Supplementary Materials

Synthesis and Properties of Energetic Hydrazinium 5-Nitro-3-dinitromethyl-2*H*-pyrazole by An Unexpected Isomerization of N-nitropyrazole

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1. ^{1}H and ^{13}C NMR spectral data

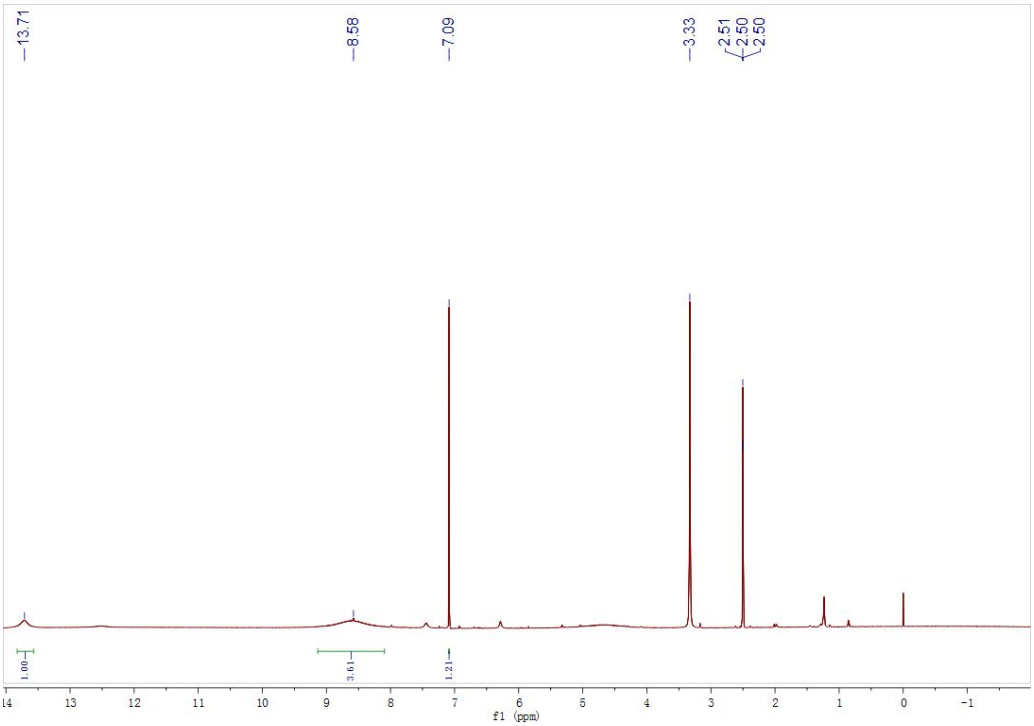


Figure S1. ^{1}H NMR spectrum of **3**

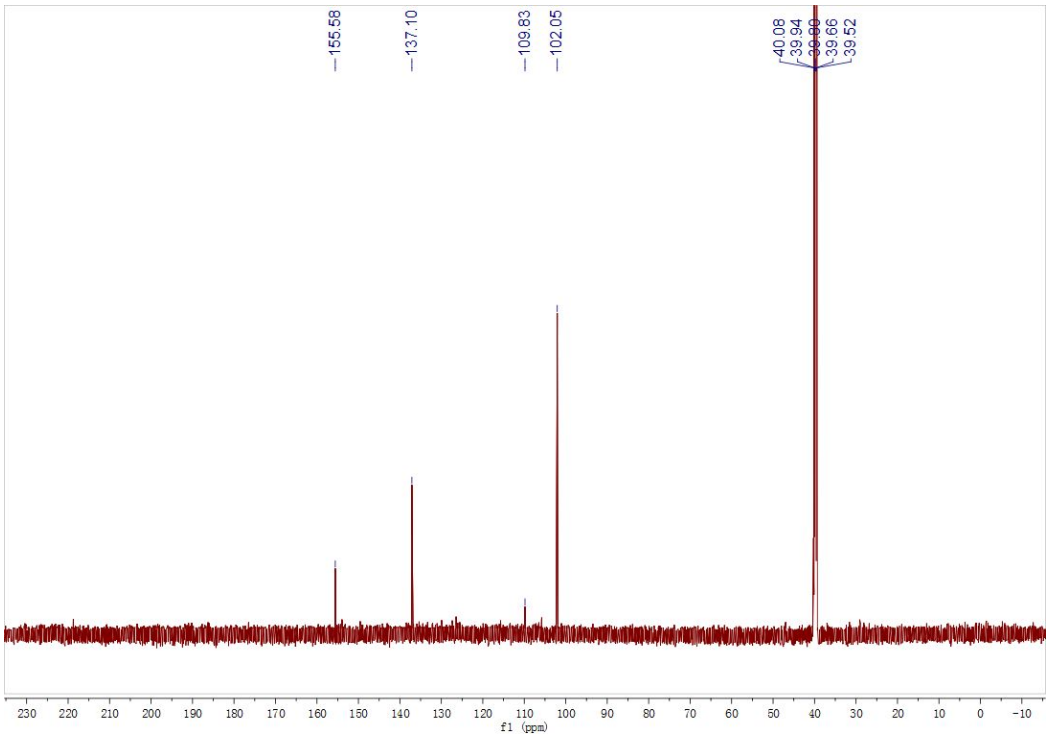


Figure S2. ^{13}C NMR spectrum of **3**

2. TG and DSC data

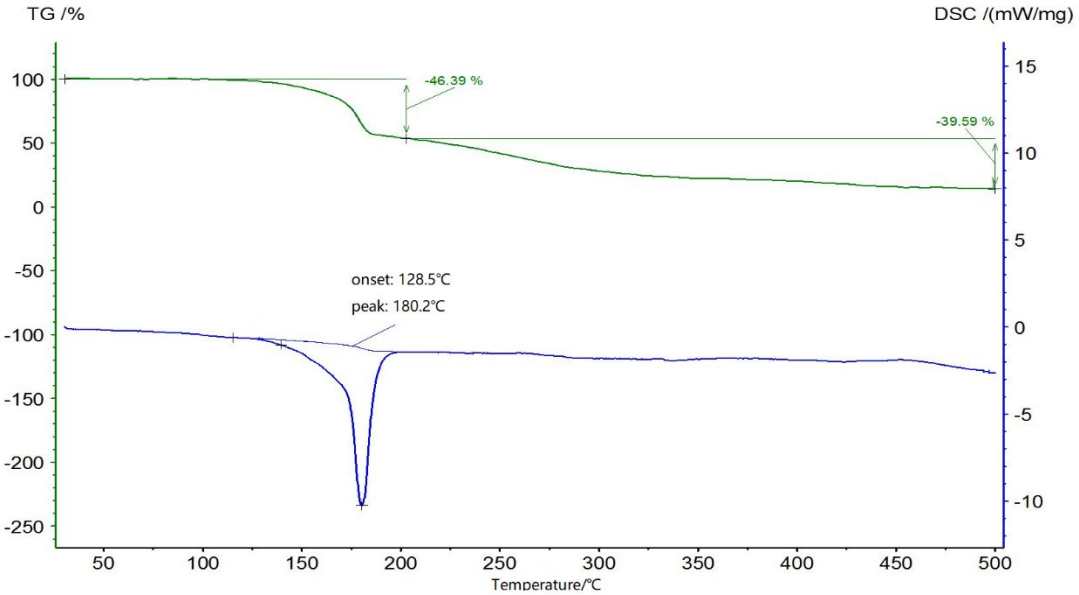


Figure S3. TG and DSC curves of **3**

3. X-ray crystallography

Table S1. Selected bond lengths [Å] and angles [°] for compound **3**

Bond	Bond length/Å	Bond	Bond angles/°
C1-C2	1.391	C1-C2-C3	103.6
C2-C3	1.398	C2-C3-N3	105.34
C3-N3	1.368	C3-N3-N4	114.35
N3-N4	1.345	N3-N4-C1	102.15
N4-C1	1.337	N4-C1-C2	114.56
C1-N5	1.436	N4-C1-N5	117.84
C3-C4	1.463	C2-C1-N5	127.6
C4-N1	1.396	C2-C3-C4	131.45
C4-N2	1.403	N3-C3-C4	123.21
N6-N7	1.442	C3-C4-N1	119.84
		C3-C4-N2	121.68

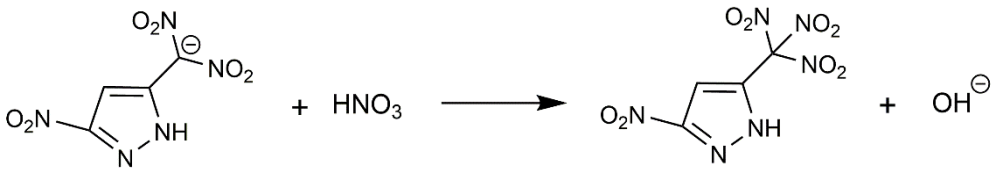
Table S2. Torsion angles [°] for **3**

Bond	Torsion angles/°	Bond	Torsion angles/°
O6-N5-C1-C2	-4.94	C4-C3-C2-C1	178.9
O6-N5-C1-N4	175.32	C4-C3-N3-N4	-178.66
O5-N5-C1-N4	-3.95	O4-N2-C4-C3	176.38
O5-N5-C1-C2	175.79	O4-N2-C4-N1	-6.27
N5-C1-N4-N3	-179.73	O1-N1-C4-C3	-1.5
N5-C1-C2-C3	-179.95	O1-N1-C4-N2	-178.9
C1-N4-N3-C3	-0.62	O2-N1-C4-C3	177.29
C1-C2-C3-N3	-0.18	O2-N1-C4-N2	-0.11
N4-N3-C3-C2	0.52	O3-N2-C4-C3	-2.88
N4-C1-C2-C3	-0.2	O3-N2-C4-N1	174.47

N3-N4-C1-C2	0.49

4. Heat of formation calculations

The isodesmic reaction which is used to calculate the HOF of the target compound is shown in Scheme S1.



Scheme S1. The isodesmic reaction for **3** anion.

The change of enthalpy for the reaction at 298 K can be expressed as Equation (1).

$\Delta H_{298K} = \Sigma\Delta_f H_P - \Sigma\Delta_f H_R$ (1)

$\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of the reactants and products at 298 K, respectively.

ΔH_{298K} can also be calculated as follows:

$\Delta H_{298K} = \Delta E_{298K} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT$ (2)

E_0 is the total energy; ZPE is the zero-point energies (ZPE); H_T is the thermal correction. On the right side of the Equation (2), it is the sum of the changes of corresponding parameters between the products and the reactants. For the isodesmic reactions, $\Delta n = 0$, so $\Delta(PV) = 0$. Combining Equation (1) and (2), the HOF of target compound can be obtained.

Based on the Born-Haber energy cycle, the heats of formation of ionic salts can be simplified by Equation (3):

ΔH_f^o(ionic salts, 298 K) = ΔH_f^o(cation, 298 K) + ΔH_f^o(anion, 298 K) - ΔH_L (3)

ΔH_L is the lattice energy of the ionic salts, which could be predicted by using the formula suggested by Jenkins et al.[1]

$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (4)

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.

The equation for lattice potential energy U_{POT} has the form Equation (5):

U_{POT} (kJ mol^{-1}) = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (5)

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

Table S3. Calculated total energy (E_0), zero-point energy (ZPE), thermal correction (H_T) and heat of formation (HOF) of target compounds.

Compd.	**E_0/a.u.**	**ZPE (kJ/mol)**	**H_T (kJ/mol)**	**HOF(g) (kJ/mol)**	**HOF(s) (kJ/mol)**
3					194.80
3 anion	-873.90	246.01	31.95	-87.58	
$N_2H_5^+$					774.1[2]

References

1. Jenkins, H. D. B.; Tudela, D.; Glasser, L. Lattice Potential Energy Estimation for Complex Ionic

Salts from Density Measurements. *Inorg. Chem.*, **2002**, 41, 2364–2367.
2. Fischer, D.; Klapoetke, T. M.; Reymann, M.; Stierstorfer, J. Dense Energetic Nitraminofurazanes. *Chem. Eur. J.*, **2014**, 20, 6401–6411.