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Supporting Information

A high density pyrazolo-triazine explosive (PTX)

Maxwell C. Schulze[†], Brian L. Scott[‡], David E. Chavez*[,†]

[†]M-7 High Explosives Sciences and Technology, Los Alamos National Laboratory, Los Alamos, NM 87544 USA

[‡]MPA-11 Materials Synthesis and Integrated Devices, Los Alamos National Laboratory, Los Alamos, NM 87544 USA

Email: dechavez@lanl.gov

Experimental

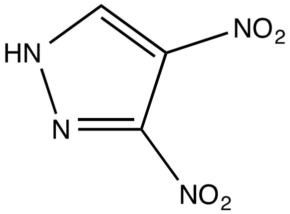
Caution: *Although we have not experienced any problems in handling the materials described in this paper, some of the described compounds are sensitive to impact and friction. Therefore, they should be handled with extreme care implementing standard safety procedures for handling energetic materials.*

General

All NMR spectra were obtained on a Bruker Ascend 400 MHz NMR spectrometer. FT-IR spectra were obtained using a Thermo Nicolet iS5 spectrometer. Elemental analyses were performed at Los Alamos National Laboratory on a Leco CHN 900 Elemental Analyzer. X-ray crystal data were collected on a Bruker D8, with APEX II CCD detector.

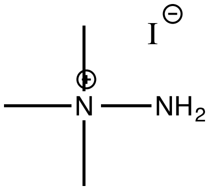
Small-scale explosive sensitivity safety tests for PTX were performed using standard procedures. Impact sensitivity was measured by using a drop hammer LANL type 12 tests using a 2.5 kg weight and the Bruceton Up/Down Method to determine the 50% drop height. Friction sensitivity was measured by a mini BAM machine (Reichel & Partner, Rhenzabern, Germany) using the Bruceton Up/Down Method to determine the 50% load. Spark sensitivity from 0 to 6 J was measured by an ABL electrostatic discharge apparatus (Safety Management Services, West Jordan, UT) connected to a diagnostic analyzer to detect NOX, CO (0–5,000 ppm), and CO_2 (0–1000 ppm) released from the sample. Thermal decomposition temperatures were measured by DSC (TA Instruments Q2000 DSC) in hermetically sealed aluminum pans that contain a pinhole lid. A typical analysis utilizes approximately 1 mg of sample with 50 mL/min ultrahigh purity nitrogen purge gas at a thermal ramp rate of 10 ºC/min.

Synthesis:



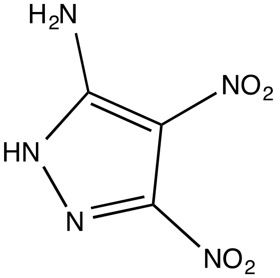
3,4-dinitropyrazole (DNP)

The compound was prepared according to a procedure reported by Ek and coworkers.[1,2] Briefly 3-nitropyrazole (5.72 g) was dissolved in sulfuric acid (100 %, 30 mL) at 40˚C. Nitric acid (100 %, 9.6 g) was added dropwise, keeping temperature below 55˚C. Solution was stirred at 40˚C for 24 hours, poured onto ice, and extracted with ethyl acetate (3 times with 150mL) washed with water (3 times with 150mL). Organic extracts were dried with $MgSO_4$ and solvent evaporated to give 3,4-dinitropyrazole (7.67g, 96% yield) as a pale yellow solid. ^1H NMR (400.13 MHz, RT, DMSO-d6) δ 14.94 (br), 9.13 ppm $^{13}C\{^1H\}$ NMR (100.61 MHz, RT, DMSO-d6) δ 148.1, 132.7, 126.3 ppm



1,1,1-Trimethylhydrazinium iodide (TMHI) general procedure

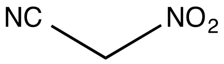
The reagent was prepared according to literature procedure and patent by Pagoria and coworkers.[3,4] Unsymmetrical dimethyl hydrazine (2.55 mL) was dissolved in 60 mL THF and cooled in and ice-water bath. Methyl iodide (2.09 mL) was added to form a thick white slurry that was stirred for 2 hours at room temperature. The white precipitate was vacuum filtered and recrystallized from ethanol to give TMHI (5.8 g, 86% yield) as a white crystalline solid. m.p. 230˚C ^1H NMR (400.13 MHz, RT, DMSO-d6) δ 3.30, 6.08 ppm $^{13}C\{^1H\}$ NMR 100.61 MHz, RT, (DMSO-d6) δ 57.3 ppm IR (KBr): n = 3287 (m), 3237 (m), 3146 (m), 3013 (m), 2935 (w), 1608 (m), 1474 (s), 1437 (w), 1395 (m), 1282 (w), 1141 (w), 1053 (s), 936 (s), 895 (s), 741 (w), 484 (w) cm^{-1}.



5-amino-3,4-dintitropyrazole (ADNP)

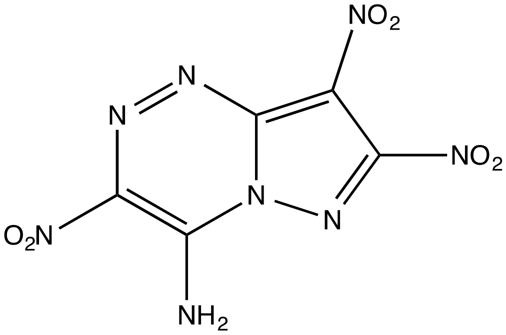
3,4-dinitropyrazole (1.58 g, 10 mmol) and TMHI (3.94 g, 19.5 mmol) were dissolved in 50 mL DMSO to form a yellow solution. Potassium t-butoxide (6.56 g, 58.5 mmol) was added in one portion to form a dark pink mixture. Reaction was stirred at room temperature for 8 hours before being quenched into 150 grams ice water with dissolved concentrated HCl (5.76 g) and $Na_2S_2O_3$ (3.08 g, 19.5 mmol) to form a yellow solution.

The solution was extracted with ethyl acetate (600 mL) and washed with water (150 mL, 3 times) before evaporating the solvent to give crude ADNP (1.168 g) as yellow/orange solid. Analysis of the crude product by NMR indicated a mixture of ADNP (78 mol%) and DNP (22 mol%) for a yield of 53.7% of ADNP. Crude product was purified by column chromatography for analysis only. m.p. ~200˚C (decomp.) ^{1}H NMR (400.13 MHz, RT, DMSO-d6) δ 13.21, 7.78 ppm ^{13}C{^{1}H} NMR (100.61 MHz, RT, DMSO-d6) δ 149.2.1, 148.2, 108.9 ppm IR (KBr): n = 3447 (m), 3386 (m), 3313 (m), 2957 (w), 2925 (w), 2851 (w), 1656 (m), 1649 (m), 1550 (w), 1524 (m), 1479 (w), 1329 (m), 1104 (s), 827 (w), 761 (w), 464 (m) cm^{-1}.



Nitroacetonitrile (NAN) general procedure

The reagent was prepared according to literature procedure by Matthews and Kubler.[5] Keeping the temperature below 55˚C, nitromethane (10 g) was added dropwise to a solution of NaOH (10 g in 20 mL water) at 45 ˚C. Waxy droplets that slowly react exothermically should be kept from building up to prevent a runaway exotherm during this step. Reaction was stirred at 45 ˚C until an amber solution was formed, which was then cooled in an ice bath and acidified with conc. HCl (20 mL) to precipitate a tan solid that was isolated by vacuum filtration. The solid was extracted with diethyl ether (200 mL) which was dried over CaCl$_2$ and the solvent evaporated to yield yellow crystals of methazonic acid as an intermediate, a substance that will decompose to a red resin within days even when stored in a freezer. The methazonic acid (nitroacetaldehyde oxime) was dissolved in freshly distilled diethyl ether (80 mL), heated to reflux, and SOCl$_2$ (2 eq. w/ respect to recovered methazonic acid) was added dropwise to ensure complete dehydration, and the solution refluxed for 4 hours. The reaction was cooled and filtered before evaporating off the solvent to give NAN (2.015 g) as amber oil. ^{1}H NMR (400.13 MHz, RT, CD_3CN) δ 5.56 ppm $^{13}C\{^{1}H\}$ NMR 119.11, 64.7 ppm MHz, RT, CD_3CN) δ 117.4, 63.2 ppm IR (KBr): n = 3422 (w), 3011 (w), 2961 (w), 2935 (w), 1578 (s), 1406 (w), 1363 (m), 1304 (w), 1218 (w), 1149 (w), 1045 (w), 978 (w), 904 (w), 714 (w) cm^{-1}.



4-amino-3,7,8-trinitropyrazolo-[5,1-c][1,2,4]triazine (PTX)

The molecule was prepared as reported by Dalinger and coworkers[6], though we found it unnecessary to purify the starting material to produce a pure sample of product. A crude mixture of ADNP (223 mg, 1.29 mmol) and 3,4-dinitropyrazole (57 mg, 0.36 mmol) was dispersed in 10 mL of 20% H_2SO_4 and cooled in an ice-water bath. $NaNO_2$ (123 mg, 1.78 mmol) dissolved in 1.2 mL water was added dropwise to the cooled dispersion and the mixture was stirred for 2 hours to form the corresponding diazonnium salt (**3**) in situ. The sodium salt of NAN was prepared by dissolving NaOH (99 mg, 2.48 mmol) and NAN (214 mg, 2.48 mmol) in 3 mL ice water and the solution was added dropwise to the cooled reaction flask. The reaction was stirred in the ice bath for 50 minutes until most of the reaction mixture was in solution. The reaction was then filtered and the filtrate stirred at room temperature. A precipitate formed from the filtrate over a few hours and was filtered, washed with water, and air-dried to give pure PTX (193 mg, 55.6% yield from

ADNP) as a yellow solid. m.p. (decomp) 260-270 ˚C ^{1}H NMR (400.13 MHz, RT, DMSO-d6) δ 10.59 (br) ppm ^{13}C{^{1}H} NMR (100.61 MHz, RT, DMSO-d6) δ 152.1, 143.4, 140.5, 138.6, 113.3 ppm IR (KBr): n = 3382 (m), 3301 (w), 3264 (m), 3217 (w), 3145 (w), 1655 (s), 1566 (s), 1523 (s), 1502 (m), 1467 (w), 1408 (w), 1375 (w), 1342 (m), 1292 (w), 1224 (m), 1198 (m), 1077 (w), 846 (m), 821 (w), 790 (w), 776 (w), 606 (w) cm^{-1}. Anal. Calc'd. for $C_5H_2N_8O_6$: C, 22.23; H, 0.75; N, 41.48. Found: C, 22.30; H, 0.58; N, 40.39.

Figure S1: DSC plot of PTX

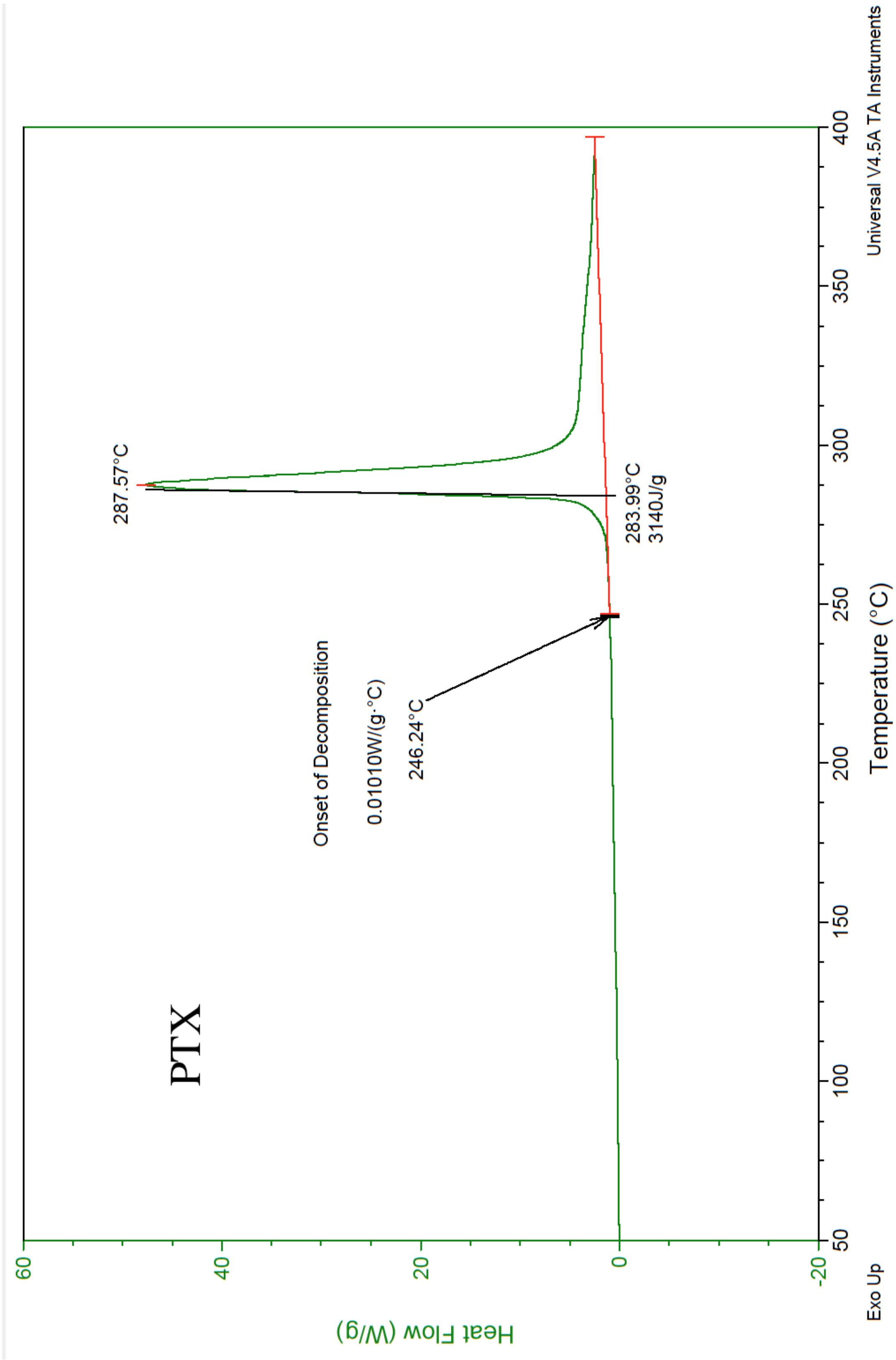


Table S1: Crystallographic data for PTX

	PTX
Empirical Formula	C5H2N8O6
Formula Weight (g mol^{-1})	270.12
Temperature (K)	300
Space Group	$P\ 2_1\ 2_1\ 2_1$
Unit Cell Lengths (Å)	**a** 5.2626(15) **b** 8.591(2) **c** 20.393(6)
Unit Cell Angles	**a** 90 **b** 90 **c** 90
Volume (Å^3)	921.988(3)
Z	4
T (K)	100
Density (100 K g cm^{-3})	2.006
Density (300 K, g cm^{-3})	1.946
Refl. Collected/2θ$_{max}$	6568/51.36
Unique Refl./ I > 2σ (I)	1682/1311
No. parameters/restrains	178/0
λ, A°/μ (Kα) (cm^{-1})	0.71073
R1/GOF	0.0465/1.014
wR2 (I > 2σ(I))	0.0953
Residual density, eÅ^{-3}	0.310/-0.221

References:

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(4)Pagoria, P. F.; Mitchell, A. R.; Schmidt, R. D. *United States Patent,* **2000,** 6069277.

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(6)Dalinger, I. L.; Vatsadse, I. A.; Shkineva, T. K.; Popova, G. P.; Ugrak, B. I.; Shevelev, S. A. *Russ. Chem. Bull. Int. Ed.* **2010,** 59, 1631-1638.