Electronic Supplementary Information

5-(4-Azidofurazan-3-yl)-1-hydroxytetrazole and its derivatives: from green primary explosive to secondary explosives

Jichuan Zhang, Ping Yin, Guangxing Pan, Zhenyuan Wang, Jiaheng Zhang*, Damon A. Parrish, Lauren A. Mitchell, and Jean'ne M. Shreeve*

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Table S1. Crystal data and structure refinement for **4-4c**

CCDC number (compound name)	1915165	1915166	1915167	1915168
Empirical formula	$C_3H_3N_9O_3$	$C_3H_4N_{10}O_2$	$C_3H_4N_{10}O_3$	$C_3H_5N_{11}O_2$
Formula weight	213.14	212.16	228.16	227.18
Temperature(K)	150	150	150	150
Wavelength(Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	P 21/n	$P2_12_12_1$	$P2_1/c$	$P2_1/c$
Unit cell dimensions	a = 10.0066(6) Å, b= 6.2343(4) Å, c = 13.5638(9) Å, α = 90°, β = 107.909(2)°, γ = 90°	a = 4.7561(5) Å, b= 12.1040(12) Å, c = 14.0172(14) Å α=90 °;β= 90 °;γ= 90 °	a = 12.1410(6) Å, b= 4.7291(2) Å, c = 15.1338(8) Å; α=90 °;β= 103.803(2) ° ;γ=90 °	a = 12.8837(9) Å, b= 4.8567(3) Å, c = 14.9766(10) Å; α=90 °;β= 103.733(2) ° ;γ=90 °
Volume	805.17(9) $Å^3$	806.94(14)$Å^3$	843.83(7) $Å^3$	909.39(10) $Å^3$
Z	4	4	4	4
Density	1.758	1.746	1.796	1.659
Mu (mm-1)	0.154	0.148	0.157	0.140
F(000)	432.0	432.0	464.0	464.0
h,k,lmax	12, 7, 16	6, 15, 18	15, 6, 19	16, 6, 19
Data completeness	0.995	1.67/1.00	0.995	0.999
Theta(max)	26.406	27.516	27.585	27.589
R(reflections)	0.0298(1284)	0.0240(1755)	0.0326(1804)	0.0303(1673)
wR2(reflections)	0.0811(1645)	0.0602(1849)	0.0863(1936)	0.0799(2112)
S	1.033	0.947	1.088	1.053
Npar	145	148	157	160

Table S2. Hydrogen bonds of crystal **4**

D-H…A	D-H(Å)	H…A(Å)	D-H…A(Å)	∠D-H…A(°)
O1S-H1S…N8	0.797(9)	2.36(1)	3.1188(16)	159.5(18)
O1S-H2S…N5	0.802(9)	2.100(11)	2.8181(16)	149.1(16)
O1-H1…O1S	0.847(9)	1.719(10)	2.5666(15)	179.(2)

Table S3. Hydrogen bonds of crystal **4a**

D-H…A	D-H	H…A	D-H…A	∠D-H…A
N2S-H2S…O1	0.95(2)	1.91(2)	2.8395(19)	167.2(19)
N2S-H3S…N4	0.88(2)	2.17(2)	3.013(2)	161.(2)
N2S-H4S…O1	0.88(2)	2.12(2)	2.9531(18)	156.2(19)

N2S-H1S…O1	0.92(2)	2.04(2)	2.896(2)	155.9(18)

Table S4. Hydrogen bonds of crystal **4b**

D-H…A	D-H	H…A	D-H…A	∠D-H…A
O2S-H4S…N4	0.929(19)	1.793(19)	2.6703(14)	156.3(17)
N1S-H3S…O1	0.904(18)	1.912(19)	2.7995(14)	166.8(15)
N1S-H3S…N2	0.904(18)	2.547(17)	3.3014(15)	141.2(13)
N1S-H3S…N3	0.904(18)	2.610(16)	3.0548(15)	111.1(12)
N1S-H2S…N5	0.927(17)	2.069(17)	2.9904(14)	172.0(15)
N1S-H1S…O1	0.877(18)	1.910(19)	2.7846(15)	174.8(16)

Table S5. Hydrogen bonds of crystal **4c**

D-H…A	D-H	H…A	D-H…A	∠D-H…A
N2S-H4S…N4	0.867(17)	2.460(16)	3.0841(15)	129.5(12)
N2S-H4S…N3	0.867(17)	2.528(16)	3.1490(15)	129.2(12)
N2S-H5S…N2S	0.882(16)	2.102(16)	2.9814(13)	174.9(13)
N1S-H3S…N5	0.889(16)	2.025(16)	2.8944(15)	165.2(13)
N1S-H2S…N2	0.917(15)	2.545(15)	3.3276(15)	143.6(11)
N1S-H2S…O1	0.917(15)	1.857(16)	2.7608(14)	168.1(13)
N1S-H1S…O1	0.922(15)	1.872(16)	2.7695(14)	163.9(12)

Table S6. Bond lengths of **4** and **4a**

4			**4a**		
Atom1	Atom2	Distance(Å)	Atom1	Atom2	Distance(Å)
O1	N2	1.3547(15)	O1	N2	1.323(2)
O1	H1	0.847(9)	N2	N3	1.339(2)
N2	N3	1.3355(17)	N2	C6	1.344(2)
N2	C6	1.3366(18)	N3	N4	1.320(2)
N3	N4	1.3039(17)	N4	N5	1.347(2)
N4	N5	1.3558(16)	N5	C6	1.338(2)
N5	C6	1.3203(17)	C6	C7	1.447(2)
C6	C7	1.4520(18)	C7	N8	1.308(2)
C7	N8	1.3047(18)	C7	C11	1.431(2)
C7	C11	1.427(2)	N8	O9	1.386(2)
N8	O9	1.3776(15)	O9	N10	1.391(2)
O9	N10	1.3883(16)	N10	C11	1.307(2)
N10	C11	1.3027(19)	C11	N12	1.389(2)
C11	N12	1.3902(18)	N12	N13	1.256(2)
N12	N13	1.2620(17)	N13	N14	1.119(2)
N13	N14	1.1168(17)	N2S	H1S	0.92(2)
O1S	H1S	0.797(9)	N2S	H2S	0.95(2)
O1S	-H2S	0.802(9)	N2S	H3S	0.88(2)
			N2S	H4S	0.88(2)

Table S7. Bond lengths of **4b** and **4c**

4b			**4c**		
Atom1	Atom2	Distance(Å)	Atom1	Atom2	Distance(Å)
O1	N2	1.311(1)	O1	N2	1.317(1)
N2	N3	1.341(1)	N2	N3	1.343(1)
N2	C6	1.350(2)	N2	C6	1.343(2)
N3	N4	1.313(2)	N3	N4	1.315(2)
N4	N5	1.342(1)	N4	N5	1.349(1)
N5	C6	1.333(2)	N5	C6	1.336(2)
C6	C7	1.448(2)	C6	C7	1.445(2)
C7	N8	1.308(2)	C7	N8	1.306(2)
C7	C11	1.434(2)	C7	C11	1.430(2)
N8	O9	1.377(1)	N8	O9	1.377(1)
O9	N10	1.390(1)	O9	N10	1.388(1)
N10	C11	1.305(2)	N10	C11	1.302(2)
C11	N12	1.394(2)	C11	N12	1.395(2)
N12	N13	1.269(2)	N12	N13	1.267(1)
N13	N14	1.117(2)	N13	N14	1.115(2)
N1S	H1S	0.88(2)	N1S	H1S	0.92(1)
N1S	H2S	0.93(2)	N1S	H2S	0.92(1)
N1S	H3S	0.91(2)	N1S	H3S	0.89(2)
N1S	O2S	1.426(1)	N1S	N2S	1.449(1)
O2S	H4S	0.93(2)	N2S	H4S	0.87(2)
			N2S	H5S	0.88(1)

Table S8. Bond angles of **4** and **4a**

4				4a			
Atom1	Atom2	Atom3	Angle(Å)	Atom1	Atom2	Atom3	Angle(Å)
H1	O1	N2	106(1)	O1	N2	N3	122.2(1)
O1	N2	N3	122.3(1)	O1	N2	C6	129.1(1)
O1	N2	C6	127.5(1)	N3	N2	C6	108.7(1)
N3	N2	C6	110.2(1)	N2	N3	N4	105.9(1)
N2	N3	N4	105.1(1)	N3	N4	N5	111.5(1)
N3	N4	N5	111.2(1)	N4	N5	C6	105.2(1)
N4	N5	C6	105.9(1)	N2	C6	N5	108.7(1)
N2	C6	N5	107.6(1)	N2	C6	C7	125.4(1)
N2	C6	C7	126.4(1)	N5	C6	C7	125.9(1)
N5	C6	C7	126.0(1)	C6	C7	N8	124.4(1)
C6	C7	N8	123.8(1)	C6	C7	C11	126.9(1)
C6	C7	C11	127.1(1)	N8	C7	C11	108.6(1)
N8	C7	C11	109.0(1)	C7	N8	O9	105.6(1)
C7	N8	O9	105.4(1)	N8	O9	N10	111.3(1)

N8	O9	N10	111.3(1)	O9	N10	C11	104.7(1)
O9	N10	C11	105.0(1)	C7	C11	N10	109.8(1)
C7	C11	N10	109.3(1)	C7	C11	N12	123.5(1)
C7	C11	N12	124.4(1)	N10	C11	N12	126.7(1)
N10	C11	N12	126.3(1)	C11	N12	N13	114.4(1)
C11	N12	N13	114.3(1)	N12	N13	N14	170.3(2)
N12	N13	N14	170.8(1)	H1S	N2S	H2S	107(2)
H1S	O1S	H2S	96(2)	H1S	N2S	H3S	113(2)
				H1S	N2S	H4S	112(2)
				H2S	N2S	H3S	108(2)
				H2S	N2S	H4S	107(2)
				H3S	N2S	H4S	108(2)

Table S9. Bond angles of **4b** and **4c**

4b				**4c**			
Atom1	Atom2	Atom3	Angle(Å)	Atom1	Atom2	Atom3	Angle(Å)
O1	N2	N3	121.6(1)	O1	N2	N3	122.0(1)
O1	N2	C6	129.7(1)	O1	N2	C6	129.0(1)
N3	N2	C6	108.7(1)	N3	N2	C6	108.9(1)
N2	N3	N4	105.71(9)	N2	N3	N4	106.24(9)
N3	N4	N5	111.7(1)	N3	N4	N5	110.7(1)
N4	N5	C6	105.6(1)	N4	N5	C6	106.2(1)
N2	C6	N5	108.3(1)	N2	C6	N5	108.0(1)
N2	C6	C7	125.8(1)	N2	C6	C7	125.8(1)
N5	C6	C7	126.0(1)	N5	C6	C7	126.2(1)
C6	C7	N8	123.5(1)	C6	C7	N8	123.4(1)
C6	C7	C11	127.8(1)	C6	C7	C11	128.0(1)
N8	C7	C11	108.7(1)	N8	C7	C11	108.5(1)
C7	N8	O9	105.7(1)	C7	N8	O9	105.8(1)
N8	O9	N10	111.30(9)	N8	O9	N10	111.15(9)
O9	N10	C11	105.0(1)	O9	N10	C11	105.0(1)
C7	C11	N10	109.3(1)	C7	C11	N10	109.5(1)
C7	C11	N12	124.9(1)	C7	C11	N12	124.9(1)
N10	C11	N12	125.7(1)	N10	C11	N12	125.6(1)
C11	N12	N13	112.0(1)	C11	N12	N13	112.4(1)
N12	N13	N14	172.4(1)	N12	N13	N14	172.4(1)
H1S	N1S	H2S	111(2)	H1S	N1S	H2S	111(1)
H1S	N1S	H3S	110(2)	H1S	N1S	H3S	110(1)
H1S	N1S	O2S	111(1)	H1S	N1S	N2S	111.9(9)
H2S	N1S	H3S	108(2)	H2S	N1S	H3S	109(1)
H2S	N1S	O2S	106(1)	H2S	N1S	N2S	108.0(9)
H3S	N1S	O2S	110(1)	H3S	N1S	N2S	107(1)
N1S	O2S	H4S	103(1)	N1S	N2S	H4S	106(1)
				N1S	N2S	H5S	108(1)

H4S	N2S	H5S	108(1)	

Table S10. Bond torsion angles of **4** and **4a**

4					**4a**				
Atom1	Atom2	Atom3	Atom4	Torsion(Å)	Atom1	Atom2	Atom3	Atom4	Torsion(Å)
H1	O1	N2	N3	73(1)	O1	N2	N3	N4	178.8(1)
H1	O1	N2	C6	-110(1)	C6	N2	N3	N4	0.3(2)
O1	N2	N3	N4	178.1(1)	O1	N2	C6	N5	-179.0(1)
C6	N2	N3	N4	0.5(2)	O1	N2	C6	C7	-1.8(3)
O1	N2	C6	N5	-177.8(1)	N3	N2	C6	N5	-0.7(2)
O1	N2	C6	C7	4.4(2)	N3	N2	C6	C7	176.5(1)
N3	N2	C6	N5	-0.4(2)	N2	N3	N4	N5	0.2(2)
N3	N2	C6	C7	-178.2(1)	N3	N4	N5	C6	-0.6(2)
N2	N3	N4	N5	-0.5(2)	N4	N5	C6	N2	0.7(2)
N3	N4	N5	C6	0.3(2)	N4	N5	C6	C7	-176.4(1)
N4	N5	C6	N2	0.1(1)	N2	C6	C7	N8	3.1(3)
N4	N5	C6	C7	177.9(1)	N2	C6	C7	C11	-177.7(2)
N2	C6	C7	N8	-9.0(2)	N5	C6	C7	N8	179.8(2)
N2	C6	C7	C11	170.0(1)	N5	C6	C7	C11	-1.0(3)
N5	C6	C7	N8	173.6(1)	C6	C7	N8	O9	178.8(1)
N5	C6	C7	C11	-7.4(2)	C11	C7	N8	O9	-0.5(2)
C6	C7	N8	O9	179.6(1)	C6	C7	C11	N10	-178.9(1)
C11	C7	N8	O9	0.4(2)	C6	C7	C11	N12	0.5(2)
C6	C7	C11	N10	-179.8(1)	N8	C7	C11	N10	0.5(2)
C6	C7	C11	N12	0.6(2)	N8	C7	C11	N12	179.9(1)
N8	C7	C11	N10	-0.6(2)	C7	N8	O9	N10	0.4(2)
N8	C7	C11	N12	179.7(1)	N8	O9	N10	C11	-0.1(2)
C7	N8	O9	N10	-0.1(1)	O9	N10	C11	C7	-0.2(2)
N8	O9	N10	C11	-0.3(1)	O9	N10	C11	N12	-179.6(1)
O9	N10	C11	C7	0.6(2)	C7	C11	N12	N13	179.9(1)
O9	N10	C11	N12	-179.8(1)	N10	C11	N12	N13	-0.8(2)
C7	C11	N12	N13	-169.1(1)	C11	N12	N13	N14	-178(1)
N10	C11	N12	N13	11.3(2)					
C11	N12	N13	N14	179.1(9)					

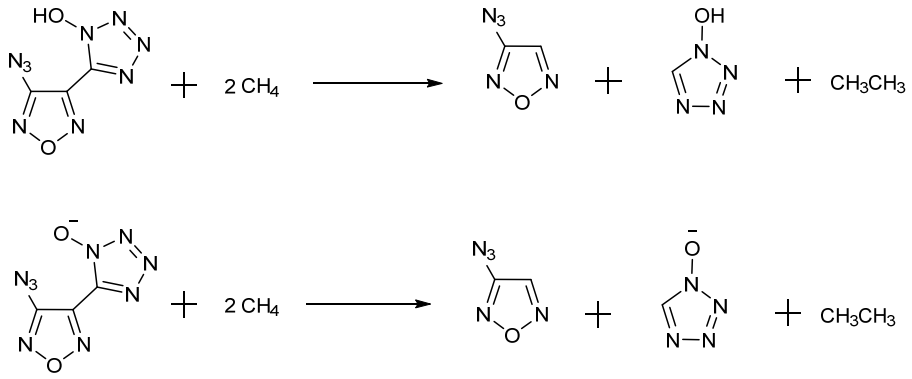
Table S11. Bond torsion angles of **4b** and **4c**

4b					4c				
Atom1	Atom2	Atom3	Atom4	Torsion(Å)	Atom1	Atom2	Atom3	Atom4	Torsion(Å)
O1	N2	N3	N4	179.2(1)	O1	N2	N3	N4	-178.0(1)
C6	N2	N3	N4	0.3(1)	C6	N2	N3	N4	-0.0(1)
O1	N2	C6	N5	-179.4(1)	O1	N2	C6	N5	177.9(1)
O1	N2	C6	C7	-1.4(2)	O1	N2	C6	C7	-1.1(2)
N3	N2	C6	N5	-0.6(1)	N3	N2	C6	N5	0.2(1)
N3	N2	C6	C7	177.4(1)	N3	N2	C6	C7	-178.8(1)

N2	N3	N4	N5	0.0(1)	N2	N3	N4	N5	-0.1(1)
N3	N4	N5	C6	-0.4(1)	N3	N4	N5	C6	0.2(1)
N4	N5	C6	N2	0.6(1)	N4	N5	C6	N2	-0.2(1)
N4	N5	C6	C7	-177.4(1)	N4	N5	C6	C7	178.8(1)
N2	C6	C7	N8	3.2(2)	N2	C6	C7	N8	-6.3(2)
N2	C6	C7	C11	-176.9(1)	N2	C6	C7	C11	174.4(1)
N5	C6	C7	N8	-179.2(1)	N5	C6	C7	N8	174.9(1)
N5	C6	C7	C11	0.7(2)	N5	C6	C7	C11	-4.4(2)
C6	C7	N8	O9	-179.9(1)	C6	C7	N8	O9	-179.6(1)
C11	C7	N8	O9	0.2(1)	C11	C7	N8	O9	-0.1(1)
C6	C7	C11	N10	179.8(1)	C6	C7	C11	N10	179.7(1)
C6	C7	C11	N12	-1.6(2)	C6	C7	C11	N12	0.4(2)
N8	C7	C11	N10	-0.3(2)	N8	C7	C11	N10	0.3(2)
N8	C7	C11	N12	178.3(1)	N8	C7	C11	N12	-179.0(1)
C7	N8	O9	N10	-0.1(1)	C7	N8	O9	N10	-0.1(1)
N8	O9	N10	C11	-0.2(1)	N8	O9	N10	C11	0.2(1)
O9	N10	C11	C7	0.3(1)	O9	N10	C11	C7	-0.3(1)
O9	N10	C11	N12	-178.3(1)	O9	N10	C11	N12	179.0(1)
C7	C11	N12	N13	-179.1(1)	C7	C11	N12	N13	-179.4(1)
N10	C11	N12	N13	-0.7(2)	N10	C11	N12	N13	1.5(2)
C11	N12	N13	N14	178(1)	C11	N12	N13	N14	-179.1(9)
H1S	N1S	O2S	H4S	34(2)	H1S	N1S	N2S	H4S	57(1)
H2S	N1S	O2S	H4S	155(2)	H1S	N1S	N2S	H5S	-58(1)
H3S	N1S	O2S	H4S	-88(2)	H2S	N1S	N2S	H4S	-66(1)
					H2S	N1S	N2S	H5S	179(1)
					H3S	N1S	N2S	H4S	177(1)
					H3S	N1S	N2S	H5S	62(1)

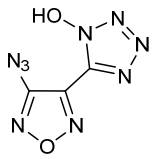
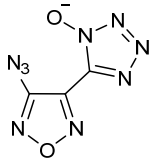
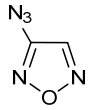
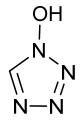
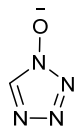
Theoretical calculations

As mentioned in the manuscript, the gas phase heats of formation for all newly prepared neutral compounds were obtained using isodesmic reactions (Scheme S1). The geometric optimization and frequency analysis of the structures were calculated using B3LYP function with 6-31+G** basis set.[1] All of the optimized structures were checked to be true local energy minima on the potential energy surface without imaginary frequencies. Single-point energies based on the optimized structures were calculated at the MP2/6-311++G** set.[2] Atomization energies for frame molecules or ions were obtained by employing the G2 *ab initio* method.[3] The conversion of gas phase enthalpies to solid phase values for neutral compounds was done by subtracting the empirical heat of sublimation obtained based on Trouton's rule. The heats of formation of other compounds in Scheme S1 were determined from the NIST WebBook.[4]



Scheme S1. Isodesmic reactions for calculating heats of formation for 4 and its anion

Table S12. Enthalpies of the gas-phase species (NIST value and G2 method).[3,4]

M	ZPE	Hr	E0	Corrected E0	ΔH_f° (kJ mol^{-1})
	0.079445	0.091127	-756.169952	-756.08200	820.9
	0.066932	0.078148	-755.6675903	-755.59212	659.7
CH_3CH_3	0.07461	0.079038	-79.5716305	-79.49558	-84.0
	0.076568	0.085227	-463.8804898	-463.79833	496.1
	0.077583	0.08517	-371.8748471	-371.79278	280.72
	0.065397	0.072166	-371.3480801	-371.27853	108.08

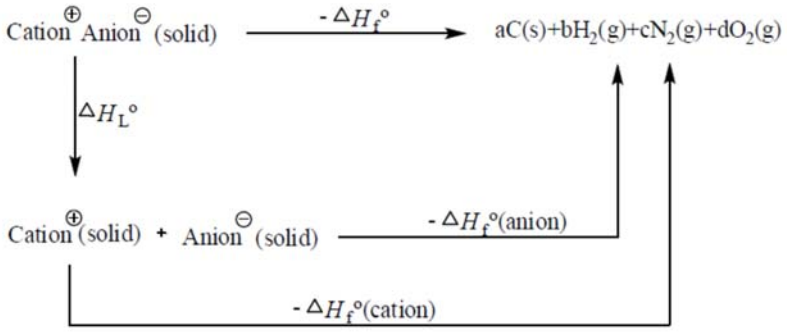
Based on the literature, the heat of sublimation is estimated with Trouton's rule.[5] The solid phase heats of formation of neutral compounds were calculated with equation 1, in which Td represents the decomposition temperature.

$$\Delta Hf\,(s) = \Delta Hf\,(g) - \Delta Hsub = \Delta Hf\,(g) - 188[J\ mol\text{-}1\ K\text{-}1] \times Td \quad (1)$$

Based on the Born-Haber energy cycle (Figure 5), the heat of formation of a salt can be simplified according to Equation (1), where ΔHL is the lattice energy of the salt.

$\triangle H_f^o$(ionic salt, 298K) = $\triangle H_f^o$(cation, 298K)＋ $\triangle H_f^o$(anion, 298K)－$\triangle$HL (1)

The $\triangle$HL value was predicted by the formula suggested by Jenkins et al [Eq. (2)], [6] where U_{POT} is the lattice potential energy and nM and nX depend on the nature of the ions Mp＋and Xq－, respectively, and are equal to three for monoatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.



$\triangle H_L = U_{POT} + [p(n_M/2\text{-}2) + q(n_X/2\text{-}2)]RT$ (2)

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ^{-1}mol^{-1}cm) and δ (kJ^{-1}mol^{-1}) are assigned literature values.

U_{POT} (kJ^{-1}mol^{-1}) = γ $(\rho_m/M_m)^{1/3} + \delta$ (3)

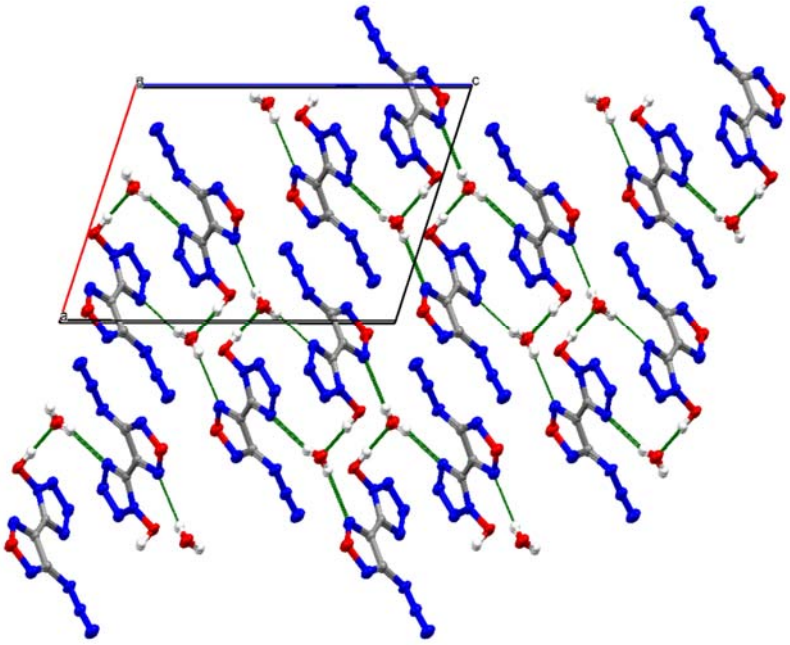


Figure S1. The packing mode of **4** from the b-axis

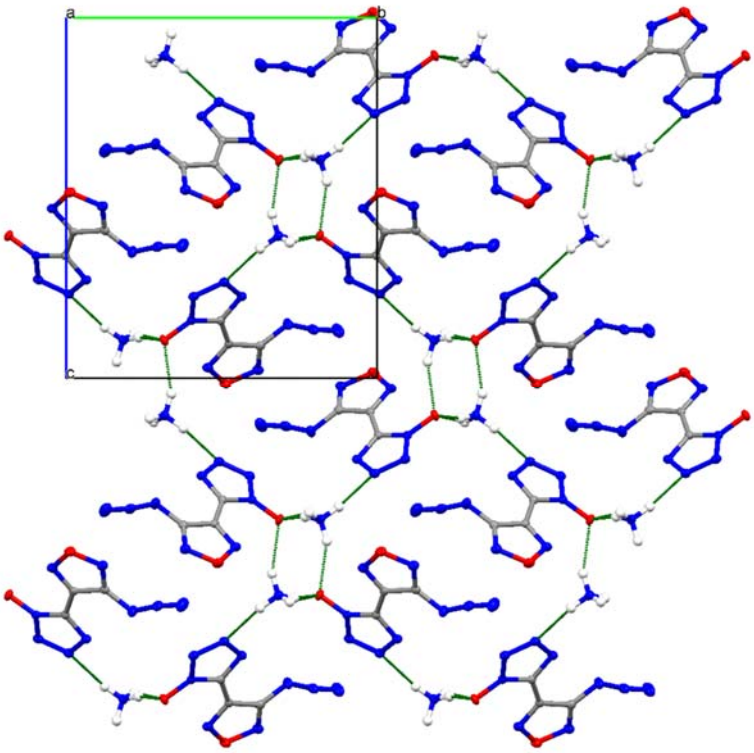


Figure S2. The packing mode of **4a** from the a-axis

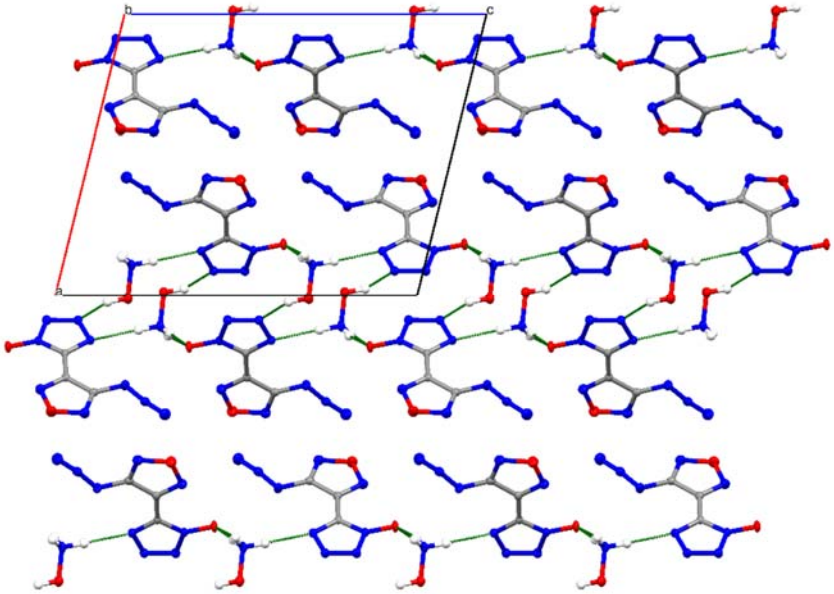


Figure S3. The packing mode of **4b** from the b-axis

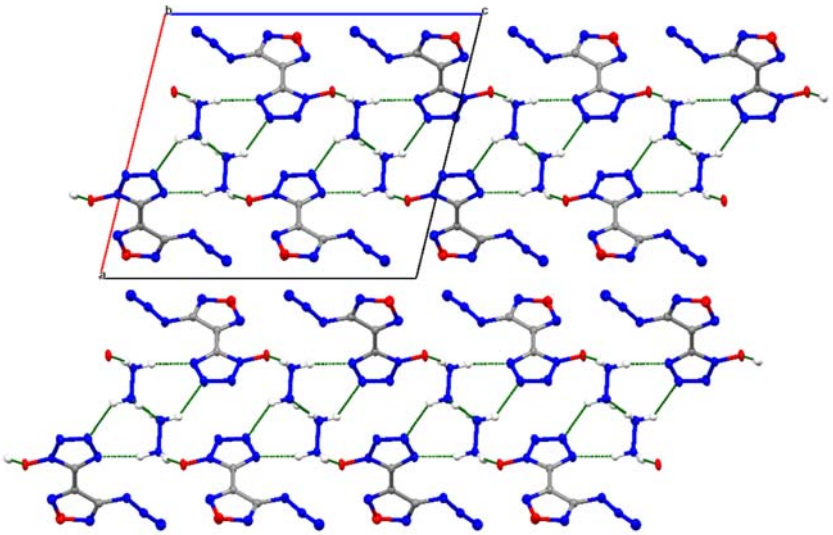


Figure S4. The packing mode of **4c** from the b-axis

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1. R. G. Parr and W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

2. Head-Gordon, M; Pople, J. A. MP2 Energy Evaluation by Direct Methods, *Chem. Phys. Lett*.1988, **153**, 503-506.

3. Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys*. 1991, **94**, 7221-7230.

4. Linstrom, P. J.; Mallard, W. G.; Eds. NIST Chemistry WebBook, NIST Standard Reference Database, 69, National Institute of Standards and Technology, 2005.

5. a) Trouton, F. Philos. Mag. 1884, **18**, 54-57; b) Westwell, M. S.; Searle, M. S.; Wales, D. J.; Williams, D. H. *J. Am. Chem. Soc*. 1995, **117**, 5013-5015.

6. (a) M. J. Kamlet, S. J. Jacobs, *J. Chem. Phys*. 1968, **48**, 23-35; (b) M. J. Kamlet, J. E. Ablard, *J. Chem. Phys*. 1968, **48**, 36-42; (c) M. J. Kamlet , C. Dicknison, *J. Chem. Phys*. 1968, **48**, 43-49. (d) H. Gao, C. Ye, C. Piekarski, J. M. Shreeve, *J. Phys. Chem. C* 2007, **111**, 10718-10731.