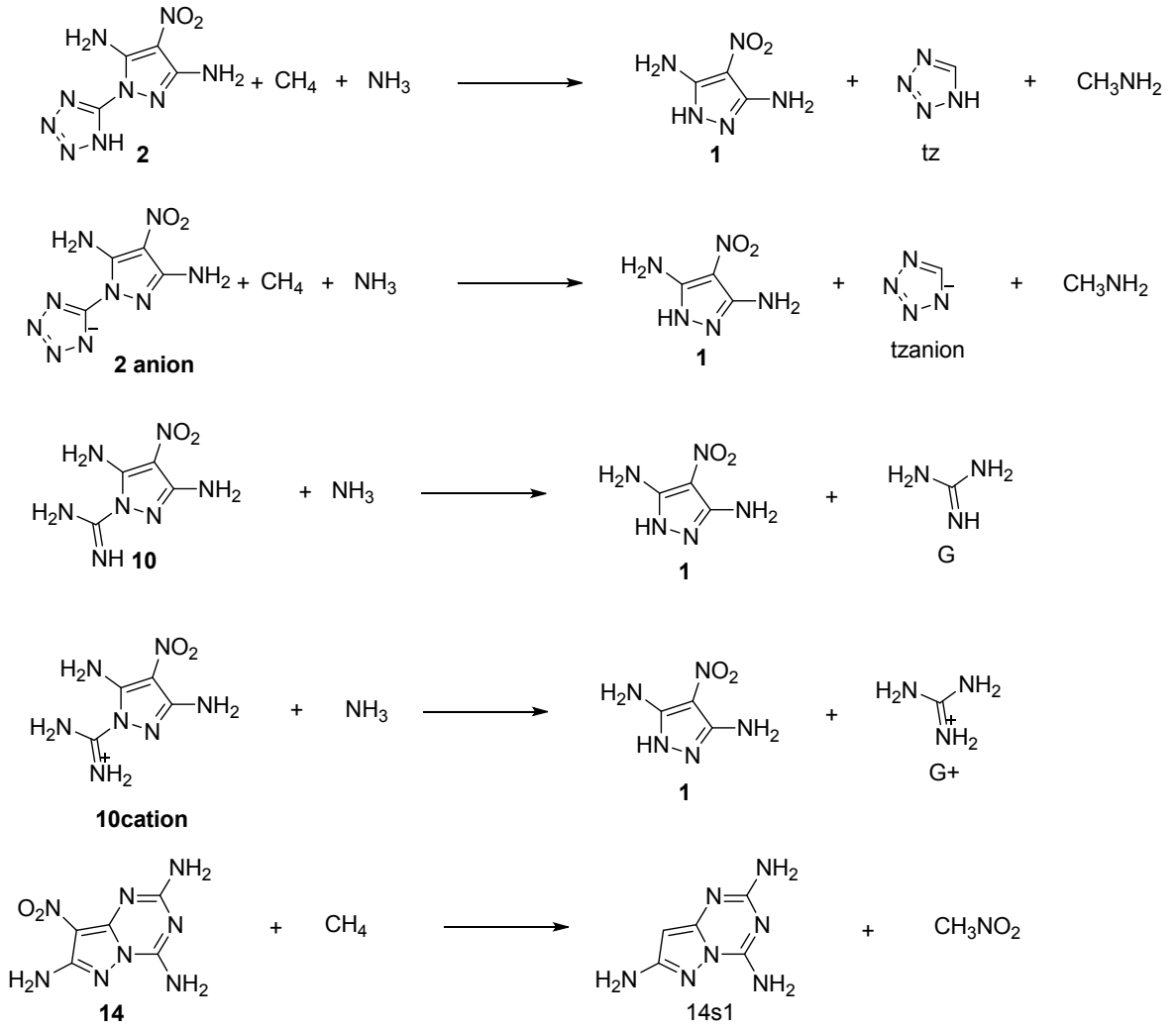
Computational Methods: The gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S1). The enthalpy of reaction is obtained by combining the MP2/6–311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid-state heats of formation were calculated based on 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]

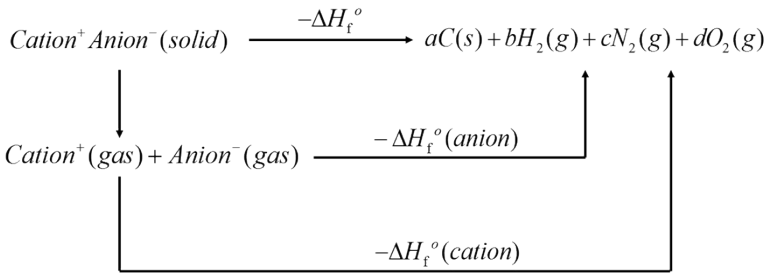
$$\Delta H_{sub} = 188 / Jmol^{-1}K^{-1} \times T \qquad (1)$$

For energetic salts, the solid-phase enthalpy of formation is obtained using a Born−Haber energy cycle (Scheme S2).[2] The solid phase heat of formation of energetic salts can be simplified by Equation (2).

$$\Delta H_{\mathrm{f}}^{o}(salt, 298K) = \Delta H_{\mathrm{f}}^{o}(cation, 298K) + \Delta H_{\mathrm{f}}^{o}(cation, 298K) - \Delta H_{\mathrm{L}} \qquad (2)$$



Scheme S1. Isodesmic reactions



Scheme S2 Born–Haber cycle for the formation of energetic salts. *a*, *b*, *c*, *d* are the number of moles of the respective products.

In Equation (2), the lattice energy (ΔH_L) could be predicted by using the formula suggested by reported methods[3] [Equation (3)].

$$\Delta H_L = U_{POT} + [p(nM/2-2) + q(n_x/2-2)]RT \quad (3)$$

in which nM and n_x depend on the nature of the ions M^{p+} and X^{q-}, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} has the form [Equation (4)]:

$$U_{POT}[kJmol^{-1}] = \gamma(\rho/M)_{1/3} + \delta \quad (4)$$

For the compound which is a hydrate (**7**·H_2O and **11**·$2H_2O$), the solid-phase enthalpy of formation is obtained by adding the gas phase heat of formation of the anhydrous compound to that of water (-241.8 kJ mol^{-1}).[4]

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

Species	*ZPE*	H_r	E_0	corrected E_0	*HOF*(kJ mol^{-1})
2	**0.134367**	**0.147753**	**-796.6755811**	**-796.53320**	**484.0076958**
2anion	**0.121462**	**0.134377**	**-796.1694654**	**-796.03995**	**268.3671766**
10	**0.146322**	**0.15925**	**-688.6467021**	**-688.49330**	**216.1391833**
10cation	**0.159492**	**0.172676**	**-689.0269266**	**-688.86063**	**775.1387349**
14	**0.146269**	**0.160562**	**-780.7199983**	**-780.56529**	**254.7325443**
1	**0.107276**	**0.117201**	**-540.1924739**	**-540.07956**	**137.09**
14s1	**0.144539**	**0.155758**	**-576.6165504**	**-576.46657**	**270.67**[a]
CH_3NH_2	**0.06403**	**0.06840**	**-95.59384**	**-95.52800**	**-23**[b]
tz	**0.046867**	**0.051296**	**-257.653854**	**-257.60443**	**335.14**[b]
tzanion	**0.033829**	**0.038053**	**-257.1242314**	**-257.08753**	**181.58**[a]
G	**0.075947**	**0.081442**	**-204.8735052**	**-204.79510**	**26**[a]
G+	**0.088414**	**0.094658**	**-205.2570327**	**-205.16591**	**575.85**[a]
CH_3NO_2	**0.04984**	**0.055138**	**-244.4784821**	**-244.42534**	**-74.3**[b]
NH_3	**0.034384**	**0.038203**	**-56.4154647**	**-56.37864**	**-45.9** [b]
CH_4	**0.044793**	**0.048605**	**-40.3796224**	**-40.33281**	**-74.6** [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.].

Crystal Structure Analysis

Table S2. Crystal data and structure refinement for **2**.

Identification code	**2**	
Empirical formula	$C_4H_7N_9O_3$	
CCDC number	1861409	
Formula weight	229.19	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.1165(4) Å	α = 90°.
	b = 14.3444(6) Å	β = 108.033(2)°.
	c = 7.2327(3) Å	γ = 90°.
Volume	899.36(7) $Å^3$	
Z	4	
Density (20°C)	1.693 Mg/m^3	
Absorption coefficient	0.144 mm^{-1}	
F(000)	472	
Crystal size	0.362 × 0.212 × 0.085 mm^3	
Theta range for data collection	2.349 to 30.034°.	
Index ranges	-12<=h<=12, -19<=k<=19, -9<=l<=10	
Reflections collected	10599	
Independent reflections	2541 [R_{int} =0.0357]	
Completeness to theta = 25.242°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.6711	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2541 / 3 / 151	
Goodness-of-fit on F^2	1.018	
Final R indices [I>2sigma(I)]	R_1 = 0.0465, wR_2 = 0.1060	
R indices (all data)	R_1 = 0.0827, wR_2 = 0.1222	
Largest diff. peak and hole	0.309 and -0.231 $e.Å^{-3}$	

Table S3. Bond lengths [Å] and angles [°] for **2**.

N(1)-C(2)	1.323(2)	N(1)-H(1A)	0.8600
N(1)-H(1B)	0.8600	C(2)-N(10)	1.3538(19)
C(2)-C(3)	1.398(2)	C(3)-N(4)	1.378(2)
C(3)-C(7)	1.433(2)	N(4)-O(5)	1.240(2)
N(4)-O(6)	1.239(2)	C(7)-N(9)	1.321(2)
C(7)-N(8)	1.336(2)	N(8)-H(8A)	0.8600
N(8)-H(8B)	0.8600	N(9)-N(10)	1.4098(17)
N(10)-C(11)	1.371(2)	C(11)-N(12)	1.319(2)
C(11)-N(15)	1.322(2)	N(12)-N(13)	1.356(2)
N(13)-N(14)	1.292(2)	N(14)-N(15)	1.348(2)
N(15)-H(15)	0.8600	O(16)-H(16B)	0.814(9)
O(16)-H(16A)	0.814(9)		
C(2)-N(1)-H(1A)	120.0	C(2)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0	N(1)-C(2)-N(10)	123.54(16)
N(1)-C(2)-C(3)	131.99(15)	N(10)-C(2)-C(3)	104.47(13)
N(4)-C(3)-C(2)	125.33(15)	N(4)-C(3)-C(7)	127.81(16)
C(2)-C(3)-C(7)	106.86(13)	O(5)-N(4)-O(6)	122.84(15)
O(5)-N(4)-C(3)	118.43(17)	O(6)-N(4)-C(3)	118.73(15)
N(9)-C(7)-N(8)	121.37(15)	N(9)-C(7)-C(3)	110.98(14)
N(8)-C(7)-C(3)	127.65(15)	C(7)-N(8)-H(8A)	120.0
C(7)-N(8)-H(8B)	120.0	H(8A)-N(8)-H(8B)	120.0
C(7)-N(9)-N(10)	104.01(12)	C(2)-N(10)-C(11)	128.20(14)
C(2)-N(10)-N(9)	113.66(13)	C(11)-N(10)-N(9)	118.13(12)
N(12)-C(11)-N(15)	110.53(14)	N(12)-C(11)-N(10)	125.34(14)
N(15)-C(11)-N(10)	124.12(14)	C(11)-N(12)-N(13)	104.11(14)
N(14)-N(13)-N(12)	111.52(14)	N(13)-N(14)-N(15)	106.37(13)
C(11)-N(15)-N(14)	107.45(13)	C(11)-N(15)-H(15)	126.3
N(14)-N(15)-H(15)	126.3	H(16B)-O(16)-H(16A)	109.0(19)

Table S4. Torsion angles [°] for **2**.

N(1)-C(2)-C(3)-N(4)	1.7(3)
N(10)-C(2)-C(3)-N(4)	-178.94(16)
N(1)-C(2)-C(3)-C(7)	-178.65(17)
N(10)-C(2)-C(3)-C(7)	0.73(18)
C(2)-C(3)-N(4)-O(5)	-2.7(3)
C(7)-C(3)-N(4)-O(5)	177.70(17)
C(2)-C(3)-N(4)-O(6)	177.34(16)
C(7)-C(3)-N(4)-O(6)	-2.3(3)
N(4)-C(3)-C(7)-N(9)	179.26(15)
C(2)-C(3)-C(7)-N(9)	-0.40(19)
N(4)-C(3)-C(7)-N(8)	-0.3(3)
C(2)-C(3)-C(7)-N(8)	-179.95(16)
N(8)-C(7)-N(9)-N(10)	179.48(15)
C(3)-C(7)-N(9)-N(10)	-0.11(17)
N(1)-C(2)-N(10)-C(11)	-2.2(3)
C(3)-C(2)-N(10)-C(11)	178.39(15)
N(1)-C(2)-N(10)-N(9)	178.59(15)
C(3)-C(2)-N(10)-N(9)	-0.86(18)
C(7)-N(9)-N(10)-C(2)	0.62(17)
C(7)-N(9)-N(10)-C(11)	-178.70(14)
C(2)-N(10)-C(11)-N(12)	11.4(3)
N(9)-N(10)-C(11)-N(12)	-169.36(15)
C(2)-N(10)-C(11)-N(15)	-169.77(16)
N(9)-N(10)-C(11)-N(15)	9.5(2)
N(15)-C(11)-N(12)-N(13)	0.14(18)
N(10)-C(11)-N(12)-N(13)	179.09(15)
C(11)-N(12)-N(13)-N(14)	-0.6(2)
N(12)-N(13)-N(14)-N(15)	0.8(2)
N(12)-C(11)-N(15)-N(14)	0.35(19)
N(10)-C(11)-N(15)-N(14)	-178.62(15)
N(13)-N(14)-N(15)-C(11)	-0.72(19)

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

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1A)...N(12)	0.86	2.24	2.858(2)	128.3
N(1)-H(1B)...O(5)	0.86	2.31	2.826(2)	118.9
N(8)-H(8A)...O(5)#2	0.86	2.20	3.056(2)	177.5
N(8)-H(8B)...O(6)	0.86	2.30	2.851(2)	121.6
N(8)-H(8B)...N(13)#3	0.86	2.30	2.984(2)	136.5
N(15)-H(15)...O(16)	0.86	1.81	2.6399(18)	161.8
O(16)-H(16B)...O(6)#2	0.814(9)	2.072(13)	2.8552(19)	161(2)
O(16)-H(16A)...N(9)#4	0.814(9)	2.162(12)	2.9615(19)	167(3)

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

Table S6. Crystal data and structure refinement for **9**.

Identification code	**9**	
CCDC number	1936195	
Empirical formula	$C_4H_{12}ClN_7O_4$	
Formula weight	257.66	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 8.5265(6) Å	α = 90°.
	b = 6.9696(5) Å	β = 96.241(2)°.
	c = 18.0794(13) Å	γ = 90°.
Volume	1068.02(13) $Å^3$	
Z	4	
Density (20°C)	1.602 Mg/m^3	
Absorption coefficient	0.374 mm^{-1}	
F(000)	536	
Crystal size	0.226 × 0.036 × 0.036 mm^3	
Theta range for data collection	2.266 to 30.073°.	
Index ranges	-9<=h<=11, -9<=k<=9, -24<=l<=24	
Reflections collected	11746	
Independent reflections	3034 [R_{int} = 0.0531]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.6917	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3034 / 6 / 161	
Goodness-of-fit on F^2	0.993	
Final R indices [I>2sigma(I)]	R_1 = 0.0438, wR_2 = 0.0958	
R indices (all data)	R_1 = 0.0986, wR_2 = 0.1136	
Largest diff. peak and hole	0.309 and -0.407 e.$Å^{-3}$	

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

O(1)-N(3)	1.245(2)	O(2)-N(3)	1.245(2)
N(3)-C(4)	1.384(2)	C(4)-C(5)	1.399(3)
C(4)-C(12)	1.429(3)	C(5)-N(6)	1.318(2)
C(5)-N(7)	1.384(2)	N(6)-H(6A)	0.8600
N(6)-H(6B)	0.8600	N(7)-C(8)	1.383(2)
N(7)-N(11)	1.414(2)	C(8)-N(10)	1.298(3)
C(8)-N(9)	1.314(3)	N(9)-H(9A)	0.8600
N(9)-H(9B)	0.8600	N(10)-H(10A)	0.8600
N(10)-H(10B)	0.8600	N(11)-C(12)	1.316(2)
C(12)-N(13)	1.338(3)	N(13)-H(13A)	0.8600
N(13)-H(13B)	0.8600	O(15)-H(15A)	0.824(9)
O(15)-H(15B)	0.830(10)	O(16)-H(16A)	0.822(10)
O(16)-H(16B)	0.823(10)		
O(2)-N(3)-O(1)	121.94(16)	O(2)-N(3)-C(4)	118.68(17)
O(1)-N(3)-C(4)	119.38(16)	N(3)-C(4)-C(5)	124.94(17)
N(3)-C(4)-C(12)	126.89(17)	C(5)-C(4)-C(12)	108.16(16)
N(6)-C(5)-N(7)	126.91(17)	N(6)-C(5)-C(4)	129.81(17)
N(7)-C(5)-C(4)	103.25(16)	C(5)-N(6)-H(6A)	120.0
C(5)-N(6)-H(6B)	120.0	H(6A)-N(6)-H(6B)	120.0
C(8)-N(7)-C(5)	129.78(17)	C(8)-N(7)-N(11)	116.84(16)
C(5)-N(7)-N(11)	113.11(15)	N(10)-C(8)-N(9)	123.77(18)
N(10)-C(8)-N(7)	117.43(19)	N(9)-C(8)-N(7)	118.80(18)
C(8)-N(9)-H(9A)	120.0	C(8)-N(9)-H(9B)	120.0
H(9A)-N(9)-H(9B)	120.0	C(8)-N(10)-H(10A)	120.0
C(8)-N(10)-H(10B)	120.0	H(10A)-N(10)-H(10B)	120.0
C(12)-N(11)-N(7)	104.69(15)	N(11)-C(12)-N(13)	122.19(18)
N(11)-C(12)-C(4)	110.76(17)	N(13)-C(12)-C(4)	127.05(17)
C(12)-N(13)-H(13A)	120.0	C(12)-N(13)-H(13B)	120.0
H(13A)-N(13)-H(13B)	120.0	H(15A)-O(15)-H(15B)	102.1(19)
H(16A)-O(16)-H(16B)	103(2)		

Table S8. Torsion angles [°] for **9**.

O(2)-N(3)-C(4)-C(5)	178.26(19)
O(1)-N(3)-C(4)-C(5)	-2.3(3)
O(2)-N(3)-C(4)-C(12)	-0.7(3)
O(1)-N(3)-C(4)-C(12)	178.79(19)
N(3)-C(4)-C(5)-N(6)	-2.3(3)
C(12)-C(4)-C(5)-N(6)	176.85(19)
N(3)-C(4)-C(5)-N(7)	179.76(18)
C(12)-C(4)-C(5)-N(7)	-1.1(2)
N(6)-C(5)-N(7)-C(8)	-2.7(3)
C(4)-C(5)-N(7)-C(8)	175.38(19)
N(6)-C(5)-N(7)-N(11)	-176.53(18)
C(4)-C(5)-N(7)-N(11)	1.5(2)
C(5)-N(7)-C(8)-N(10)	-152.5(2)
N(11)-N(7)-C(8)-N(10)	21.1(3)
C(5)-N(7)-C(8)-N(9)	27.8(3)
N(11)-N(7)-C(8)-N(9)	-158.58(19)
C(8)-N(7)-N(11)-C(12)	-176.03(17)
C(5)-N(7)-N(11)-C(12)	-1.3(2)
N(7)-N(11)-C(12)-N(13)	-179.14(18)
N(7)-N(11)-C(12)-C(4)	0.5(2)
N(3)-C(4)-C(12)-N(11)	179.49(19)
C(5)-C(4)-C(12)-N(11)	0.4(2)
N(3)-C(4)-C(12)-N(13)	-0.9(3)
C(5)-C(4)-C(12)-N(13)	-180.0(2)

Table S9. Hydrogen bonds for **9** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...O(15)#1	0.86	2.10	2.846(2)	144.6
N(6)-H(6B)...O(1)	0.86	2.25	2.791(2)	121.4
N(6)-H(6B)...O(15)#2	0.86	2.26	3.055(2)	154.2
N(10)-H(10B)...O(16)	0.86	2.03	2.876(3)	167.3
N(13)-H(13B)...O(2)	0.86	2.25	2.808(2)	122.7
O(15)-H(15A)...O(16)	0.824(9)	2.027(10)	2.850(3)	175(3)
O(15)-H(15B)...Cl(14)#6	0.830(10)	2.388(10)	3.217(2)	177(3)

Symmetry transformations used to generate equivalent atoms:
#1 x-1,y,z #2 -x+1,-y+1,-z+1 #3 -x+1,y-1/2,-z+1/2
#4 x,-y+3/2,z-1/2 #5 -x+2,-y+2,-z+1 #6 x,y-1,z
#7 -x+2,y-1/2,-z+1/2

Table S10. Crystal data and structure refinement for **13**.

Identification code	**13**	
CCDC number	1936194	
Empirical formula	$C_5H_9ClN_8O_3$	
Formula weight	264.65	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.8649(6) Å	α = 87.756(2)°.
	b = 7.8722(6) Å	β = 74.218(2)°.
	c = 8.8770(6) Å	γ = 73.265(2)°.
Volume	506.04(6) $Å^3$	
Z	2	
Density (20°C)	1.737 Mg/m^3	
Absorption coefficient	0.393 mm^{-1}	
F(000)	272	
Crystal size	0.408 × 0.223 × 0.060 mm^3	
Theta range for data collection	2.386 to 30.019°.	
Index ranges	-11<=h<=11, -11<=k<=10, -12<=l<=11	
Reflections collected	6095	
Independent reflections	2773 [R_{int} = 0.0200]	
Completeness to theta = 25.242°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7460 and 0.6981	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2773 / 3 / 160	
Goodness-of-fit on F^2	1.029	
Final R indices [I>2sigma(I)]	R_1 = 0.0395, wR_2 = 0.0981	
R indices (all data)	R_1 = 0.0552, wR_2 = 0.1063	
Largest diff. peak and hole	0.336 and -0.285 e.$Å^{-3}$	

Table S11. Bond lengths [Å] and angles [°] for **13**.

O(1)-N(3)	1.2377(19)	O(2)-N(3)	1.2339(18)
N(3)-C(4)	1.398(2)	C(4)-C(15)	1.378(2)
C(4)-C(5)	1.438(2)	C(5)-N(7)	1.332(2)
C(5)-N(6)	1.338(2)	N(6)-H(6A)	0.8600
N(6)-H(6B)	0.8600	N(7)-N(8)	1.3947(19)
N(8)-C(15)	1.352(2)	N(8)-C(9)	1.376(2)
C(9)-N(10)	1.305(2)	C(9)-N(11)	1.330(2)
N(10)-H(10B)	0.8600	N(11)-C(12)	1.338(2)
C(12)-N(13)	1.308(2)	C(12)-N(14)	1.370(2)
N(13)-H(13A)	0.8600	N(13)-H(13B)	0.8600
N(14)-C(15)	1.343(2)	N(14)-H(14)	0.8600
O(17)-H(17A)	0.822(10)	O(17)-H(17B)	0.817(10)
O(2)-N(3)-O(1)	123.11(14)	O(2)-N(3)-C(4)	118.61(14)
O(1)-N(3)-C(4)	118.28(14)	C(15)-C(4)-N(3)	124.98(15)
C(15)-C(4)-C(5)	105.95(14)	N(3)-C(4)-C(5)	128.74(15)
N(7)-C(5)-N(6)	122.20(16)	N(7)-C(5)-C(4)	110.99(14)
N(6)-C(5)-C(4)	126.77(15)	C(5)-N(6)-H(6A)	120.0
C(5)-N(6)-H(6B)	120.0	H(6A)-N(6)-H(6B)	120.0
C(5)-N(7)-N(8)	103.76(13)	C(15)-N(8)-C(9)	121.67(14)
C(15)-N(8)-N(7)	113.36(13)	C(9)-N(8)-N(7)	124.78(13)
N(10)-C(9)-N(11)	123.16(15)	N(10)-C(9)-N(8)	117.72(15)
N(11)-C(9)-N(8)	119.12(14)	C(9)-N(10)-H(10A)	120.0
C(9)-N(10)-H(10B)	120.0	H(10A)-N(10)-H(10B)	120.0
C(9)-N(11)-C(12)	119.36(14)	N(13)-C(12)-N(11)	120.46(15)
N(13)-C(12)-N(14)	117.47(15)	N(11)-C(12)-N(14)	122.06(15)
C(12)-N(13)-H(13A)	120.0	C(12)-N(13)-H(13B)	120.0
H(13A)-N(13)-H(13B)	120.0	C(15)-N(14)-C(12)	119.07(14)
C(15)-N(14)-H(14)	120.5	C(12)-N(14)-H(14)	120.5
N(14)-C(15)-N(8)	118.52(14)	N(14)-C(15)-C(4)	135.54(15)
N(8)-C(15)-C(4)	105.92(14)	H(17A)-O(17)-H(17B)	105(2)

Table S12. Torsion angles [°] for **13**.

O(2)-N(3)-C(4)-C(15)	-172.53(16)
O(1)-N(3)-C(4)-C(15)	7.2(2)
O(2)-N(3)-C(4)-C(5)	-0.1(3)
O(1)-N(3)-C(4)-C(5)	179.63(16)
C(15)-C(4)-C(5)-N(7)	0.39(19)
N(3)-C(4)-C(5)-N(7)	-173.15(16)
C(15)-C(4)-C(5)-N(6)	178.21(17)
N(3)-C(4)-C(5)-N(6)	4.7(3)
N(6)-C(5)-N(7)-N(8)	-177.83(16)
C(4)-C(5)-N(7)-N(8)	0.10(18)
C(5)-N(7)-N(8)-C(15)	-0.60(18)
C(5)-N(7)-N(8)-C(9)	174.44(15)
C(15)-N(8)-C(9)-N(10)	178.83(15)
N(7)-N(8)-C(9)-N(10)	4.2(2)
C(15)-N(8)-C(9)-N(11)	-1.5(2)
N(7)-N(8)-C(9)-N(11)	-176.16(14)
N(10)-C(9)-N(11)-C(12)	177.79(16)
N(8)-C(9)-N(11)-C(12)	-1.8(2)
C(9)-N(11)-C(12)-N(13)	-178.29(17)
C(9)-N(11)-C(12)-N(14)	1.9(3)
N(13)-C(12)-N(14)-C(15)	-178.41(17)
N(11)-C(12)-N(14)-C(15)	1.4(3)
C(12)-N(14)-C(15)-N(8)	-4.6(2)
C(12)-N(14)-C(15)-C(4)	174.20(18)
C(9)-N(8)-C(15)-N(14)	4.8(2)
N(7)-N(8)-C(15)-N(14)	179.98(14)
C(9)-N(8)-C(15)-C(4)	-174.36(15)
N(7)-N(8)-C(15)-C(4)	0.85(18)
N(3)-C(4)-C(15)-N(14)	-5.8(3)
C(5)-C(4)-C(15)-N(14)	-179.62(18)
N(3)-C(4)-C(15)-N(8)	173.13(15)
C(5)-C(4)-C(15)-N(8)	-0.72(18)

Table S13. Hydrogen bonds for **13** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(6)-H(6A)...Cl(16)#1	0.86	2.44	3.2856(17)	166.0
N(6)-H(6B)...O(2)	0.86	2.34	2.884(2)	121.7
N(10)-H(10B)...O(17)	0.86	2.03	2.865(2)	164.0
N(13)-H(13A)...N(11)#5	0.86	2.13	2.987(2)	179.3
O(17)-H(17A)...Cl(16)#4	0.822(10)	2.386(10)	3.2072(15)	178(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1 #2 -x+1,-y+1,-z+1 #3 x-1,y+1,z
#4 -x,-y+2,-z+1 #5 -x+1,-y+2,-z #6 -x+2,-y+1,-z
#7 x+1,y,z #8 -x+1,-y+1,-z

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