

Supporting information

Energetic furazan-triazole with high thermal stability and low sensitivity: facile synthesis, crystal structures and energetic properties

Yang Liu, Yuangang Xu, Qi Sun, Ming Lu*

School of Chemical Engineering, Nanjing University of Science and Technology,
Nanjing 210094, China

Email: luming@njust.edu.cn

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1. General methods

All reagents and solvents were purchased from Aladdin and Energy Chemical as analytical grade and were used as received. ^1H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts for ^1H and ^{13}C NMR are reported relative to Me_4Si as external standards. The melting and decomposition (onset) points were obtained at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ on a differential scanning calorimeter (Mettler Toledo DSC823e) in closed Al containers with a nitrogen flow of 50 ml min^{-1} . IR spectra were recorded using KBr pellets for solids on a Thermo Nicolet iS10 spectrometer. Elemental analyses were carried out on a vario EL III CHNOS elemental analyzer. Impact and friction sensitivity measurements were made using a standard BAM fallhammer and a BAM friction tester.

2. X-ray crystallography detail

A colorless crystal (**2a**) of dimensions 0.35×0.28×0.26 mm³, a colorless crystal (**2c**·H₂O) of dimensions 0.25×0.22×0.02 mm³, a needle-like crystal (**3**) of dimensions 0.22×0.20×0.18 mm³, a colorless crystal (**3a**) of dimensions 0.22×0.21×0.18mm³ were collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo-K α radiation (λ =0.071073 nm). The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data Reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Empirical absorption corrections were applied by using the SADABS (v2008/1) program. The structures were solved by direct methods and refined by the full matrix least-squares based on F² using SHELXTL--2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands were generated geometrically and refined using a riding model.

Table S2. Crystallographic data.

Compound	2a	2c ·H ₂ O	3	3a
CCDC number	1915061	1915062	1887194	1887195
formula	C ₄ H ₈ N ₁₀ O ₃	C ₄ H ₁₁ N ₁₁ O ₄	C ₄ H ₄ N ₁₀ O ₅	C ₄ H ₁₀ N ₁₂ O ₅
Mw	244.20	277.24	272.17	306.24
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	C2/c	P2 ₁ /c	P2 ₁ /c	P2 ₁ /c
a [Å]	18.7451(9)	9.0312(4)	10.0899(7)	14.260(2)
b [Å]	7.3716(4)	18.6286(7)	7.7440(5)	4.9236(7)
c [Å]	14.7077(6)	6.5567(3)	13.7323(9)	17.854(2)
α [°]	90	90	90°	90°
β [°]	110.5010(10)	96.737(2)	110.922(2)°	103.382(4)°
γ [°]	90	90	90°	90°
V [Å ³]	1903.61(16)	1095.47(8)	1002.24(12)	1219.5(3)
Z	8	4	4	4
T [K]	296	296	296	296
λ [Å]	0.71073	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.704	1.681	1.804	1.668
μ [mm ⁻¹]	0.145	0.145	0.162	0.148
F [000]	1008	576	552	632
θ range [°]	2.320-27.498	2.187-27.488	3.073- 27.535	2.345- 27.546
GOF on F	1.038	1.062	1.047	1.041
R ₁ [I>2 σ (I)]	0.0479	0.0495	0.0367	0.0440
wR ₂ [I>2 σ (I)]	0.1314	0.1327	0.0942	0.1081
R ₁ [all data]	0.0597	0.0634	0.0430	0.0690
wR ₂ [all data]	0.1393	0.1411	0.0978	0.1201

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

C(1)-N(1)	1.324(2)	N(1)-C(1)-N(8)	128.48(16)
C(1)-N(8)	1.337(2)	N(1)-C(1)-N(3)	109.89(15)
C(1)-N(3)	1.361(2)	N(8)-C(1)-N(3)	121.63(15)
C(2)-N(2)	1.307(2)	N(2)-C(2)-N(3)	109.71(15)
C(2)-N(3)	1.372(2)	N(2)-C(2)-C(3)	126.56(16)
C(2)-C(3)	1.453(2)	N(3)-C(2)-C(3)	123.63(15)
C(3)-N(4)	1.296(2)	N(4)-C(3)-C(4)	109.39(15)
C(3)-C(4)	1.444(2)	N(4)-C(3)-C(2)	121.32(16)
C(4)-N(5)	1.312(2)	C(4)-C(3)-C(2)	129.26(16)
C(4)-N(6)	1.370(2)	N(5)-C(4)-N(6)	131.06(16)
N(1)-N(2)	1.391(2)	N(5)-C(4)-C(3)	108.26(15)
N(3)-N(9)	1.4014(19)	N(6)-C(4)-C(3)	120.62(15)
N(4)-O(1)	1.375(2)	C(1)-N(1)-N(2)	106.86(13)
N(5)-O(1)	1.397(2)	C(2)-N(2)-N(1)	107.92(14)
N(6)-N(7)	1.312(2)	C(1)-N(3)-C(2)	105.61(14)
N(7)-O(3)	1.238(2)	C(1)-N(3)-N(9)	122.38(14)
N(7)-O(2)	1.270(2)	C(2)-N(3)-N(9)	131.91(14)
N(8)-H(8A)	0.8600	C(3)-N(4)-O(1)	105.96(14)
N(8)-H(8B)	0.8600	C(4)-N(5)-O(1)	105.28(14)
N(9)-H(9A)	0.8600	N(7)-N(6)-C(4)	116.53(15)
N(9)-H(9B)	0.8600	O(3)-N(7)-O(2)	119.96(15)
N(10)-H(10A)	0.9212	O(3)-N(7)-N(6)	124.49(16)
N(10)-H(10B)	1.0182	O(2)-N(7)-N(6)	115.56(15)
N(10)-H(10C)	0.9582	C(1)-N(8)-H(8A)	120.0
N(10)-H(10D)	0.9990	C(1)-N(8)-H(8B)	120.0
		H(8A)-N(8)-H(8B)	120.0
		N(3)-N(9)-H(9A)	120.0
		N(3)-N(9)-H(9B)	120.0
		H(9A)-N(9)-H(9B)	120.0
		H(10A)-N(10)-H(10B)	108.8
		H(10A)-N(10)-H(10C)	112.4
		H(10B)-N(10)-H(10C)	110.4
		H(10A)-N(10)-H(10D)	109.1
		H(10B)-N(10)-H(10D)	104.9
		H(10C)-N(10)-H(10D)	110.9
		N(4)-O(1)-N(5)	111.10(12)

Table S4 Bond lengths [Å] and angles [°] for compound **2c**·H₂O

C(1)-N(2)	1.319(2)	N(2)-C(1)-N(7)	126.64(17)
C(1)-N(7)	1.347(2)	N(2)-C(1)-N(1)	110.06(15)
C(1)-N(1)	1.357(2)	N(7)-C(1)-N(1)	123.29(17)
C(2)-N(3)	1.304(2)	N(3)-C(2)-N(1)	109.93(16)

C(2)-N(1)	1.376(2)	N(3)-C(2)-C(3)	125.63(16)
C(2)-C(3)	1.453(2)	N(1)-C(2)-C(3)	124.44(16)
C(3)-N(4)	1.297(2)	N(4)-C(3)-C(4)	109.72(16)
C(3)-C(4)	1.447(2)	N(4)-C(3)-C(2)	122.47(16)
C(4)-N(5)	1.314(2)	C(4)-C(3)-C(2)	127.81(16)
C(4)-N(8)	1.373(2)	N(5)-C(4)-N(8)	131.89(17)
N(1)-N(6)	1.404(2)	N(5)-C(4)-C(3)	108.08(16)
N(2)-N(3)	1.389(2)	N(8)-C(4)-C(3)	120.02(16)
N(4)-O(1)	1.378(2)	C(1)-N(1)-C(2)	105.24(14)
N(5)-O(1)	1.400(2)	C(1)-N(1)-N(6)	124.00(15)
N(6)-H(6A)	0.8600	C(2)-N(1)-N(6)	130.75(15)
N(6)-H(6B)	0.8600	C(1)-N(2)-N(3)	107.16(14)
N(7)-H(7A)	0.8600	C(2)-N(3)-N(2)	107.57(15)
N(7)-H(7B)	0.8600	C(3)-N(4)-O(1)	105.68(14)
N(8)-N(9)	1.322(2)	C(4)-N(5)-O(1)	105.31(14)
N(9)-O(2)	1.240(2)	N(1)-N(6)-H(6A)	120.0
N(9)-O(3)	1.244(2)	N(1)-N(6)-H(6B)	120.0
N(10)-N(11)	1.442(3)	H(6A)-N(6)-H(6B)	120.0
N(10)-H(10A)	0.8253	C(1)-N(7)-H(7A)	120.0
N(10)-H(10B)	0.8796	C(1)-N(7)-H(7B)	120.0
N(11)-H(11A)	0.8900	H(7A)-N(7)-H(7B)	120.0
N(11)-H(11B)	0.8900	N(9)-N(8)-C(4)	116.29(16)
N(11)-H(11C)	0.8900	O(2)-N(9)-O(3)	120.36(17)
O(4)-H(4A)	0.79(3)	O(2)-N(9)-N(8)	123.31(17)
O(4)-H(4B)	0.83(3)	O(3)-N(9)-N(8)	116.32(17)
		N(11)-N(10)-H(10A)	104.6
		N(11)-N(10)-H(10B)	102.8
		H(10A)-N(10)-H(10B)	110.1
		N(10)-N(11)-H(11A)	109.5
		N(10)-N(11)-H(11B)	109.5
		H(11A)-N(11)-H(11B)	109.5
		N(10)-N(11)-H(11C)	109.5
		H(11A)-N(11)-H(11C)	109.5
		H(11B)-N(11)-H(11C)	109.5
		N(4)-O(1)-N(5)	111.20(13)
		H(4A)-O(4)-H(4B)	110(3)

Table S5 Bond lengths [\AA] and angles [$^\circ$] for compound **3**

C1-N2	1.297(2)	N2-C1-N3	126.23(14)
C1-N3	1.378(2)	N2-C1-C2	109.27(13)
C1-C2	1.4278(19)	N3-C1-C2	124.48(13)
C2-N1	1.2947(19)	N1-C2-C1	109.03(12)
C2-C3	1.4529(18)	N1-C2-C3	124.49(12)

C3-N5	1.2951(17)	C1-C2-C3	126.47(13)
C3-N6	1.3806(16)	N5-C3-N6	111.15(11)
C4-N8	1.3186(19)	N5-C3-C2	122.03(12)
C4-N7	1.3224(19)	N6-C3-C2	126.81(12)
C4-N6	1.3525(16)	N8-C4-N7	129.14(13)
N1-O1	1.3727(17)	N8-C4-N6	124.75(13)
N2-O1	1.3894(19)	N7-C4-N6	106.08(12)
N3-N4	1.3507(17)	C2-N1-O1	105.64(12)
N3-H3	0.86	C1-N2-O1	104.93(12)
N4-O2	1.2200(19)	N4-N3-C1	123.15(14)
N4-O3	1.225(2)	N4-N3-H3	118.4
N5-N7	1.3710(17)	C1-N3-H3	118.4
N6-N9	1.4001(15)	O2-N4-O3	126.52(14)
N7-H7	0.93(2)	O2-N4-N3	119.08(15)
N8-H8A	0.86	O3-N4-N3	114.40(15)
N8-H8B	0.86	C3-N5-N7	104.53(11)
N9-N10	1.3200(16)	C4-N6-C3	106.39(11)
N10-O5	1.2488(14)	C4-N6-N9	120.66(11)
N10-O4	1.2568(15)	C3-N6-N9	131.79(11)
		C4-N7-N5	111.86(11)
		C4-N7-H7	127.9(12)
		N5-N7-H7	120.2(12)
		C4-N8-H8A	120
		C4-N8-H8B	120
		H8A-N8-H8B	120
		N10-N9-N6	110.21(10)
		O5-N10-O4	120.97(11)
		O5-N10-N9	115.65(11)
		O4-N10-N9	123.36(11)
		N1-O1-N2	111.12(11)

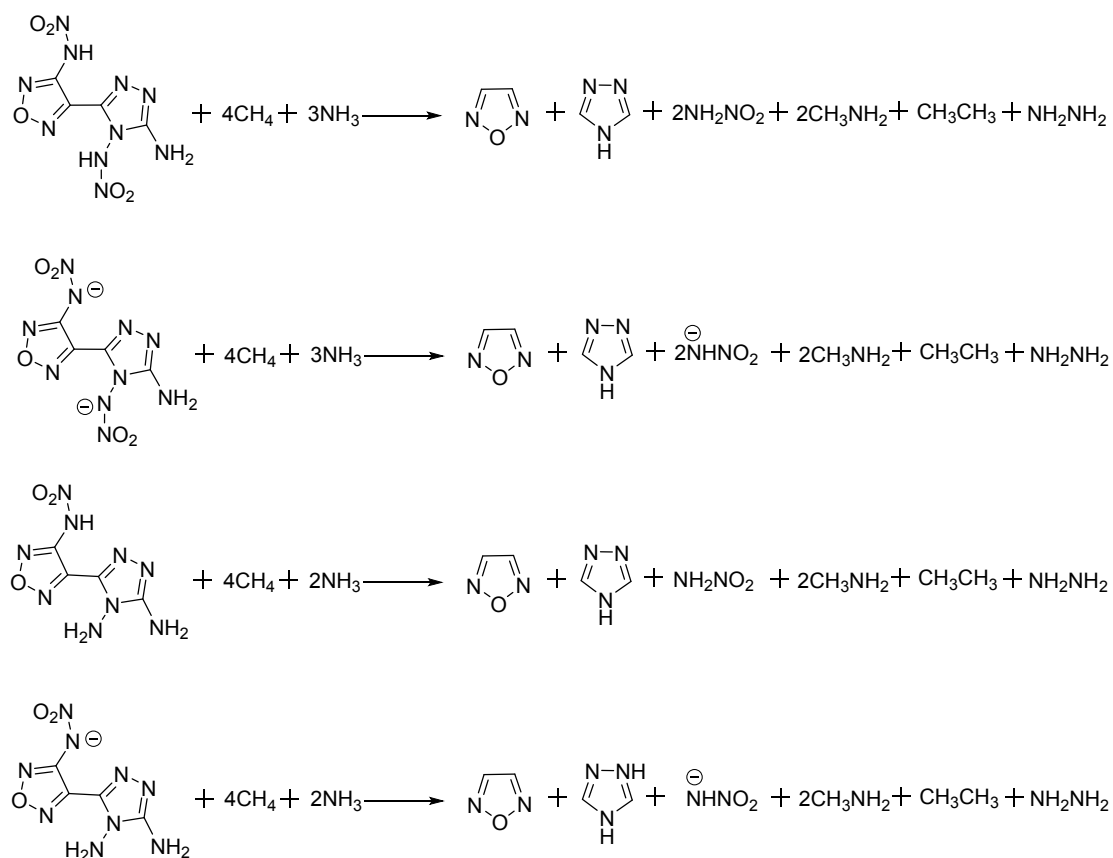
Table S6 Bond lengths [\AA] and angles [$^\circ$] for compound **3a**

C1-N2	1.315(2)	N2-C1-N1	127.14(15)
C1-N1	1.343(2)	N2-C1-N4	109.83(14)
C1-N4	1.362(2)	N1-C1-N4	122.93(15)
C2-N3	1.301(2)	N3-C2-N4	109.93(14)
C2-N4	1.377(2)	N3-C2-C3	126.22(15)
C2-C3	1.456(2)	N4-C2-C3	123.84(14)
C3-N7	1.297(2)	N7-C3-C4	109.64(15)
C3-C4	1.441(2)	N7-C3-C2	122.07(15)
C4-N8	1.316(2)	C4-C3-C2	128.28(15)
C4-N9	1.375(2)	N8-C4-N9	130.71(16)
N1-H1A	0.93(2)	N8-C4-C3	108.08(14)

N1-H1B	0.95(2)	N9-C4-C3	121.21(15)
N2-N3	1.400(2)	C1-N1-H1A	115.8(13)
N4-N5	1.3974(17)	C1-N1-H1B	119.3(14)
N5-N6	1.318(2)	H1A-N1-H1B	116(2)
N6-O1	1.233(2)	C1-N2-N3	107.24(13)
N6-O2	1.2629(18)	C2-N3-N2	107.47(13)
N7-O5	1.3745(19)	C1-N4-C2	105.52(13)
N8-O5	1.3930(19)	C1-N4-N5	124.55(13)
N9-N10	1.316(2)	C2-N4-N5	129.87(13)
N10-O3	1.228(2)	N6-N5-N4	108.64(13)
N10-O4	1.2808(19)	O1-N6-O2	120.87(15)
N11-H11C	0.862(14)	O1-N6-N5	124.43(14)
N11-H11D	0.878(14)	O2-N6-N5	114.70(14)
N11-H11B	0.856(14)	C3-N7-O5	105.71(13)
N11-H11A	0.897(13)	C4-N8-O5	105.26(14)
N12-H12A	0.864(14)	N10-N9-C4	116.65(15)
N12-H12D	0.843(14)	O3-N10-O4	120.63(15)
N12-H12C	0.817(14)	O3-N10-N9	125.37(16)
N12-H12B	0.850(14)	O4-N10-N9	113.99(15)
		H11C-N11-H11D	109.4(16)
		H11C-N11-H11B	112.5(17)
		H11D-N11-H11B	107(2)
		H11C-N11-H11A	113(2)
		H11D-N11-H11A	106.3(17)
		H11B-N11-H11A	107.7(16)
		H12A-N12-H12D	111.6(19)
		H12A-N12-H12C	103(2)
		H12D-N12-H12C	118(2)
		H12A-N12-H12B	110.3(19)
		H12D-N12-H12B	96(2)
		H12C-N12-H12B	118(2)
		N7-O5-N8	111.31(12)

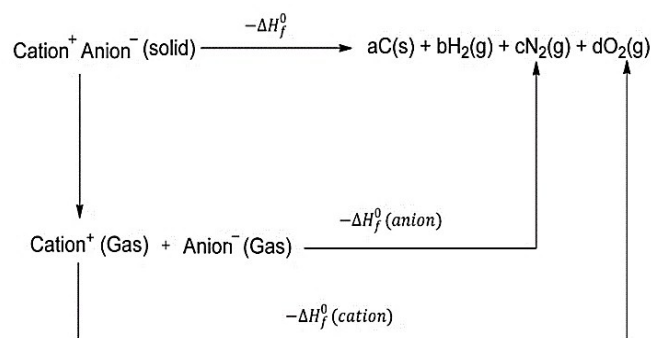
3. Theoretical study

All of the ab initio calculations involved in this work were carried out using the Gaussian 09 suite of programs.^[1] The geometric optimization and frequency analysis of the structures are based on available single-crystal structures and using the B3LYP functional with the 6-311++G (d, p) basis set. The geometrical were optimized with no constraints imposed under default convergence criteria. Total energy (E0) and zero-point energy (ZPE) were calculated with vibrational frequency analysis. The heats of formation were obtained by using the isodesmic reaction approach. Atomization energies were obtained by employing the G2 ab initio method. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.



Scheme S1. Isodesmic reactions for calculating heats of formation for new compounds.

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Scheme S2) [2]. The number is simplified by equation 1:



Scheme S2. Born-Haber Cycle for the formation of energetic salts.

$$\Delta H_f^\circ (\text{salt, 298 K}) = \Delta H_f^\circ (\text{cation, 298K}) + \Delta H_f^\circ (\text{anion, 298K}) - \Delta H_L \quad (1)$$

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al.^[2] [Eq. (2)]

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

where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-} , respectively. The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

$$U_{\text{POT}} [\text{kJ mol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for γ and the coefficients γ ($\text{kJ mol}^{-1} \text{ cm}$) and δ (kJ mol^{-1}) are assigned literature values.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature^[3, 4], the heat of sublimation can be estimated with Trouton's rule according to supplementary equation 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{\text{sub}} = 188/\text{J mol}^{-1}\text{K}^{-1} \times T$$

4. References

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