Supplementary Information

Novel dinitromethyl-featured polynitro energetic salts

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X-ray crystallography

The relevant data and parameters for the X-ray measurements and refinements of the salt **5** are summarized in Table S1.

Table S1 Crystallographic data for salt **5**·1.5H_2O

	5·1.5H_2O
CCDC	1484784
Formula	$C_{10}H_{24}N_{18}O_{21}$
FW (g mol^{-1})	732.47
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	P -1
Z	2
a (Å)	6.8808(18)
b (Å)	13.354(3)
c (Å)	15.942(4)
α (°)	89.832(6)
β (°)	81.391(6)
γ (°)	75.199(6)
V (Å^3)	1399.3(6)
D_c (g cm^{-3})	1.738
μ (mm^{-1})	0.167
F(000)	756
θ (°)	1.578-25.000
Refl. coll.	7773
Independ. refl. [R_{int}]	4926 [0.0376]
S	1.021
R_1, wR_2 [I>2s(I)]	0.0693, 0.1579
R_1, wR_2 (all)	0.1098, 0.1805

Theoretical study

Heat of formation

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

ΔH_f^o(ionic salt, 298K) = ΔH_f^o(cation, 298K) ＋ ΔH_f^o(anion, 298K) － ΔH_L (1)

The ΔH_L value could be predicted by the formula suggested by Jenkins et al [Eq. (2)],[1] where U_{POT} is the lattice potential energy and n_M 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.

$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (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.[1]

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

Table S2 Ab Initio computational data

Compounds	E_0[a] (Hartree)	ZPE[b] (Hartree)	H_T[c] (Hartree)	HOF[d] (kJ/mol)
CH_4	-40.39849	0.044793	0.003812	-74.6[2a]
NH_3	-56.43418	0.034372	0.003818	-45.9[2a]
CH_3CH_3	-79.60944	0.074599	0.004428	-83.8[2b]
CH_3NO_2	-244.5544	0.049856	0.005273	-74.3[2a]
CH_3NH_2	- 95.63188	0.064032	0.004369	-23.0[2d]
FOX-7	-597.2172	0.091946	0.010218	-134.1[2*]
Urea	-224.8302	0.062316	0.005299	-235.5[2a]
$CH_3CH_2^-$	-78.92410	0.057501	0.004496	133.1[2a]
ATNP Anion	-1157.362	0.121910	0.017947	-543.1

[a] Total energy (E_0) calculated by B3LYP/6-31+G**/MP2/6-311++G** method (Hartree/Particle); [b] Zero-point correction (ZPE) (Hartree/Particle); [c] Values of thermal correction (H_T) (Hartree/Particle); [d] Heat of formation (HOF) (kJ/mol).

Energetic properties

Detonation pressures (P) and detonation velocities (D) were calculated according to the Kamlet-Jacobs equations (Eq. 4 and 5),[3]

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

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

For compound with the molecular formula of $C_aH_bO_cN_d$, c≥2a+b/2 (suitable for the salt **1** in this study), Q can be calculated according to Eq. 6.

$$Q = \frac{28.9b + 94.05a + 0.239\Delta H_f^0}{M} \times 10^3 \quad (6)$$

For compound with the molecular formula of $C_aH_bO_cN_d$, 2a+b/2＞c≥b/2 (suitable for all the salts in this study except **1**), Q can be calculated according to Eq. 7.

$$Q = \frac{28.9b + 94.05(\frac{c}{2} - \frac{b}{4}) + 0.239\Delta H_f^0}{M} \times 10^3 \quad (7)$$

where each term in Eq. 4, 5, 6 and 7 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; $\overline{M}$, the average molecular weight of these gases (g mol^{-1}); Q, the heat of detonation (J g^{-1}); M, molecular weight of the compound (g mol^{-1}); and ρ, the loaded densities of explosives (g cm^{-3}). Density measured by gas pycnometer at 25°C.

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