

Supporting Information (SI)

Advanced ultra heat-resistant explosives with multiple heterocyclic skeletons of hydrogen bond network

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1. Experimental sections

General methods

Caution!

Compounds reported in this work are highly explosive compounds, thus appropriate safety precaution are necessary. Proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthed equipment) should be always used. Additionally, the small-scale experiment and real time monitoring is indispensable.

^1H and ^{13}C NMR spectra were recorded on 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 500 and 126 MHz, respectively, by using DMSO- d_6 as the solvent and locking solvent unless otherwise stated. Chemical shifts in ^1H and ^{13}C NMR spectra are reported relative to DMSO. DSC was performed in closed Al containers with a nitrogen flow of 30 mL min^{-1} on an STD-Q600 instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR equipped with an ATR unit at $25\text{ }^\circ\text{C}$. Impact sensitivity and friction sensitivity of samples are measured by using the standard BAM methods. X-ray intensity data were collected on a Bruker D8 VENTURE PHOTON II system equipped with an Incoatecius 3.0 Microfocus sealed tube. The structures were solved and refined using Bruker SHELXTL Software Package. The data were refined against F2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed to their parent atoms using a riding model and refined isotropically.

Synthesis

6-(3,5-diamino-4-nitro-1H-pyrazol-1-yl)-1,3,5-triazine-2,4-diamine (**H1**):

3,5-diamino-4-nitro-4-pyrazole (0.14 g, 1.0 mmol) was dissolved in 5 mL of DMF, and 6-chloro-1,3,5-triazine-2,4-diamine (**1**) (0.15 g, 1.0 mmol) was added. The reaction was carried out at $100\text{ }^\circ\text{C}$ for 12 hours, and 100 mL of water was added to the DMF solution to generate a large amount of precipitate. The precipitate was collected through filtration, washed with water to obtain 0.15 g (59.2 %) of compound **H1** as a brown solid. ^1H NMR (500 MHz, DMSO- d_6): $\delta = 8.59$ (s, 4H) ppm. ^{13}C NMR (126 MHz, DMSO- d_6): $\delta = 133.02, 133.41, 135.10, 136.19, 149.72, 157.71$ ppm. IR (KBr): $\tilde{\nu}$ 3502.5, 3500.6, 3428.4, 3308.7, 3425.8, 1643.6, 1580.9, 1563.8, 1537.7, 1508.1, 1470.6, 1449.1, 1406.4, 1374.4, 1304.3, 1230.6, 1197.4, 787.9, 752.3, 729.8, 400.5, 392.7, 232.7, 226.1, 208.4, 148.0 cm^{-1} . Elemental analysis for $\text{C}_6\text{H}_8\text{N}_{10}\text{O}_2$ (252.08): calcd C, 28.58; H, 3.20; N, 55.54%. Found: C 28.50, H 3.10, N 55.72%.

1,1'-(6-amino-1,3,5-triazine-2,4-diyl)bis(4-nitro-1H-pyrazole-3,5-diamine) (**H2**):

3,5-diamino-4-nitro-4-pyrazole (0.28 g, 2.0 mmol) was dissolved in 10 mL of DMF, and 4,6-dichloro-1,3,5-triazin-2-amine (**2**) (0.17 g, 1.0 mmol) was added. The reaction was carried out at 100 °C for 12 hours, and 200 mL of water was added to the DMF solution to generate a large amount of precipitate. The precipitate was collected through filtration, washed with water to obtain 0.26 g (68.6 %) of compound **H2** as a yellow solid. ¹H NMR (500 MHz, DMSO-d₆): δ = 8.56 (s, 8H) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 132.69, 136.64, 137.59, 1151.24, 157.66 ppm. IR (KBr): $\tilde{\nu}$ 3487.6, 3458.6, 3426.7, 3336.0, 1647.6, 1624.0, 1517.4, 1472.2, 1439.0, 1407.4, 1387.6, 1369.7, 1363.6, 1210.0, 1195.6, 751.4, 732.3, 726.0, 388.4, 370.6, 319.3, 302.9, 283.5, 193.5 cm⁻¹. Elemental analysis for C₉H₁₀N₁₄O₄ (378.27): calcd C, 28.58; H, 2.66; N, 51.84%. Found: C 28.55, H 2.61, N 51.92%.

1,1',1''-(5-nitropyrimidine-2,4,6-triyl)tris(4-nitro-1H-pyrazole-3,5-diamine) (**H3**):

3,5-diamino-4-nitro-4-pyrazole (0.63 g, 3.0 mmol) was dissolved in 20 mL of DMF, and 2,4,6-trichloro-5-nitropyrimidine (**3**) (0.23 g, 1.0 mmol) was added. The reaction was carried out at 100 °C for 24 hours, and 500 mL of water was added to the DMF solution to generate a large amount of precipitate. The precipitate was collected through filtration, washed with water to obtain 0.36 g (66.8 %) of compound **H3** as a yellow solid. ¹H NMR (500 MHz, DMSO-d₆): δ = 8.73 (s, 12H) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 109.15, 146.61, 148.50, 1449.10, 150.02, 150.68, 151.07, 151.14, 151.59 ppm. IR (KBr): $\tilde{\nu}$ 3478.0, 3449.0, 342.4, 3321.0, 1716.5, 1655.2, 1652.6, 1638.8, 1620.1, 1531.0, 1471.2, 1406.8, 1390.1, 1386.1, 1366.5, 1364.5, 1322.9, 1297.1, 1242.6, 1196.3, 808.0, 798.6, 735.3, 708.3, 604.6, 566.4, 490.7, 368.7, 290.6, 207.5 cm⁻¹. Elemental analysis for C₁₃H₁₂N₁₈O₈ (548.36): calcd C, 28.47; H, 2.21; N, 45.98%. Found: C 28.40, H 2.20, N 46.06%.

N2-(5-amino-4-nitro-1H-pyrazol-3-yl)-N6-(3-amino-4-nitro-1H-pyrazol-5-yl)-3,5-dinitropyridine-2,4,6-triamine (**H4**):

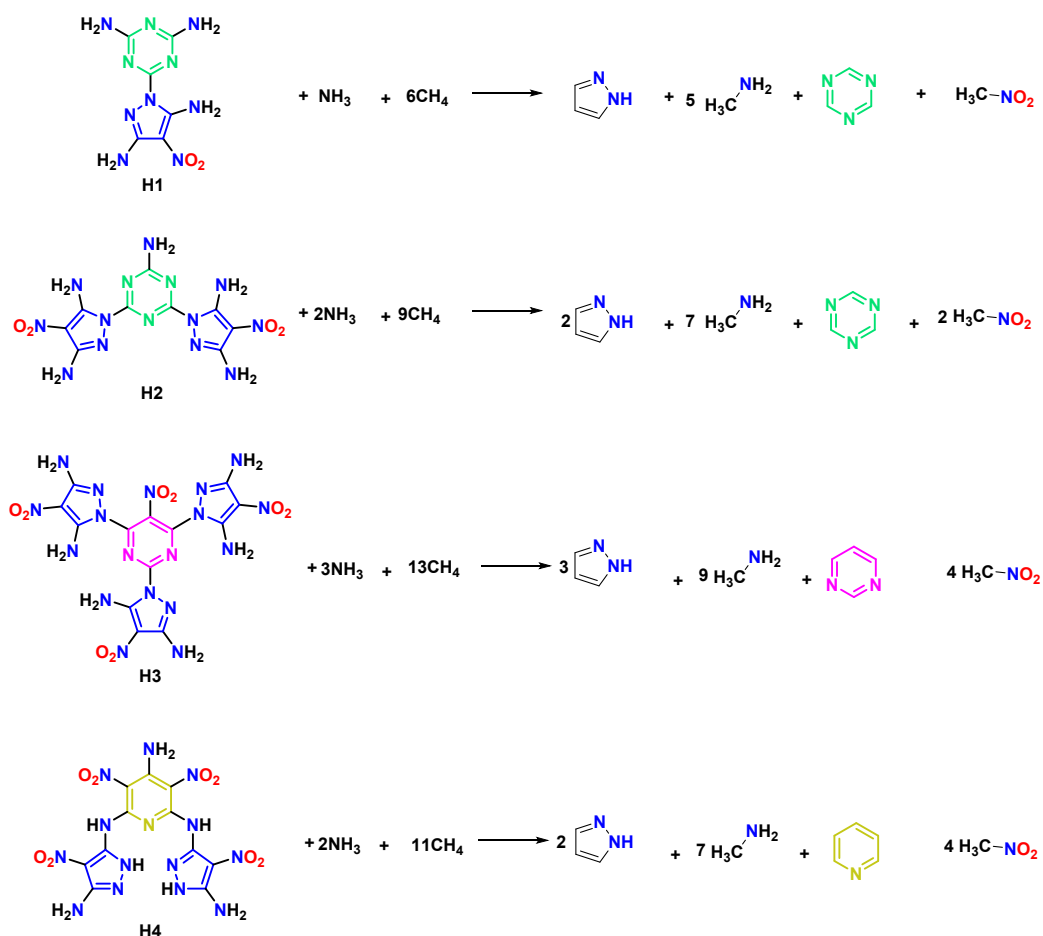
3,5-diamino-4-nitro-4-pyrazole (0.42 g, 2.0 mmol) was dissolved in 10 mL of DMF, and 2,6-dichloro-3,5-dinitropyridin-4-amine (**4**) (0.25 g, 1.0 mmol) was added. The reaction was carried out at 100 °C for 12 hours, and 500 mL of water was added to the DMF solution to generate a large amount of precipitate. The precipitate was collected through filtration, washed with water to obtain 0.41 g (88.9 %) of compound **H4** as a brown solid. ¹H NMR (500 MHz, DMSO-d₆): δ = 7.32 (s, 2H), 8.39 (s, 6H) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 114.04, 139.91, 141.65, 147.15, 147.95, 151.32 ppm.

IR (KBr): $\tilde{\nu}$ 3351.5, 3325.6, 3255.4, 3061.7, 3058.1, 1645.3, 1593.4, 1571.7, 1514.8, 1509.3, 1473.0, 1441.0, 1393.8, 1358.7, 1340.7, 1315.7, 1248.3, 1235.3, 1192.0, 1184.3, 1050.7, 798.9, 747.8, 738.6, 650.3, 328.0, 379.7, 277.4, 273.0, 237.5, 185.0 cm^{-1} . Elemental analysis for $\text{C}_{11}\text{H}_{10}\text{N}_{14}\text{O}_8$ (466.29): calcd C, 28.33; H, 2.16; N, 42.05%. Found: C 28.31, H 2.20, N 42.03%.

2. Computational details of HOF

Computations were performed by using the Gaussian09 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.²⁻⁴ 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.⁵ All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF shown in Scheme S1.



Scheme S1. The isodesmic reactions for calculating heat of formation.

The change of enthalpy for the reactions at 298K can be expressed by Equation (1):

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

Where $\sum \Delta_f H_P$ and $\sum \Delta_f H_R$ are the *HOF* of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression in Equation (2):

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

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 the thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Equation(2) is the *PV* work term. It equals ΔnRT for the reactions of an ideal gas. For the isodesmic reactions $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Equation (2), apart from target compound all the others are called reference compounds. The *HOF* of reference compounds are available either from experiments or from the high level computing such as CBS-4M.

3. Crystallographic data

Table S1. Crystallographic data for H1-H4

Crystal	4H1 ⁺ ·4ClO ₄ ⁻ ·3H ₂ O	H2 ⁺ ·ClO ₄ ⁻ ·H2 ²⁺ ·2ClO ₄ ⁻ ·H ₂ O	H3·2.25DMF·H ₂ O	2H4·DMF·3H ₂ O
CCDC number	2368016	2368017	2368018	2368019
Empirical Formula	C ₂₄ H ₄₂ Cl ₄ N ₄₀ O ₂₁	C ₁₈ H ₂₅ Cl ₃ N ₂₈ O ₂₁	C _{19.75} H _{29.75} N _{20.25} O _{11.25}	C ₂₅ H ₃₃ N ₂₉ O ₂₀
Formula weight	1464.77	1076.01	730.89	1059.80
Temperature [K]	223.0	223.0	223.0	223.0
Crystal system	monoclinic	monoclinic	tetragonal	monoclinic
Space group	P2/n	P21/n	I41/a	P2 ₁ /n
<i>a</i> /Å	14.2998(8)	7.686(2)	29.9543(14)	13.494(6)
<i>b</i> /Å	9.2251(4)	11.614(3)	29.9543(14)	19.039(9)
<i>c</i> /Å	20.3851(9)	44.234(14)	14.6802(10)	16.146(8)
<i>α</i> /°	90	90	90	90
<i>β</i> /°	95.234(3)	90.115(17)	90	103.069(14)
<i>γ</i> /°	90	90	90	90
Cell volume (Å ³)	2677.9(2)	3948.6(19)	13172.0(15)	4041(3)
Formula Z	2	4	16	4
Density (g cm ⁻³)	1.817	1.810	1.474	1.742
<i>μ</i> (mm ⁻¹)	3.157	3.099	1.059	1.323
F (000)	1500.0	2192.0	6080.0	2184.0
Crystal Size (mm ³)	0.11×0.12×0.13	0.10×0.11×0.13	0.13×0.11×0.10	0.12×0.11×0.1
2θ range for data collection (°)	7.25 to 136.486	7.87 to 137.292	12.764 to 137.382	7.29 to 133.184
Index ranges	-17 ≤ <i>h</i> ≤ 15, -9 ≤ <i>k</i> ≤ 11, -24 ≤ <i>l</i> ≤ 24	-9 ≤ <i>h</i> ≤ 9, -13 ≤ <i>k</i> ≤ 13, 0 ≤ <i>l</i> ≤ 53	-36 ≤ <i>h</i> ≤ 36, -36 ≤ <i>k</i> ≤ 36, -197 ≤ <i>l</i> ≤ 14	-16 ≤ <i>h</i> ≤ 15, -22 ≤ <i>k</i> ≤ 22, -19 ≤ <i>l</i> ≤ 19
Reflections collected	18543 4900	12710 7003	33633 6028	23233 7095
Independent reflections	[<i>R</i> _{int} = 0.0830, <i>R</i> _{sigma} = 0.0812]	[<i>R</i> _{int} = 0.0843, <i>R</i> _{sigma} = 0.0967]	[<i>R</i> _{int} = 0.1089, <i>R</i> _{sigma} = 0.0568]	[<i>R</i> _{int} = 0.0866, <i>R</i> _{sigma} = 0.0633]
Data/restraints/parameters	4900/176/490	7003/19/633	6028/318/613	7095/0/680
Final <i>R</i> indexes [<i>I</i> ≥ 2σ (<i>I</i>)]	<i>R</i> ₁ = 0.0979, w <i>R</i> ₂ = 0.0950	<i>R</i> ₁ = 0.0874, w <i>R</i> ₂ = 0.02175	<i>R</i> ₁ = 0.0808, w <i>R</i> ₂ = 0.1649	<i>R</i> ₁ = 0.0999, w <i>R</i> ₂ = 0.1783
Goodness-of fit on <i>F</i> ²	1.082	1.048	1.178	0.993
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0979,	<i>R</i> ₁ = 0.1264,	<i>R</i> ₁ = 0.1129,	<i>R</i> ₁ = 0.1761,

 $wR_2 = 0.0950$ $wR_2 = 0.2570$ $wR_2 = 0.1833$ $wR_2 = 0.2246$

Table S2. Hydrogen bonds for **H3**

D-H \cdots A	d(D-H)/ Å	d(H \cdots A)/ Å	d(D \cdots A)/ Å	\angle (DHA)/ °
N1-H1A \cdots O10	0.8700	2.0800	2.934(7)	165.00
N1-H1B \cdots O1	0.8700	2.2500	2.812(5)	122.00
N1-H1B \cdots O3	0.8700	2.1900	3.011(4)	158.00
N5-H5A \cdots N6	0.8700	2.2000	2.749(4)	120.00
N5-H5A \cdots N3	0.8700	2.5800	3.339(4)	146.00
N5-H5B \cdots O2	0.8700	2.2200	2.773(4)	146.00
N9-H5A \cdots O12	0.8700	2.0400	2.890(6)	164.00
N9-H5A \cdots O4	0.8700	2.2800	2.840(5)	122.00
N11-H11A \cdots N6	0.8700	2.1700	2.742(4)	123.00
N11-H11A \cdots O3	0.8700	2.2100	2.766(4)	121.00
N11-H11A \cdots O12	0.8700	2.1700	3.057(5)	129.00

Table S3. Torsion angles for **H3**

Parameter	Bond angles (Å)	Parameter	Bond angles (Å)
N4-N3-C2-N1	-178.6(3)	C3-N4-C4-N6	-26.0(5)
N4-N3-C2-C1	0.1(4)	C3-N4-C4-C5	155.8(3)
O1-N2-C1-C2	-3.1(7)	C7-N6-C4-N4	-176.6(3)
O1-N2-C1-C3	176.3(4)	C7-N6-C4-C5	1.8(4)
O2-N2-C1-C2	176.1(4)	C4-N6-C4-N7	179.1(3)
O2-N2-C1-C3	-4.6(7)	C4-N6-C7-N12	-1.2(5)
N3-N4-C3-N5	-179.6(3)	C7-N7-N8-C10	-179.7(3)
N3-N4-C3-C1	1.5(4)	C8-N7-N8-C10	-1.2(5)

Table S4. Hydrogen bonds for **H4**

D-H \cdots A	d(D-H)/ Å	d(H \cdots A)/ Å	d(D \cdots A)/ Å	\angle (DHA)/ °
N1-H1A \cdots O17	0.8700	1.9200	2.767(11)	165.00

D-H...A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
N1-H1B...O1	0.8700	2.2700	2.811(8)	120.00
N1-H1B...O4	0.8700	2.4600	3.301(4)	162.00
N5-H5...O2	0.8700	2.0700	2.726(7)	131.00
N5-H5...O3	0.8700	1.8100	2.521(7)	131.00
N7-H7A...O4	0.8700	1.8700	2.534(8)	132.00
N7-H7B...O5	0.8700	1.8700	2.524(9)	131.00
N7-H7A...N6	0.8700	2.6000	3.162(8)	124.00
N10-H10...O6	0.8700	1.8600	2.551(8)	135.00
N11-H11...N3	0.8700	1.9500	2.775(8)	157.00
N11-H11...N9	0.8700	2.1500	2.674(8)	119.00

Table S5. Torsion angles for **H4**

Parameter	Bond angles (Å)	Parameter	Bond angles (Å)
N4-C2-C3-N5	-0.9(11)	C3-N5-C4-N9	-0.1(10)
N4-C2-C3-N3	178.7(7)	C3-N5-C4-C5	179.2(7)
O1-N4-C2-C1	-0.6(11)	C4-N5-C3-N3	-0.8(11)
O1-N4-C2-C3	180.0(7)	C4-N5-C3-C2	178.7(7)
O2-N4-C2-C1	179.6(7)	C4-N9-C8-N7	-179.2(6)
O2-N4-C2-C3	0.2(11)	C4-N9-C8-N10	0.2(10)
N3-N2-C1-N1	179.0(6)	C9-N10-C8-C7	178.9(6)
N3-N2-C1-C2	-0.7(7)	C8-N10-C9-N11	0.9(11)

4. Spectrums of compounds

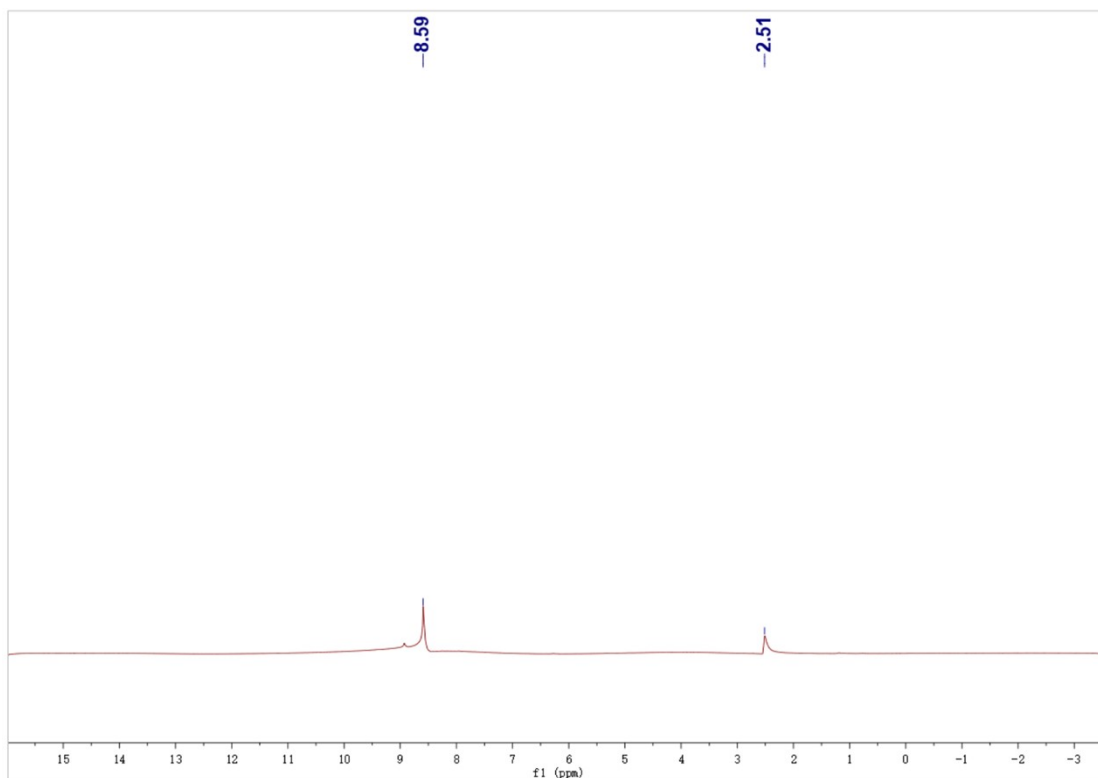


Figure S1. ^1H NMR spectra in DMSO- d_6 for **H1**.

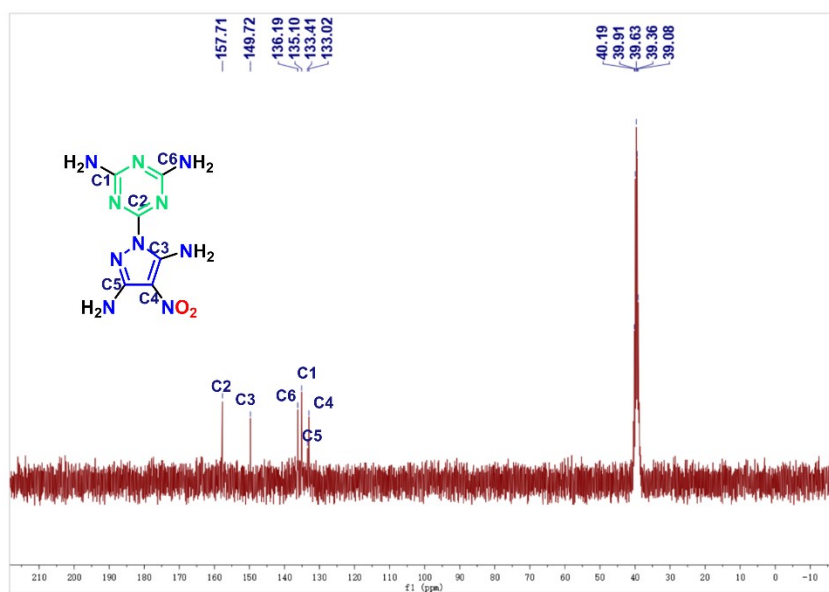


Figure S2. ^{13}C NMR spectra in DMSO- d_6 for **H1**.

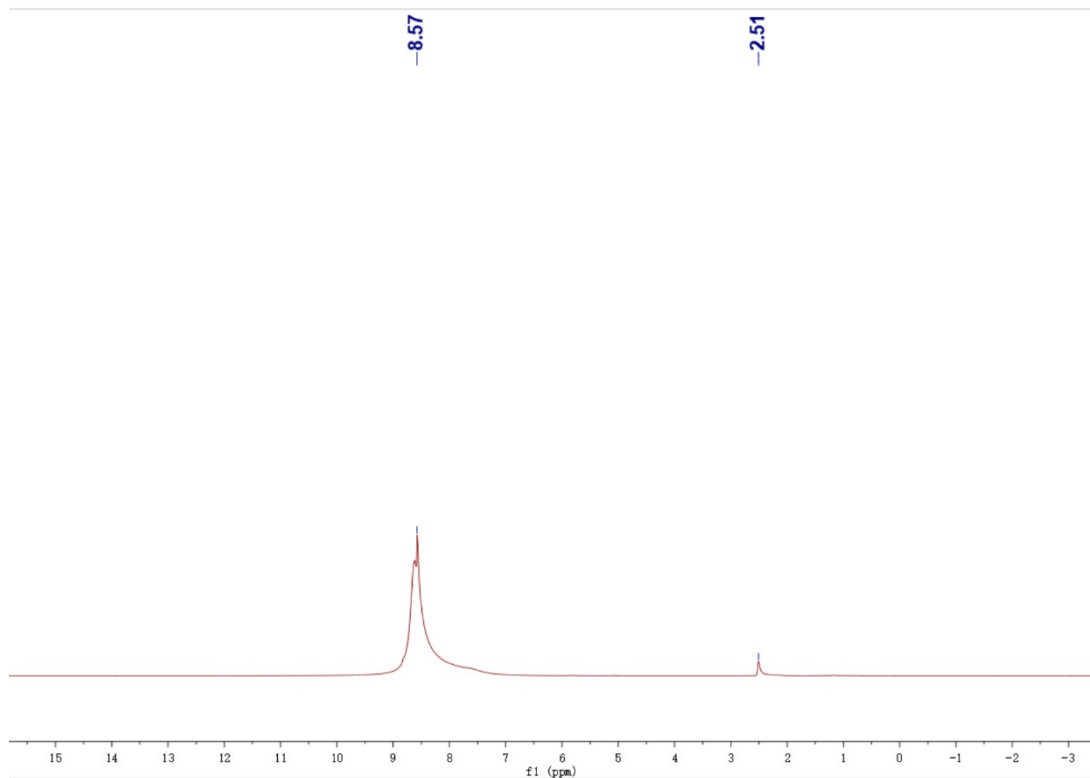


Figure S3. ^1H NMR spectra in DMSO- d_6 for H2.

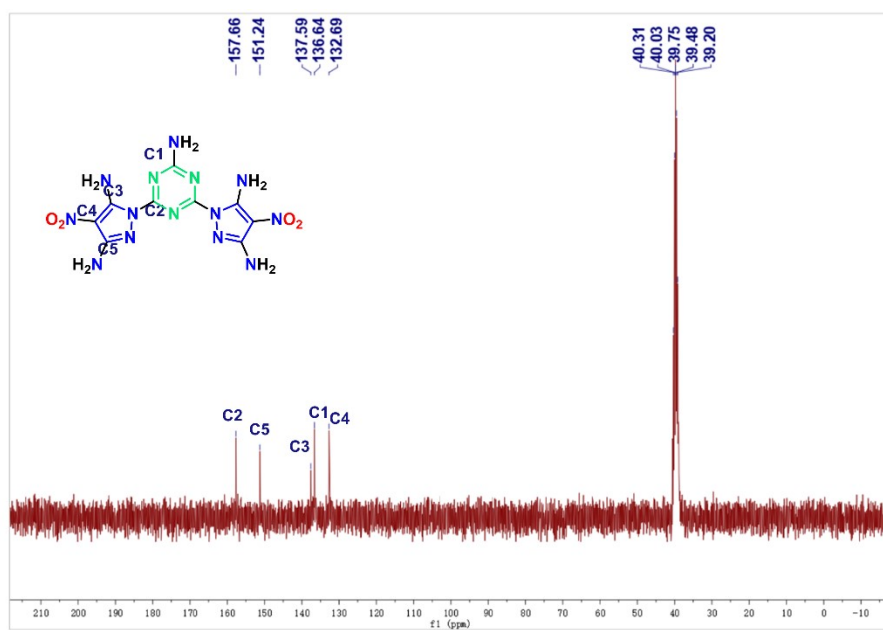


Figure S4. ^{13}C NMR spectra in DMSO- d_6 for H2.

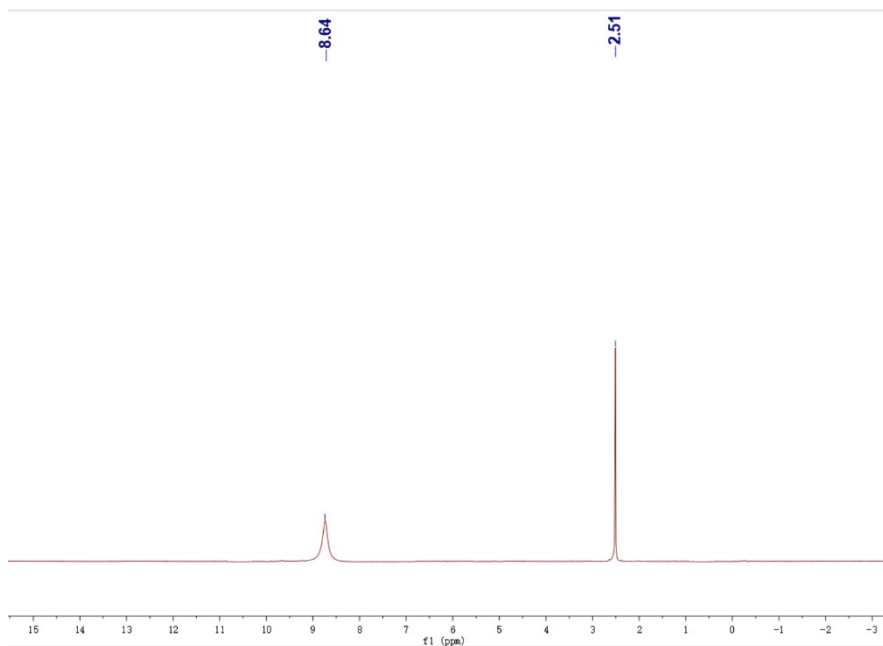


Figure S5. ^1H NMR spectra in DMSO- d_6 for H3.

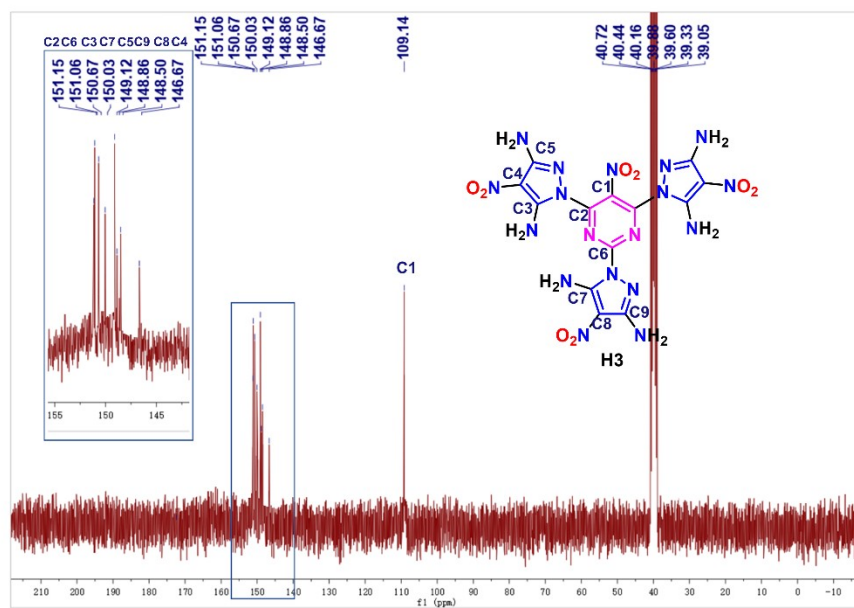


Figure S6. ^{13}C NMR spectra in DMSO- d_6 for H3.

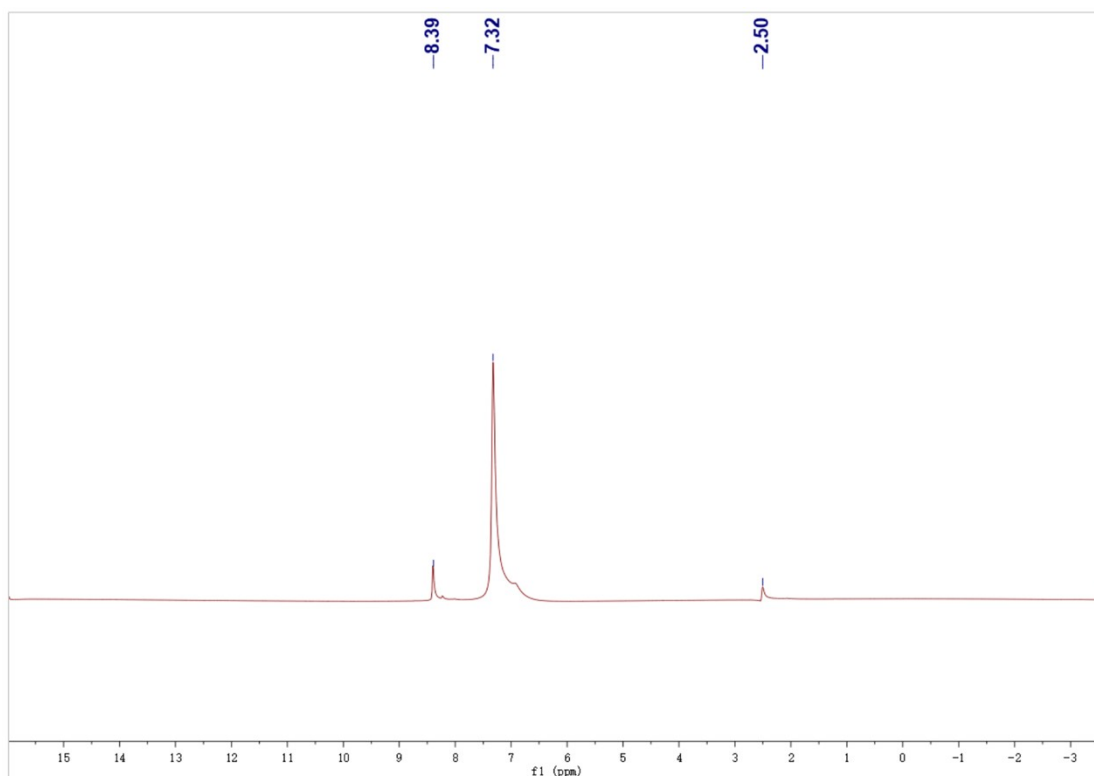


Figure S7. ¹H NMR spectra in DMSO-d₆ for **H4**.

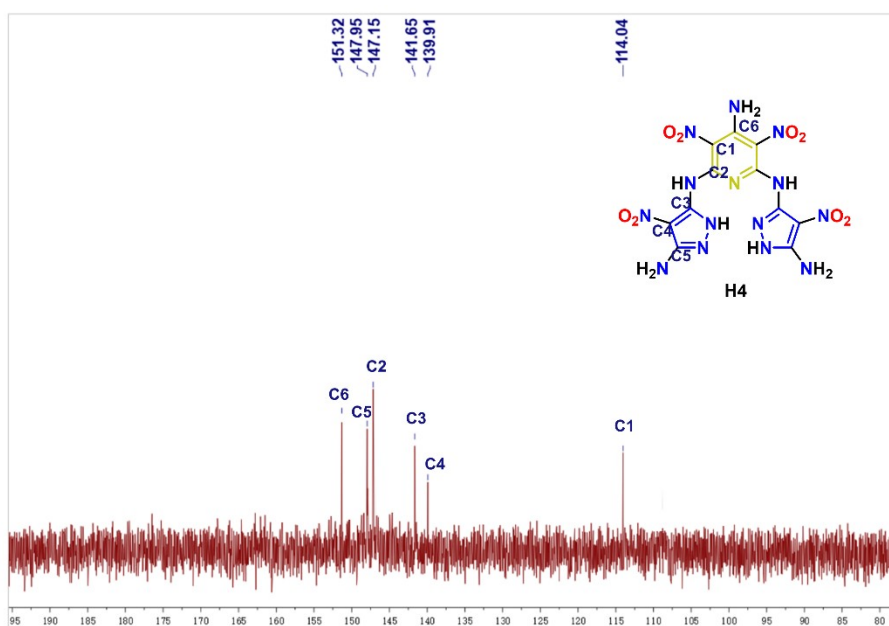


Figure S8. ¹³C NMR spectra in DMSO-d₆ for **H4**.

5. DSC and TG of compounds

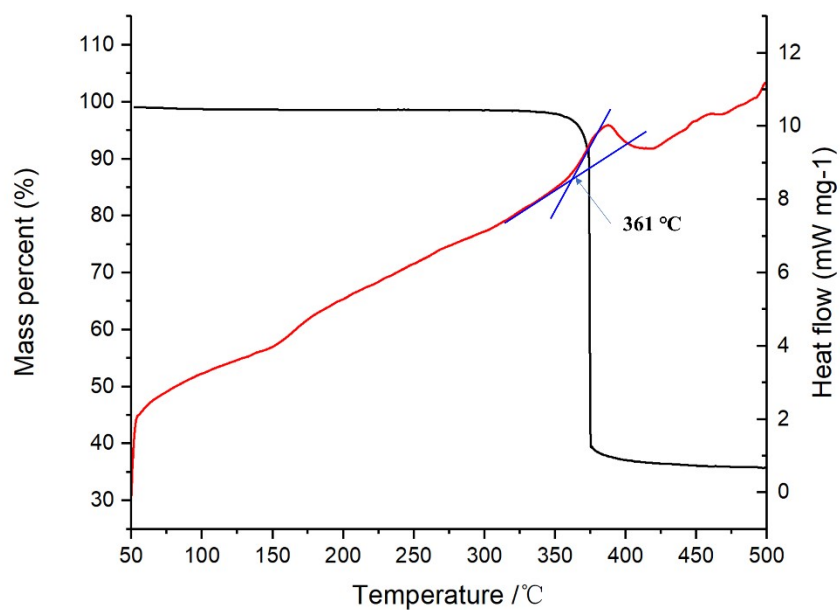


Figure S9 TG and DSC of H1.

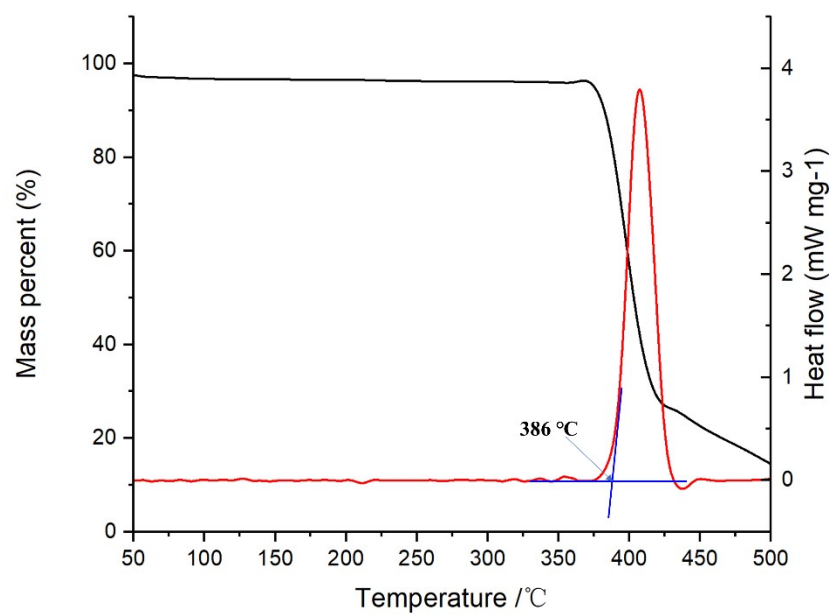


Figure S10 TG and DSC of H2.

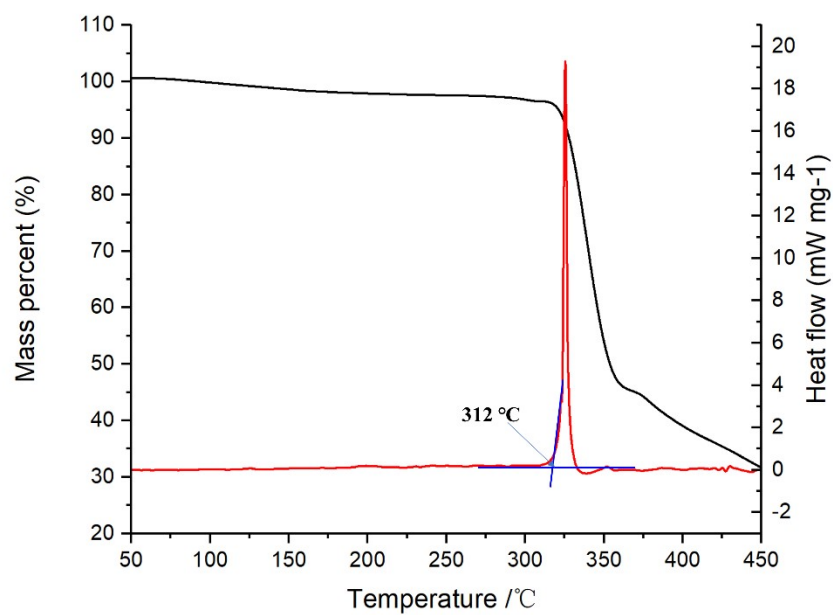


Figure S11 TG and DSC of **H3**.

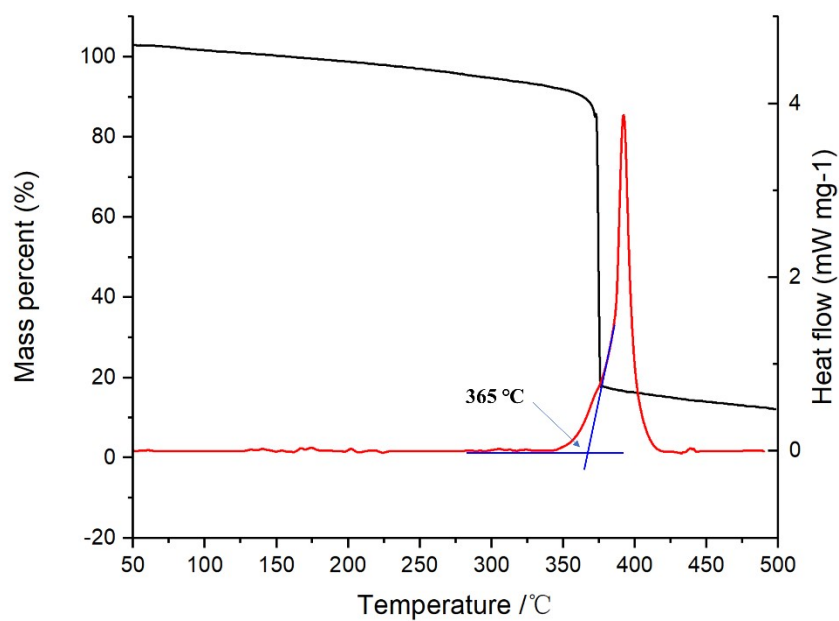


Figure S12 TG and DSC of **H4**.

6. Selected ultra heat-resistant explosives

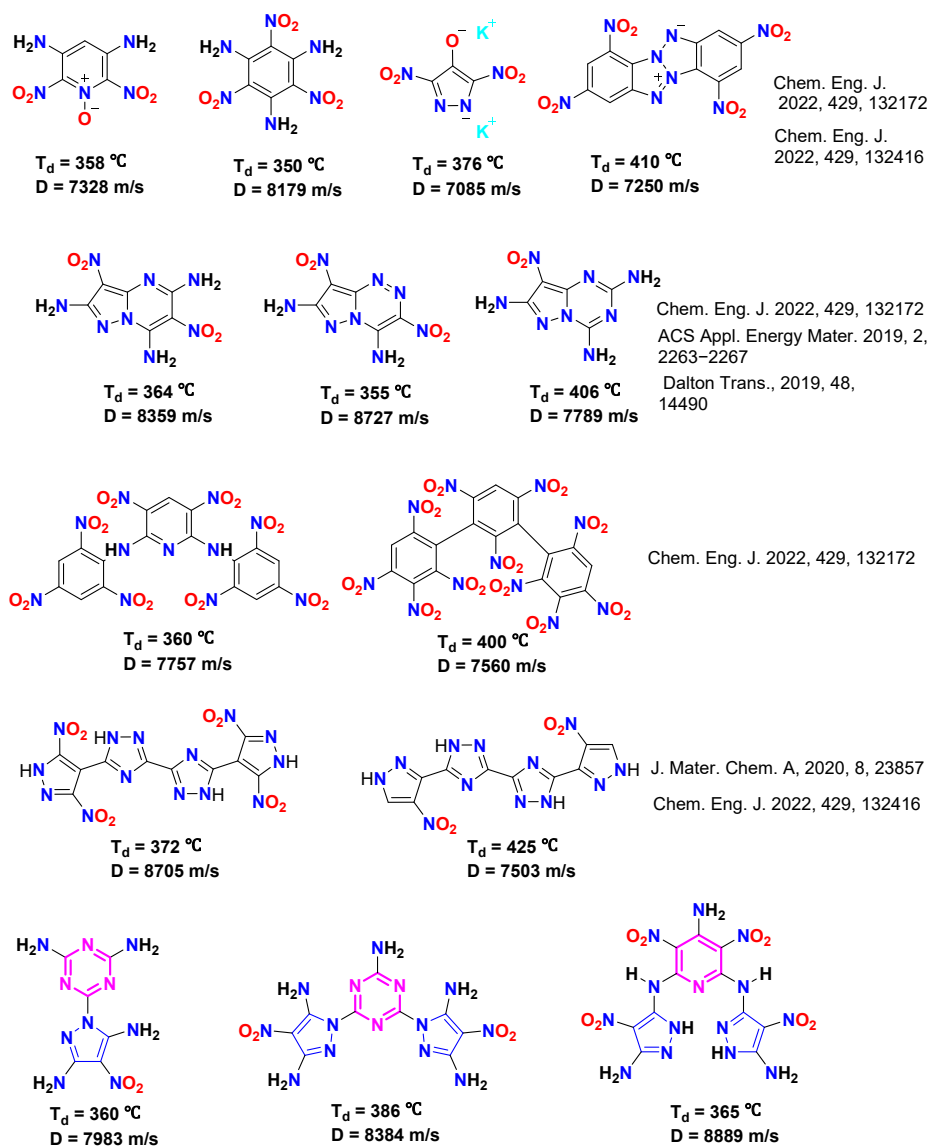


Figure S13 The selected typical heat-resistant explosives with $T_d > 350\text{ }^\circ\text{C}$.

7. Refences

- [1] M. J. Frisch. Gaussian 09, Revision D. 01 (Gaussian Inc., 2009).
- [2] A. D. Becke, J. Chem. Phys. **1993**, 98, 5648-5652
- [3] P. J. Stephens; F. J. Devlin; C. F. Chabalowski; M. J. Frisch. J. Phys. Chem. **1994**, 98, 11623-11627.
- [4] P. C. Hariharan; J. A. Pople, Theor. Chim. Acta. **1973**, 28, 213-222.
- [5] J. W. Ochterski; G. A. Petersson; J. A. Montgomery, J. Chem. Phys. **1996**, 104,

2598-2619.