

New Journal of Chemistry

Supporting Information

Simple methods for the introduction of nitrate ester, amino and diazo-oxide substituents into dinitromethylpyrazole

1. Experimental Section
2. Reaction Mechanism
3. NMR Spectrum of The Prepared Compounds
4. DSC Curves of The Title Compounds
5. High Resolution Mass Spectrometry of Compounds **B** and **B3**
6. Crystallographic Data for Compounds potassium **A**, **C·H₂O** and **C1**
7. Computational Section

1. Experimental Section

General methods: All reagents are commercially available and were used without any purification. ^1H and ^{13}C NMR spectra were obtained by using a 500 MHz (Bruker Avance III) NMR spectrometer. Differential scanning calorimeter (DSC) was conducted on DSC823E thermal analyzer (Mettler Toledo). The FT-IR spectra were recorded with a NICOLETIS10 infrared spectrometer. The results of elemental analyses were gained by Elementar Vario MICRO CUBE (Germany) elemental analyzer. Density was measured by using UltraPYC 1200e gas pycnometer at 25 °C. BAM drop hammer (BFH-PEx) and BAM friction tester (FSKM-10) were performed to measure Impact and friction sensitivity, respectively. X-ray diffractions were carried out on a Bruker D8 VENTURE diffractometer using Mo-K α radiation ($\lambda=0.71073$ Å) at 170K. Details of the data collection and refinement are given in Table S1. High resolution mass spectral data were acquired on Acquity UPLC-Xevo G2 QTof (electrospray ionization: EI).

Caution: Although we have not encountered any difficulties in the synthesis of these new energetic compounds, standard safety precautions must be used. All compounds should be handled with extreme care.

1-Acetyl-4-chloro-3,5-dinitropyrazole (1)

CIDNP (4.62 g, 24 mmol) was dissolved in 80 mL DMF at room temperature, and NaHCO_3 (2.02 g, 24 mmol) was added. After the mixture was heated to 70 °C from room temperature. KBr (4.28 g, 36 mmol) and chloroacetone (3.33 g, 36 mmol) were added in turn. Subsequently, the reaction suspension was stirred for another 2 h. Ice water (200 mL) was poured into the reaction mixture and the precipitate was filtered and washed with ice water to give **1** (5.81 g, yield 97%) as a white solid after drying in air. FT-IR (KBr pellet, cm^{-1}): 3014, 2973, 2900, 1736, 1556, 1501, 1447, 1407, 1316, 1174, 1071, 894, 788, 744, 631; ^1H NMR (500 MHz, DMSO-d_6): $\delta=2.31$ (s, 3H), 5.81 (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta=200.07$, 149.12, 142.99, 106.56, 64.58, 27.39 ppm; Anal. Calcd. For $\text{C}_6\text{H}_5\text{ClN}_4\text{O}_5$: C 28.99, H 2.03, N 22.54; found: C 28.86, H 2.06, N 22.43.

3,5-Dinitro-4-chloro-1-(dinitromethyl)pyrazole (A)

Compound **1** (2.4 g, 9.67 mmol) was dispersed in H_2SO_4 (36 mL) at 0 °C. Then fuming HNO_3 (30 mL) was added dropwise, maintaining the internal temperature not exceeding 20 °C. The mixture was stirred at 30 °C for 5 h before pouring into ice water (300 mL), and the resulting mixture was stirred for 30 min. The precipitated was separated from the solution and dried to get **A** (2.41 g, yield 84%) as a white solid. FT-IR (KBr pellet, cm^{-1}): 2872, 2360, 1631, 1581, 1537, 1432, 1380, 1312, 1268, 1250, 1091, 985, 856, 829, 816, 793, 725, 619; ^1H NMR (500 MHz, DMSO-d_6): $\delta=7.12$ (s, 1H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta=156.14$, 133.56, 115.16, 112.12 ppm; Anal. Calcd. For $\text{C}_4\text{HClN}_6\text{O}_8$: C 16.20, H 0.34, N 28.34; found: C 16.31, H 0.35, N 28.18.

Silver 3,5-dinitro-4-nitroso-1-(dinitromethyl)pyrazole (B1)

Compound **A** (1.29 g, 4.3 mmol) was dissolved in methanol (9 mL) followed by addition of KI (0.75 g, 4.5 mmol) at room temperature. Then the mixture was stirred for about 20 minutes. A large amount of yellow solid precipitated from the reaction mixture and was collected by filtration followed by washing with a small amount of ethanol to give potassium salt. Subsequently, AgNO_3 (2.45 g, 14.4 mmol) was added into a suspension of potassium salt and water (30mL). The mixture was stirred in the dark for 3 h at room temperature. Then the insoluble solid was filtered, and the filtrate was evaporated under vacuum to get a yellow solid **B1** (0.68 g, 44%). FT-IR (KBr pellet, cm^{-1}): 3659, 1621, 1567, 1496, 1423, 1371, 1317, 1276, 1217, 1149, 1007, 867, 815, 702, 641, 612; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta=150.58$, 141.24, 131.39, 107.38 ppm; Anal. Calcd. For $\text{C}_4\text{AgN}_7\text{O}_{11}$: C 11.17, N 22.80; found: C 11.05, N 22.57.

3,5-Dinitro-4-nitroso-1-(dinitromethyl)pyrazole (B)

Compound **B1** (1.28 g, 3.0 mmol) was dissolved in water, and 20% sulfuric acid solution was added dropwise into the solution until the pH value reached 1. Subsequently, the mixture was dried at low temperature and recrystallized from acetonitrile to give **B** (0.51 g, 52%) as a white solid. FT-IR (KBr pellet, cm^{-1}): 3033, 2913, 1613, 1595, 1575, 1529, 1432, 1355, 1311, 1262, 1060, 938, 841, 799, 748; ^1H NMR (500 MHz, DMSO-d_6): $\delta=4.26$ (s, 2H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta=150.65$, 141.31, 131.44, 107.47 ppm; Anal. Calcd. For $\text{C}_4\text{HN}_7\text{O}_{11}$: C 14.87, H 0.31, N 30.35; found: C 14.74, H 0.39, N 30.29; HRMS (EI) m/z : ($\text{M}+\text{H}^+$) Calcd for $\text{C}_4\text{H}_2\text{N}_7\text{O}_{11}$ 323.9807; Found 323.9804.

General procedures for the preparation of salts B2-B3:

The obtained monosilver salt **B1** (107 mg, 0.25 mmol) was suspended in water (7mL), and one equivalent of the corresponding hydrochloride salt was added. The mixture was stirred at room temperature overnight. After removing the insoluble solids, the filtrate was concentrated to get **B2** and **B3**.

Hydroxylammonium 3,5-dinitro-4-nitroso-1-(dinitromethyl)pyrazole (B2). Light yellow solid; Yield: 71 mg (81%); FT-IR (KBr pellet, cm^{-1}): 3659, 3564, 3480, 2987, 2900, 1616, 1566, 1507, 1423, 1373, 1329, 1318, 1213, 1146, 1007, 868, 825, 701; ^1H NMR (500 MHz, DMSO-d_6): $\delta=10.34$ (s, 3H) ppm; ^{13}C NMR (125 MHz, DMSO-d_6): $\delta=150.98$, 141.61, 131.80, 107.87 ppm; Anal. Calcd. For $\text{C}_4\text{H}_4\text{N}_8\text{O}_{12}$: C 13.49, H 1.13, N 31.47; found: C 13.43, H 1.24, N 31.36.

Guanidinium 3,5-dinitro-4-nitroso-1-(dinitromethyl)pyrazole (B3). White powder; Yield: 78 mg (83%); FT-IR (KBr pellet, cm^{-1}): 3639, 3463, 3441, 3362, 3284, 3198, 2987, 2900, 1660, 1562, 1514, 1482, 1422, 1329, 1230, 1147, 1097, 1007, 867, 814, 760, 700; ^1H NMR (500 MHz, DMSO-d_6): $\delta=7.01$ (s, 6H) ppm; ^{13}C NMR (125MHz, DMSO-d_6): $\delta=158.12$, 150.63, 141.28,

131.44, 107.47 ppm; Anal. Calcd. For $C_5H_6N_{10}O_{11}$: C 15.71, H 1.58, N 36.65; found: C 15.69, H 1.54, N 36.63; HRMS (EI) m/z: (M^+H^+) Calcd for $C_4HN_7O_{11}$ 322.9734; found 322.9749.

Ammonium 3,5-dinitro-4-amino-1-(dinitromethyl)pyrazole (C)

Compound **A** (1.25 g, 4.23 mmol) was dissolved in ammonia (25%, 25 mL), and the mixture was heated at 60 °C in hydrothermal reactor. After 10 h, the solution was concentrated to 10 mL and placed at 2 °C for 1 h. Many needle-like crystals were obtained in the orange solution. The precipitate was filtered followed by drying in air to give **C** (0.77g, 62%) as orange needles. FT-IR (KBr pellet, cm^{-1}): 3589, 3454, 3238, 2914, 1639, 1573, 1509, 1467, 1429, 1320, 1281, 1202, 1185, 1232, 979, 875, 816, 735, 662; 1H NMR (500MHz, DMSO- d_6): δ =7.44 (br, 2H), 7.10 (br, 4H) ppm; ^{13}C NMR (125MHz, DMSO- d_6): δ =143.09, 132.15, 130.10, 129.45 ppm; Anal. Calcd. For $C_4H_6N_8O_8$: C 16.33, H 2.06, N 38.10; found: C 16.37, H 2.21, N 38.34.

4-Diazo-3-nitro-5-one-1-(dinitromethyl)pyrazole zwitterion (C1)

Compound **C** (100 mg, 0.34 mmol) was dispersed in water (3 mL), the mixture was stirred at 50 °C until the mixture became clear. Then the sulfuric acid solution (20%) was added into the solution. After stirring for 0.5 h, the solution was allowed to stand for 1 h at 2 °C, and the yellow precipitates were collected by filtration to give **C1** (48 mg, 51%). FT-IR (KBr pellet, cm^{-1}): 3674, 3445, 3002, 2987, 2900, 2175, 1715, 1601, 1581, 1536, 1416, 1370, 1300, 1113, 1065, 967, 804, 741, 701, 591; 1H NMR (500MHz, CD_3CN): δ =8.13 (s, 1H) ppm; ^{13}C NMR (125MHz, CD_3CN): δ =161.19, 149.40, 104.54, 67.02 ppm; Anal. Calcd. For $C_4HN_7O_7$: C 18.54, H 0.39, N 37.84; found: C 18.35, H 0.41, N 37.79.

2. Reaction Mechanism

The structure of **A** with a chloro group adjacent to two nitro groups, gives rise to good reactivity to nucleophiles such as ammonia, nitrate ion, et al. When nitrate ion or ammonia is added to compound **A**, the nucleophile attacks the 4-position carbon atom to form an intermediate product, and finally chloride ion or hydrogen chloride leaves to obtain the final corresponding product (Figure S1).

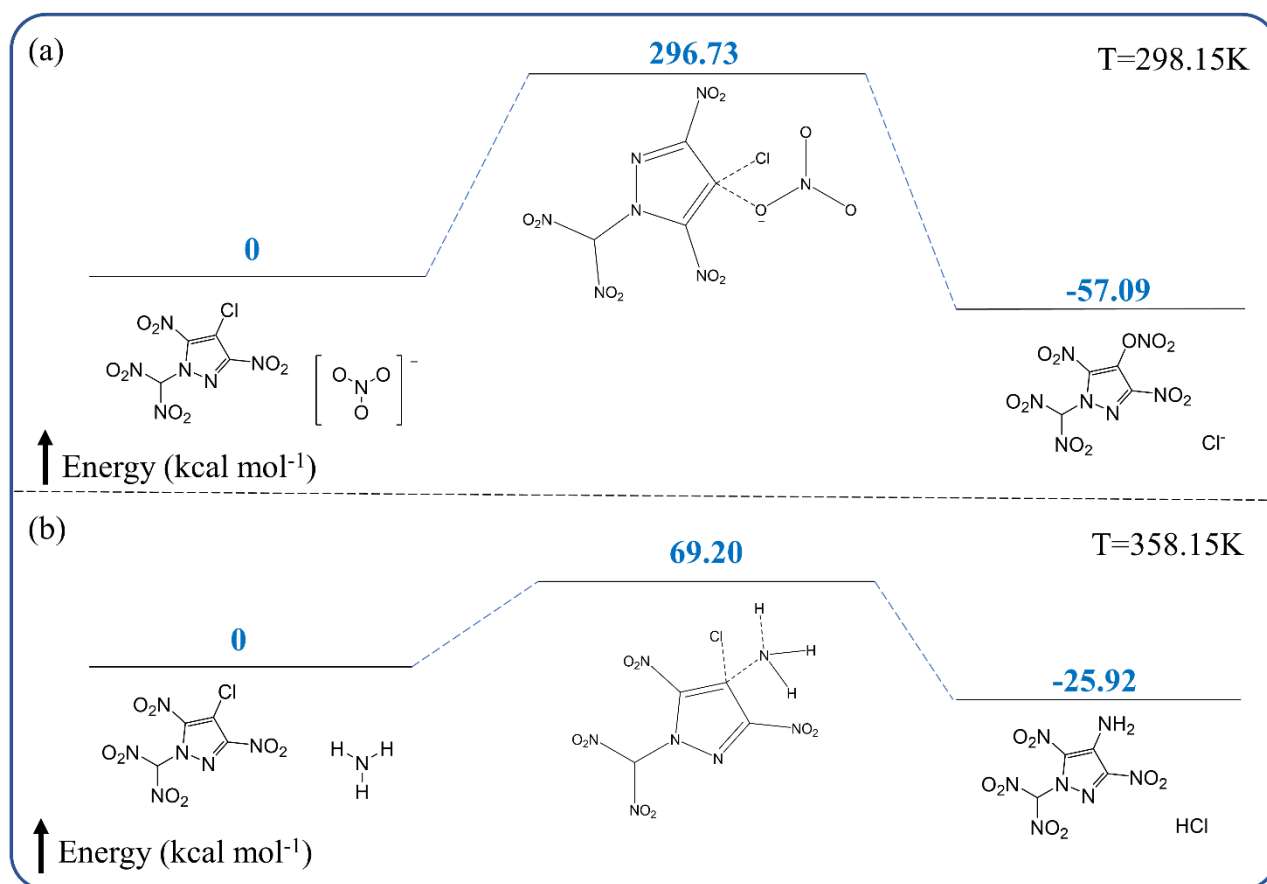


Figure S1. The free energies relative to the reactants.

3. NMR Spectrum of The Prepared Compounds

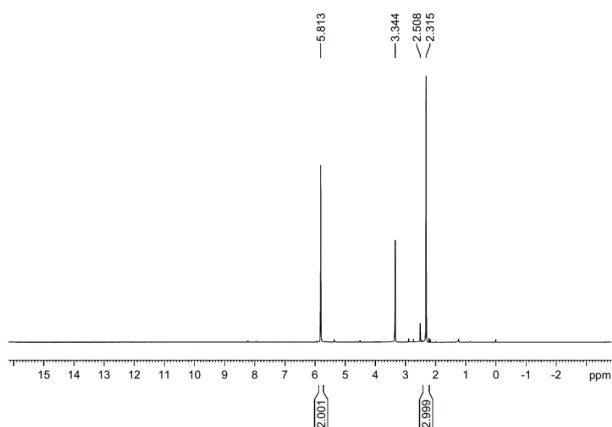


Figure S2. ^1H NMR spectrum of compound 1.

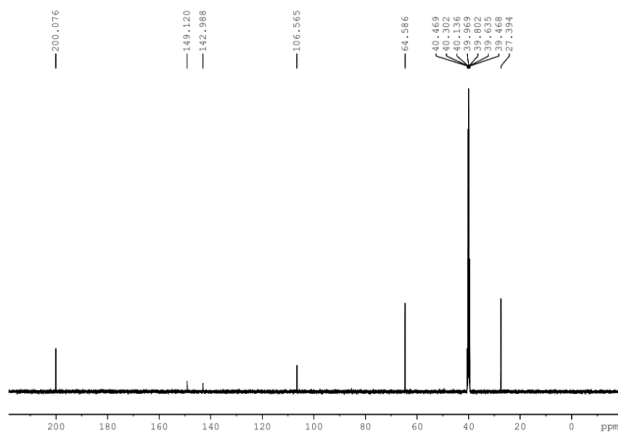


Figure S3. ^{13}C NMR spectrum of compound 1.

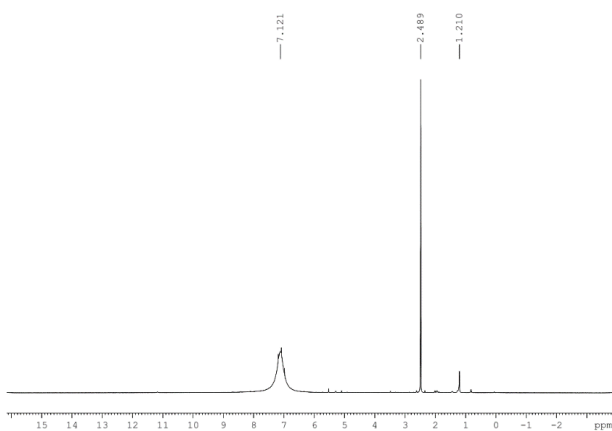


Figure S4. ^1H NMR spectrum of compound A.

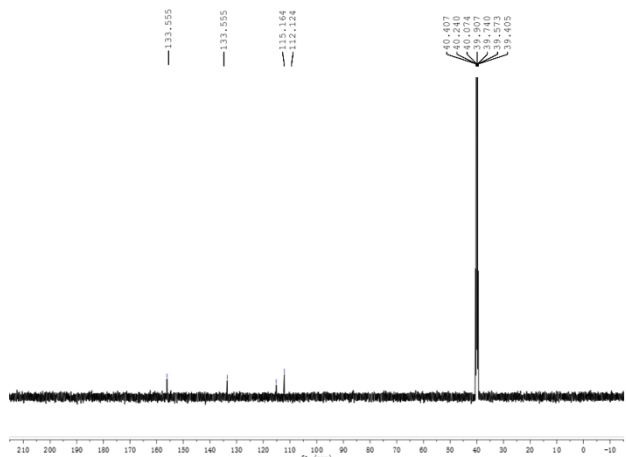


Figure S5. ^{13}C NMR spectrum of compound A.

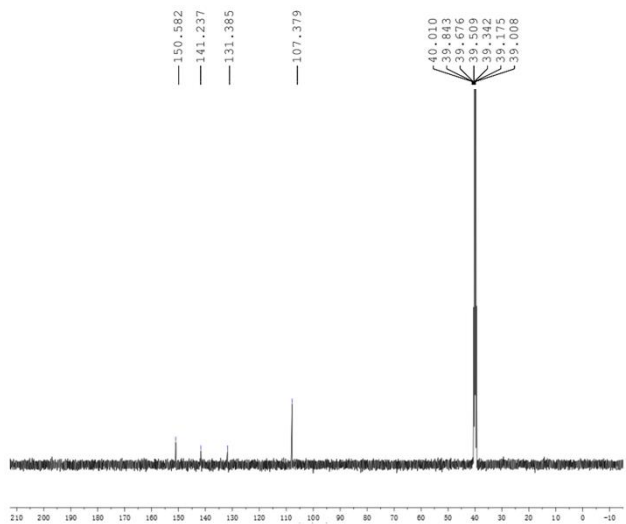


Figure S6. ^{13}C NMR spectrum of compound B1.

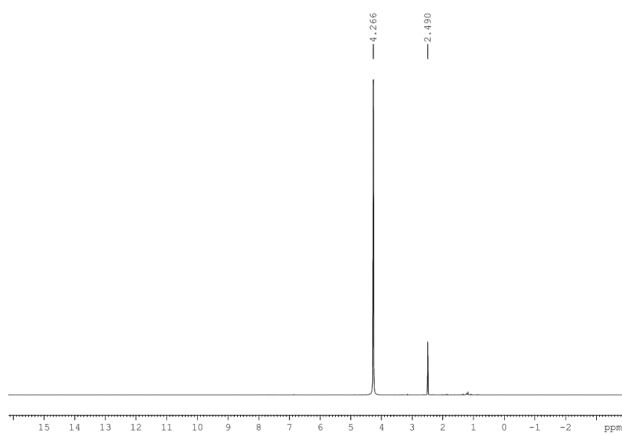


Figure S7. ^1H NMR spectrum of compound B.

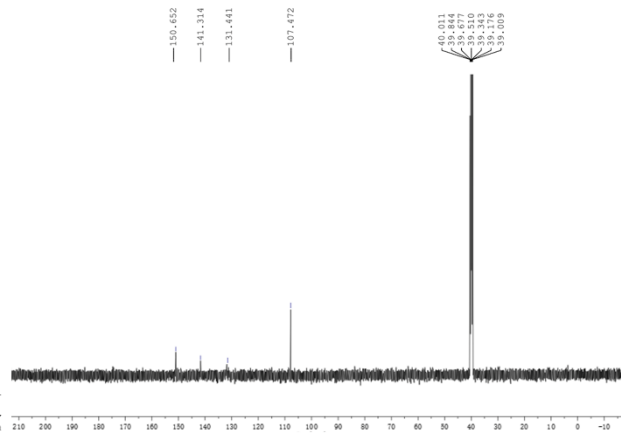


Figure S8. ^{13}C NMR spectrum of compound B.

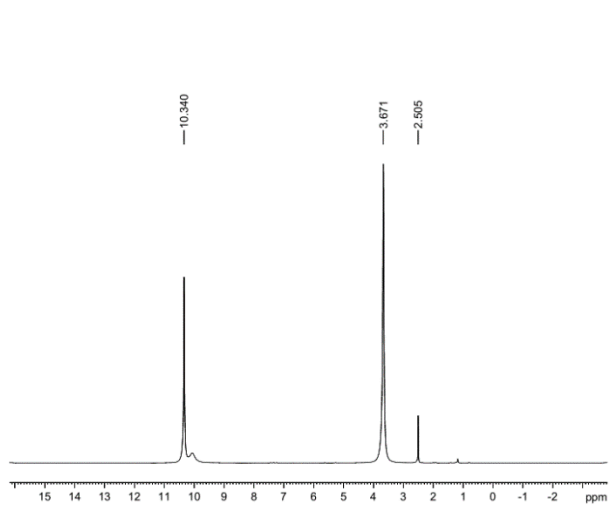


Figure S9. ^1H NMR spectrum of compound B2.

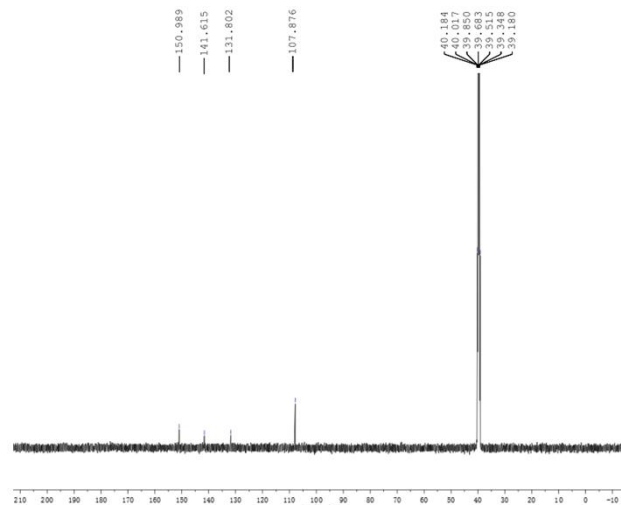


Figure S10. ^{13}C NMR spectrum of compound B2.

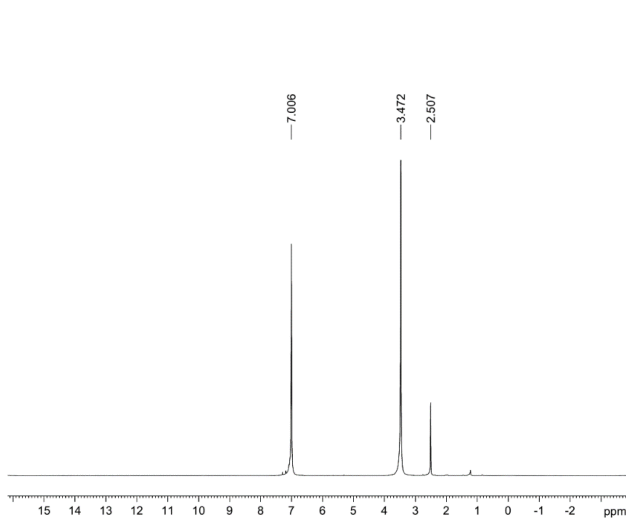


Figure S11. ^1H NMR spectrum of compound B3.

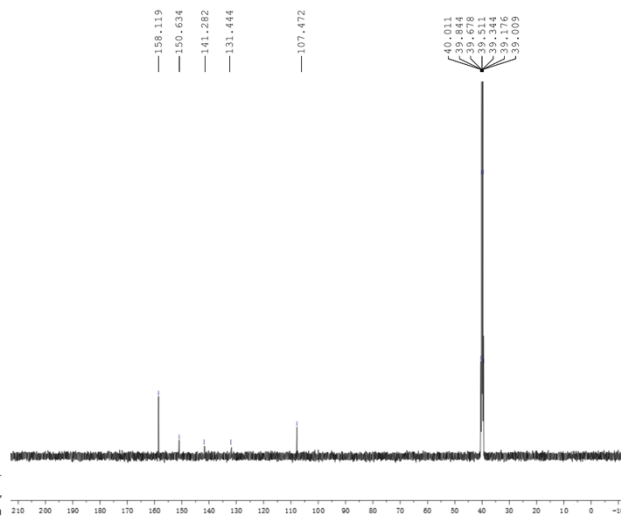


Figure S12. ^{13}C NMR spectrum of compound B3.

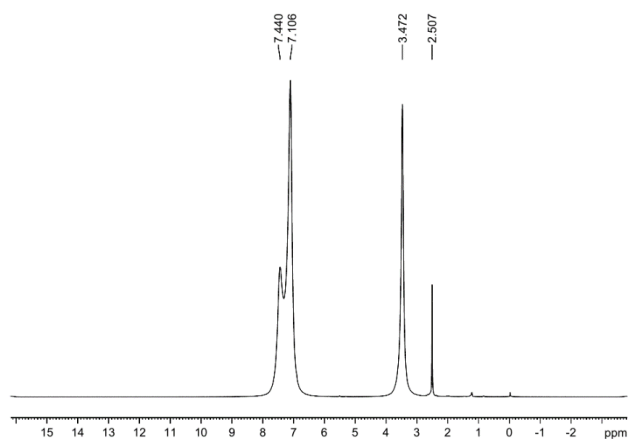


Figure S13. ¹H NMR spectrum of compound C.

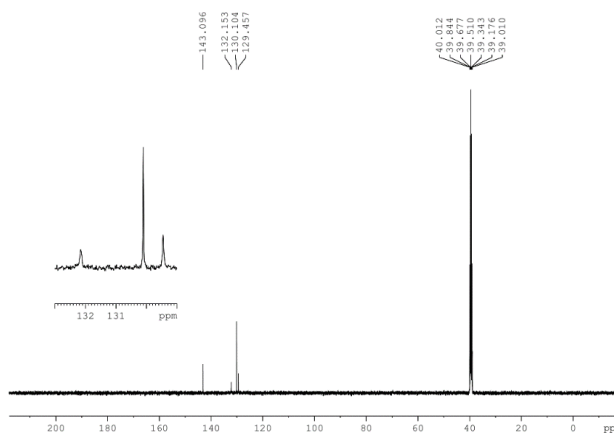


Figure S14. ¹³C NMR spectrum of compound C.

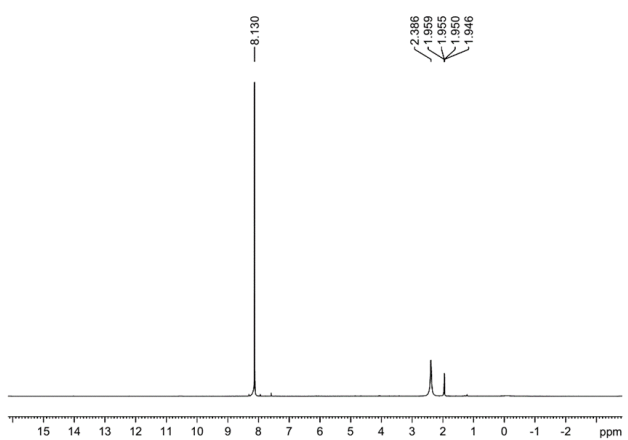


Figure S15. ¹H NMR spectrum of compound C1.

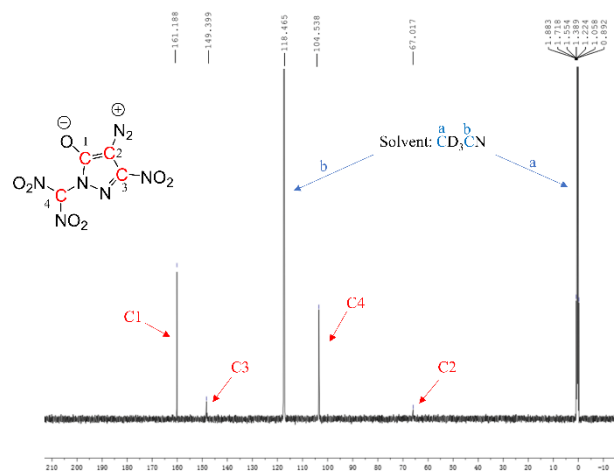


Figure S16. ¹³C NMR spectrum of compound C1.

4. DSC Curves of The Title Compounds

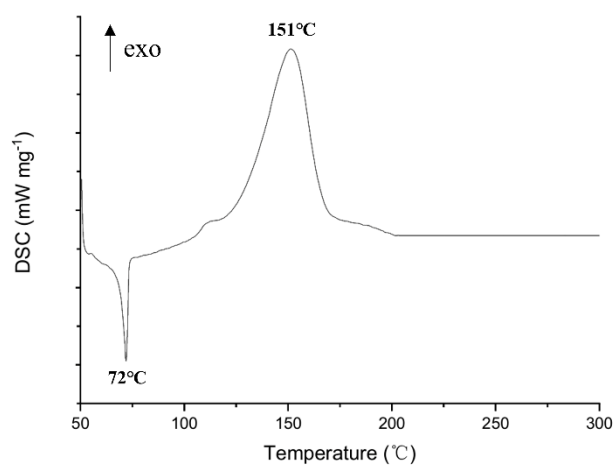


Figure S17. DSC curves of compound A.

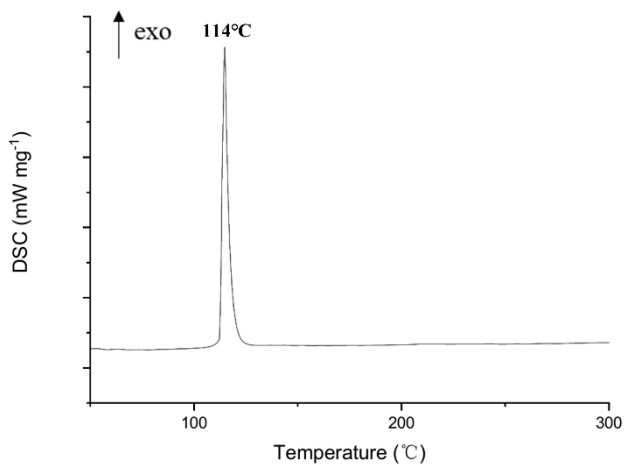


Figure S18. DSC curves of compound B.

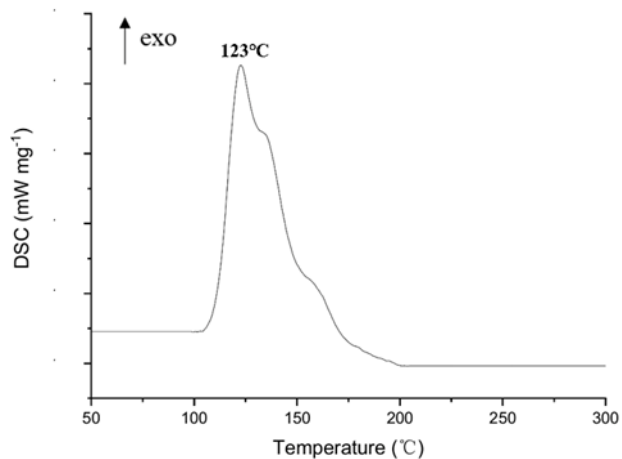


Figure S19. DSC curves of compound B1.

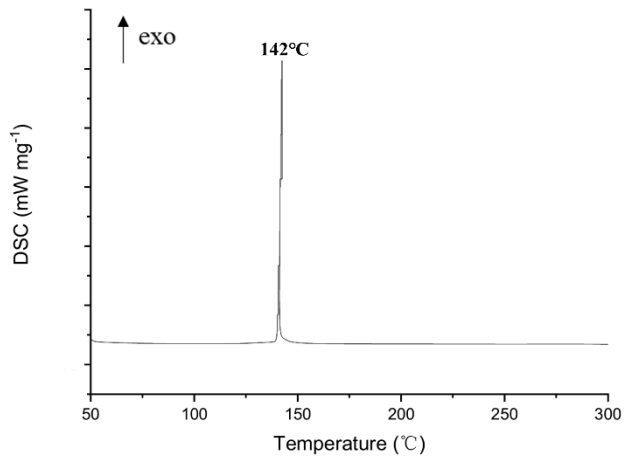


Figure S20. DSC curves of compound B2.

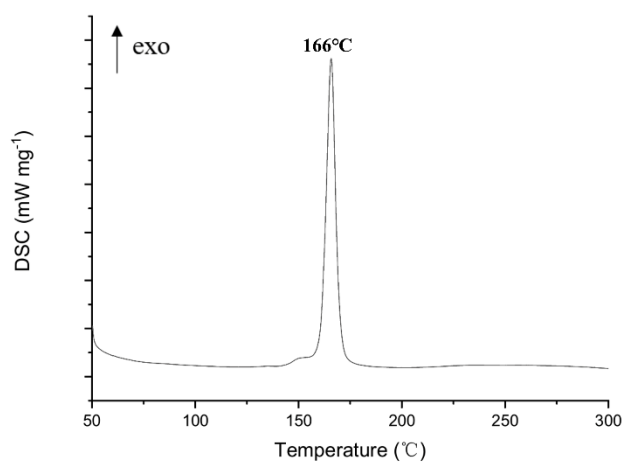


Figure S21. DSC curves of compound B3.

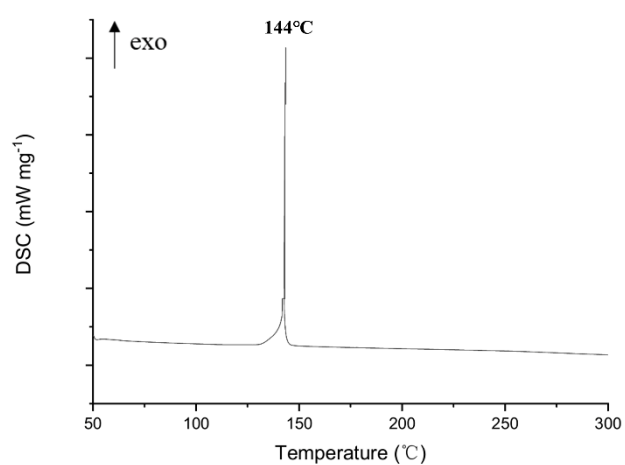


Figure S22. DSC curves of compound C.

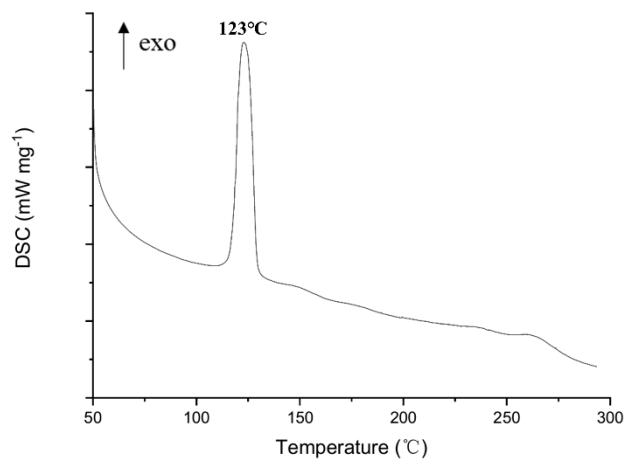


Figure S23. DSC curves of compound C1.

5. High Resolution Mass Spectrometry of Compounds B and B3

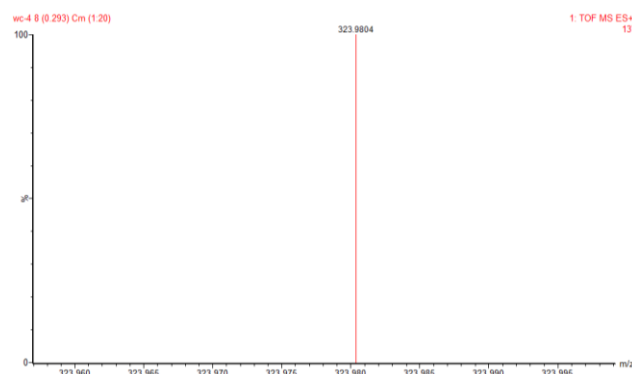


Figure S24. Mass spectrometry of compound B.

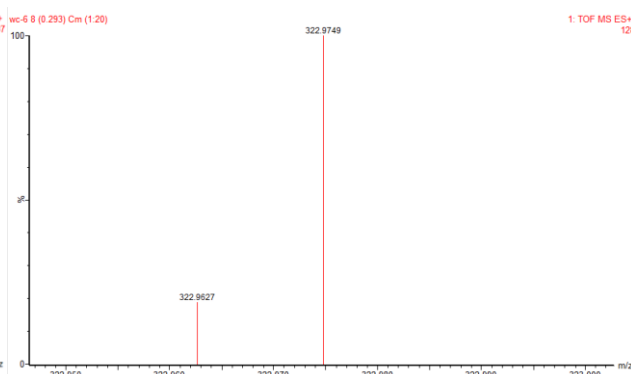


Figure S25. Mass spectrometry of compound B3.

6. Crystallographic Data for Compounds potassium A, C and C1

We refine the crystal structure by using NoSpherA2,^[1] an implementation of non-spherical atom-form-factors in Olex2, with improved structural quality and precision.

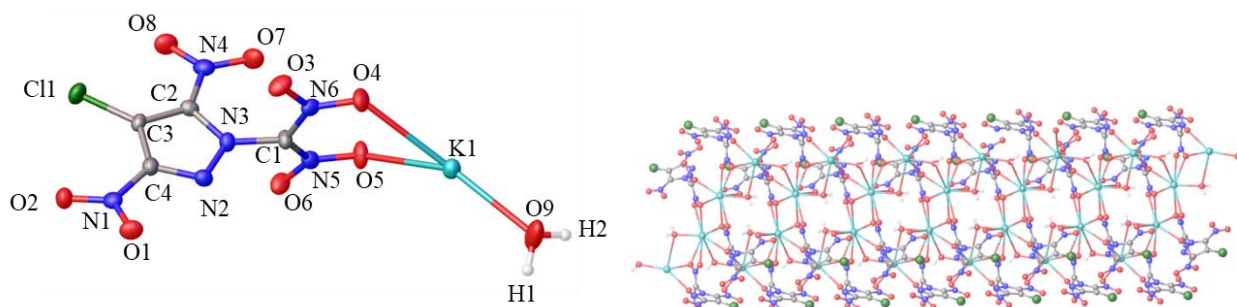


Figure S26. X-ray crystal structure and packing diagram of potassium A.

Table S1. Crystal data and structure refinement for compounds potassium A, C-H₂O and C1.

Compound	potassium A	C-H ₂ O	C1
CCDC	CCDC-2127242	CCDC-2127241	CCDC-2129989
Empirical formula	C ₄ H ₂ ClKN ₆ O ₉	C ₄ H ₈ N ₈ O ₉	C ₄ HN ₇ O ₇
Formula weight	352.67	312.16	259.096
Temperature	170 K	170 K	150 K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 2 ₁ /c	P 2 ₁ /c	P 2 ₁ /c
Unit cell dimensions	a = 11.100(3) Å	a = 10.9418(19) Å	a = 5.4325(3) Å
	b = 15.461(3) Å	b = 15.988(3) Å	b = 13.6955(8) Å
	c = 6.9205(19) Å	c = 6.7678(10) Å	c = 12.3557(7) Å
	α = 90°	α = 90°	α = 90°
	β = 102.99(1)°	β = 100.161(6)°	β = 93.876(2)°
	γ = 90°	γ = 90°	γ = 90°
Volume	1157.3(5) Å ³	1165.4(3) Å ³	917.17(9) Å ³

Z	4	4	4
Density (calculated)	2.024 mg/m ³	1.779 Mg/m ³	1.876 Mg/m ³
Absorption coefficient	0.755 mm ⁻¹	0.172 mm ⁻¹	0.179 mm ⁻¹
F(000)	705.9	640.7	520.4
Crystal size	0.11 x 0.08 x 0.03 mm ³	0.15 x 0.08 x 0.05 mm ³	0.15 x 0.08 x 0.05 mm ³
2 θ range for data collection	3.76 to 50.88°	4.56 to 52.06°	4.44 to 52.86°
Index ranges	-13 ≤ h ≤ 13, -18 ≤ k ≤ 18, -8 ≤ l ≤ 7	-13 ≤ h ≤ 11, -19 ≤ k ≤ 19, -8 ≤ l ≤ 7	-6 ≤ h ≤ 6, -17 ≤ k ≤ 16, -15 ≤ l ≤ 14
Reflections collected	7926	11341	6875
Independent reflections	2128 [R(int) = 0.0849]	2274 [R(int) = 0.0733]	1848 [R(int) = 0.0405]
Data / restraints / parameters	2128 / 2 / 198	2274 / 9 / 262	1848 / 0 / 163
Goodness-of-fit on F ²	1.129	1.115	1.083
Final R indices [I > 2σ(I)]	R1 = 0.0501, wR2 = 0.0804	R1 = 0.0406, wR2 = 0.0490	R1 = 0.0387, wR2 = 0.0814
Final R indices (all data)	R1 = 0.0975, wR2 = 0.1027	R1 = 0.0801, wR2 = 0.0604	R1 = 0.0576, wR2 = 0.0938
Largest diff. peak and hole	0.71 and -0.82 e.Å ⁻³	0.41 and -0.52 e.Å ⁻³	0.33 and -0.31 e.Å ⁻³

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound potassium A. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
K1	10306.4(9)	3584.9(7)	3687.3(14)	25.2(3)
O7	3108(3)	3022(2)	4546(4)	27.8(8)
O1	7468(3)	5211(2)	6608(4)	28.6(8)
O4	7616(3)	2356(2)	7586(4)	29.6(8)
O3	9201(3)	2901(2)	6635(5)	31.4(8)
O2	9143(3)	4586(2)	6172(5)	31.8(8)
O6	6821(3)	4465(2)	12400(4)	31.5(8)
N2	8162(3)	2980(2)	7014(5)	21.9(9)
O8	2462(3)	3580(2)	7007(4)	30.8(8)
O5	8224(3)	4272(2)	10689(4)	35.3(9)
N1	8090(3)	4542(2)	6522(5)	22.1(9)
N4	6430(3)	3790(2)	7429(5)	20.2(9)
N6	3279(3)	3366(2)	6178(5)	21.4(9)
N5	5398(3)	3547(2)	6139(5)	20.5(9)
N3	7153(4)	4249(2)	10898(5)	25.4(9)

C2	6213(4)	3943(3)	9266(6)	18.7(10)
C3	4986(4)	3804(3)	9185(6)	18.2(10)
C1	7559(4)	3760(3)	6837(6)	21.0(10)
O9	10968(4)	3456(4)	159(6)	61.0(13)
C4	4542(4)	3568(3)	7196(6)	20.9(10)
Cl1	4225.4(10)	3889.2(8)	11037.2(16)	26.1(3)

Table S3. Bond lengths [Å] and angles [°] for potassium A.

K(1)-O(7) ¹	3.154(3)
K(1)-O(1) ²	3.136(3)
K(1)-O(4) ³	3.255(3)
K(1)-O(3)	2.812(3)
K(1)-O(3) ³	2.831(3)
K(1)-O(2)	2.831(3)
K(1)-O(2) ²	2.891(3)
K(1)-O(8) ¹	2.921(3)
K(1)-O(5) ⁴	2.936(3)
K(1)-N(6) ¹	3.379(4)
K(1)-O(9) ⁵	3.346(5)
K(1)-O(9)	2.710(4)
O(7)-N(6)	1.224(4)
O(1)-N(1)	1.253(4)
O(4)-N(2)	1.250(4)
O(3)-N(2)	1.246(4)
O(2)-N(1)	1.247(4)
O(6)-N(3)	1.225(4)
N(2)-C(1)	1.371(5)
O(8)-N(6)	1.224(4)
O(5)-N(3)	1.230(4)
N(1)-C(1)	1.384(5)
N(4)-N(5)	1.338(5)
N(4)-C(2)	1.367(5)
N(4)-C(1)	1.454(5)
N(5)-C(4)	1.323(5)
C(2)-C(3)	1.367(5)
C(3)-Cl(1)	1.692(4)
O(7) ^{1*} -K(1)-O(4) ^{2*}	137.27(9)
O(7) ^{1*} -K(1)-N(6) ^{1*}	21.23(7)
O(7) ^{1*} -K(1)-O(9) ^{3*}	62.80(9)

O(1) ^{4*} -K(1)-O(7) ^{1*}	54.44(8)
O(1) ^{4*} -K(1)-O(4) ^{2*}	160.86(8)
O(1) ^{4*} -K(1)-N(6) ^{1*}	53.10(8)
O(4) ^{2*} -K(1)-O(9) ^{3*}	77.10 (10)
O(3)-K(1)-O(7) ^{1*}	109.38(9)
O(3) ^{2*} -K(1)-O(7) ^{1*}	99.69(9)
O(3) ^{2*} -K(1)-O(1) ^{4*}	138.50(9)
O(3) ^{2*} -K(1)-O(1) ^{4*}	135.04(8)
O(3)-K(1)-O(4) ^{2*}	41.28(8)
O(3)-K(1)-O(4) ^{2*}	58.32(9)
O(3)-K(1)-O(2) ^{4*}	117.84(9)
O(3) ^{2*} -K(1)-O(2) ^{4*}	151.08(10)
O(3) ^{2*} -K(1)-O(2) ^{4*}	122.86(9)
O(3) ^{2*} -K(1)-O(2)	55.40(9)
O(3)-K(1)-O(8) ^{1*}	80.92(9)
O(3) ^{2*} -K(1)-O(8) ^{1*}	125.35(10)
O(3)-K(1)-O(5) ^{5*}	104.25(9)
O(3) ^{2*} -K(1)-O(5) ^{5*}	75.85(10)
O(3)-K(1)-N(6) ^{1*}	97.33(9)
O(3) ^{2*} -K(1)-N(6) ^{1*}	115.97(10)
O(3)-K(1)-O(9) ^{3*}	61.71(9)
O(3) ^{2*} -K(1)-O(9) ^{3*}	55.14(10)
O(2)-K(1)-O(7) ^{1*}	126.97(9)
O(2) ^{4*} -K(1)-O(7) ^{1*}	94.10(9)
O(2)-K(1)-O(1) ^{4*}	100.89(9)
O(2) ^{4*} -K(1)-O(1) ^{4*}	42.08(8)
O(2) ^{4*} -K(1)-O(4) ^{2*}	128.41(9)
O(2)-K(1)-O(4) ^{2*}	82.33(8)
O(2) ^{4*} -K(1)-O(8) ^{1*}	81.15(10)
O(2)-K(1)-O(8) ^{1*}	85.90(9)
O(2) ^{4*} -K(1)-O(5) ^{5*}	78.27(10)
O(2)-K(1)-O(5) ^{5*}	80.63(10)
O(2)-K(1)-N(6) ^{1*}	105.76(9)
O(2) ^{4*} -K(1)-N(6) ^{1*}	84.60(9)
O(2) ^{4*} -K(1)-O(9) ^{3*}	151.89(11)
O(2)-K(1)-O(9) ^{3*}	115.41(9)
O(8) ^{1*} -K(1)-O(7) ^{1*}	41.64(8)
O(8) ^{1*} -K(1)-O(1) ^{4*}	62.28(8)
O(8) ^{1*} -K(1)-O(4) ^{2*}	136.83(9)

O(8) ^{1*} -K(1)-O(5) ^{5*}	158.79(10)
O(8) ^{1*} -K(1)-N(6) ^{1*}	20.81(8)
O(8) ^{1*} -K(1)-O(9) ^{3*}	70.93(11)
O(5) ^{5*} -K(1)-O(7) ^{1*}	145.00(9)
O(5) ^{5*} -K(1)-O(4) ^{2*}	57.39(9)
O(5) ^{5*} -K(1)-N(6) ^{1*}	156.95(9)
O(5) ^{5*} -K(1)-O(9) ^{3*}	129.82(11)
O(9)-K(1)-O(7) ^{1*}	72.19 (11)
O(9)-K(1)-O(1) ^{4*}	66.93(11)
O(9)-K(1)-O(4) ^{2*}	100.15(11)
O(9)-K(1)-O(3) ^{2*}	70.29(12)
O(9)-K(1)-O(3)	151.20(13)
O(9)-K(1)-O(2)	147.17(14)
O(9)-K(1)-O(2) ^{4*}	90.25(13)
O(9)-K(1)-O(8) ^{1*}	111.63(11)
O(9)-K(1)-O(5) ^{5*}	73.73(12)
O(9)-K(1)-N(6) ^{1*}	68.15(10)
O(9) ^{3*} -K(1)-N(6) ^{1*}	91.19(11)
N(6)-O(7)-K(1) ^{6*}	89.8(2)
N(1)-O(1)-K(1) ^{6*}	92.1(2)
N(2)-O(4)-K(1) ^{4*}	86.2(2)
N(2)-O(3)-K(1) ^{3*}	107.0(2)
N(2)-O(3)-K(1) ^{3*}	133.8(3)
N(1)-O(2)-K(1)	131.6(3)
N(1)-O(2)-K(1) ^{4*}	104.3(2)
O(4)-N(2)-K(1) ^{3*}	86.2(2)
O(4)-N(2)-C(1)	116.4(3)
O(3)-N(2)-K(1) ^{3*}	52.6(2)
O(3)-N(2)-O(4)	121.9(4)
O(3)-N(2)-C(1)	121.6(4)
N(6)-O(8)-K(1) ^{6*}	101.2(2)
N(3)-O(5)-K(1) ^{7*}	122.3(2)
O(1)-N(1)-C(1)	117.1(3)
O(2)-N(1)-O(1)	121.0(4)
O(2)-N(1)-C(1)	121.9(4)
N(5)-N(4)-C(2)	111.4(3)
N(5)-N(4)-C(1)	118.8(3)
C(2)-N(4)-C(1)	129.3(4)
O(7)-N(6)-C(4)	118.3(3)

O(8)-N(6)-C(4)	116.8(4)
C(4)-N(5)-N(4)	103.8(3)
O(6)-N(3)-O(5)	125.1(4)
O(6)-N(3)-C(2)	117.0(3)
O(5)-N(3)-C(2)	117.9(3)
N(4)-C(2)-N(3)	122.7(4)
N(4)-C(2)-C(3)	108.5(3)
C(3)-C(2)-N(3)	128.7(4)
C(2)-C(3)-C(4)	102.0(3)
C(2)-C(3)-C(1)	128.3(3)
C(4)-C(3)-C(1)	129.7(3)
N(2)-C(1)-N(1)	124.4(4)
N(2)-C(1)-N(4)	117.0(4)
N(1)-C(1)-N(4)	117.2(4)
N(5)-C(4)-N(6)	117.4(4)
N(5)-C(4)-C(3)	114.3(4)
C(3)-C(4)-N(6)	128.3(4)

Symmetry transformations used to generate equivalent atoms:

11+X,+Y,+Z; 22-X,1-Y,1-Z; 3+X,1/2-Y,-1/2+Z; 4+X,+Y,-1+Z; 5+X,1/2-Y,1/2+Z

1*1+X,+Y,+Z; 2*+X,1/2-Y,-1/2+Z; 3*+X,1/2-Y,1/2+Z; 4*2-X,1-Y,1-Z; 5*+X,+Y,-1+Z; 6*-1+X,+Y,+Z; 7*+X,+Y,1+Z

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for potassium **A**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2}U_{11} + \dots + 2hka^* b^* U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
K ₁	22.7(6)	29.9(6)	23.2(5)	-3.3(5)	5.7(4)	-2.5(5)
O ₇	33(2)	27(2)	20.1(17)	-4.1(15)	0.7(15)	-3.7(15)
O ₁	36(2)	21(2)	33.0(19)	3.6(15)	16.3(16)	6.4(16)
O ₄	44(2)	20(2)	27.6(18)	1.9(15)	13.0(16)	-4.0(16)
O ₃	26(2)	34(2)	38.0(2)	1.5(15)	15.7(16)	9.1(16)
O ₂	23(2)	33(2)	45(2)	-7.3(17)	18.2(16)	-6.3(16)
O ₆	36(2)	36(2)	21.3(18)	-7.7(15)	2.9(15)	2.4(16)
N ₂	28(2)	21(2)	17(2)	-0.3(17)	7.2(17)	4.4(18)
O ₈	22.5(19)	44(2)	27.7(18)	2.4(16)	9.5(15)	2.7(16)
O ₅	23(2)	53(3)	27.9(19)	5.6(17)	-0.1(15)	-9.1(17)
N ₁	22(2)	24(2)	20(2)	-2.1(17)	4.4(17)	2.0(18)
N ₄	19(2)	19(2)	23(2)	-2.1(17)	7.3(17)	-0.9(16)
N ₆	23(2)	18(2)	22(2)	3.8(17)	3.4(18)	-2.0(16)
N ₅	21(2)	21(2)	18.5(19)	-1.8(16)	2.1(16)	1.4(17)
N ₃	27(2)	23(2)	24(2)	5.7(18)	1.1(18)	-0.2(18)
C ₂	20(3)	15(2)	19(2)	-1.2(18)	0.9(19)	0.6(19)
C ₃	20(2)	17(3)	20(2)	1.5(19)	9.0(19)	-0.7(19)
C ₁	18(3)	19(3)	28(3)	3(2)	10(2)	1(2)

O ₉	29(2)	121(4)	37(2)	-2(3)	15(2)	-19(3)
C ₄	20(2)	20(3)	23(2)	1(2)	8(2)	3(2)
Cl ₁	28.9(7)	31.2(7)	21.0(6)	-3.6(5)	11.4(5)	-2.9(5)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for potassium A.

Atom	x	y	z	U(eq)
H9A	11660(40)	3660(40)	0(110)	120(30)
H9B	10450(60)	3640(60)	-890(80)	160(40)

Table S6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound C-H₂O. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
O5	739.9(13)	3096.2(8)	3159(2)	28.0(4)
O6	2319.3(14)	2432.7(8)	2388(2)	28.9(4)
O4	1169.2(14)	4668.8(8)	4244(2)	31.6(4)
O1	7021.7(13)	3024.6(8)	5943(2)	31.6(4)
O3	2916.3(14)	5149.2(8)	3627(2)	29.6(4)
O7	2181.5(14)	4261.0(8)	-616(2)	29.2(4)
O2	7774.1(14)	3431.7(9)	3357(2)	34.2(4)
O8	3735.1(14)	4335.2(9)	-2234(2)	34.0(4)
N3	3772.6(16)	3712.9(9)	2790(2)	19.9(4)
N2	4749.7(16)	3481.3(9)	4134(2)	20.9(4)
O9	-884(2)	4159.1(17)	10346(3)	45.1(6)
N8	1853(16)	3077.7(10)	2950(2)	20.3(4)
N6	2197.3(17)	4561.3(10)	3750(2)	21.8(4)
N1	6907.6(17)	3300.0(10)	4236(3)	23.2(4)
N4	3295.2(18)	4173.3(10)	-724(2)	23.8(4)
N7	-124(3)	3608.1(19)	6819(5)	26.2(6)
N5	6115(2)	3856.7(12)	-253(3)	29.7(5)
C1	2606.3(19)	3768.2(11)	3322(3)	20.0(5)
C4	5699.5(19)	3501.6(11)	3173(3)	20.0(5)
C2	4111(2)	3880.8(11)	950(3)	20.7(5)
C3	5388(2)	3755.7(11)	1120(3)	20.6(5)

Table S7. Bond lengths [\AA] and angles [$^\circ$] for compound C-H₂O.

O5-N8	1.251(2)
N3-C2	1.387(2)
O6-N8	1.2396(18)
N2-C4	1.320(2)
O4-N6	1.241(2)
N8-C1	1.374(2)
O1-N1	1.222(2)

N6-C1	1.392(2)
O3-N6	1.2378(19)
N1-C4	1.426(3)
O7-N4	1.242(2)
N4-C2	1.393(2)
O2-N1	1.223(2)
N5-C3	1.336(3)
O8-N4	1.2312(19)
C4-C3	1.430 (2)
N3-N2	1.328(2)
C2-C3	1.396(3)
N3-C1	1.388(2)

N2-N3-C1	120.41(16)
O8-N4-O7	123.82(18)
N2-N3-C2	111.02(16)
O8-N4-C2	117.21(18)
C1-N3-C2	128.57(17)
N3-C1-N6	117.12(16)
C4-N2-N3	105.34(16)
N8-C1-N3	116.76(16)
O5-N8-C1	121.64(16)
N8-C1-N6	124.44(18)
O6-N8-O5	121.06(16)
N2-C4-N1	119.09(18)
O6-N8-C1	117.29(17)
N2-C4-C3	114.34(18)
O4-N6-C1	121.49(17)
C3-C4-N1	126.55(18)
O3-N6-O4	122.00(16)
N3-C2-N4	124.14(18)
O3-N6-C1	116.51(17)
C3-C2-N3	108.8(2)
O1-N1-O2	124.28(18)
C3-C2-N4	127.09(17)
O1-N1-C4	119.30(17)
N5-C3-C4	129.9(2)
O2-N1-C4	116.40(17)
N5-C3-C2	129.5(2)
O7-N4-C2	118.97(16)

C2-C3-C4 100.63(16)

Table S8. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **C·H₂O**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [$h^2a^{*2}U_{11} + \dots + 2hka^* b^* U_{12}$]

Atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
O5	20.4(9)	27.8(8)	35.9(9)	-6.8(7)	5.8(7)	-2.1(7)
O6	30.3(10)	19.6(8)	37.6(9)	-1.8(7)	8.4(8)	-5.5(7)
O4	28.9(10)	24.7(8)	44.2(10)	5.9(7)	15.0(8)	1.7(7)
O1	26.8(10)	30.8(8)	33.2(9)	-0.6(7)	-5.6(7)	6.3(7)
O3	38.7(11)	20.5(8)	31.7(9)	-7.6(7)	12.0(8)	-1.7(7)
O7	23.3(10)	35.2(9)	26.6(9)	5.1(7)	-1.9(7)	-1.3(7)
O2	18.9(10)	49.8(10)	33.3(9)	-0.7(8)	2.8(8)	-8.4(7)
O8	38.8(11)	42.8(9)	20.2(8)	4.1(8)	4.9(8)	4.4(7)
N3	14.7(11)	25.6(10)	19.9(9)	0.6(8)	4.3(8)	-0.2(7)
N2	18.3(11)	25.3(9)	19.3(10)	0.0(8)	3.6(8)	0.3(8)
O9	50.2(15)	56.7(15)	29.7(12)	19.4(13)	10.5(11)	4.9(12)
N8	19.4(12)	19.9(10)	21.7(9)	-2.0(8)	3.7(8)	-0.4(8)
N6	24.6(12)	20.0(10)	21.1(9)	0.8(9)	4.8(8)	1.6(7)
N1	19.4(12)	24.1(10)	25.1(10)	0.5(8)	1.5(9)	-4.0(8)
N4	27.4(13)	24.5(10)	17.9(10)	2.2(9)	0.1(9)	-1.3(8)
N7	24.7(17)	27.9(15)	25.5(15)	3.7(12)	3.4(13)	-1.8(13)
N5	28.0(15)	35.7(12)	28.7(12)	2.0(11)	14.3(12)	2.6(9)
H5a	33(5)	75(19)	28(12)	11(3)	14(3)	-2(9)
H5b	43(13)	90(20)	36(6)	8(9)	10(4)	17(5)
C1	18.1(13)	16.9(10)	24.8(12)	-0.2(9)	3.2(10)	-0.1(9)
C4	15.8(13)	23.3(11)	20.1(11)	-1.0(9)	1.3(10)	-0.8(9)
C2	20.5(13)	23.9(11)	17.4(11)	1.9(10)	2.2(10)	-0.0(9)
C3	21.1(14)	21.5(11)	20.0(12)	0.7(9)	5.9(10)	-0.2(9)
H7a	120(40)	80(30)	50(20)	0(20)	30(20)	-30(20)
H7b	80(30)	90(30)	60(20)	-30(20)	40(20)	10(20)
H7c	100(30)	36(17)	12(15)	12(15)	7(16)	-12(13)
H7d	90(30)	90(30)	80(30)	0(30)	10(20)	-20(20)
H9a	210(50)	50(20)	40(20)	-30(30)	-40(20)	10(20)
H9b	90(30)	120(40)	40(20)	0(20)	-10(20)	20(20)

Table S9. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **C·H₂O**.

Atom	x	y	z	U(eq)
H5a	6990(20)	3739(15)	60(30)	44(8)
H5b	5680(20)	4020(16)	-1680(40)	57(8)
H7a	330(40)	3090(20)	7120(50)	82(12)

H7b	370(30)	3990(20)	6190(50)	74(12)
H7c	-350(30)	3852(14)	8030(40)	48(9)
H7d	-770(30)	3450(20)	5770(60)	89(13)
H9a	-1010(40)	4707(19)	10660(50)	110(17)
H9b	-380(30)	3980(20)	11540(50)	88(14)

Table S10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **C1**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	$U(\text{eq})$
O7	10264(2)	4791.6(10)	3825.4(11)	26.6(3)
O4	6415(3)	1709.5(10)	5574.8(12)	33.4(4)
O1	2026(3)	4381.7(11)	1369.3(12)	36.3(4)
O6	7142(3)	3424.2(11)	6913.6(12)	36.6(4)
O5	4295(3)	3886.7(12)	5709.7(13)	41.9(4)
N3	7202(3)	3627.7(11)	4082.3(12)	23.4(4)
O2	1331(3)	2949.7(12)	2047.4(13)	43.7(4)
N1	5024(3)	3281.5(11)	3572.1(13)	24.3(4)
N5	6311(3)	3549.4(12)	5989.5(14)	26.6(4)
N4	7854(3)	2137.2(12)	5035.7(13)	26.3(4)
N2	2513(3)	3703.8(13)	1993.7(13)	28.4(4)
O3	9211(3)	1778.4(11)	4412.0(13)	47.7(5)
N6	6647(3)	5242.0(13)	1892.1(14)	28.2(4)
C4	8318(3)	4410.3(13)	3543.2(15)	21.4(4)
C2	4677(3)	3833.3(13)	2730.5(15)	22.0(4)
C1	7976(3)	3252.0(13)	5098.1(15)	22.8(4)
N7	6735(3)	5832.5(15)	1284.3(16)	43.2(5)
C3	6538(3)	4543.1(13)	2638.1(15)	22.6(4)

Table S11. Bond lengths [\AA] and angles [$^\circ$] for compound **C1**.

O7-C4	1.209(2)
N1-C2	1.289(2)
O4-N4	1.212(2)
N5-C1	1.527(2)
O1-N2	1.225(2)
N4-O3	1.206(2)
O6-N5	1.211(2)
N4-C1	1.530(2)
O5-N5	1.217(2)
N2-C2	1.448(2)
N3-N1	1.386(2)

N6-N7	1.107(2)
N3-C4	1.419(2)
N6-C3	1.333(2)
N3-C1	1.395(2)
C4-C3	1.440(3)
O2-N2	1.221(2)
C2-C3	1.413(2)
N1-N3-C4	115.05(15)
N7-N6-C3	179.0(2)
N1-N3-C1	118.62(15)
O7-C4-N3	125.70(17)
C1-N3-C4	126.06(16)
O7-C4-C3	134.24(17)
C2-N1-N3	103.89(15)
N3-C4-C3	100.03(15)
O6-N5-O5	126.33(17)
N1-C2-N2	120.24(16)
O6-N5-C1	116.16(16)
N1-C2-C3	113.72(16)
O5-N5-C1	117.51(16)
C3-C2-N2	126.04(17)
O4-N4-C1	118.81(15)
N3-C1-N5	113.18(15)
O3-N4-O4	126.80(18)
N3-C1-N4	108.27(15)
O3-N4-C1	114.36(16)
N5-C1-N4	106.08 (14)
O1-N2-C2	115.79(16)
N6-C3-C4	124.69(17)
O2-N2-O1	125.70(17)
N6-C3-C2	127.99(17)
O2-N2-C2	118.51(16)
C2-C3-C4	107.28(16)

Table S12. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **C1**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2hka^* b^* U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O7	21.8(7)	31.8(7)	26.1(8)	-5.3(6)	1.0(6)	-2.4(6)
O4	37.1(8)	31.2(8)	31.9(8)	-5.8(6)	1.8(7)	4.6(6)

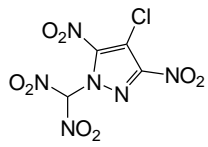
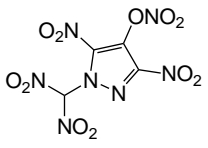
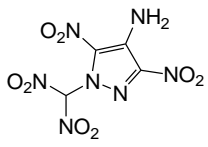
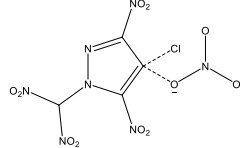
O1	33.2(8)	45.6(9)	29.1(8)	4.5(7)	-6.1(7)	7.2(7)
O6	48.0(9)	41.0(9)	20.9(8)	4.8(7)	3.4(7)	0.4(7)
O5	30.9(8)	52.9(10)	41.7(10)	14.6(7)	-0.2(7)	-12.9(8)
N3	20.6(8)	27.9(9)	20.8(9)	-4.0(6)	-4.5(7)	3.2(7)
O2	36.3(9)	48.5(10)	44.5(10)	-17.2(7)	-9.7(7)	4.4(8)
N1	20.3(8)	27.0(9)	25.3(9)	-2.3(6)	-0.7(7)	-0.6(7)
N5	29.5(9)	24.6(9)	26.0(10)	0.1(7)	3.4(8)	-4.0(7)
N4	29.7(9)	27.7(9)	21.2(9)	5.4(7)	-1.1(8)	1.2(7)
N2	23.5(8)	38.9(10)	22.4(9)	-0.5(7)	-1.1(7)	-0.6(8)
O3	61.6(11)	40.1(9)	44.0(10)	18.1(8)	21.8(9)	-2.4(8)
N6	25.7(9)	33.3(10)	25.7(9)	-0.5(7)	1.9(7)	2.4(8)
C4	22.1(9)	22.6(10)	19.9(10)	1.8(7)	3.9(8)	-2.8(8)
C2	21.0(9)	24.5(10)	20.5(10)	1.2(7)	0.8(8)	-2.8(8)
C1	22.1(9)	25.8(10)	20.6(10)	2.1(8)	1.7(8)	0.8(8)
N7	38.6(11)	48.7(12)	41.8(12)	-5.3(9)	0.3(9)	17.7(10)
C3	23.9(10)	24.3(10)	19.7(10)	-0.5(7)	2.5(8)	1.9(8)

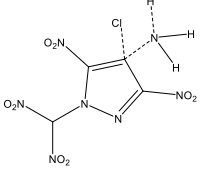
Table S13. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for compound **C1**.

Atom	x	y	z	U(eq)
H1	9709(3)	3463.1(13)	5298.8(15)	27.4(5)

7. Computational Section

Table S14. Computational data of the changes in Gibbs Free Energy (ΔG)

Species	E_0^a (Hartree)	G^c (Hartree)
	-1542.9831026	-1543.0403405
	-1363.0599637	-1362.9997068
	-1138.775444	-1138.8186181
	-1822.752603	-1822.7057871

	-1598.4753453	-1599.4857844
NO ₃ ⁻	-280.2353798	-280.2455836
NH ₃	-56.5473487	-56.5557897
Cl ⁻	-460.2549123	-460.269935
HCl	-460.7926246	-460.8188455

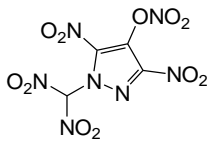
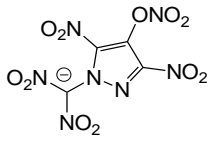

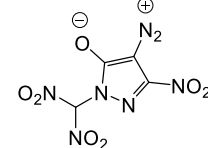

^a Total energy (E_0) calculated by M062X/TZVP method (Hartree/Particle);

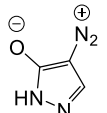
^b Values of thermal correction to Gibbs Free Energy (GT) (Hartree/Particle);

^c Values of Gibbs Free Energy (G) (Hartree/Particle).

The changes in Gibbs Free Energy were calculated by using the Gaussian 09 (Revision D.01) suite of programs.^[2] The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-31+G* basis set. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The single-point energies were calculated at the M062X/TZVP at 298.15K or 358.15K.

Table S15. Computational data of heats of formation

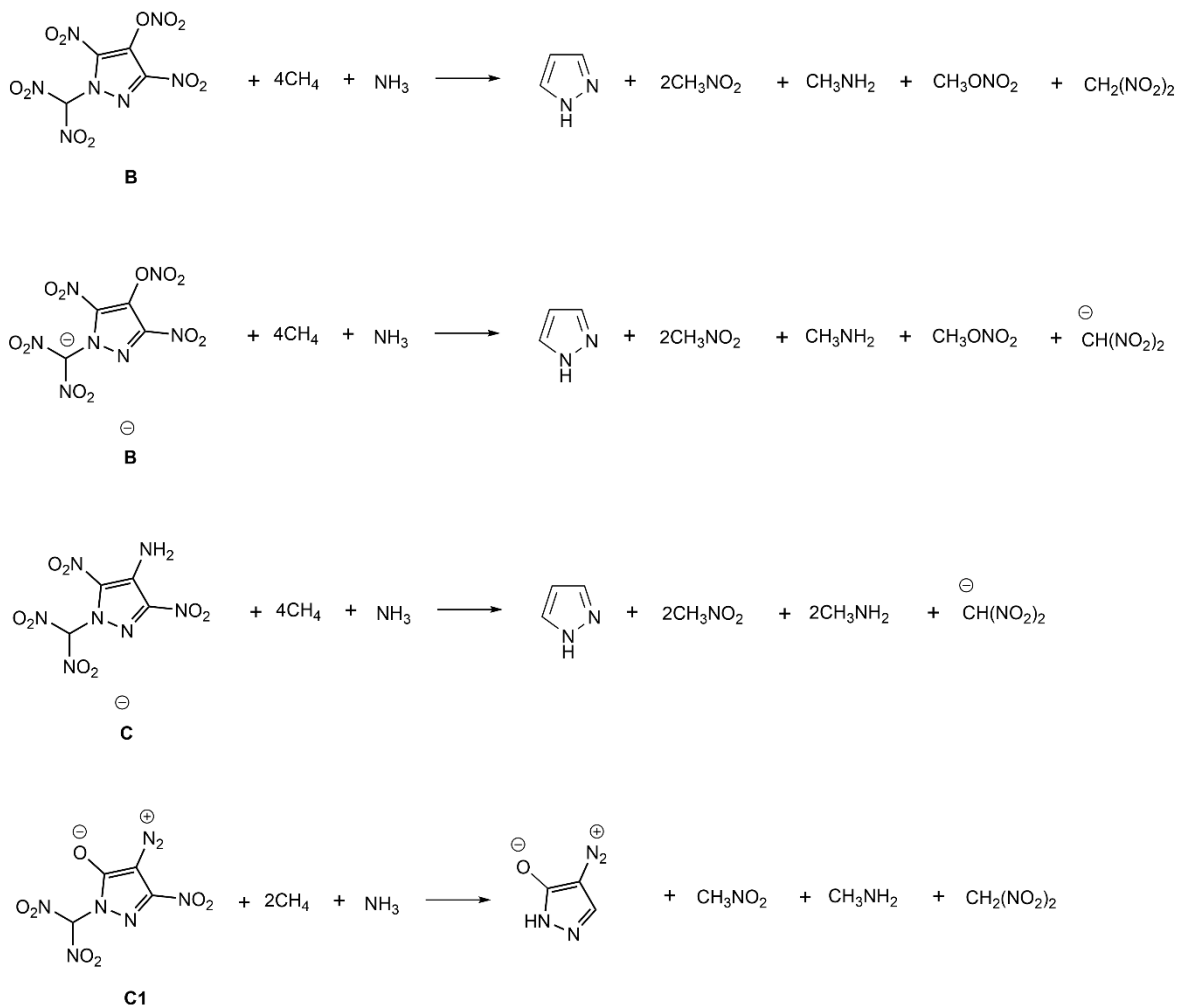
Species	E_0^a (Hartree)	H_{corr}^b (Hartree)	ZPE ^c (Hartree)	HOF ^d (kJ/mol)
	-1360.742129	0.133519	0.113519	26.38
	-1360.245361	0.120414	0.100566	-246.64
	-1136.287541	0.129335	0.112145	-158.21
	-1060.554851	0.112694	0.096359	651.16
CH ₄	-40.3984857	0.048605	0.044793	-74.6
NH ₃	-56.4341763	0.038190	0.034372	-45.9
	-225.7180666	0.075955	0.071265	105.4
CH ₃ NO ₂	-244.5543604	0.055129	0.049856	-74.3
CH ₂ (NO ₂) ₂	-448.698143	0.059333	0.052836	-58.9
CH(NO ₂) ₂ ⁻	-448.1640752	0.046605	0.039726	-233
CH ₃ ONO ₂	-319.5931968	0.058954	0.053585	-122
CH ₃ NH ₂	-95.6318759	0.068401	0.064032	-23.0

	-408.8785442	0.068881	0.061643	682.37
---	--------------	----------	----------	--------

^a Total energy (E_0) calculated by MP2/6-311++G* method (Hartree/Particle);

^b Values of thermal correction (H_T) (Hartree/Particle); ^c Zero-point correction (ZPE) (Hartree/Particle); ^d Heat of formation (HOF) (kJ/mol).

For the heats of formation, the energies were refined by MP2(full)/6-311++G*level single-point calculations. The heats of formation (HOFs) of all compounds were calculated by the isodesmic reactions (Scheme S1).



Scheme S1. Isodesmic reactions for calculation of the heats of formation of compounds **B**, **C** and the corresponding anions.

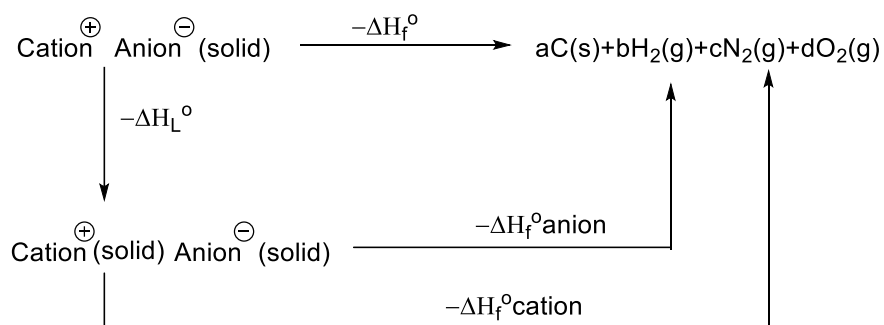


Figure S27. Born-Haber cycle for the formation for energetic salts.

Based on the Born-Haber energy cycle (Figure S27), the heat of formation of a salt can be simplified according to Equation (1), where ΔH_L is the lattice energy of the salt.

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

The ΔH_L value could be predicted by the formula suggested by Jenkins et al [Equation (2)],^[3] where U_{POT} is the lattice potential energy and nM and nX 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.

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

The equation for the lattice potential energy, U_{POT} , takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), Mm is the chemical formula mass of the ionic material (g), and the coefficients γ ($\text{kJ}^{-1}\text{mol}^{-1}\text{cm}$) and δ ($\text{kJ}^{-1}\text{mol}^{-1}$) are assigned literature values (1:1 salts $\gamma=1981.2$ $\delta=103.8$).

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

Detonation pressure (P) and detonation velocity (D) were calculation according to the Kamlet-Jacobs equations.^[4]

$$D = 1.01(N\bar{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (4)$$

$$P = 1.558\rho^2\bar{M}^{1/2}Q^{1/2} \quad (5)$$

where each term in Equations 4 and 5 is defined as follows: D , the detonation velocity (km s^{-1}); P , the detonation pressure (GPa); N , the moles of detonation gases per gram explosive; M , the average molecular weight of these gases (g mol^{-1}); Q , the heat of detonation (cal g^{-1}); and ρ , the loaded density of explosives (g cm^{-3}). The measured density was used for the calculation here.

References

- [1] F. Kleemiss, O. V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, L. Midgley, L. J. Bourhis, A. Genoni, L. A. Malaspina, D. Jayatilaka, J. L. Spencer, F. White, B. Grundkötter-Stock, S. Steinhauer, D. Lentz, H. Puschmann, S. Grabowskyet, *Chem. Sci.*, 2021, **12**, 1675-1692.
- [2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Rev. D.01; Gaussian, Inc., Wallingford, CT, 2013.
- [3] H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364–2367.
- [4] Y. Tang, C. He, J. M. Shreeve, *J. Mater. Chem. A.*, 2017, **5**, 4314-4319.