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Supporting Information

A Novel Facile transformation to 1,2-Bis(3-nitro-1-(1*H*-tetrazol-5-yl)-1*H*-1,2,4-triazol-5-yl)hydrazine Salts

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1. Theoretical study

Calculations were performed using the Gaussian 03 (Revision E.01) suite of programs.[S1] The geometric optimization of the structures and frequency analyses were conducted using the B3LYP functional with the 6–31+G** basis set,[S2] and single-point energies were calculated at the MP2(full)/6–311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.In the present study, theoretical enthalpies of formation at 0 K are calculated according to Equation 1,

$$\Delta_f H^o(M,0K) = \sum_{\text{atoms}} x\Delta_f H^o(X,0K) - \sum D_0(M) = \sum_{\text{atoms}} x\Delta_f H^o(X,0K) - \left(\sum_{\text{atoms}} x\varepsilon_0(X) - \varepsilon_0(M)\right) \quad \text{(Equation 1)}$$

In the Equation 1, M will be used to stand for the molecule, and X to represent each element which makes up M, and x will be the number of atoms of X in M. $\varepsilon_0(X)$ and $\varepsilon_0(M)$ are the total energies of the atom and molecule, respectively. $D_0(M)$ is the atomization energy of the molecule, which are readily calculated from the total energies of the molecule $\varepsilon_0(X)$ and $\varepsilon_0(M)$. $\Delta_f H^0(X, 0K)$ is the heats of formation of the atoms at 0K, which can be taken directly from experimental data[S3]. $\Delta_f H^0(M,0K)$ is the heat of formation of the molecule at 0 K.Theoretical enthalpies of formation at 298 K, $\Delta_f H^0(M,298K)$, are calculated by correction to $\Delta_f H^0(M, 0 K)$ as follows:

$$\Delta_f H^o(M,298K) = \Delta_f H^o(M,0K) + \left(H_M^o(298K) - H_M^o(0K)\right) - \sum_{\text{atoms}} x\left(H_X^o(298K) - H_X^o(0K)\right) \quad \text{(Equation 2)}$$

In the Equation 2, $(H^0_X(298K) - H^0_X(0K))$ is the enthalpy corrections of the atomic elements, they are taken directly from experimental data.[S4] $(H^0_M(298K) - H^0_M(0K))$ is the enthalpy corrections of the molecule.

Table S1 The enthalpies of formation ($\Delta_f H$) and total energies after zero-point energy correction (E_{ZPE}, in hartree) calculated by the Gaussian-3 (G3) method.

	$\Delta_f H$(298K)[kJ mol^{-1}]	E_{ZPE}[in hartree]
BNTD	683.62	0.167379
BNTH anion	340.72	0.165072

Based on the Born-Haber energy cycle (**Fig. S1**), the heat of formation of a salt can be simplified according to Equation. (1), where ΔH_L is the lattice energy of the salt.

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

The ΔH_L value could be predicted by the formula suggested by Jenkins et al. [Eq. 2],[S2] in which 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 monatomic ions, five for linear polyatomic ions, and six for nonlinear polyatomic ions.

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

The equation for the lattice potential energy, U_{POT}, takes the form of Equation (3), where ρ_m is the density (g cm^{-3}), M_m is the chemical formula mass of the ionic material (g), and the coefficients γ (kJ mol^{-1} cm) and δ (kJ mol^{-1}) are assigned literature values.[S4]

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

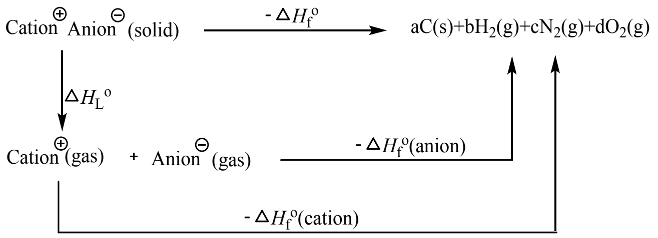

Fig. S1. Born-Haber cycle for the formation for energetic salts.

Oxygen bomb calorimetry calculation of enthalpies of formation of energetic compounds

The constant-volume combustion energies ($\Delta_c U$) for the compounds were measured by an oxygen bomb calorimeter. The enthalpy of formation ($\Delta_c H^o$) was calculated from ΔcU and a correction for change in gas volume during combustion was included (Scheme S1). The standard enthalpies of formation ($\Delta_f H^o$) of these energetic compounds were back calculated from the heats of combustion on the basis of combustion equations, Hess's Law as applied in thermochemical equations, and known standard heats of formation for water and carbon dioxide [$\Delta_f H^o$ (CO_2, g) = -393.51 kJ mol^{-1}, $\Delta_f H^o$ (H_2O, l) = -285.83 kJ mol^{-1}]. According to Hess's law, the standard molar enthalpies of formation ($\Delta_f H^o$) f (**2**, **4-12**) at 298.15 K are calculated as (473.5), (323.6), (415.3), (598.7), (492.1), (763.9), (856.1), (726.2), (1165.3), and (395.6) kJ mol^{-1}, respectively.

$$\Delta_c H^0 = \Delta_c U + \Delta nRT$$

$$\Delta_f H^0 \text{ (reactant, s)} = \Delta_f H^0 \text{ (product 1, l/s)} + \Delta_f H^0 \text{ (product 2, l)} + \Delta_f H^0 \text{ (product 3, g)} - \Delta_c H^0 \text{ (reactant, s)}$$

[$\Delta n = \Delta n_i$(products,g)-Δn_j(reactants,g), Δn_i or Δn_j is the total amounts of gases in the products or reactants]

Scheme S1. Combustion reaction

2. Experimental Section

Caution! Although we have experienced no difficulties in handling these energetic materials, small-scale and best safety practices (Kevlar gloves, ear protection and face shield) are strongly encouraged!

General methods: The ^{1}H and ^{13}C NMR spectra were recorded on a 700 MHz NMR spectrometer operating at 400 and 176 MHz, respectively. Chemical shifts are reported relative to TMS. The solvent used was dimethylsulfoxide-d_6 (DMSO-d_6) unless otherwise specified. The melting and decomposition points were recorded by DSC at a scan rate of 5 °C min^{-1} in a dynamic nitrogen atmosphere (flow rate = 50 mL min^{-1}). The IR spectra were recorded using a Bruker Alpha with an ATR-Ge device. Densities were measured at 25°C using a Micromeritics Accupyc II 1340 gas pycnometer. Elemental analyses were obtained on an ElementarVario MICRO CUBE (Germany) elemental analyzer. For initial safety testing, the IS was measured using a BAM Fall Hammer BFH-10; the FS was measured using BAM Friction Apparatus FSKM-10. The constant-volume combustion energies of the compounds were determined using a precise rotating-bomb calorimeter (Parr 6200).

X-ray crystallography

Crystals of **2**, **4**, and **8** were removed from the flask and covered with a layer of hydrocarbon oil. A suitable crystal was then selected, attached to a glass fiber, and placed in the low-temperature nitrogen stream. Data for **2**, **4**, and **8** were collected at 153(2) K using Rigaku Saturn724 CCD (AFC10/Saturn724+) diffractometer equipped with a graphite-monochromatized MoKα radiation (λ = 0.71073 Å) using omega scans. Data collection and reduction were performed and the unit cell was initially refined by using CrystalClear-SM Expert 2.0 r2 (ref. S5) software. The reflection data were also corrected for Lp factors. The structure was solved by direct methods and refined by the least squares method on F^2 using the SHELXTL-97 system of programs.[S6] Structure were solved in the space group $P2_1/n$ for **2**, $P2_1/c$ for **4**, and $P2$ for **8** by analysis of systematic absences. In this all-light-atom structure the value of the Flack parameter did not allow the direction of polar axis to be determined and

Friedel reflections were then merged for the final refinement. Details of the data collection and refinement are given in Table S2.

Table S2. Crystallographic data for compound **2, 4** and **8**.

Compound	**2**·CH_3OH	**4**·$CH_3OH·H_2O$	**8**
CCDC	1561563	1561564	1561565
Formula	$C_8H_{10}N_{18}O_6$	$C_7H_{16}N_{20}O_6$	$C_8H_{20}N_{30}O_4$
Mr	454.34	476.40	600.54
crystal system	Monoclinic	Monoclinic	Monoclinic
space group	*P2₁/n*	*P2₁/c*	*P2*
a [Å]	12.368(3)	15.406(3)	11.727(2)
b [Å]	6.1353(12)	8.9944(18)	7.3404(15)
c [Å]	13.010(3)	15.496(3)	13.670(3)
β [Å]	99.24(3)	119.61(3)	90.36(3)
V [$Å^3$]	974.5(3)	1866.9(8)	1176.6(4)
Z	2	4	2
T [K]	153(2)	153(2)	153(2)
ρ_{calcd} [$mg·m^{-3}$]	1.548	1.695	1.695
Crystal size/mm^3	0.24 × 0.21 × 0.13	0.26 × 0.24 × 0.21	0.16 × 0.14 × 0.1
F(000)	464	984.0	620.0
θ [°]	3.173 - 27.477	5.258 - 54.956	2.98 - 54.974
index range	$-10 \le h \le 16$	$-19 \le h \le 20$	$-15 \le h \le 15$
	$-7 \le K \le 6$	$-11 \le k \le 11$	$-9 \le k \le 9$
	$-16 \le l \le 16$	$-20 \le l \le 19$	$-11 \le l \le 17$
reflections collected	6580	12354	8524
data/restraints/parameters	2204/0/146	4224/0/299	5137/1/379

GOF on F2	1.136	1.149	1.131
R1 [I>2σ(I)]	0.0555	0.0742	0.0532
wR2 [I>2σ(I)]	0.1278	0.1564	0.1050
R1(all data)	0.0621	0.0909	0.0604
wR2(all data)	0.1325	0.1664	0.1221
largest diff. peak and hole [e Å^{-3}]	0.21/-0.22	0.38/-0.35	0.36/-0.33

(**2**). Bright yellow solid (304 mg, 78%). ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ = 8.22 (s, 3H); ^{13}C NMR (176 MHz, DMSO-d$_6$): δ = 165.2, 158.2, 156.1 ppm. IR (neat): 3064, 2905, 2791, 1566, 1434, 1321, 1015, 841 cm^{-1}. Anal. calcd for $C_4H_4N_8O_7$: C 18.47, H 0.52, N 64.61; found: C 18.33, H 0.50, N 64.09. HRMS: calc. for $C_6H_2N_{18}O_4$ [M+H]$^+$: 391.0579; found: 391.0587.

(12). Pale yellow solid (357 mg, 91%). ^{1}H NMR (400MHz, DMSO-*d*$_6$): δ = 10.36 (s, 2H), 7.09 (s, 2H) ppm; ^{13}C NMR (176 MHz, DMSO-d$_6$): δ = 161.3, 157, 155.3 ppm. IR (neat): 3590, 3265, 2940, 2640, 1990, 1630, 1605, 1380, 1308, 1036 cm^{-1}. Anal. calcd for $C_7H_7N_{15}O_6$: C 18.37, H 1.03, N 64.28; found: C 18.03, H 1.01, N 64.01. HRMS: calc. for $C_6H_4N_{18}O_4^-$ [M]$^-$: 391.0590; found: 391.0595.

General procedure for the preparation of energetic salts 4–11:

(3) (606 mg, 1 mmol) was added to a solution of the corresponding hydrochloride (1 mmol) in H_2O (30 mL) and the resulting mixture was stirred at 80 °C for 10 h. The hot solution was filtered and evaporated in vacuo and the residue was recrystallized from ethanol-water solution to get the target product.

(**4**). Bright yellow solid (192 mg, 45%). ^{1}H NMR (400MHz, DMSO-d_6): δ = 9.92 (s, 2H), 7.13 (t, J = 48 Hz, 8H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ = 16..5, 157, 156 ppm. IR (neat): 3112, 3002, 2801, 2003, 1746, 1642, 1544, 1391, 1309, 1153 cm^{-1}. Anal. calcd for $C_4H_4N_8O_7$: C 16.91, H 2.36, N 65.72; found: C 16.83, H 2.30, N 65.33.

(5). Yellow solid (178 mg, 39%). ^{1}H NMR (400MHz, DMSO-d_6): δ = 10.30 (s, 8H) 10.11 (s, 2H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ = 161.0, 156.6, 156.0 ppm. IR (neat): 3132, 2922, 2704, 1606, 1539, 1402, 1308, 1151 cm^{-1}. Anal. calcd for $C_4H_4N_8O_6$: C 15.79, H 2.65, N 67.53; found: C 15.70, H 2.61, N 67.31.

(6). Bright yellow solid (220 mg, 48%). ^{1}H NMR (400MHz, DMSO-d_6): δ = 9.95 (s, 2H), 6.19 (s, 10H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ = 160.5, 157.2, 156.1 ppm. IR (neat): 3150, 2840, 2701, 1608, 1542, 1398, 1308, 1148, 1037 cm^{-1}. Anal. calcd for $C_4H_4N_8O_7$: C 15.73, H 2.20, N 61.13; found: C 15.56, H 2.13, N 60.78.

(7). Pale yellow solid (205 mg, 38%). ^{1}H NMR (400MHz, DMSO-d_6): δ = 9.92 (s, 2H), 8.57 (s, 2H), 7.26 (s, 4H) , 6.75 (s, 4H), 4.69 (s, 4H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ = 160.6, 158.3, 157.1, 156.1 ppm. IR (neat): 3378, 3326, 3152, 3089, 1720, 1666, 1605, 1304, 1147 cm^{-1}. Anal. calcd for $C_4H_5N_9O_6$: C 17.78, H 2.98, N 67.39; found: C 17.59, H 2.71, N 67.22.

(8). Pale yellow solid (268 mg, 47%). ^{1}H NMR (400MHz, DMSO-d_6): δ = 9.93 (s, 2H), 8.58 (s, 4H), 7.16 (s, 4H), 4.61 (s, 8H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ = 160.5, 160.1, 157.3, 156.0 ppm. IR (neat): 3429, 3206, 1668, 1603, 1537, 1391, 1301, 1171, 1009 cm^{-1}. Anal.calcd for $C_5H_8N_{12}O_6$: C 16.85, H 3.18, N 68.76; found C16.74, H 3.10, N 68.55.

(9). Pale yellow solid (288 mg, 48%). ^{1}H NMR (400MHz, DMSO-d_6): δ = 9.93 (s, 2H), 8.61 (s, 6H), 4.41 (s, 12H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ = 160.5, 159.5, 157.3, 156.0 ppm. IR (neat): 3345, 3321, 3196, 1675, 1599, 1533, 1304, 1137 cm^{-1}. Anal.calcd for $C_5H_8N_{12}O_6$: C 16.00, H 3.36, N 69.98 found C15.93, H 3.31, N 69.74.

(10). Bright yellow solid (266 mg, 45%). ^{1}H NMR (400MHz, DMSO-d_6): δ = 9.92 (s, 2H), 6.98 (s, 8H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ = 160.5, 157.3, 156.0, 152.0 ppm. IR (neat): 3461, 3176, 3643, 1670, 1596, 1302, 1151, 988 cm^{-1}. Anal.calcd for $C_5H_9N_{13}O_6$: C 20.34, H 2.39, N 66.43; found C 20.21, H 2.38, N 66.41.

(11). Pale yellow solid (273 mg, 39%). ^{1}H NMR (400MHz, DMSO-d_6): δ = 9.9 (s, 1H), 8.2 (s, 2H), 7.2 (s, 2H), 5.8 (s, 2H) ppm; ^{13}C NMR (176 MHz, DMSO-d_6): δ = 160.6, 160.5, 157.3, 156.0, 147.9, 141.6 ppm. IR (neat): 3444, 3324, 3092, 2745, 1688, 1544, 1479, 1300, 1144 cm^{-1}. Anal. calcd for $C_5H_4N_{12}O_6$: C 20.58, H 2.30, N 67.99; found: C 20.48, H 2.35, N 67.81.

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