Supporting Information

Constructing heat-resistant and insensitive energetic compounds with the introduction of cyano group into fused pyrazolotriazine skeleton

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Experimental Section

Synthesis of 7-diamino-8-nitropyrazole [5, 1-C][1,2,4] triazine-3-cyanide (2)

HCl (12.5 mL, 50.0 mmol) in dioxane (4 M) was added into a suspension of **1** (1.43 g, 10 mmol) in methanol (30 mL) at 0 ℃. Tert-butyl nitrite (1.72 g, 15.0 mmol) was added dropwise to the suspension. After stirring 1 h at 0 ℃, diethyl ether (200 mL) was added to the reaction mixture and the diazonium salt precipitated. After filtration and washing with diethyl ether (20 mL × 2), the orange solid (**2**) was suspended in sulfuric acid (20%, 16 mL). Then a solution of potassium malononitrile (prepared by adding 10.5 g potassium acetate to a solution of 0.924 g malononitrile (15.0 mmol) in 35 mL water at 0-5 ℃) was added to the above suspension while maintaining the temperature below 5 ℃. The resulting suspension was stirred for 1 d. A orange precipitate which formed was filtered. Compound **2** was obtained in a yield of 94%. **2:** Yellow solid. ^{1}H NMR (d_6-DMSO): 9.29 (s, 2H), 7.41 (s, 2H) ppm. ^{13}C NMR (d_6-DMSO): δ 155.35, 148.77, 141.06, 114.91, 114.25, 109.71 ppm. IR (KBr): 3433.27, 3159.28, 2246.62, 1629.48, 1570.07, 1526.33, 1432.31, 1301.98, 1209.19, 1121.54, 810.44, 769.66.751.31, 670.94, 596.44 cm^{-1}. Elemental analysis (%) for $C_6H_4N_8O_4$ (220.56): calcd: C, 32.72; H, 1.80; N, 50.90; found: C 30.259, H 2.97, N 48.27.

Synthesis of 4-amino-7, 8-dinitropyrazole [5, 1-C][1,2,4] triazine-3-cyanide (3)

To a solution of ADNP (0.346 g, 2.00 mmol) in 12 mL water and 0.6 mL 37% hydrochloric acid was added a solution of sodium nitrite (0.162 g, 2.35 mmol) in 3 mL water under stirring at -2 °C. The reaction mixture was kept for 0.5 h at this temperature. Then, malononitrile (0.155 g, 2.35 mmol) and sodium acetate (0.964 g, 11.75 mmol) in 5 mL water was added drop-wise to the reaction mixture. The reaction system was stirred at -2 °C for 1 h and then warmed to 30 °C for 2 h. The precipitate was filtered off, washed with water and dried in air afford compound **3** (0.329 g,

1.31 mmol) in a yield of 66%. ^{1}H NMR(500MHz, d_6-DMSO) δ: 10.64 (S,2H); ^{13}C NMR(500MHz, d_6-DMSO) δ: 152.40, 143.22, 142.59, 115.68, 114.06, 112.97 ppm. IR (KBr): 3129.86, 2252.69, 1658.39, 1514.53, 1491.52, 1410.15, 1379.86, 1337.52, 1294.01, 1072.58, 948.62, 912.50752.35, 690.89 cm^{-1}. Elemental analysis (%): $C_6H_2N_8O_4$ (250.71), calculated value: C 28.71, H 0.79, N 44.67; Measured value: C 28.56, H 0.86, N 44.39.

2. Crystalline parameters

Table S1. Crystal data and structure refinement for compound **2.**

Identification code	CCDC 2073483
Empirical formula	$C_6H_4N_8O_2$
Formula weight	220.56
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1$
a/Å	4.9560(2)
b/Å	4.8398(2)
c/Å	17.0120(6)
α/°	90
β/°	91.769(4)
γ/°	90
Volume/Å^3	407.85(3)
Z	4
ρ_{calc}g/cm^3	1.794
μ/mm^{-1}	0.722
F(000)	182.0
Crystal size/mm^3	1 × 0.8 × 0.7
Radiation	CuKσ(λ= 1.54184)
2θ range for data collection/°	5.198 to 155.324
Index ranges	$-6 \le h \le 6$, $-6 \le k \le 6$, $-21 \le l \le 15$
Reflections collected	4929
Independent reflections	1655 [R_{int} = 0.0392, R_{sigma} = 0.0401]
Data/restraints/parameters	1655/1/146
Goodness-of-fit on F^2	1.062
Final R indexes [I>=2σ(I)]	R_1 = 0.0408, wR_2 = 0.1089
Final R indexes [all data]	R_1 = 0.0431, wR_2 = 0.1102
Largest diff. peak/hole / e Å^{-3}	0.22/-0.19

Flack parameter	0.6(2)

Table S2 Bond Lengths for **2.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.381(4)	C5	C4	1.417(4)
N1	C4	1.347(4)	C5	N6	1.349(4)
N1	N2	1.374(4)	C5	C6	1.431(5)
N8	C6	1.142(5)	C1	N5	1.360(4)
N7	C4	1.316(4)	N5	N6	1.312(4)
N3	C3	1.338(4)	C3	N2	1.332(4)
C2	C1	1.391(4)	O1	N4	1.232(4)
C2	C3	1.418(4)	O2	N4	1.232(4)
C2	N4	1.405(4)			

Table S3 Bond Angles for **2.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	N1	C1	122.9(3)	N1	C4	C5	112.3(3)
C4	N1	N2	122.7(3)	N7	C4	N1	119.2(3)
N2	N1	C1	114.4(2)	N7	C4	C5	128.5(3)
C1	C2	C3	107.5(2)	N3	C3	C2	128.0(3)
C1	C2	N4	126.4(3)	N2	C3	N3	121.0(3)
N4	C2	C3	126.1(3)	N2	C3	C2	111.0(3)
C4	C5	C6	119.8(3)	N5	N6	C5	121.9(3)
N6	C5	C4	124.0(3)	C3	N2	N1	104.0(2)
N6	C5	C6	116.2(3)	N8	C6	C5	179.2(4)
N1	C1	C2	103.2(3)	O1	N4	C2	118.8(3)
N5	C1	N1	122.1(3)	O1	N4	O2	122.8(3)
N5	C1	C2	134.7(3)	O2	N4	C2	118.3(3)
N6	N5	C1	116.8(3)				

Table S4. Crystal data and structure refinement for compound **3.**

Identification code	CCDC 2089297
Empirical formula	$C_6H_2N_8O_4$
Formula weight	250.16
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.4198(5)

b/Å	8.7088(9)
c/Å	19.3747(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	914.48(15)
Z	4
ρ_{calc}g/cm^3	1.817
μ/mm^{-1}	0.156
F(000)	504.0
Crystal size/mm^3	0.2 × 0.11 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.29 to 51.992
Index ranges	$-5 \le h \le 6$, $-10 \le k \le 10$, $-23 \le l \le 21$
Reflections collected	4524
Independent reflections	1789 [R_{int} = 0.0490, R_{sigma} = 0.0635]
Data/restraints/parameters	1789/0/164
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0445, wR_2 = 0.1023
Final R indexes [all data]	R_1 = 0.0583, wR_2 = 0.1108
Largest diff. peak/hole / e Å^{-3}	0.24/-0.16
Flack parameter	1.8(10)

Table S5 Bond Lengths for **3.**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N7	1.199(5)	N4	C5	1.337(5)
O2	N7	1.212(4)	N5	C4	1.297(4)
O3	N8	1.211(5)	N6	C6	1.118(5)
O4	N8	1.219(5)	N7	C1	1.461(5)
N1	N2	1.350(4)	N8	C2	1.429(5)
N1	C1	1.316(4)	C1	C2	1.386(5)
N2	C3	1.377(4)	C2	C3	1.399(5)
N2	C4	1.363(4)	C4	C5	1.408(5)
N3	N4	1.318(4)	C5	C6	1.444(5)
N3	C3	1.343(5)			

Table S6 Bond Angles for **3.**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	N2	102.7(3)	C2	C1	N7	129.2(3)
N1	N2	C3	114.4(3)	C1	C2	N8	129.2(3)

N1	N2	C4	123.3(3)	C1	C2	C3	105.0(3)
C4	N2	C3	122.3(3)	C3	C2	N8	125.5(4)
N4	N3	C3	116.0(3)	N2	C3	C2	103.7(3)
N3	N4	C5	122.1(3)	N3	C3	N2	123.3(3)
O1	N7	O2	125.1(4)	N3	C3	C2	133.1(3)
O1	N7	C1	117.2(3)	N2	C4	C5	111.5(3)
O2	N7	C1	117.6(4)	N5	C4	N2	119.7(3)
O3	N8	O4	124.3(4)	N5	C4	C5	128.8(3)
O3	N8	C2	117.9(4)	N4	C5	C4	124.8(3)
O4	N8	C2	117.8(4)	N4	C5	C6	115.3(3)
N1	C1	N7	116.2(3)	C4	C5	C6	119.9(3)
N1	C1	C2	114.2(3)	N6	C6	C5	179.1(4)

3. NMR spectra

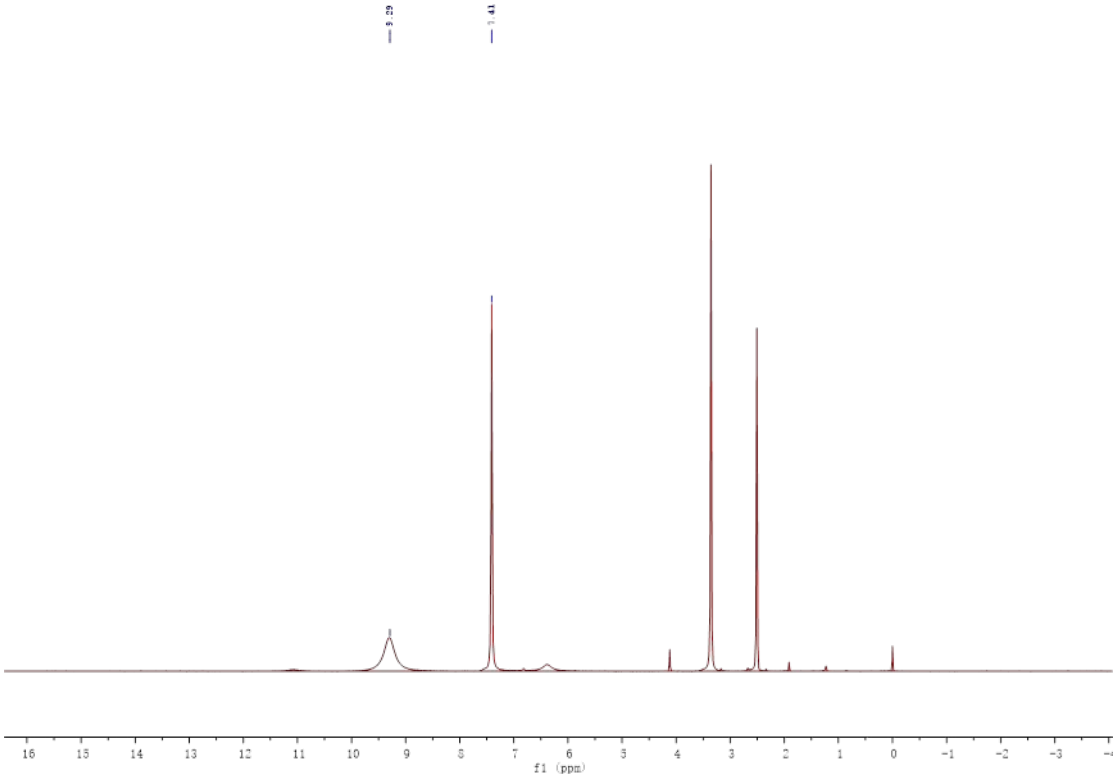


Figure S1. ^{1}H NMR of energetic compound **2**

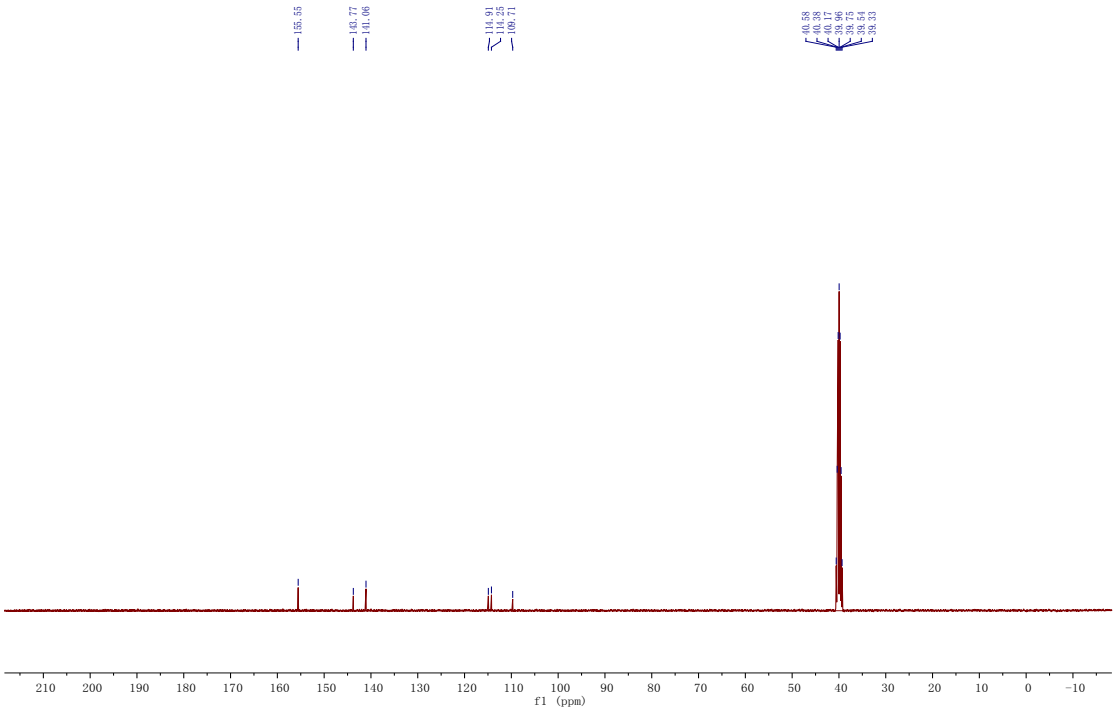


Figure S2. ^{13}C NMR of energetic compound **2**

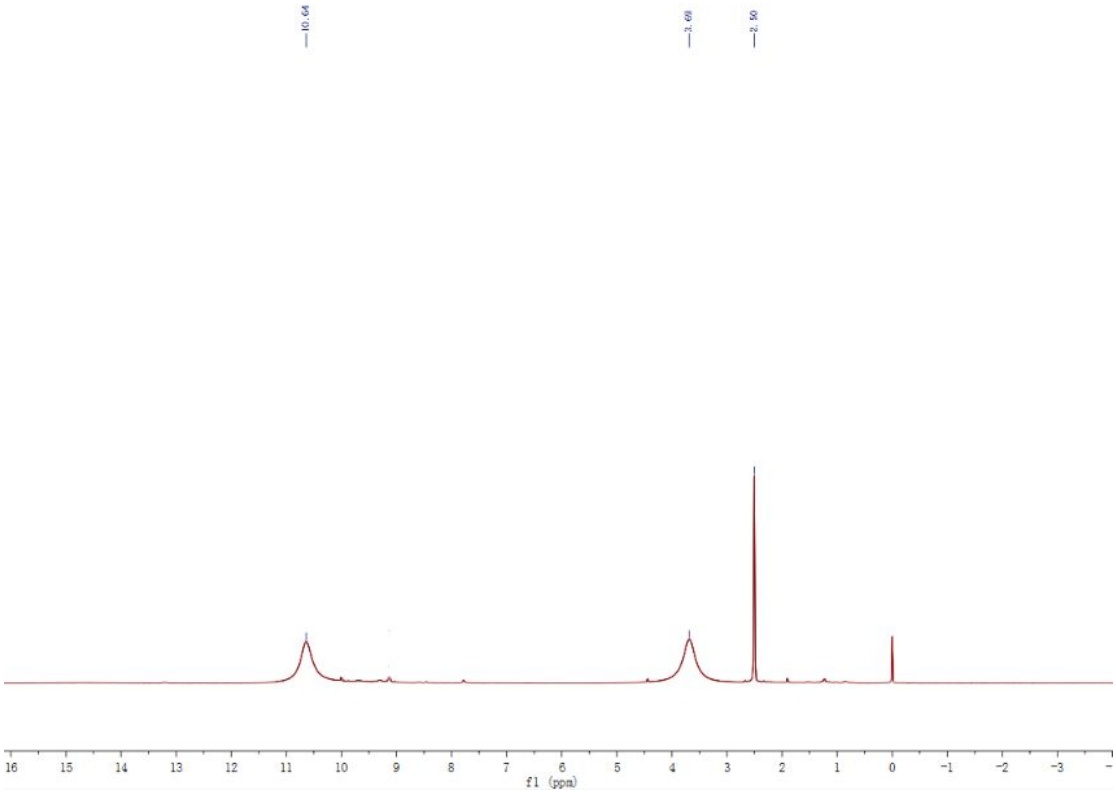


Figure S3. ^{1}H NMR of energetic compound **3**

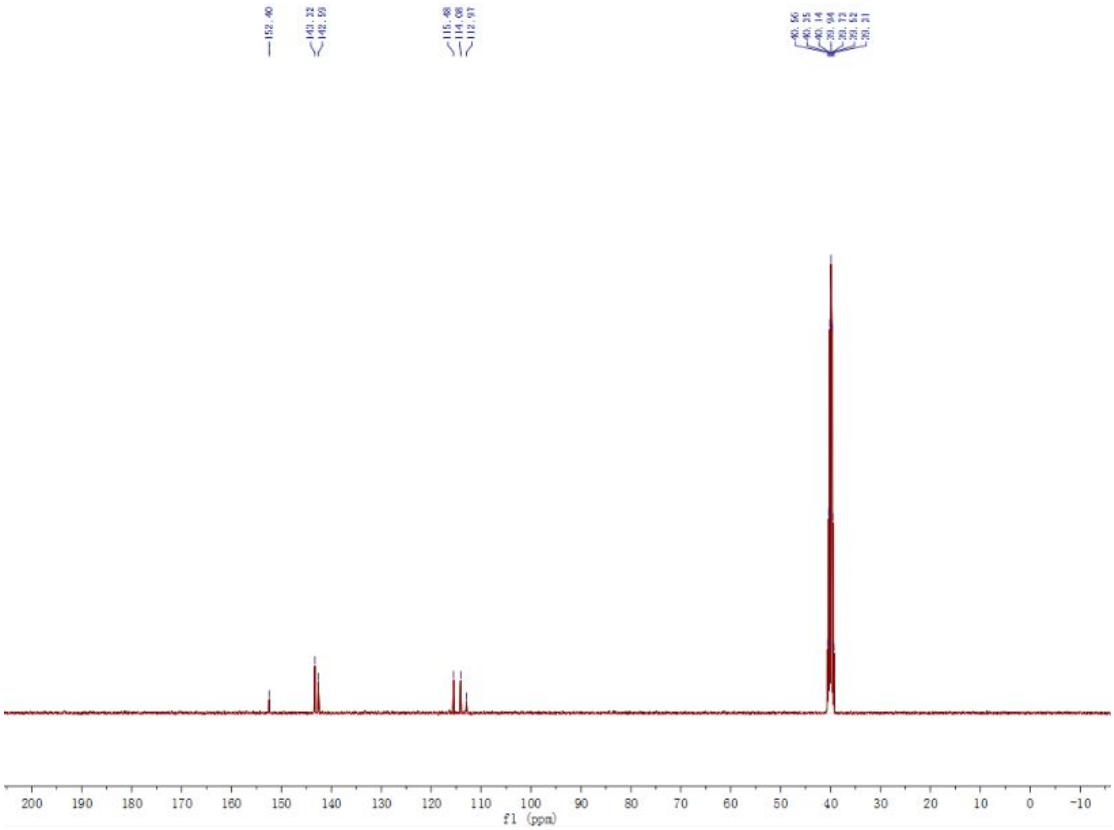


Figure S4. ^{13}C NMR of energetic compound **3**

4. DSC-TG curves

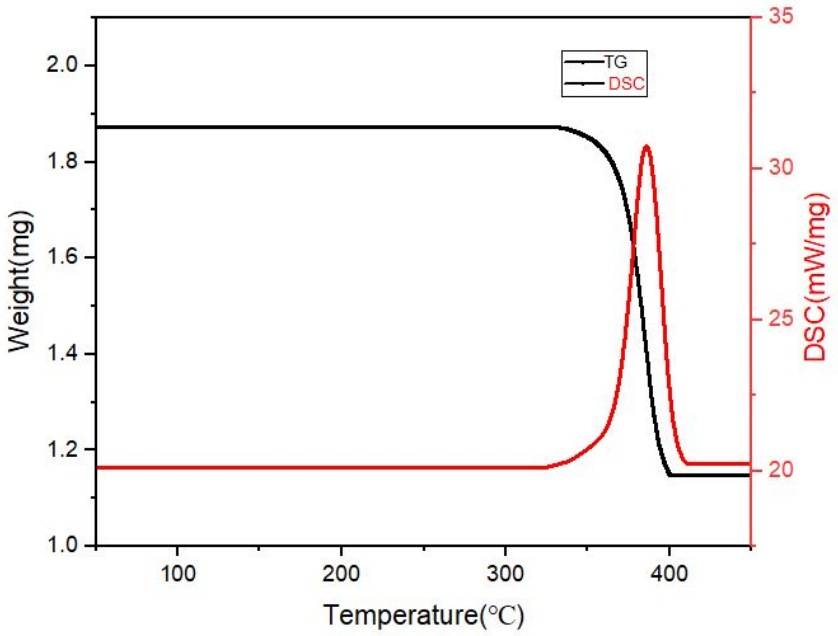


Figure S5. TG-DSC curves of **2.**

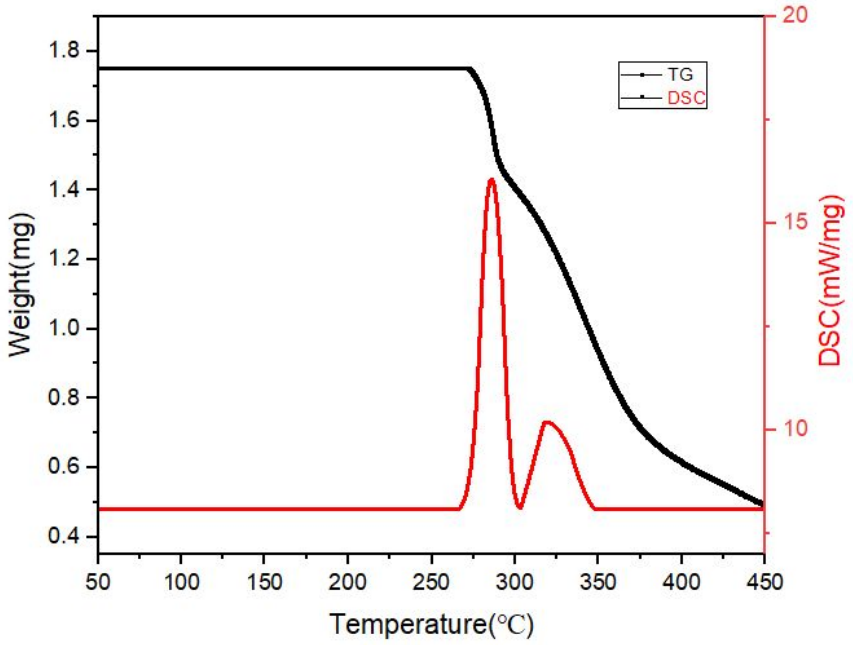


Figure S6. TG-DSC curves of **3.**

5. Theoretical study

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.[1] The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP) functional with the 6-311+G** basis set.[2] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.[3] All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.[4]

The predictions of heat of formation (*HOF*) adopt the hybrid DFT-B3LYP methods with 6-311+G** basis set via designed isodesmic reactions. The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of the title

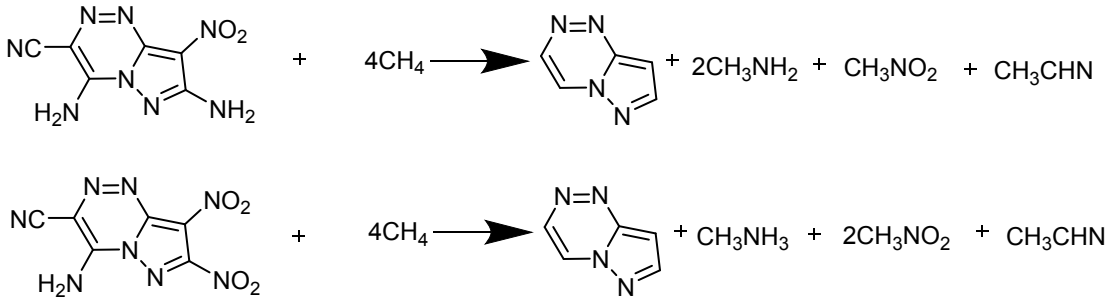
compounds are in Scheme S1. The change of enthalpy for the reactions at 298 K can be expressed as

$$\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R \quad (1)$$

Where $\sum \Delta_f H_P$ and $\sum \Delta_f H_R$ are the HOF of reactants and products at 298 K, respectively, and ΔH298 can be calculated using the following expression

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

Where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K; ΔH_T is thermal correction from 0 to 298 K. The Δ(PV) value in Eq. (2) is the PV work term. It equals Δ(nRT) for the reactions of ideal gas. For the isodesmic reaction, Δn = 0, so Δ(PV) = 0. On the left side of Eq. (1), apart from target compound, all the others are called reference compounds. The HOF of reference compounds is available from the experiments.



Scheme S1. Isodesmic reactions of target compounds.

4 References

[1] Frisch MJ, Trucks GW, Schlegel HB, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J, Fox DJ. Gaussian 09, Revision D. 01, Gaussian. Inc. Wallingford CT, 2009.

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[3] Ochterski JW, Petersson GA, Montgomery JA, Lattice dynamics and hyperfine interactions of $C_{60}Fe(CO)_4$, J Chem Phys. 1996; 104, 7, 2598-2619.

[4] Jenkins HDB, Tudeal D, Glasser L, Lattice potential energy estimation for complex ionic salts from density measurements, Inorg Chem. 2002; 41, 9, 2364-2367.