Energetic Materials

Synthesis and Investigation of 2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX) and Its Salts

Thomas M. Klapötke,* Jörg Stierstorfer, Michael Weyrauther, and Tomasz G. Witkowski[a]

Abstract: 2,6-Bis(picrylamino)pyridine (**1**; pre-PYX) and 2,6-bis(picrylamino)-3,5-dinitropyridine (**2**; PYX) were synthesized using an improved literature method. Compounds **1** and **2** were reinvestigated in detail and the X-ray structures (**1**: $\rho = 1.698\ \mathrm{g\,cm^{-3}}$ at 173 K; **2**: $\rho = 1.757\ \mathrm{g\,cm^{-3}}$ at 298 K) are given. The reactions of **2** with different bases, such as alkali metal hydroxides (sodium, potassium, rubidium, cesium), and *N*-bases (ammonia, hydrazine, hydroxylamine, guanidinium carbonate, aminoguanidine bicarbonate) are reported, as well as metathesis reactions producing energetic salts. Several energetic compounds were synthesized and characterized for the first time using vibrational (IR, Raman) and multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, and DSC. The crystal structures of four energetic salts were determined using low temperature single-crystal X-ray diffraction. Heats of formation for the metal-free species were calculated using the Gaussian 09 software. Detonation parameters were estimated using the EXPLO5 program. The sensitivities towards impact, friction, and electrostatic discharge were also determined.

Introduction

Thermally stable (heat-resistant) explosives are particularly interesting, because they are stable at the high temperatures encountered in drilling deep oil wells (e.g., thermally stable perforators) or in space exploration (e.g., in achieving stage separation in space rockets).[1] In this area, the following explosives have received special attention: 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 2,2′,4,4′,6,6′-hexanitrostilbene (HNS), and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX), shown in Figure 1.

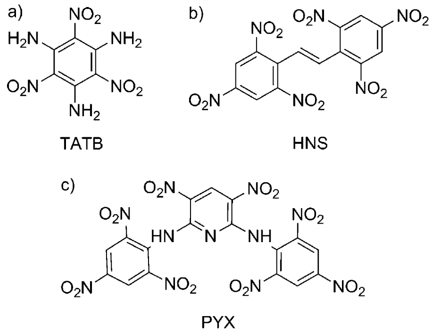

Figure 1. Most known heat resistant explosives: a) 1,3,5-triamino-2,4,6-trinitrobenzene (TATB); b) 2,2′,4,4′,6,6′-hexanitrostilbene (HNS); c) 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX).

In 1888, Jackson and Wing prepared TATB by the reaction of 1,3,5-tribromo-2,4,6-trinitrobenzene with ammonia, yielding TATB as a pale yellow solid.[2] TATB shows a high theoretical maximum density ($\rho_{\mathrm{TMD}} = 1.93\ \mathrm{g\,cm^{-3}}$)[3] and has a high thermal stability (310 °C).[4] In addition, TATB has a high Chapman–Jouguet (C-J) detonation velocity and pressure ($D_{\mathrm{C\text{-}J}} = 7.66\ \mathrm{km\,s^{-1}}$, $P_{\mathrm{C\text{-}J}} = 28.7$ GPa at a density of $1.854\ \mathrm{g\,cm^{-3}}$; cylinder test).[5] TATB is insensitive towards impact (IS) (50 J), friction (FS) (353 N) and electrostatic discharge ignition (ESD) (2.56 J).[6] However, TATB is difficult to initiate, since its initiation sensitivity is relatively high.[7] For example, a detonation wave generated by a cyclotol (75/25) booster did not propagate into a diameter 0.64 cm TATB charge section (length: 1.27 cm, density: $1.881\ \mathrm{g\,cm^{-3}}$).[8] It could be concluded that initiation of small TATB charges by a weak initiator causes a low reaction extent at the Chapman–Jouguet plane and results in low-order detonation.

2,2′,4,4′,6,6′-Hexanitrostilbene (HNS) was prepared by Shipp through the reaction of 2,4,6-trinitrobenzyl chloride with an alcoholic potassium hydroxide solution.[9] HNS has only a moderately high theoretical maximum density ($\rho_{\mathrm{TMD}} = 1.745\ \mathrm{g\,cm^{-3}}$)[10] and melts with subsequent decomposition at 318 °C.[6b, 11] Two polymorphs of HNS are known: HNS-I (thin, very fragile plates) and HNS-II (rectangular shape, has a higher bulk density than HNS-I).[12] In comparison to TATB, HNS shows lower values for the detonation parameters ($D_{\mathrm{C\text{-}J}} = 7000\ \mathrm{m\,s^{-1}}$ at $\rho = 1.70\ \mathrm{g\,cm^{-3}}$; $D_{\mathrm{C\text{-}J}} = 6800\ \mathrm{m\,s^{-1}}$ at $\rho = 1.60\ \mathrm{g\,cm^{-3}}$, $P_{\mathrm{C\text{-}J}} = 20.0$ GPa at $\rho = 1.60\ \mathrm{g\,cm^{-3}}$).[12,13] Despite this, HNS has a uniquely small critical diameter (ca. 1.0 mm)[14] and is sensitive to several initiation sources (IS, FS, and ESD: 5 J, >240 N, 0.66 J, respectively).[6]

The search for explosives that are thermally more stable than HNS, but with lower sensitivities and better performances is an ongoing process in many research groups worldwide. The other interesting thermally stable explosives are: 3,3′-di-

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amino-4,4′-azofurazan (DAAzF),[15] 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105),[16] tetraazapentalenes [1,3,7,9-tetranitro-6*H*-benzotriazolo[2,1-*a*]benzotriazol-5-ium inner salt (*Z*-TACOT),[17] 2,4,8,10-tetranitro-5*H*-benzotriazolo[1,2-*a*]benzotriazol-6-ium inner salt (*T*-TACOT),[17c] and 2,4,8,10-tetranitro-5*H*-pyrido[3′,2′:4,5][1,2,3]-triazolo[1,2-*a*]benzotriazol-6-ium inner salt (BPTAP)[18]], 2,2′,2′′,4,4′,4′′,6,6′,6′′-nonanitroterphenyl (NONA),[19] and 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX).[1a]

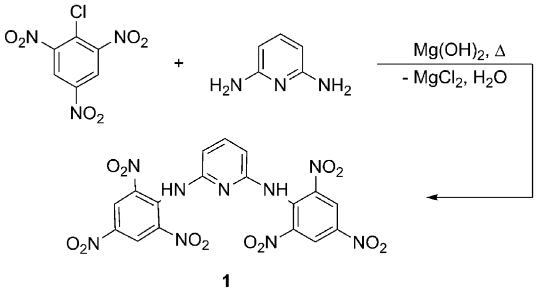
The first synthesis of PYX was reported by Coburn and Singleton in 1970[20] in which 2,6-diaminopyridine was reacted with picryl chloride and sodium fluoride (in situ generation of picryl fluoride) in a polar, aprotic solvent to yield 2,6-bis(picrylamino)pyridine (*Pre*-PYX). Many different reaction conditions were studied. Kuboszek and Pawłowski found that using magnesium hydroxide instead of sodium fluoride in nitrobenzene gives pre-PYX in high yields (87 %) and purity.[21] The subsequent nitration of pre-PYX using fuming nitric acid results in the formation of PYX.[20–22] PYX is characterized by an excellent thermal stability ($T_{decomp}=373\,^{\circ}C$), a theoretical maximum density that is slightly higher than that of HNS ($\rho=1.757\,g\,cm^{-3}$), and good detonation parameters ($D_{C\text{-}J}=7500\,m\,s^{-1}$, $P_{C\text{-}J}=25.19\,GPa$ at $\rho=1.75\,g\,cm^{-3}$, calculated).[22] Also PYX shows only moderate sensitivity towards IS, FS, and ESD (8 J, 360 N, and 1.00 J, respectively).

Out of the thermally stable explosives described above, PYX shows the highest thermal stability. Furthermore, only PYX possesses acidic protons that can be deprotonated to form ionic species. This is advantageous, since energetic materials can often achieve higher thermal stability by the formation of ionic compounds. Therefore, we decided to investigate these ionic derivatives as the part of our studies on thermally stable energetic materials.[20–22]

Results and Discussion

Synthesis

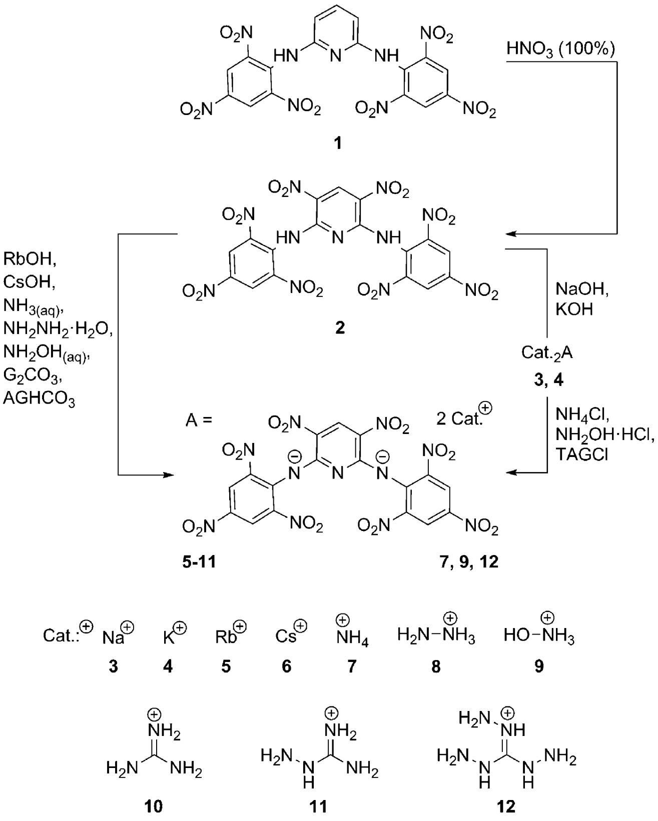
2,6-Bis(picrylamino)pyridine (pre-PYX, **1**) was synthesized in a similar manner as described by Kuboszek and Pawłowski, in which picrylation of 2,6-diaminopyridine in nitrobenzene at 190 °C was performed.[21a] After the reaction was complete, the crude product was boiled in methanol in order to remove impurities. This yielded an orange product which was identified as **1** (Scheme 1).



Scheme 1. Synthesis of 2,6-bis(picrylamino)pyridine (pre-PYX, **1**).

The highest yield of pure **1**, which did not involve recrystallization, was obtained using sodium carbonate (Na_2CO_3) and nitrobenzene at 140 °C for 3 h (yield 83 %). The highest yield for the synthesis of **1**, in which further purification by recrystallization was carried out, was achieved using NaF and dimethylformamide at 140 °C for 3 h (yield 88 %). The characterization data are consistent with that published by Kuboszek and Pawłowski.[21a] Nitration of **1** using fuming nitric acid yielded PYX (**2**) (Scheme 2).[20–22]

The reaction of **2** with different bases (alkali metal hydroxides, *N*-bases) or/and by metathesis reactions resulted in the formation of salts of PYX containing the following cations: sodium (**3**), potassium (**4**), rubidium (**5**), cesium (**6**), ammonium (**7**), hydrazinium (**8**), hydroxylammonium (**9**), guanidinium (**10**), aminoguanidinium (**11**), and triaminoguanidinium (**12**) (Scheme 2).



Scheme 2. Synthesis of 2,6-bis(picryl-amino)-3,5-dinitropyridine (PYX, **2**) and its salts.

Single-crystal X-ray analysis

The structures of **1**, **2**, the guanidinium monohydrate salt **10**$\cdot H_2O$, and the mono-deprotonated potassium monohydrate **4b**$\cdot H_2O$, rubidium **5b**, and cesium **6b** salts in the crystalline state were determined by using low-temperature single-crystal X-ray diffraction.[23] Compound **1** crystallizes in the monoclinic space group $P2_1$ with a density of $1.698\,g\,cm^{-3}$ at 173 K and four molecules in the unit cell. The molecular structure of **1** is shown in Figure 2. Nitration of **1** yielded **2** which crystallizes in the orthorhombic space group $P2_12_12_1$ with a density of

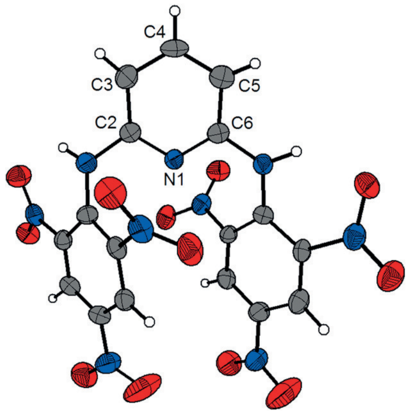


Figure 2. Molecular structure of **1** shown with 50 % probability thermal ellipsoids.

1.757 g cm^{-3} at 298 K and eight molecules in the unit cell. The introduction of two nitro groups in the pyridine moiety at the 3- and 5-positions in **2** has a positive impact on both the density and the thermal stability (Table 1) in comparison with **1**. The molecular structure of **2** is shown in Figure 3.

The potassium salt of mono-deprotonated **2** crystallizes with one water molecule per **4b** molecule in the monoclinic space group $P2_1$, with a density of 1.860 g cm^{-3} at 173 K and two molecules in the unit cell. The molecular structure of **4b**·H_2O is shown in Figure 4. The rubidium salt of **2** is anhydrous and crystallizes in the triclinic space group $P\bar{1}$ with a density of 1.959 g cm^{-3} at 173 K and two molecules in the unit cell. The molecular structure of **5b** is shown in Figure 5. The cesium salt of **2** crystallizes in the monoclinic space group $P2_1/c$ with a density of 2.077 g cm^{-3} at 173 K and four molecules in the unit cell. The molecular structure of **6b** is shown in Figure 6.

The guanidinium salt crystallizes with one water molecule per molecule in the triclinic space group $P\bar{1}$ with a density of 1.714 g cm^{-3} at 173 K and two molecules in the unit cell. The molecular structure of **10**·H_2O is shown in Figure 7.

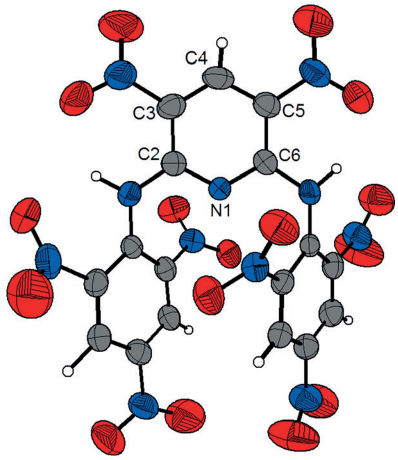


Figure 3. Molecular structure of **2** shown with 50 % probability thermal ellipsoids.

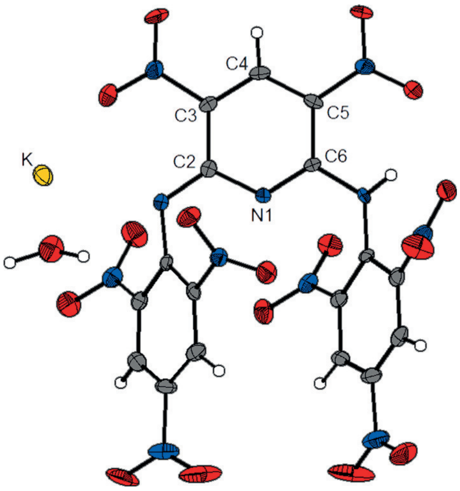


Figure 4. Molecular structure of **4b**·H_2O in which only a single deprotonation of PYX has occurred. The thermal ellipsoids are shown with 50 % probability.

Table 1. Physicochemical properties of PYX, and its salts in comparison to HNS.

	PYX (**2**)	**7**	**8**	**9**	**10**	**11**	**12**	HNS
formula	$C_{17}H_7N_{11}O_{16}$	$C_{17}H_{13}N_{13}O_{16}$	$C_{17}H_{15}N_{15}O_{16}$	$C_{17}H_{13}N_{13}O_{18}$	$C_{19}H_{17}N_{17}O_{16}$	$C_{19}H_{19}N_{19}O_{16}$	$C_{19}H_{23}N_{23}O_{16}$	$C_{14}H_6N_6O_{12}$
M_W [g mol^{-1}]	621.34	655.36	685.69	687.36	739.44	769.47	829.53	450.23
IS[a] [J]	10	40	10	5	40	40	20	5[1a, 6b]
FS[b] [N]	360	360	360	324	360	360	360	240[1a, 6b]
N[c] [%]	24.80	27.8	30.7	26.5	32.2	34.6	38.8	18.67
Ω[d] [%]	−55.36	−59.8	−59.5	−52.4	−66.0	−65.5	−64.6	−67.6
T_{decomp}[e] [°C]	360	276	205	333	227	183	233	318[1a, 6b]
ρ[f] [g cm^{-3}]	1.757	1.72	1.65	1.71	1.62	1.67	1.62	1.74[6b]
$\Delta H_{(s)}^{\ominus}$[g] [kJ mol^{-1}]	43.7	273.5	553.9	382.1	169.0	384.2	799.0	78.2
EXPLO5 V6.02								
$-\Delta_E U^{\ominus}$[h] [kJ kg^{-1}]	4993	5286	5486	5659	4716	4907	5171	5263
$T_{C\text{-}J}$[i] [K]	3651	3634	3758	3896	3328	3364	3481	3723
$P_{C\text{-}J}$[j] [GPa]	24.5	24.9	23.8	26.4	20.3	22.6	22.4	23.6
$D_{C\text{-}J}$[k] [m s^{-1}]	7713	7815	7715	7910	7343	7682	7710	7545
V_0[l] [dm^3 kg^{-1}]	618	664	699	671	701	712	754	589

[a] Impact sensitivity (BAM drophammer, method 1 of 6). [b] Friction sensitivity (BAM drophammer, method 1 of 6). [c] Nitrogen content. [d] Oxygen balance. [e] Temperature of decomposition. [f] Density at 298 K. [g] Standard molar enthalpy of formation. [h] Heat of detonation. [i] Detonation temperature. [j] Detonation pressure. [k] Detonation velocity. [l] Volume of detonation gases at standard temperature and pressure conditions.

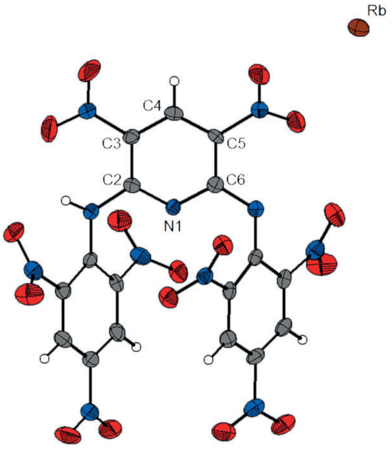


Figure 5. Molecular structure of **5 b** shown with 50 % probability thermal ellipsoids.

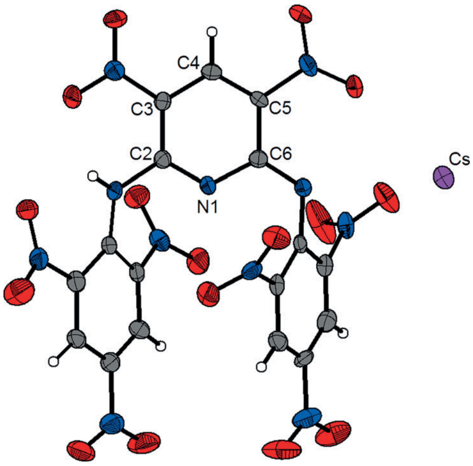


Figure 6. Molecular structure of **6 b** shown with 50 % probability thermal ellipsoids.

Selected crystallographic data, measurement parameters and refinement details are given in the Supporting Information (Tables S1 and S2).

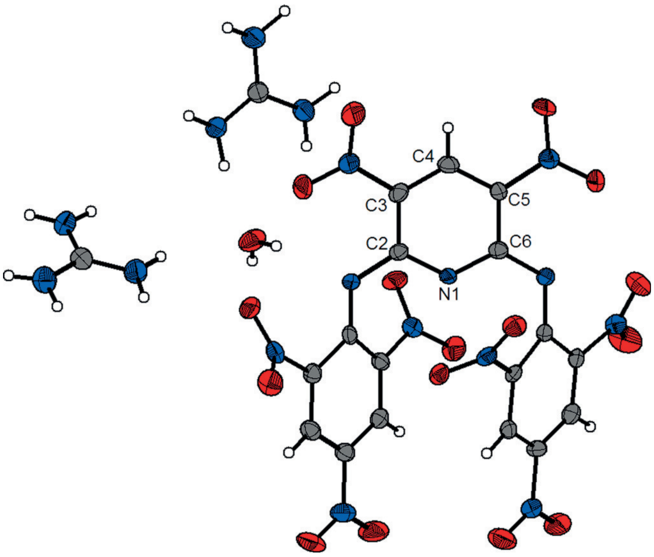


Figure 7. Molecular structure of **10**$\cdot H_2O$ shown with 50 % probability thermal ellipsoids.

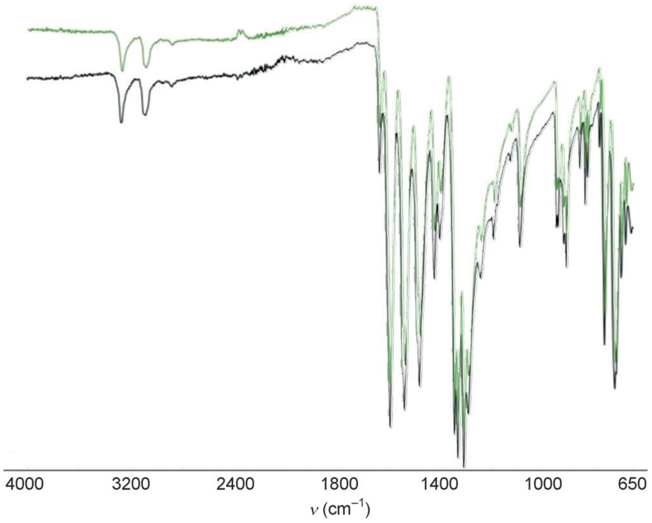


Figure 8. IR-spectra recorded for **2** before (black) and after (green) the isothermal long term experiment.

Thermal stabilities, sensitivities, and energetic properties

2,6-Bis(picrylamino)pyridine (*Pre*-PYX, **1**) has a high thermal stability and decomposes at 304 °C. However, the introduction of two further nitro groups in the 3- and 5-positions of the pyridine moiety increases the thermal stability with decomposition occurring at 360 °C. The results of the isothermal long-term experiment (RADEX, 100 h, 260 °C) show that neither decomposition nor thermal rearrangement of compound **2** occurred (Figure 8). The highest thermal stability within the series of alkali metal salts is shown by the sodium salt (**3**, $T_{\text{decomp}}=$ 349 °C). However, out of the salts investigated, the hydroxylammonium salt (**9**, $T_{\text{decomp}}=333$ °C) has the highest thermal stability. The decomposition temperature of **9** is, however, still lower than that of covalent **2** ($T_{\text{decomp}}=360$ °C; Table 1).

Furthermore, the sensitivities of the compounds to impact (IS) and friction (FS) were investigated. Surprisingly, the introduction of two nitro groups to **1** decreases the impact and friction sensitivity from IS = 9 J and FS = 324 N (**1**) to IS = 10 J and FS = 360 N (**2**). The most sensitive compounds towards impact are the sodium (**3**, IS = 3 J), cesium (**6**, IS = 10 J) and hydroxylammonium (**9**, IS = 10 J) salts of PYX. All of the salts which were investigated have friction sensitivities higher than 300 N.

Since the amount of gaseous products liberated during detonation strongly depends on the composition of the explosive being initiated, we decided to investigate only non-metal energetic materials. The gas-phase absolute molar enthalpies at 298 K and 1 atm for the non-metal species were calculated theoretically using the modified complete basis set method (CBS-4M) with the Gaussian 09 software.[24] The atomization-energy method was applied in order to calculate the gas phase standard molar enthalpies of formation ($\Delta H_{(g)}^{\ominus}$) at

298.15 K.[24c, 25] In order to obtain the standard molar enthalpy of formation ($\Delta H_{(s)}^{\ominus}$) for the prepared covalent compounds, the values of the standard molar enthalpies of sublimation (estimated using Trouton's rule) were subtracted from $\Delta H_{(g)}^{\ominus}$.[26] In the case of the salts, $\Delta H_{(g)}^{\ominus}$ of the ions as well as the calculated standard molar lattice enthalpies were used to calculate $\Delta H_{(s)}^{\ominus}$.[27] The Chapman–Jouguet (C-J) characteristics, based on the calculated $\Delta H_{(s)}^{\ominus}$ value and either the theoretical maximum densities (obtained either from X-ray diffraction measurements at 298 K) or from recalculation of the values obtained at 173 K (using the following equation:[28] $\rho_{298} = \rho T \cdot (1+\alpha_v(298-T))^{-1}$; $\alpha_v = 1.5\times10^{-4}$; $T = 173$ K) were calculated using the EXPLO5 V6.02 thermochemical computer code.[29] The Becker–Kistiakowsky–Wilson equation of state (BKW EOS) with the following sets of constants: $\alpha = 0.5$, $\beta = 0.38$, $\kappa = 9.4$, and $\Theta = 4120$ for gaseous detonation products and the Murnaghan equation of state for condensed products (compressible solids and liquids) were applied (Table 1).

Conclusion

The synthetic routes for the preparation of 2,6-bis(picrylamino)-3,5-dinitropyridine (PYX) and its salts with detailed characterizations are reported. Furthermore, the crystal structures for *Pre*-PYX (**1**), PYX (**2**) and four energetic salts were determined using low-temperature single-crystal X-ray diffraction. Surprisingly, compound **2** shows lower sensitivities toward impact and friction than the non-nitrated **1**. Compound **2** also shows a higher thermal stability than **1**. Moreover, an isothermal long time stability test (RADEX) of **2** showed that no chemical changes occurred after 100 h at 260 °C. All of the salts investigated showed lower thermal stabilities than **2**. Using the calculated heats of formation and experimentally determined densities, the detonation parameters (heat of explosion, explosion temperature, detonation pressure, and velocity) were calculated for non-metal species. The hydroxylammonium salt **9** showed the highest thermal stability and was calculated to possess the best detonation performance out of the nitrogen-based (non-metal) salts investigated. Furthermore, values of **9** are superior to corresponding values for HNS. Therefore, the hydroxylammonium salt **9** is the most promising candidate for further investigation and potential application among the salts which were investigated.

Experimental Section

Differential scanning calorimetry (DSC) was performed on a LINSEIS DSC PT10 using about 1 mg substance in a perforated aluminum vessel with a heating rate of 5 K min^{-1} and a nitrogen flow of 5 dm^3 h^{-1}. NMR spectra were recorded at 25 °C on a JEOL Eclipse 400 and JEOL ECX 400 instrument. Tetramethylsilane (^{1}H and ^{13}C) and nitromethane (^{14}N) were used as external standards. As an additional standard in ^{1}H and ^{13}C NMR spectroscopy, the solvent signal was used as locking signal. Mass spectrometric data were obtained with a JEOL MStation JMS 700 spectrometer (DEI^{+}/FAB$^{+/-}$). Raman spectra were recorded with a Bruker MultiRAM FT-Raman instrument fitted with a liquid-nitrogen-cooled germanium detector and an Nd:YAG laser ($\lambda = 1064$ nm). Infrared spectra were measured with a PerkinElmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. The following abbreviations were used to characterize the relative signal intensities: vs (very strong), s (strong), m (middle), w (weak), vw (very weak). All spectra were recorded at ambient temperature. Elemental analyses were performed on a Vario EL and a Vario Micro from Elementar Company. The sensitivities towards mechanical stimuli were determined according to the BAM (Bundesanstalt für Materialforschung und Prüfung, English: Federal Institute for Materials Research and Testing) standard for friction and impact.[30] The impact sensitivity was tested according to STANAG 4489 modified instructions using a BAM drophammer. The friction sensitivity was tested according to STANAG 4487 modified instructions using a BAM friction tester. The single-crystal X-ray diffraction measurements of pre-PYX (**1**), PYX (**2**), guanidinium monohydrate (**12**·H_2O) and mono-deprotonated (potassium monohydrate **4b**·H_2O, rubidium **5b**, and cesium **6b**) salts were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA), enhanced molybdenum $K\alpha$ radiation source ($\lambda = 0.71073$ Å), Oxford Cryosystems Cryostream cooling unit, four-circle kappa platform, and a Sapphire CCD detector. Data collection and reduction were performed by using the CrysAlisPro software.[31] The structure was solved with SIR-92,[32] refined by full-matrix least-squares on *F*2 with SHELXL-97,[33] checked with PLATON,[34] and all integrated into the WinGX software suite.[35] The finalized CIF files were checked with checkCIF.[36] Intra- and intermolecular contacts were analyzed with MERCURY.[37] The CCDC deposition numbers are given in reference [23].

Picryl chloride:[38] Picric acid (5.04 g, 22 mmol) was dissolved in phosphoryl chloride (50 mL) and *N*,*N*-diethylaniline (3.98 mL, 25 mmol) was added drop wise under vigorous stirring. The resulting solution was allowed to stir at ambient temperature for 15 min before being poured into iced water (500 mL) and stirred vigorously until all the phosphoryl chloride was hydrolyzed and picryl chloride precipitated. Picryl chloride was washed with water and dried over calcium chloride. Yield: 92.73 %, 5.05 g; DSC (5 °C min^{-1}): 86 °C (melt.); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 9.17$ ppm (s, 2 H, CH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta =$ 149.7, 146,8, 125.8, 123.3 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta = -15$ ppm (CNO$_2$); MS (DEI^{+}): *m*/*z*: 247.2 [*M*]$^{+}$; IR (ATR): $\tilde{\nu} = 3086$ (m), 1605 (m), 1533 (vs), 1407 (w), 1341 (vs), 1186 (w), 1063 (s), 936 (m), 920 (vs), 825 (w), 753 (m), 732 (s), 720 (vs), 645 cm^{-1} (m); Raman (1064 nm, 300 mW): $\tilde{\nu} =$ 3089 (15), 1604 (54), 1554 (34), 1547 (37), 1370 (62), 1353 (100), 1197 (22), 1065 (29), 937 (11), 924 (11), 824 (40), 765 (7), 754 cm^{-1} (9); elemental analysis calcd (%) for $C_6H_2ClN_3O_6$ (247.55): C 29.11, H 0.81, N 16.97; found: C 28.82, H 0.94, N 16.78; IS: 15 J; FS: 360 N.

2,6-Bis(picrylamino)pyridine (*Pre*-PYX, 1):[21b] To a solution of picryl chloride (4.95 g, 20 mmol) in *p*-xylene (40 mL), magnesium hydroxide (1.05 g, 18 mmol) and 2,6-diaminopyridine (0.98 g, 9 mmol) were added. The reaction mixture was heated at 140 °C for 3 h and then allowed to cool to room temperature. Toluene (30 mL) was then added and the product collected by filtration, washed with methanol, 10 % HCl, and with water until it was acid free. Yield: 60.00 %, 2.97 g; DSC (5 °C min^{-1}): 304 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 10.37$ (s, 2 H, NH), 8.77 (s, 4 H, CH), 7.75 (t, 1 H, $J = 8.02$ Hz, CH), 7.75 ppm (d, 2 H, $J = 8.02$ Hz, CH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta = 154.7$, 143.1, 139.4, 139.1, 136.7, 125.7, 99.2 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta = -13$ (CNO$_2$), -273 ppm (CNH); MS (DEI^{+}): *m*/*z*: 531.2 [*M*]$^{+}$; IR (ATR): $\tilde{\nu} = 3334$ (w), 3306 (w), 3098 (w), 3080 (w), 1739 (w), 1623 (m), 1596 (s), 1586 (s), 1540 (s), 1518 (m), 1480 (s), 1452 (s), 1394 (w), 1335 (vs), 1294 (vs), 1527 (s), 1216 (m), 1171 (m), 1151 (s), 1086 (s), 998 (w), 933 (m), 921 (s), 844 (w), 828 (w), 793 (s), 773 (m), 751 (m), 740 (m), 721 (vs), 702 cm^{-1} (s); Raman (1064 nm, 300 mW): $\tilde{\nu}=1622$ (33), 1544 (20), 1529 (14), 1503 (12), 1455 (11), 1354 (49), 1340 (100), 1301 (25), 1278 (20), 1173 (17), 1000 (23), 827 cm^{-1} (13); elemental analysis calcd (%) for $C_{17}H_9N_9O_{12}$ (531,31): C 38.43, H 1.71, N 23.73; found: C 38.29, H 1.88, N 23.57; IS: 9 J; FS: 324 N; ESD: 0.5 J.

2,6-Bis(picrylamino)-3,5-dinitropyridine (PYX, 2):[21a] 2,6-Bis(picrylamino)pyridine (1.06 g, 2 mmol) was carefully added to fuming nitric (11 mL) stirred acid at −20 °C. The resulting solution was allowed to warm to room temperature, stirred for 2 h, then heated under reflux for 5 h before being cooled and diluted with 65% nitric acid (21 mL) at 0 °C. The precipitated product was filtered off, washed with 70% nitric acid (3 mL), water until acid free, and methanol (21 mL). The product obtained was dried at 150 °C. Yield: 66.80%, 0.83 g; DSC (5 °C min^{-1}): 360 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=11.25$ (s, br, 2H, NH), 9.19 (s, 1H, CH), 8.90 ppm (s, 4H, CH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=161.2$, 144.4, 142.3, 137.7, 131.2, 125.1, 124.0 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-6$ (CNO$_2$), −48 (CNO$_2$) −292 ppm (CNH); MS (DEI$^+$): m/z: 621.4 $[M]^+$; IR (ATR): $\tilde{\nu}=3271$ (w), 3087 (w), 1739 (w), 1636 (m), 1594 (vs), 1539 (vs), 1481 (s), 1422 (s), 1402 (s), 1344 (vs), 1331 (vs), 1308 (vs), 1292 (s), 1244 (m), 1194 (w), 1091 (m), 949 (m), 940 (m), 922 (m), 911 (m), 858 (w), 838 (w), 826 (w), 780 (w), 762 (s), 721 (s), 696 (m), 679 (w), 639 (m), 608 cm^{-1} (m); Raman (1064 nm, 300 mW): $\tilde{\nu}=3102$ (4), 1626 (55), 1606 (19), 1542 (20), 1523 (16), 1483 (12), 1347 (100), 1334 (83), 1310 (37), 1294 (49), 1266 (29), 1177 (13), 1094 (8), 942 (7), 859 (4), 838 (25), 827 (13), 741 (5), 697 (4), 641 cm^{-1} (5); elemental analysis calcd (%) for $C_{17}H_7N_{11}O_{16}$ (621.30) : C 32.86, H 1.14, N 24.80; found: C 32.68, H 1.38, N 24.29; IS: 10 J; FS: 360 N; ESD: 0.5 J.

Sodium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (3): A solution of sodium hydroxide (60.0 mg, 1.50 mmol) in ethanol (10 mL) was added to 2,6-bis(picrylamino)-3,5-dinitropyridine (466.0 mg, 0.75 mmol) dissolved in ethanol (10 mL). Instantly a bright red solid precipitated. Yield: 93.80%, 468.0 mg; DSC (5 °C min^{-1}): 349 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.74$ (s, 1H, CH), 8.34 (s, 4H, CH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=153.5$, 145.6, 143.6, 134.0, 131.2, 126.0, 122.9 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-20$ ppm (CNO$_2$); MS (FAB$^-$): m/z: 620.3 $[C_{17}H_6N_{11}O_{16}]^-$; (FAB$^+$): m/z: 23.0 [Na]$^+$; IR (ATR): $\tilde{\nu}=3084$ (w), 2289 (vw), 1607 (m), 1556 (m), 1520 (s), 1504 (m), 1466 (w), 1443 (w), 1413 (w), 1346 (s), 1266 (vs), 1185 (vs), 1166 (vs), 1126 (s), 1087 (s), 940 (m), 931 (m), 914 (m), 848 (w), 826 (w), 806 (vw), 782 (vw), 769 (w), 755 (m), 738 (m), 719 (vs), 678 cm^{-1} (m); Raman (1064 nm, 300 mW): $\tilde{\nu}=3088$ (2), 1612 (28), 1541 (19), 1441 (14), 1368 (67), 1340 (86), 1325 (92), 1309 (57), 1292 (60), 1233 (33), 1187 (100), 1131 (20), 1091 (9), 945 (6), 916 (7), 832 (52), 769 (12), 739 (16), 720 (25), 385 (9), 190 (21), 170 (25), 85 cm^{-1} (68); elemental analysis calcd (%) for $C_{17}H_5N_{11}Na_2O_{16}$ (665.27): C 30.69, H 0.76, N 23.16; found: C 30.36, H 1.09, N 22.63; IS: 3 J; FS: 360 N.

Potassium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (4): A solution of potassium hydroxide (40.4 mg, 0.72 mmol) in ethanol (10 mL) was added to 2,6-bis(picrylamino)-3,5-dinitropyridine (223.7 mg, 0.36 mmol) in ethanol (10 mL). Immediately a red solid precipitated. Yield: 96.38%, 242.0 mg; DSC (5 °C min^{-1}): 280 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.75$ (s, 1H, CH), 8.34 ppm (s, 4H, CH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=151.3$, 144.1, 143.0, 134.4, 134.0, 124.2,123.0 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-32$ ppm (CNO$_2$); MS (FAB$^-$): m/z: 620.3 $[C_{17}H_6N_{11}O_{16}]^-$; (FAB$^+$): m/z: 39.0 [K]$^+$; IR (ATR): $\tilde{\nu}=3084$ (w), 2892 (vw), 2349 (vw), 2281 (vw), 1840 (vw), 1611 (w), 1594 (w), 1564 (m), 1528 (s), 1485 (m), 1444 (m), 1345 (m), 1321 (m), 1296 (s), 1252 (vs), 1216 (s), 1192 (s), 1168 (s), 1119 (m), 1088 (m), 961 (vw), 937 (w), 922 (m), 910 (w), 857 (vw), 846 (vw), 824 (w), 802 (vw), 780 (vw), 755 (m), 738, (vw), 730 (vw), 720 (s), 704 (vw), 678 cm^{-1} (m); Raman (1064 nm, 300 mW, 25 °C): $\tilde{\nu}=3084$ (2), 1613 (18), 1595 (19), 1578 (34), 1535 (18), 1501 (20), 1432 (14), 1359 (58), 1343 (54), 1323 (100), 1300 (58), 1270 (34), 1243 (36), 1203 (38), 1174 (25), 1120 (21), 1081 (12), 945 (11), 827 (76), 803 (6), 753 (11), 741 (14), 720 cm^{-1} (11); elemental analysis calcd (%) for $C_{17}H_5K_2N_{11}O_{16}$, (697.48): C 29.27, H 0.72, N 22.09; found: C 29.05, H 1.06, N 21.65; IS: 10 J; FS: 360 N.

Rubidium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (5): A solution of rubidium hydroxide (102.5 mg, 1.00 mmol, 50 wt.% in water) in ethanol (10 mL) was added to 2,6-bis(picrylamino)-3,5-dinitropyridine (310.7 mg, 0.50 mmol) in ethanol (10 mL). Immediately a red solid precipitated. Yield: 90.86%, 359 mg; DSC (5 °C min^{-1}): 208 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.76$ (s, 1H, CH), 8.42 ppm (s, 4H, CH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=151.6$, 144.3, 143.6, 133.6, 133.8, 124.0,122.6 ppm; MS (FAB$^-$): m/z: 620.2 $[C_{17}H_6N_{11}O_{16}]^-$; (FAB$^+$): m/z: 85.0 [Rb]$^+$; IR (ATR): $\tilde{\nu}=3083$ (w), 2358 (vw), 1610 (m), 1556 (m), 1527 (s), 1482 (m), 1466 (w), 1428 (w), 1365 (w), 1345 (s), 1325 (vs), 1251 (vs), 1215 (vs), 1167 (s), 1087 (s), 935 (m), 927 (m), 907 (w), 824 (w), 768 (vw), 756 (m), 729 (m), 718 (s), 678 cm^{-1} (m); Raman (1064 nm, 300 mW): $\tilde{\nu}=1611$ (14), 1536 (14), 1446 (13), 1431 (15), 1360 (36), 1323 (100), 1239 (21), 1202 (45), 1174 (16), 1122 (9), 1083 (9), 945 (8), 827 (41), 769 (9), 752 (7), 740 (9), 721 (10), 627 cm^{-1} (7); elemental analysis calcd (%) for $C_{17}H_5N_{11}O_{16}Rb_2$ (790.22): C 25.84, H 0.64, N 19.50; found: C 26.03, H 0.34, N 19.89; IS: 10 J; FS: 360 N.

Cesium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (6): A solution of cesium hydroxide monohydrate (167.9 mg, 1.00 mmol) in ethanol (10 mL) was added to 2,6-bis(picrylamino)-3,5-dinitropyridine (310.7 mg, 0.50 mmol) dissolved in ethanol (10 mL). Immediately a red solid precipitated. Yield: 93.37%, 413.2 mg; DSC (5 °C min^{-1}): 337 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.77$ (s, 1H, CH), 8.47 ppm (s, 4H, CH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=163.5$, 153.9, 148.9, 148.5, 144.3, 143.2, 139.9, 138.6, 134.1, 128.5, 125.7, 124.7, 122.9 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-3$ ppm (CNO$_2$); IR (ATR): $\tilde{\nu}=3083$ (vw), 1608 (w), 1550 (s), 1525 (s), 1479 (m), 1448 (w), 1425 (w), 1343 (m), 1326 (s), 1255 (vs), 1213 (s), 1166 (s), 1086 (m), 936 (w), 920 (w), 908 (w), 857 (vw), 836 (vw), 824 (w), 779 (vw), 756 (m), 717 (s), 695 (m), 678 (m), 660 cm^{-1} (m); Raman (1064 nm, 300 mW): $\tilde{\nu}=3240$ (8), 2563 (17), 2269 (12), 2242 (14), 2221 (16), 2208 (17), 2185 (19), 2158 (21), 2136 (24), 2092 (22), 2075 (20), 2059 (21), 2043 (18), 2023 (22), 1925 (22), 1796 (22), 1625 (29), 1328 (66), 1204 (35), 1123 (34), 1090 (22), 826 (40), 723 (36), 641 (42), 98 cm^{-1} (100); MS (FAB$^-$): m/z: 620.5 $[C_{17}H_6N_{11}O_{16}]^-$; (FAB$^+$): m/z: 133.0 [Cs]$^+$; elemental analysis calcd (%) for $C_{17}H_5Cs_2N_{11}O_{16}$ (885.10): C 23.07, H 0.57, N 17.41; found: C 22.98, H 0.87, N 17.27; IS: 5 J; FS: 360 N.

Ammonium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (7): Method 1: The sodium (**3**; 0.50 mmol, 332,6 mg) or potassium (**4**; 0.50 mmol, 348.7 mg) salt of 2,6-bis(picrylamino)-3,5-dinitropyridine was added to ethanol (10 mL) followed by the dropwise addition of ammonium chloride (53.5 mg, 1.00 mmol) in water (1 mL). After stirring at room temperature for 5 h the reaction mixture was filtered and the product was obtained as brown solid. Yield: 80.32% (263.2 mg), 80.20% (262.8 mg), respectively. Method 2: 2,6-Bis(picrylamino)-3,5-dinitropyridine (1.00 g, 1.61 mmol) was dissolved in ethanol (40 mL) and ammonia gas was slowly bubbled through the solution for 15 min at room temperature. After stirring for 1 h, the reaction mixture was filtered and the product was obtained as a brown solid. Yield: 47.08%, 496.8 mg; DSC (5 °C min^{-1}): 276 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=9.04$ (s, 4H, CH), 8.98 (s, 1H, CH), 7.14 ppm (s, 4H, NH$_4$); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=154.7$, 143.6, 134.2, 132.6, 128.0, 125.2, 120.2 ppm; ^{14}N NMR

(29 MHz, [D$_6$]DMSO): $\delta=-18$ (CNO$_2$), −355 ppm (NH$_4$); IR (ATR): $\tilde{\nu}=3436$ (w), 3326 (w), 3085 (w), 1633 (m), 1580 (m), 1523 (m), 1455 (m), 1419 (m), 1346 (m), 1269 (vs), 1161 (m), 1089 (m), 1039 (m), 933 (m), 897 (m), 827 (m), 777 (w), 763 (m), 738 (m), 727 (s), 707 (m), 689 cm^{-1} (m); Raman (1064 nm, 300 mW): $\tilde{\nu}=2620$ (40), 1628 (52), 1530 (58), 1338 (100), 1282 (75), 1224 (56), 1166 (53), 1092 (32), 1055 (50), 940 (62), 829 cm^{-1} (90); MS (FAB$^-$): *m/z*: 620.3 [$C_{17}H_6N_{11}O_{16}$]$^-$; (FAB$^+$): *m/z*: 18.0 [NH$_4$]$^+$; elemental analysis calcd (%) for $C_{17}H_{13}N_{13}O_{16}$ (655.36): C 31.16, H 2.00, N 27.78; found: C 30.76, H 1.61, N 28.16; IS: 40 J; FS: 360 N.

Hydrazinium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (8): 2,6-Bis(picrylamino)-3,5-dinitropyridine (453.5 mg, 0.73 mmol) was dissolved in ethanol (10 mL) and hydrazine monohydrate (0.07 mL, 1.46 mmol) was added dropwise. Afterwards, the reaction mixture was heated under reflux for 3 h, cooled, and the resulting dark-red precipitate was filtered off. Yield: 62.91 %, 663.8 mg; DSC (5 °C min^{-1}): 205 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.97$ (s, 1H, CH), 8.81 (s, 4H, CH), 7.31 ppm (br, 10H, NH$_2$-NH$_3$); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=155.2$, 139.2, 135.8, 130.7, 120.7, 117.6, 116.7 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-15$ (CNO$_2$), −359 ppm (NH$_2$); IR (ATR): $\tilde{\nu}=3474$ (m), 3357 (m), 3088 (w), 2840 (vw), 2740 (vw), 2648 (vw), 2360 (vw), 1606 (vs), 1552 (w) 1526 (w), 1508 (m), 1455 (m), 1436 (m), 1389 (w) 1373 (m), 1328 (s), 1281 (s), 1269 (vw), 1217 (vs), 1180 (m), 1330 (w), 1106 (vw), 1086 (m), 1060 (vw), 1036 (s), 944 (vw), 934 (m), 922 (vw), 902 (w), 877 (vw), 864 (vw), 828 (w), 802 (m), 742 (m), 717 (m), 706 (m), 684 cm^{-1} (vw); Raman (1064 nm, 300 mW): $\tilde{\nu}=3347$ (8), 3297 (6), 3085 (7), 2476 (7), 1598 (17), 1554 (12), 1358 (13), 1323 (86), 1253 (9), 1185 (17), 1111 (5), 1061 (7), 1010 (5), 805 (12), 791 (7), 751 (7), 726 (6), 381 (17), 348 (6), 87 cm^{-1} (43); MS (FAB$^-$): *m/z*: 620.3 [$C_{17}H_6N_{11}O_{16}$]$^-$; (FAB$^+$): *m/z*: 33.1 [N_2H_5]$^+$; elemental analysis calcd (%) for $C_{17}H_{15}N_{15}O_{16}$ (685.69): C 29.79, H 2.21, N 30.65; found: C 28.99, H 2.72, N 36.64; IS: 10 J; FS: 360 N; ESD: 0.35 J.

Hydroxylammonium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (9): Method 1: The sodium (**3**; 0.50 mmol, 332.6 mg) or potassium (**4**; 0.50 mmol, 348.7 mg) salt of 2,6-bis(picrylamino)-3,5-dinitropyridine was added to ethanol (10 mL) and hydroxylammonium chloride (69.5 mg 1.00 mmol) in water (10 mL) was added dropwise. After heating at 60 °C for 3 h, the hot reaction mixture was filtered and the product obtained as an orange solid. Yield: 68.55 % (235.6 mg), 72.68 % (249.8 mg), respectively. Method 2: 2,6-Bis(picrylamino)-3,5-dinitropyridine (1.00 g, 1.61 mmol) was dissolved in ethanol (40 mL) and hydroxylamine (3.22 mmol, 0.21 mL, 50 wt. % in H$_2$O) was added to the reaction mixture. After stirring at room temperature for 5 h, the reaction mixture was filtered and the product obtained as an orange solid. Yield: 62.96 %, 696.8 mg; DSC (5 °C min^{-1}): 333 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=9.08$ (s, 1H, CH), 8.85 (s, 4H, CH), 4.55 ppm (brs, 4H, NH$_3$OH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=149.1$, 145.6, 142.8, 136.4,127.3, 124.5, 122.4 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-18$ (NO$_2$), −292 ppm (NH$_3$); IR (ATR): $\tilde{\nu}=3270$ (vw), 3089 (vw), 1635 (w), 1593 (vs), 1538 (s), 1480 (s), 1422 (m), 1400 (m), 1343 (vs), 1330 (vs), 1330 (vs), 1307 (vs), 1290 (s), 1243 (m), 1193 (w), 1091 (m), 948 (m), 921 (w), 910 (m), 858 (vw), 837 (w), 826 (w), 779 (vw), 761 (m), 720 (s), 695 (m), 678 cm^{-1} (w); Raman (1064 nm, 300 mW): $\tilde{\nu}=3263$ (3), 3102 (4), 1627 (62), 1605 (18), 1542 (20), 1524 (19), 1483 (12), 1357 (84), 1347 (89), 1333 (100), 1309 (43), 1293 (64), 1293 (65), 1267 (29), 1177 (14), 942 (7), 838 (27), 827 (13), 640 cm^{-1} (6); MS (FAB$^-$): *m/z*: 620.6 [$C_{17}H_6N_{11}O_{16}$]$^-$; (FAB$^+$): *m/z*: 34.0 [NH$_3$OH]$^+$; elemental analysis calcd (%) for $C_{17}H_{13}N_{13}O_{18}$ (687.36): C 29.71, H 1.91, N 26.49; found: C 29.45, H 1.48, N 26.38; IS: 5 J; FS: 324 N.

Guanidinium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (10): 2,6-Bis(picrylamino)-3,5-dinitropyridine (310.7 mg, 0.50 mmol) and guanidinium carbonate (90.1 mg, 1.00 mmol) were added to ethanol (15 mL) and heated under reflux for 3 h. After cooling and filtering, the product was obtained as a dark-red solid. Yield: 62.67 %, 215.4 mg; DSC (5 °C min^{-1}): 227 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.82$ (s 1H, CH), 8.66 (s, 4H, CH), 6.90 ppm (s, br, 6H, NH$_2$); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=158.4$, 154.1, 145.3, 143.1, 134.5, 125.7 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-15$ (CNO$_2$), −364 ppm (CNH$_2$); IR (ATR): $\tilde{\nu}=3604$ (vw), 3436 (w), 3360 (w), 3190 (w), 3080 (w), 2360 (vw), 2341 (vw),1668 (m), 1006 (w), 1540 (m), 1521 (s), 1496 (m),1464 (w), 1439 (w), 1415 (w), 1341 (m), 1267 (s), 1203 (s), 1165 (s), 1084 (m), 932 (m), 924 (m), 906 (w), 824 (w), 766 (vw), 758 (w), 718 (m), 700 (vw), 683 (w), 668 cm^{-1} (vw); Raman (1064 nm, 300 mW): $\tilde{\nu}=3087$ (1), 1609 (23), 1573 (7), 1535 (17), 1469 (2), 1435 (11), 1364 (53), 1327 (100), 1230 (40), 1202 (58), 1173 (20), 1124 (18), 1087 (7), 1010 (3), 943 (3), 827 (39), 771 (8), 741 (8), 719 cm^{-1} (8); MS (FAB$^-$): *m/z*: 620.3 [$C_{17}H_6N_{11}O_{16}$]$^-$; (FAB$^+$): *m/z*: 60.1 [CN_3H_6]$^+$; elemental analysis calcd (%) for $C_{19}H_{17}N_{17}O_{16}$ (739.44): C 30.86, H 2.32, N 32.20; found: C 30.43, H 2.51, N 31.27; IS: 40 J; FS: 360 N.

Aminoguanidinium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (11): 2,6-Bis(picrylamino)-3,5-dinitropyridine (403.8 mg, 0.65 mmol) and aminoguanidinium bicarbonate (176.9 mg, 1.30 mmol) were added to ethanol (10 mL) and heated under reflux for 3 h. After cooling and filtering, the product was obtained as a dark-red solid. Yield: 61.72 %, 308.7 mg; DSC (5 °C min^{-1}): 183 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.75$ (s, 1H, CH), 8.58 (s, br, 2H, NH) 8.34 (s, 4H, CH), 7.26 (s, br, 2H, N-NH$_2$), 6.79 ppm (s, br, 4H, NH$_2$); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=159.2$, 153.4, 145.5, 143.6, 134.0, 131.2, 126.0, 122.9 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-20$ (CNO$_2$), −264 (CNH) −369 ppm (CNH$_2$); IR (ATR): $\tilde{\nu}=3334$ (w), 3082 (w), 2280 (vw), 1682 (w), 1666 (m), 1625 (m), 1572 (m), 1527 (s), 1497 (m), 1444 (w), 1389 (w), 1344 (s), 1310 (s), 1289 (s), 1247 (m), 1184 (m), 1116 (m), 1081 (m), 957 (m), 938 (m), 924 (m), 857 (w), 923 (m), 767 (vw), 758 (m), 717 (m), 685 cm^{-1} (m); Raman (1064 nm, 300 mW,): $\tilde{\nu}=3065$ (8), 2748 (7), 1617 (32), 1581 (78), 1503 (49), 1456 (13), 1368 (73), 1346 (100), 1317 (43), 1298 (46), 1242 (66), 1174 (41), 1119 (52), 1082 (28), 946 (10), 824 (70), 747 cm^{-1} (21); MS (FAB$^-$): *m/z*: 620.3 [$C_{17}H_6N_{11}O_{16}$]$^-$; (FAB$^+$): *m/z*: 75.1 [CN_4H_7]$^+$; elemental analysis calcd. (%) for $C_{19}H_{19}N_{19}O_{16}$ (769.47): C 29.66, H 2.49, N 34.59; found: C 29.61, H 2.31, N 34.71; IS: 40 J; FS: 360 N.

Triaminoguanidinium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (12): The sodium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (322.6 mg, 0.50 mmol) or the potassium salt of 2,6-bis(picrylamino)-3,5-dinitropyridine (348.7 mg, 0.50 mmol) together with triaminoguanidine hydrochloride (140.6 mg, 1.00 mmol) were added to ethanol (10 mL) and heated under reflux for 2 h. The hot mixture was filtered and the product obtained as a dark-red solid. Yield: 71.44 %, 296.3 mg; DSC (5 °C min^{-1}): 233 °C (decomp); ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta=8.81$ (s, 4H, CH), 8.68 (s, 1H, CH), 8.59 (brs, 6H, NH), 4.49 ppm (brs, 12H, NH$_2$); ^{13}C NMR (101 MHz, [D$_6$]DMSO): $\delta=160.9$, 159.5, 144.7, 134.1, 130.7, 124.7, 123.5, 114.5 ppm; ^{14}N NMR (29 MHz, [D$_6$]DMSO): $\delta=-19$ (NO$_2$), −170 (NH), −279 ppm (NH$_2$); IR (ATR): $\tilde{\nu}=3319$ (vw), 3193 (w), 3082 (w), 1681 (w), 1623 (m), 1583 (m), 1531 (s), 1500 (m), 1439 (m), 1412 (m), 1348 (vs), 1306 (vs), 1251 (s), 1200 (s), 1130 (m), 1093 (w), 1056 (w), 945 (m), 931 (m), 913 (m), 858 (w), 825 (w), 758 (m), 721 (s), 684 cm^{-1} (m); MS (FAB$^-$): *m/z*: 620.4 [$C_{17}H_6N_{11}O_{16}$]$^-$; (FAB$^+$): *m/z*: 105.2 [CN_6H_9]$^+$; elemental analysis calcd (%) for $C_{19}H_{23}N_{23}O_{16}$ (829.53): C 27.51, H 2.79, N 38.84; found: C 27.84, H 3.25, N 38.90; IS: 20 J; FS: 360 N.

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