Supporting Information

Synthesis and detonation characters of 3,4,5-1*H*-trinitropyrazole and its nitrogen-rich energetic salts

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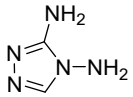
1. Experimental Part

All chemicals and solvents were employed as received. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE(III) 400 M spectrometer. The infrared spectra (in KBr) were recorded on a Nicolet 6700 FT-IR spectrophotometer. ESI-MS was performed in a Bruker Daltonik GmbH, Bremen mass spectrometer equipped with an electrospray ionization (ESI) source. The density was measured by gas pycnometer (25 °C). The thermal behavior of the compound (0.2 mg, aluminium crucibles) was analyzed by differential scanning calorimeter (TGA/DSC, METTLER TOLEDO STAR system), with the heating rate of 5 °C·min^{-1} and N_2 gas atmosphere with a heat flow 80 mL/min. The mechanical sensitivities (including impact sensitivity and friction sensitivity) were determined by the standard step method of the drop weight device with a BAM DFH-10 device with a weight drop of 5 kg. The molecular structure in the crystalline state was determined by using Bruker smart Apex 2, Bruker D8 Venture. The solution and refinement of the structure was performed using the program OLEX2 software[1] (SHELEX-97[2] was implemented) and finally checked with the PLATON software[3]. CCDC-2240955 (**1a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

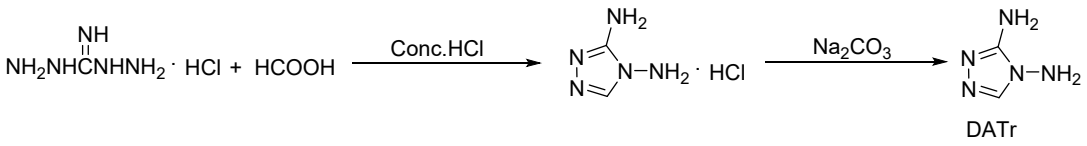
Caution! All of these compounds are potentially energetic materials. This necessitates additional meticulous safety precautions (ear plugs, face shield and Kevlar gloves etc).

1.1. 3,4-diamino-1,2,4-1H-triazole (DATr)



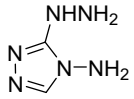
DATr

Diaminoguanidine hydrochloride (5 g, 40 mmol) and formic acid (8 mL, 85%) was added to a 100 mL two necked bottle, the mixture was stirred and refluxed at 110 °C for 1 h, then concentrated hydrochloric acid (12 mL) was added and continue reflux for 1 h. Depressurize the reaction solution to half, Freeze in the refrigerator overnight to precipitate white solids, The precipitated solid was filtered, washed with ethanol and diethyl ether, and dried in air to give DATr·HCl (5.13 g, 95.0%)。Dissolve DATr·HCl (0.27 g, 2 mmol) in 5mL of water, sodium bicarbonate (0.168 g, 2 mmol) was added to adjust the solution to pH=7, and then spin dry the solvent. Extract the DATr with methanol, and concentrated to get a white powder DATr (0.16 g, 82%)[4]. ^{1}H NMR (400 MHz, DMSO): δ = 8.42 (1H, s), 8.25 (2H, s), 6.16 (2H, s) ppm.



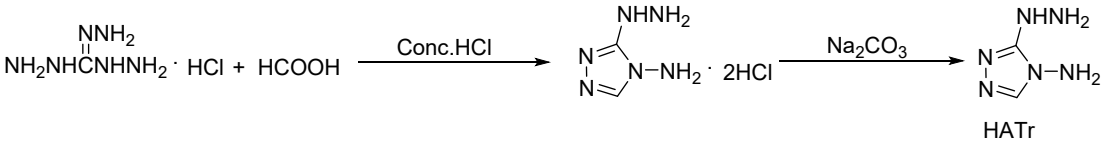
Scheme 1. Synthetic pathway towards DATr.

1.2. 3-hydraziono-4-amino-1,2,4-1H-triazole(HATr)



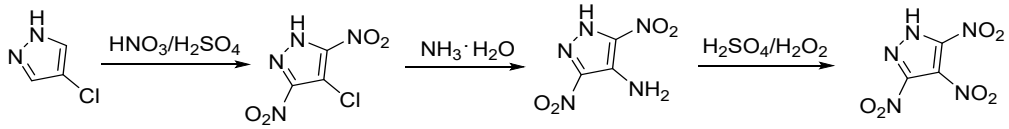
HATr

Triaminoguanidine hydrochloride (5.64 g, 40 mmol) and formic acid (8 mL, 85%) was added to a 100 mL two necked bottle, the mixture was stirred and refluxed at 110 ℃ for 1 h, then concentrated hydrochloric acid (12 mL) was added and continue reflux for 0.5 h. Depressurize the reaction solution to half, Freeze in the refrigerator overnight to precipitate white solids, The precipitated solid was filtered, washed with ethanol and methanol, and dried in air to give HATr·2HCl (6.99 g, 94.0%)。Dissolve HATr·2HCl (0.27 g, 2 mmol) in 5mL of water, sodium bicarbonate (0.168 g, 2 mmol) was added to adjust the solution to pH=7, and then spin dry the solvent. Extract the HATr with methanol, and concentrated to get a white powder HATr[5]. ^{1}H NMR (400 MHz, DMSO): δ = 9.61 (1H, s), 8.78 (1H, s), 5.88 (2H, s), 5.75 (2H, s) ppm.



Scheme 2. Synthetic pathway towards HATr.

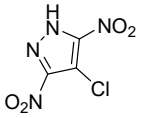
1.3. 3,4,5-trinitro-1H-pyrazole (HTNP)



HTNP

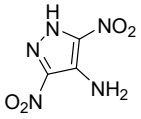
Scheme 3. Synthetic pathway towards HTNP.

1.3.1 4-chloro-3,5-dinitro-1H-pyrazole



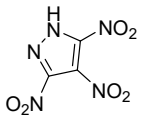
4-chloro-1H-pyrazole (15.6 g，0.12 mol) was dissolved in concentrated sulfuric acid (190 mL), then concentrated nitric acid (20 mL) was added dropwise at 15-25 ℃, the temperature was slowly raised to 100 ℃ After stirring for 5 h, the mixture was added to ice water (1L), extracted with EtOAc, the combined organic layers were dried over Na_2SO_4 and concentrated to get light yellow solid; yield: 75%.

1.3.2 3,5-dinitro-1H-pyrazol-4-amine



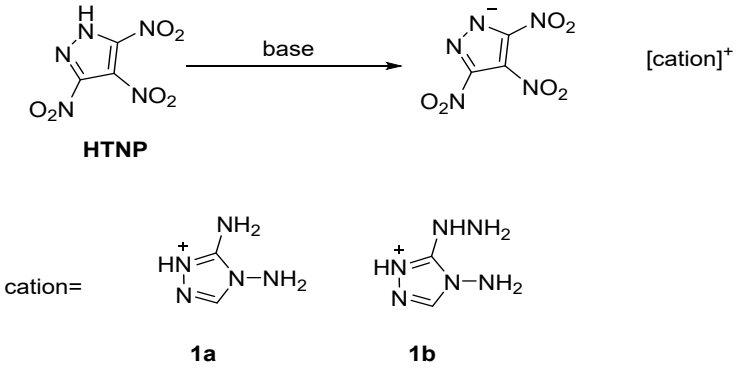
4-chloro-3,5-dinitro-1H-pyrazole (5.3g，27.6 mmol) was dissolved in aqueous 25% NH_3 (50 mL)，the mixture was kept in a stainless steel bomb at an external temperature of 170 °C for 10 h，After cooling, the solution was acidify with 20% H_2SO_4 to pH=1. The resulting mixture is extracted with EtOAc, and the combined organic layers were dried over Na_2SO_4. The solvent was removed in vacuo and the yellow solid was crystallized and filtered; yield: 80%.

1.3.3 3,4,5-trinitro1H-pyrazole (HTNP)



3,5-dinitro-1H-pyrazol-4-amine (1.04 g，6 mmol) was dissolved in concentrated sulfuric acid (13.6 mL), then slowly add 30% H_2O_2 (7 ml) in an ice water bath and react at room temperature .After 24 h，the reaction mixture was poured into cold water and extract with EtOAc. The combined organic layers were dried over Na_2SO_4 and concentrated to get light yellow solid HTNP[6]; yield: 75%.

1.4. Synthesis of Energetic Salts of 3,4,5-trinitro-1H-pyrazole



Scheme 5. Synthetic pathway towards energetic salts.

1.4.1 Synthesis of 1a

DATr (100 mg, 1mmol) was dissolved in water (5 mL), then TNP aqueous solution (10 mL) was added dropwise, the mixture was stirred at room temperature for 2 h and concentrated to get the product; yield: 85%. ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.44 (1H, s), 8.18 (1H, s), 6.07 (2H, s), ppm; ^{13}C NMR (125 MHz, DMSO-d6): δ = 151.15, 147.29, 142.20, 122.49 ppm; IR (KBr): v = 3355, 3288, 3138, 1697, 1523, 1516, 1458, 1317, 1230, 962, 846, 623 cm^{-1}; MS(ESI+): m/z=199.12 [$C_2H_6N_5^+$]; MS(ESI-): m/z= 201.98 [$C_3N_5O_6^-$].

1.4.2 synthesis of 1b

HATr (100 mg, 1mmol) was dissolved in water (5 mL)，then TNP aqueous solution (10 mL) was added dropwise, the mixture was stirred at room temperature for 2 h and concentrated to get the product；yield:80%. ^{1}H NMR (400 MHz, DMSO-d6): δ = 8.54 (1H, s), 4.40 (2H, s) ppm; ^{13}C NMR (125 MHz, DMSO-d6): δ = 153.09, 147.13, 143.00, 122.47 ppm; IR (KBr): v = 3423, 3365, 1704, 1535, 1508, 1454, 1363, 1216, 956, 850 cm^{-1}; MS(ESI+): m/z=229.14 [$C_2H_7N_6^+$]; MS(ESI-): m/z= 201.98 [$C_3N_5O_6^-$].

2. X-ray Crystallographic Data

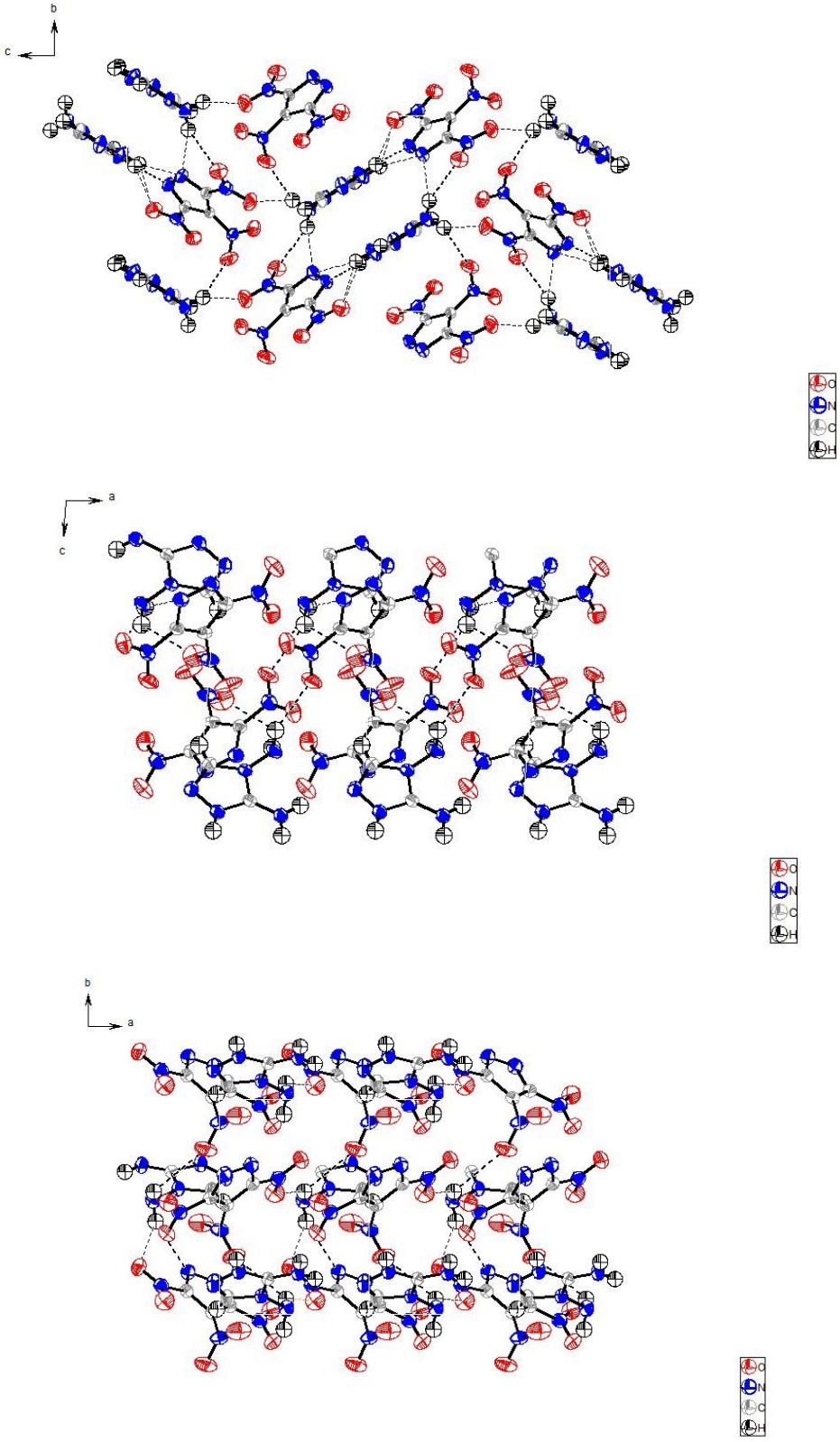


Figure S1. Crystallographic packing diagram graph of **1a**, direction from a, b, c axis, respectively.

Table S1. Crystallographic data of **1a**

Crystal	**1a**
Chemical formula	$C_5H_6N_{10}O_6$
Formula mass	302.20
Crystal system	monoclinic
a/Å	6.1145(5)
b/Å	8.7498(8)
c/Å	21.6564(19)
α/o	90
β/o	94.974(6)
γ/o	90
Volume/Å3	1154.27(17)
Temperature/K	296.15
Space group	$P2_1/c$
Z	4
Radiation type	MoKα (λ = 0.71073)
μ/mm-1	0.157
$Density_{calcd}$ /g cm^{-3}	1.739
F(000)	616
2θ range for data collection/°	3.776 to 55.076
Index ranges	$-7 \leq h \leq 7$, $-11 \leq k \leq 11$, $-27 \leq l \leq 28$
Reflections collected	14294
Independent reflections	2635 [R_{int} = 0.0355, R_{sigma} = 0.0280]
Data/restraints/parameters	2635/0/190
R1 / wR2 [all data]	0.0562/ 0.1021
R1 / wR2 [I > 2σ(I)]	0.0382/ 0.0921
Goodness-of-fit on F2	1.025
CCDC number	2240955

Table S2. Selected bond lengths [Å] and angles [°] for compound **1a**

Parameter	Bond length (Å)	Parameter	Bond length (Å)
O5-N3	1.2228(18)	N5-C3	1.432(2)
O2-N5	1.2195(18)	C4-C5	1.378(2)
O3-N4	1.2033(19)	C4-C3	1.378(2)
O6-N3	1.2223(19)	N10-N7	1.4033(17)
O1-N5	1.2277(18)	N10-C1	1.3501(19)
O4-N4	1.2115(19)	N10-C2	1.365(2)
N2-N1	1.3443(19)	N8-N9	1.3819(19)
N2-C5	1.3385(19)	N8-C1	1.3221(19)
N1-C3	1.336(2)	N6-C1	1.311(2)
N4-C4	1.4494(19)	N9-C2	1.287(2)
N3-C5	1.436(2)		
Parameter	Bond angle (°)	Parameter	Bond angle (°)
C5-N2-N1	106.85(13)	N2-C5-C4	111.81(13)
C3-N1-N2	107.95(12)	C4-C5-N3	127.38(14)
O3-N4-O4	124.92(15)	N1-C3-N5	120.35(13)
O3-N4-C4	118.09(14)	N1-C3-C4	111.21(14)
O4-N4-C4	116.99(15)	C4-C3-N5	128.37(15)
O5-N3-C5	116.36(14)	C1-N10-N7	121.46(13)
O6-N3-O5	125.22(15)	C1-N10-C2	107.25(12)
O6-N3-C5	118.41(14)	C2-N10-N7	131.28(13)
O2-N5-O1	124.40(15)	C1-N8-N9	111.40(13)
O2-N5-C3	117.56(13)	C2-N9-N8	104.48(14)
O1-N5-C3	118.03(14)	N8-C1-N10	105.59(13)
C5-C4-N4	128.91(14)	N6-C1-N10	124.95(13)
C5-C4-C3	102.17(13)	N6-C1-N8	129.42(14)
C3-C4-N4	128.90(14)	N9-C2-N10	111.27(15)
N2-C5-N3	120.72(14)		

Table S3. Hydrogen bonds present in compound **1a**

D-H···A	d(D-H)/ Å	d(H···A)/ Å	d(D···A)/ Å	<(D-H-A)/ °
N(8) -H(8)···O(1)	0.86	2.54	3.125(2)	126.4
N(8)-H(8)···N(1)	0.86	1.98	2.810(18)	160.6
N(6)-H(6A) ···O(1)	0.86	2.51	3.112(19)	128.7
N(6)-H(6A) ···N(2^1)	0.86	2.43	3.166(19)	144.8
N(6)-H(6B) ···N(9^1)	0.86	2.14	2.976(19)	163.0
N(7)-H(7A) ···O(6^2)	0.86	2.43	3.156(19)	142.1
N(7)-H(7A) ···N(2^2)	0.86	2.48	3.252(2)	149.6
N(7)-H(7B) ···O(5^3)	0.87	2.32	3.017(17)	137.5
N(7)-H(7B)···O(4^4)	0.87	2.89	3.475(2)	126.3
C(2)-H(2) ···O(3^5)	0.93	2.68	2.360(2)	130.5

3. Characterization analysis

3.1. ^{1}H NMR spectra

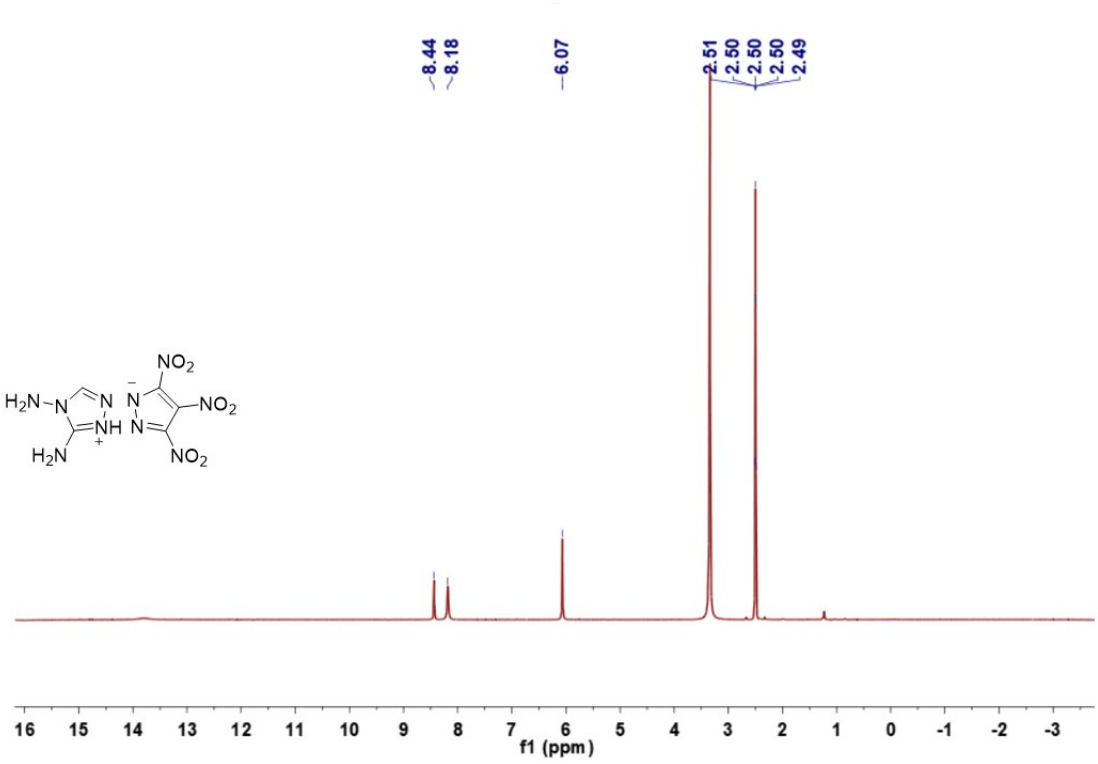


Figure S2. ^{1}HNMR spectra (400 MHz) of **1a** in [D_6] DMSO

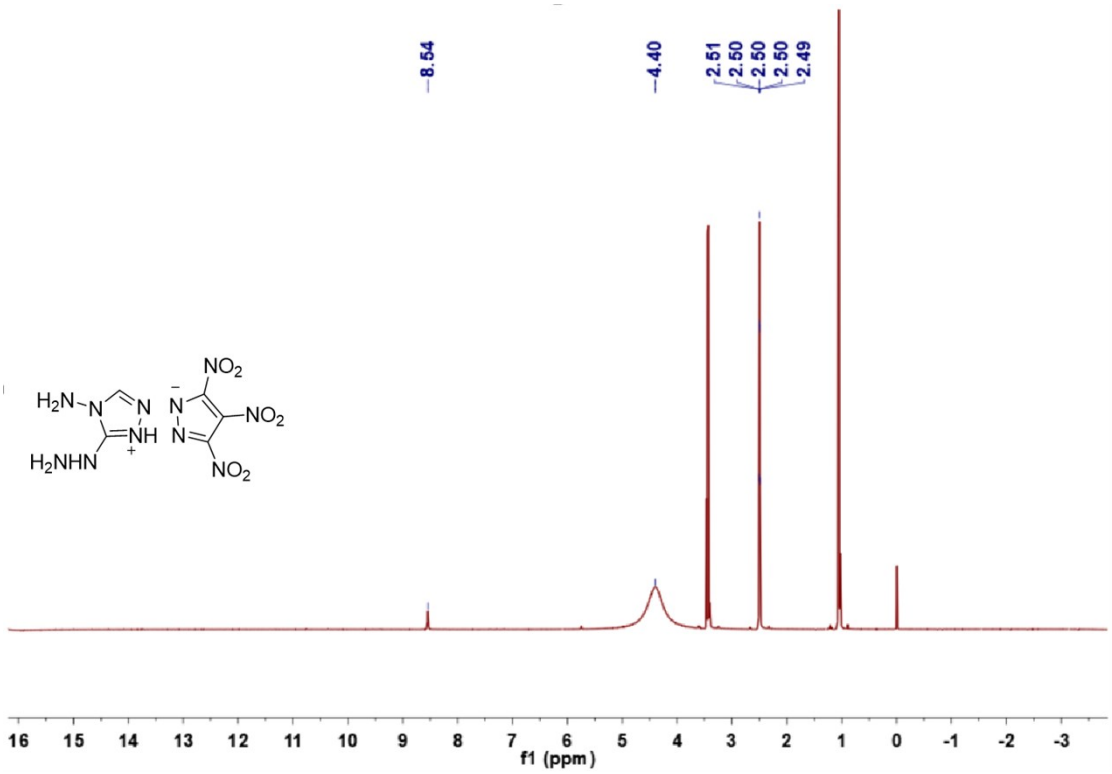


Figure S3. ^{1}H NMR spectra (400 MHz) of **1b** in [D_6] DMSO

3.2. ^{13}C NMR spectra

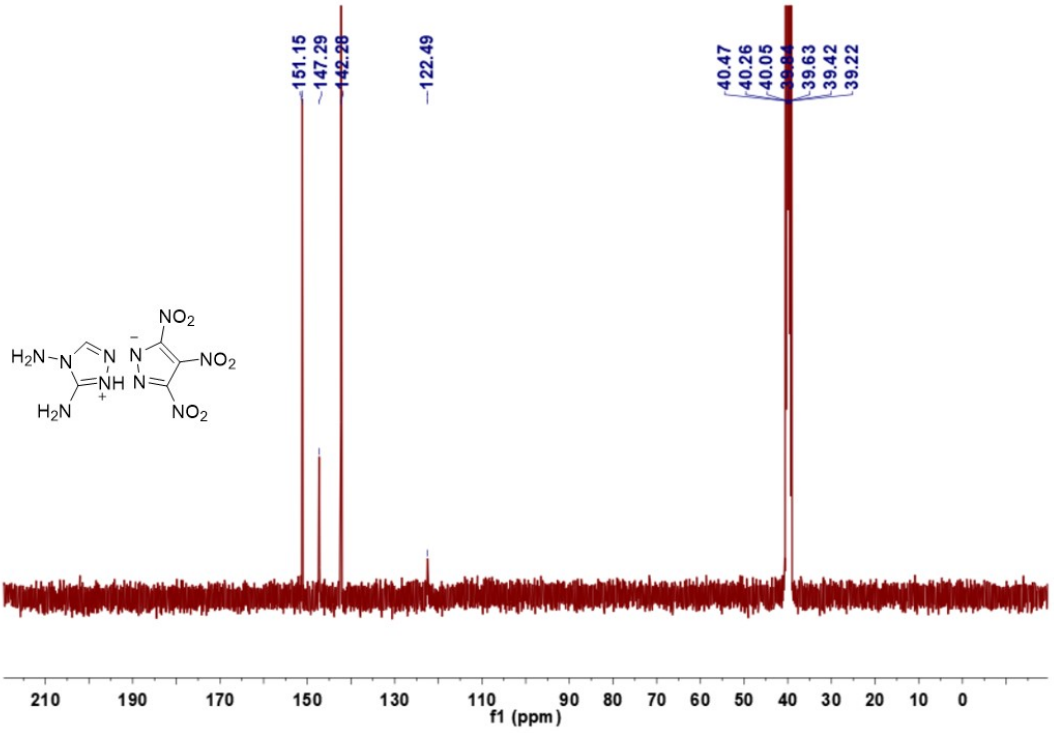


Figure S4. ^{13}C NMR spectra (125 MHz) of **1a** in [D_6] DMSO

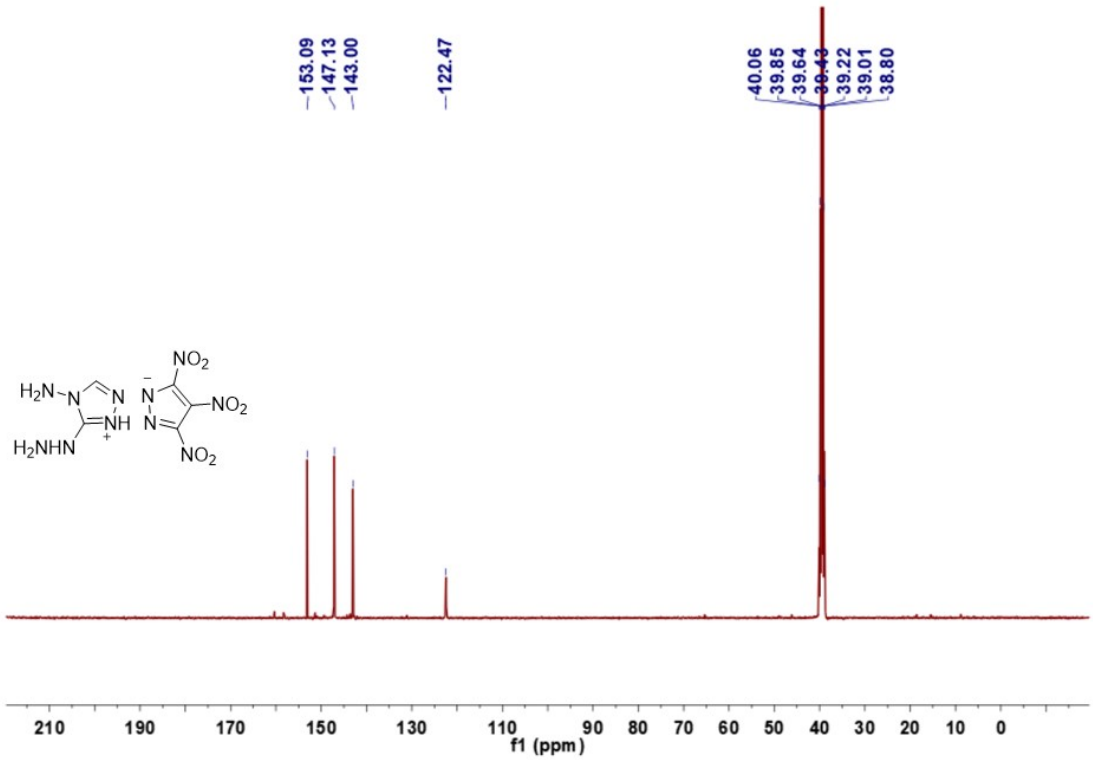


Figure S5. ^{13}C NMR spectra (125 MHz) of **1b** in [D_6] DMSO

3.3. Mass spectra

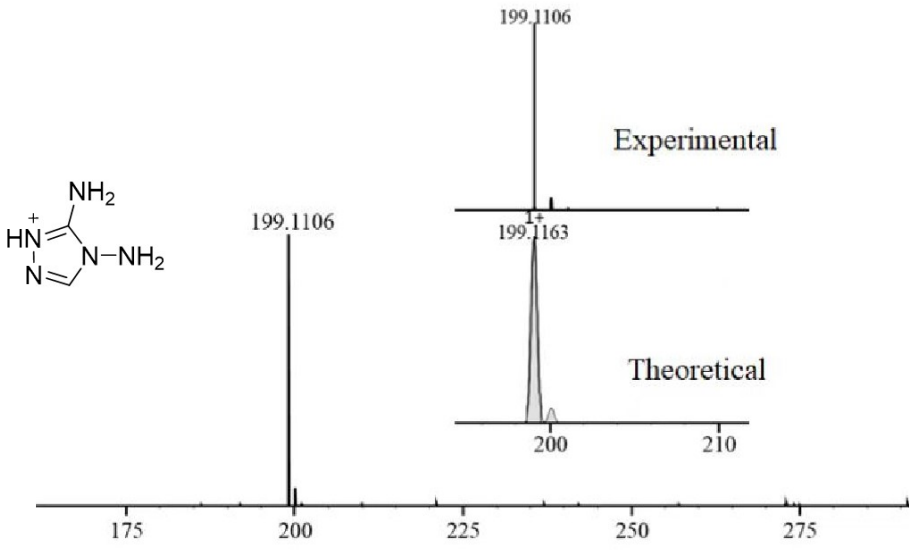


Figure S6. ESI-MS(DEI$^+$) spectrum of complex **1a**

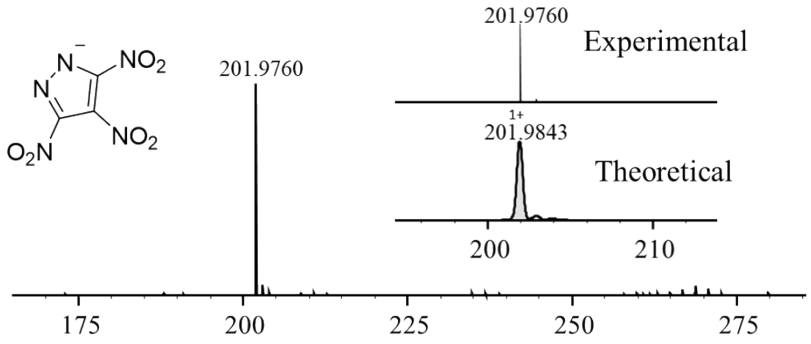


Figure S7. ESI-MS(DEI$^-$) spectrum of complex **1a**

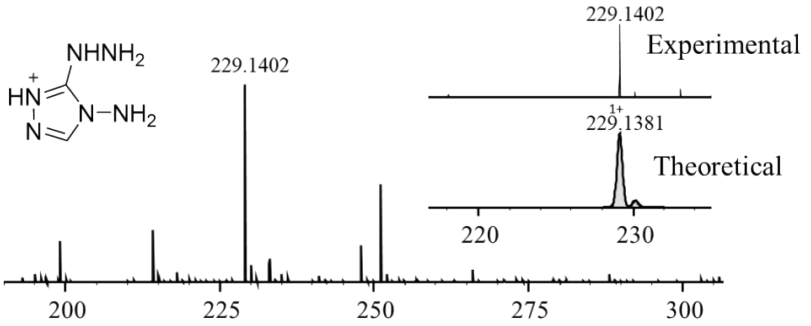


Figure S8. ESI-MS(DEI$^+$) spectrum of complex **1b**

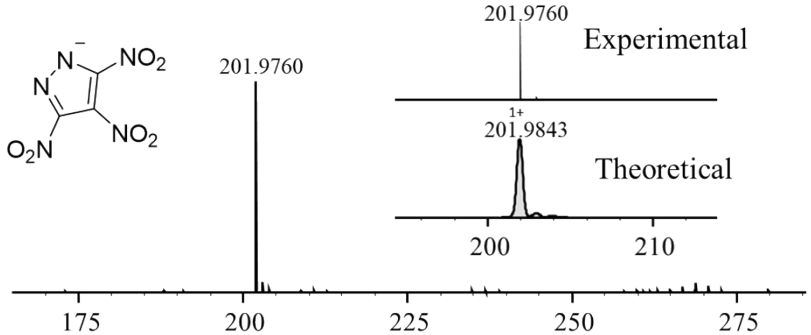


Figure S9. ESI-MS(DEI$^-$) spectrum of complex **1b**

3.4. IR spectra

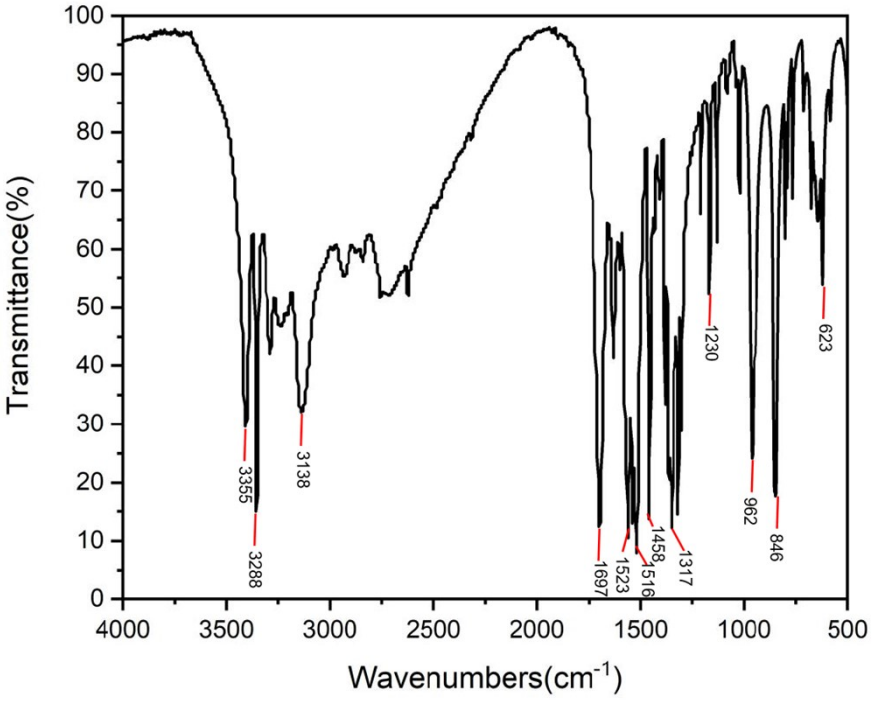


Figure S10. IR spectrum of complex **1a**

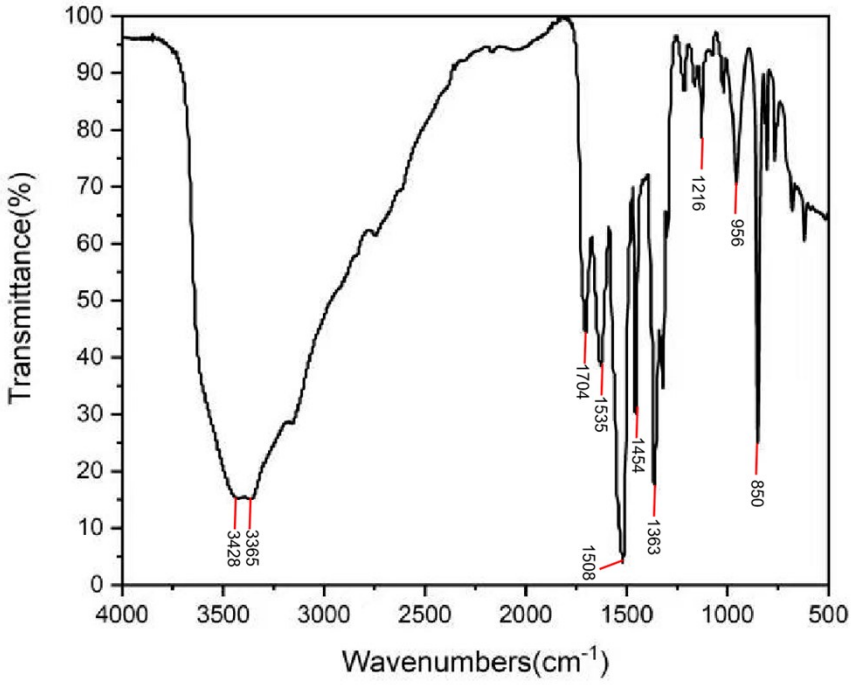


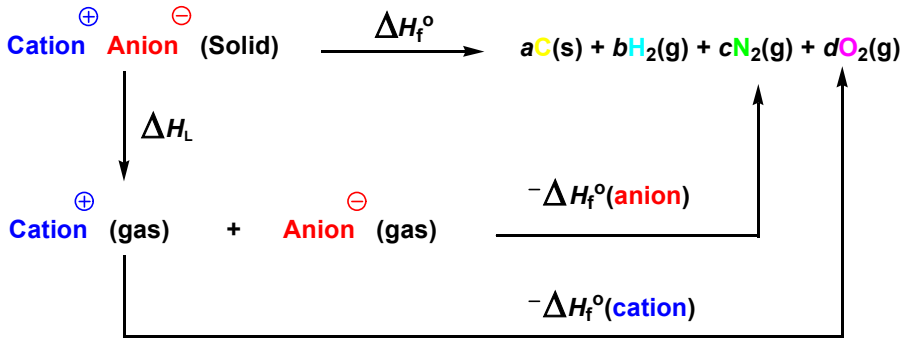
Figure S11. IR spectrum of complex **1b**

4. Computational Datils

The geometric optimization and frequency analyses were carried out by using B3LYP functional analyses with the 6-31+G** basis set. All of the optimized structures were determined to be the local energy minima on the potential energy surface without imaginary frequencies. Single-point energies were calculated at the MP2/6-311++G** level. All computations in this work were performed by using the Gaussian 09 suites of program[7]. The gas-phase heats of formation were calculated using the isodesmic reaction method[8]. In order to explore the effect on mechanical sensitivity, the Hirshfeld surface analysis was commutated based upon the optimized geometry.

5. Heat of Formation Calculation

The heats of formation of energetic materials mostly are calculated theoretically, thus avoid the experimental complication. The heats of formation of all cations and anions were computed by the isodesmic reaction method[8]. The lattice energy (U_L) and lattice enthalpy (ΔH_L) were calculated by the equation provided by Jenkins and Glasser[9]. According to the Born-Haber energy cycles[10], the heats of formation of energetic salts can be obtained by Eq.1. And the heats of formation (ΔH_m) for solid state were used to calculate the energies of formation (ΔU_m) according to Eq. 2.



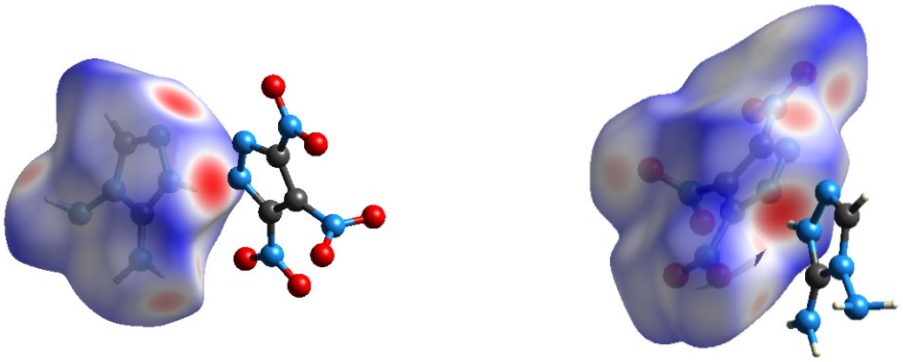
Scheme 6. Born-Haber Cycle for the formation of DNABT-based energetic salts

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

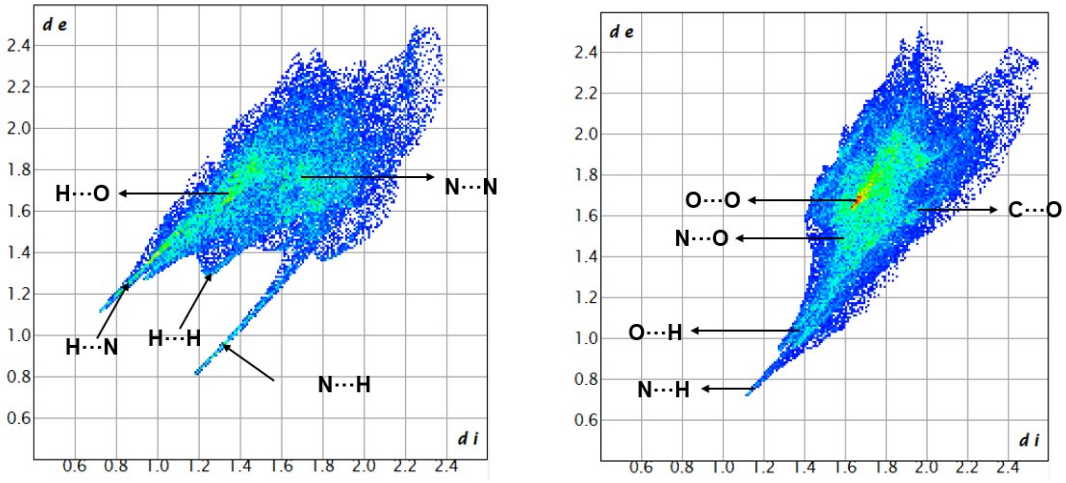
$$\Delta U_m = \Delta H_m - \Delta n\,RT \quad (2)$$

6. Hirshfeld Analysis

(a)



(b)



(c)

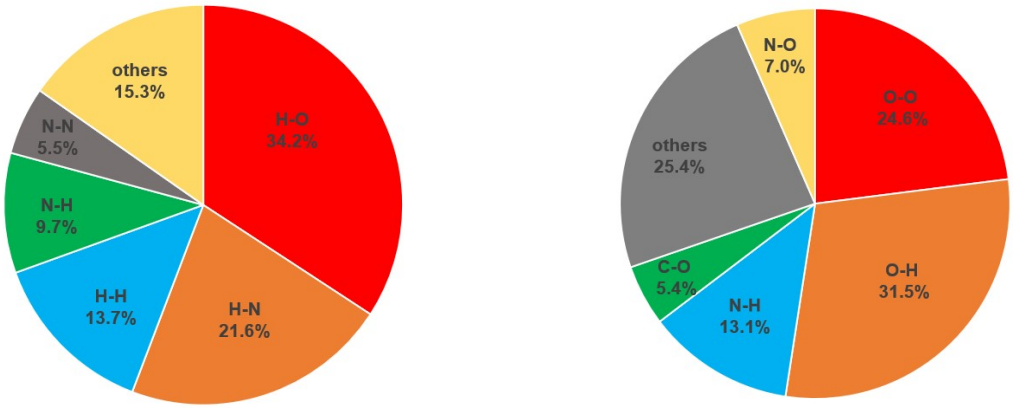


Figure S12. (a) Hirshfeld surface of **1a** mapped on d_{norm}, red and blue parts indicate strong and weak close contacts, respectively; (b) the two-dimensional fingerprint plot of **1a**, (c) indicidual atomic contacts percentage contribution to Hirshfeld surface for **1a**.

7. Optimization

TNP^-

E= -834.865233 (a.u.)

-1 0

O	2.75504600	0.85388900	0.00110300
O	-2.75500800	0.85395700	-0.00036900
O	0.00104400	2.19914000	-1.09193700
O	3.31760300	-1.26104800	-0.00114000
O	-3.31766300	-1.26096000	-0.00041900
O	-0.00091400	2.19913800	1.09175500
N	0.00003500	1.63613800	-0.00005800
N	2.47784800	-0.35742600	0.00003200
N	-2.47787300	-0.35736500	-0.00021400
C	-0.00001500	0.18047500	-0.00006400
C	1.08673500	-0.69788600	0.00015700
C	-1.08678300	-0.69787900	0.00021800
N	-0.66207200	-1.98790400	0.00056900
N	0.66199300	-1.98789900	0.00055600

8. References

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