



Energetic derivatives of 4,4',5,5'-tetranitro-2H,2'H-3,3'-bipyrazole (TNBP): synthesis, characterization and promising properties

Journal:	<i>Journal of Materials Chemistry A</i>
Manuscript ID	TA-ART-12-2017-011172.R1
Article Type:	Paper
Date Submitted by the Author:	24-Feb-2018
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Energetic derivatives of 4,4',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole (TNBP): synthesis, characterization and promising properties

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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4,4',5,5'-Tetranitro-2*H*,2'*H*-3,3'-bipyrazole (TNBP, **1**) is an excellent precursor to new energetic derivatives (**3** and **5–14**). The monotrinitromethyl substituted compound (**3**) was obtained by alkylation with bromoacetone and subsequent nitration. Nitration of the aminated compound (**4**) with nitronium tetrafluoroborate (NO₂BF₄) in the presence of potassium acetate results in the monopotassium salt (**5**). Dianionic salts of **1** with potassium and nitrogen rich cations (**6–14**) were prepared by neutralization. These compounds were fully characterized using NMR and infrared spectra and elemental analyses as well with single crystal X-ray diffraction for **3**, **5**, **8** and **10**. The detonation properties, determined from the calculated heats of formation and measured densities, show that some (**3**, **7** and **13**) are superior to those of 1,3,5-trinitrotriazacyclohexane (RDX). In addition, given the high thermal stability (323 °C) and good detonation performance of **6**, it could be a promising green primary explosive.

Introduction

Energetic materials, well known as propellants, high explosives and pyrotechnics, are widely used in civil and military applications. The key to the development of energetic materials is to design and synthesize high energy density compounds (HEDCs). In consideration of the high toxicity of traditional energetic compounds such as TNT and RDX, interest in nitrogen-rich energetic compounds has increased markedly because decomposition to dinitrogen gas gives rise to very promising environmentally friendly materials.^[1] The design strategy for HEDCs is largely focused on the modification of azoles using explosophore groups.^[2] The formation of energetic salts is also an efficient approach for stabilizing molecules and improving sensitivities towards external stimuli.^[3]

The chemistry of fully C-nitrated mono/bi nitrogen rich heterocyclic rings (Fig. 1) has been investigated.^[4] The results show that these compounds are highly interesting energetic compounds. However, the derivatives of 4,4',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole (TNBP, **1**) have not been reported perhaps since the synthetic details were not available until recent studies by our group.^[5] In our continuing efforts to synthesize high performance and insensitive energetic compounds, we choose **1** as the starting material in order to

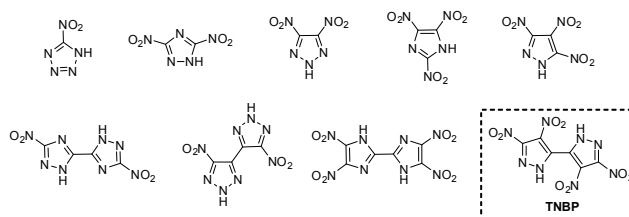


Fig. 1 Fully C-nitrated mono/bi nitrogen-rich heterocyclic compounds

investigate and expand its chemistry. In this study, the alkylation/nitration, amination/nitration and neutralization reactions were examined. Many energetic derivatives (**3** and **5–14**) of **1** were prepared and fully characterized. Some of them (**3**, **5**, **8** and **10**) were confirmed by single crystal X-ray diffraction. Potential application as energetic materials was examined both theoretically and experimentally.

Results and discussion

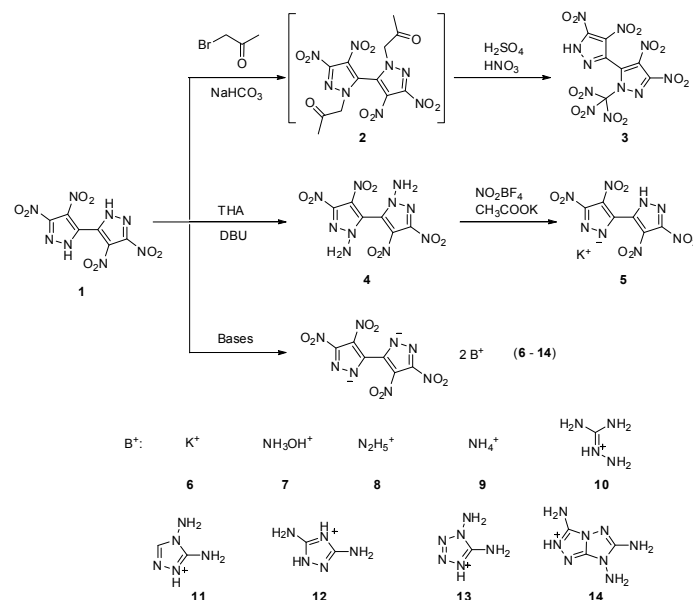
Synthesis

The starting material 4,4',5,5'-tetranitro-2*H*,2'*H*-3,3'-bipyrazole (TNBP, **1**) was prepared based on the literature.^[5,6] The alkylation of **1** with bromoacetone (Scheme 1) in a mixture of acetone and water in the presence of sodium bicarbonate gave the very hygroscopic product (**2**). The next step was commenced immediately with stirring for seven days in a mixture of concentrated sulfuric acid and 100% nitric acid. The precipitate, mono-N-trinitromethyl substituted pyrazole (**3**) rather than the di-N-trinitromethyl substituted, was isolated after the reaction mixture was poured into ice water. The

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Electronic Supplementary Information (ESI) available: Includes theoretical calculation, crystallographic data (CCDC: 1811781-1811784) and NMR spectra. See DOI: 10.1039/x0xx00000x



Scheme 1 Synthesis of different energetic derivatives (**3** and **5-14**) based on **1**

structure of **3** was confirmed by single crystal X-ray diffraction analysis.

In order to synthesize the N-nitramino functionalized derivative, attempts to nitrate the aminated compound (**4**) by using NO_2BF_4 in the presence of potassium acetate were made.^[7] However, due to the weak N-NH₂ bonds in **4** and even though NO_2BF_4 is a mild nitrating reagent, only the monopotassium tetranitro-bipyrazolate (**5**) was isolated, and subsequently well characterized and a single crystal X-ray structure obtained.

Energetic salts (**6-14**) were prepared by reacting **1** with potassium bicarbonate and several nitrogen rich bases. Those salts are readily isolated in high yield and are stable in air. The structures of **8** and **10** were confirmed by single crystal X-ray diffraction.

¹⁵N NMR spectra

Several compounds were characterized by ¹⁵N NMR (Fig. 2). The assignments are based on the literature,^[5] and HMBC spectra as well as comparison with theoretical calculations.^[8] The signals for the anion in these compounds are observed at low field. The two nitro groups bonded to the pyrazole ring are essentially in the same place, while the nitrogen atoms (N3 and N4), especially the negative nitrogen atom (N4), are shifted due to the presence of different cations. The signal of the hydrazinium cation in **8** is at $\delta = -331.2$ ppm. In the spectrum of **12**, all the signals are easily observed. In comparison with **8**, the signals (N1-N4) for the anion are shifted to higher field, especially for N4, with the presence of a different cation. The signals for the anion in **14** shift little relative to those in **8**. All the signals for the cation are well detected except one amino group (N12). However, the signal

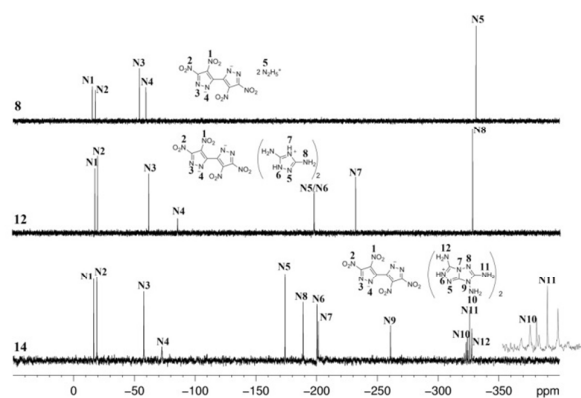


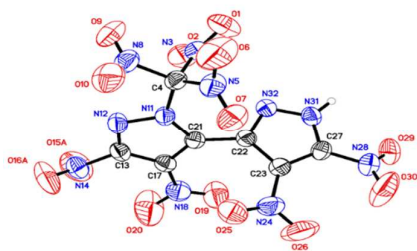
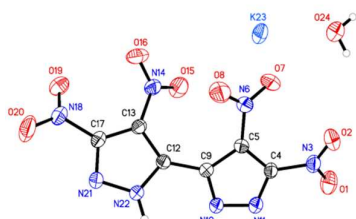
Fig. 2 ¹⁵N NMR spectra of **8**, **12** and **14**

for N12 ($\delta: -329.6$ ppm) was observed in the ¹H-¹⁵N HSQC spectrum (ESI). The signals (N10 and N11) for the other two amino groups were observed as triplets at high field.

Single crystal X-ray diffraction studies

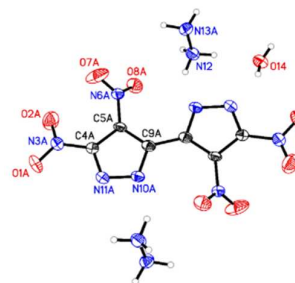
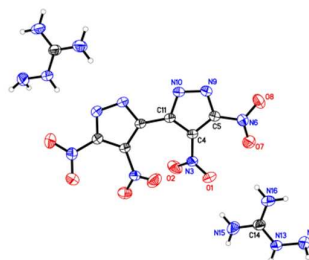
Compound **3** crystallizes in the monoclinic space group *C2/c* with a density of 1.891 g cm^{-3} at 293K and eight molecules per unit cell. The crystal structure is shown in Fig. 3. The nitro groups are distorted with respect to the pyrazole rings due to steric hindrance. The dihedral angle between the two pyrazole rings is 57° . The hydrogen atom is bonded to N31 (near C27-N28) rather than N32. The parameters for the nitro groups and bipyrazole are comparable to those in the literature.^[9]

Compound **5** crystallizes as a monohydrate in the triclinic space group *P-1* with a density of 1.924 g cm^{-3} at 293 K and

Fig. 3 The molecular structure of **3**Fig. 4 The molecular structure of **5**

two molecules per unit cell (Fig. 4). In comparison with **3**, the hydrogen atom is bonded to N22 which is near the bond (C12–C9) connecting the two pyrazole moieties. The dihedral angle between the two pyrazole rings is 35° . In addition, each of the nitro groups is twisted out of the plane of the pyrazole ring to which it is bonded.

Compound **8** crystallizes as a monohydrate in the monoclinic space group C2/c with a calculated density of 1.802 g cm^{-3} at 293 K and four molecules per unit cell (Fig. 5). This structure is whole-molecule disordered and was fixed at 85:15. The structure of **8** consists of many hydrogen bonds that generate dense 3D hydrogen networks (Fig. 5). The details are given in the ESI.

Fig. 5 The molecular structure of **8**Fig. 6 The molecular structure of **10**

Compound **10** crystallizes in the monoclinic space group P2/n with two molecules per unit cell (Fig. 6). The crystal density at 293 K is 1.693 g cm^{-3} , which is low due to the poor molecular packing in the crystal lattice. The parameters are similar to those in **8**. The bispyrazole backbone is not coplanar. The dihedral angle between the two pyrazole rings is 16.53° . In addition, the nitro groups are also out of the plane of the bonded pyrazole rings because of steric hindrance.

Physical and detonation properties

Thermal stabilities were determined by differential scanning calorimetry (DSC) at a heating rate of $5^\circ \text{C min}^{-1}$. The results are given in Table 1. The mono-N-trinitromethyl-substituted

Table 1. Physicochemical and energetic properties of **3**, **5**–**14** compared with RDX and $\text{Pb}(\text{N}_3)_2$.

Compds	$\rho^a (\text{g cm}^{-3})$	$Dv^b (\text{m s}^{-1})$	$P^c (\text{GPa})$	$\Delta H_f^d (\text{kJ mol}^{-1}/\text{kJ g}^{-1})$	$T_m^e (^\circ \text{C})$	$T_{dec}^f (^\circ \text{C})$	$IS^g (\text{J})$	$FS^h (\text{N})$
3	1.882	8987	36.0	347.4/0.75		150	5	240
5	1.916	8035	28.9	-50.7/-0.14	150(-H ₂ O)	228	6	120
6	2.029	7769	27.3	-125.2/-0.31		323	4	40
7	1.854	8851	35.8	220.6/0.58		137	8	240
8	1.769	8670	31.5	220.9/0.56	94(-H ₂ O)	155	10	240
9	1.764	8343	29.4	116.2/0.33		193	10	240
10	1.692	8136	25.2	353.3/0.76		196	15	360
11	1.750	8306	27.3	791.9/1.55	185	186	16	360
12	1.763	8219	26.5	565.4/1.10		206	12	360
13	1.809	8952	34.2	1359.4/2.64	187	193	10	360
14	1.795	8542	28.9	1269.7/2.04		250	18	360
RDX ⁱ	1.800	8795	34.9	70.3/0.32	-	204	7.4	120
$\text{Pb}(\text{N}_3)_2^i$	4.800	5877	33.4	450.1/1.55		315	2.5-4	0.1-1

^a Density (measured with a gas pycnometer at 25°C .) ^b Detonation velocity calculated with EXPLO5 v6.01. ^c Detonation pressure calculated with EXPLO5 v6.01. ^d Heat of formation. ^e Melting point. ^f Decomposition temperature (onset temperature). ^g Impact sensitivity. ^h Friction sensitivity. ⁱ ref. 10

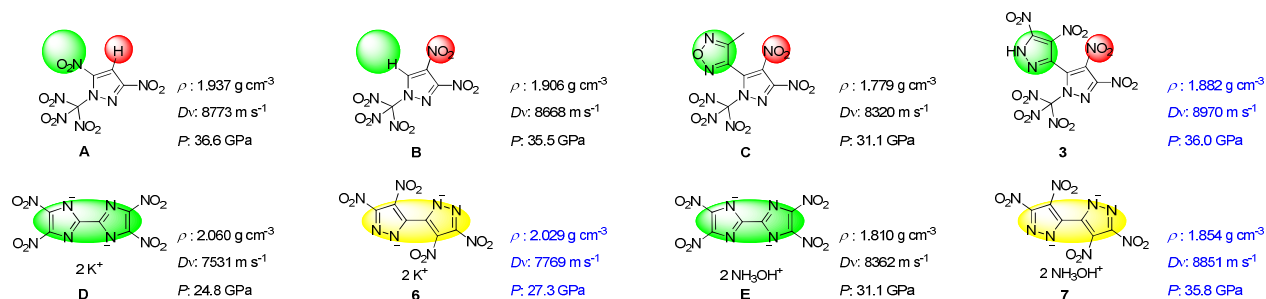


Fig. 7 A comparison of **3**, **6**, **7** and their similar compounds (**A–E**)

compound **3** has a decomposition temperature of 150 °C. Although the hydroxylammonium (**7**), and hydrazinium (**8**) salts decompose at 137 °C and 155 °C, respectively, the others show good thermal stability (> 180 °C), e.g., **14** with the triamino fused cation shows a high decomposition temperature of 250 °C. The potassium salts (**5** and **6**) also have good thermal stabilities; the monopotassium salt **5** loses water at 150 °C and decomposes at 228 °C, while the dipotassium salt **6** shows the highest decomposition temperature at 323 °C, which is higher than that (315 °C) of the commonly used primary explosive, lead azide^[11] (Table 1).

The densities were measured by using a gas pycnometer at 25 °C. The densities of the potassium salts **5** and **6** are 1.916 and 2.029 g cm⁻³. Compound **3** with a trinitro moiety also shows a high density at 1.882 g cm⁻³. In these energetic salts (**7–14**), the densities range from 1.692 g cm⁻³ (**10**) to 1.854 g cm⁻³ (**7**). The heats of formation were calculated with Gaussian03 software^[12] by using isodesmic reactions (ESI). Compounds **13** and **14** have high heats of formation.

On the basis of measured densities and heats of formation, the detonation performance was calculated by using the computer code EXPLO5 (v 6.01).^[13] Compounds **3**, **7** and **13** have high detonation velocities that exceed those of RDX (Table 1). The other energetic salts also show good detonation velocities (7769 m s⁻¹ to 8670 m s⁻¹) and detonation pressures (25.2 GPa to 31.5 GPa). These values fall in the range of well-known explosives such as RDX and TNT.^[10]

Sensitivity is especially important for handling or transportation of energetic materials. The sensitivities to impact and friction were obtained using BAM technology.^[14] The dipotassium salt **6** could be classified as sensitive compound since the impact and friction sensitivities are 4 J and 40 N, respectively. Compounds **3** and **5** are also sensitive and their impact sensitivities are 5 and 6 J, respectively. The others (**7–14**) are slightly less sensitive than RDX.

Trinitromethyl substituted compounds always show high density. The recently reported representative compounds **A**^[15] – **C**^[16] were selected for comparison with **3** in this study (Fig. 7). As can be seen, the difference in the structures from **A–C** to **3** is that they have different functional groups bonded at the 4/5 position in 1-trinitromethyl-3-nitro-pyrazole. In comparison with **3**, since the hydrogen atom at the 4/5 position in **A** and **B** is smaller than the dinitropyrazole moiety in **3**, they are more dense. However, the combination of dinitropyrazole in **3** leads

to a higher heat of formation, thus improving the detonation performance. **C** with a methyl-furazan moiety shows a density of 1.779 g cm⁻³, which is lower than that of **3**. As expected, the detonation performance is also lower than those of **3** accordingly. Although 4,4',5,5'-tetranitro-2,2'-bisimidazole (TNBI)^[4e] and TNBP have the same elemental composition, the backbone in TNBI is bisimidazole while that in **7** is bipyrazole. Their dipotassium salts (**D** and **6**) and hydroxylammonium salts (**E** and **7**) are also given in Fig. 7. It is seen that their densities are fairly similar, but the bipyrazole has two N–N bonds, which increases the heat of formation. Therefore, the potassium and hydroxylammonium salts (**6** and **7**) based on TNBP exhibit a little better detonation performance than those (**D** and **E**) based on TNBI.

Conclusions

In conclusion, a variety of energetic compounds were synthesized from 4,4',5,5'-tetranitro-2H,2'H-3,3'-bipyrazole (**1**) and thoroughly characterized, including single crystal X-ray diffraction for **3**, **5**, **8** and **10**. Some of them, such as **3**, **7** and **13**, have high densities and good detonation velocities. These calculated values are superior to the well-known secondary explosive RDX, which suggests their use in high energetic density materials (HEDM). The monopotassium salt **5** and dipotassium salt **6** may find application in the field of primary explosives. Especially for **6**, since it has a high density of 2.029 g cm⁻³ and excellent thermal stability of 323 °C.

Experimental section

Caution! The compounds in this study are potentially energetic materials which may be sensitive to impact and friction. Although we did not encounter explosions during preparation and handling of these compounds, mechanical actions of these energetic materials, involving scratching or scraping, must be avoided. Manipulations must be carried out by using appropriate standard safety precautions.

General methods

All reagents were purchased from AKSci or Alfa Aesar in analytical grade and were used as received. ¹H, ¹³C and ¹⁵N NMR spectra were recorded on a Bruker 300 MHz NMR

spectrometer or 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts for ^1H , and ^{13}C NMR spectra are reported relative to $(\text{CH}_3)_4\text{Si}$. $[\text{D}_6]\text{DMSO}$ was used as a locking solvent unless otherwise stated. Infrared (IR) spectra were recorded on an FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. Density was determined at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Melting and decomposition (onset) points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q2000) at a scan rate of $5\text{ }^\circ\text{C min}^{-1}$. Elemental analyses (C, H, N) were performed on a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made using a standard BAM Fallhammer and a BAM friction tester.

Computational Methods

The gas phase enthalpies of formation were calculated based on isodesmic reactions (Scheme S1, ESI). The enthalpy of reaction is obtained by combining the MP2/6-311++G** energy difference for the reactions, the scaled zero point energies (ZPE), values of thermal correction (HT), and other thermal factors. The solid state heat of formation of **3** was calculated with Trouton's rule according to equation (1) (T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition).^[16]

$$\Delta H_{\text{sub}} = 188 / \text{Jmol}^{-1}\text{K}^{-1} \times T \quad (1)$$

For energetic salts **5–14**, the solid-phase enthalpy of formation is obtained using a Born–Haber energy cycle.^[17] For the compounds (**5**· H_2O and **8**· H_2O), which are hydrates, the solid-phase enthalpy of formation is obtained by adding the gas phase heat of formation of the anhydrous compound to that of water ($-241.8\text{ kJ mol}^{-1}$).^[18]

X-Ray crystallography data

A clear colorless needle crystal (**3**) of dimensions $0.247 \times 0.086 \times 0.020\text{ mm}^3$ was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a PHOTON 100 CMOS detector. The crystals were irradiated using a $1\mu\text{s}$ microfocus $\text{CuK}\alpha$ source ($\lambda = 1.54178\text{ \AA}$) with Helios optics.

A clear yellow plate crystal (**5**) of dimensions $0.231 \times 0.198 \times 0.080\text{ mm}^3$, a clear yellow needle crystal (**8**) of dimensions $0.062 \times 0.023 \times 0.020\text{ mm}^3$, or a clear yellow plate crystal (**10**) of dimensions $0.198 \times 0.185 \times 0.030\text{ mm}^3$ was mounted on a MiteGen MicroMesh using a small amount of Cargille immersion oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). Data were collected at room temperature (20°C).

Data collection was performed and the unit cell was initially refined using APEX3 [v2015.5-2].^[19] Data reduction was

performed using SAINT [v8.34A]^[20] and XPREP [v2014/2].^[21] Corrections were applied for Lorentz, polarization, and absorption effects using SADABS [v2014/5].^[22] The structure was solved and refined with the aid of the programs SHELXL-2014/7.^[23] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model. In case of **8**, whole-molecule two-component disorder observed for cation and anion with a 85:15 ratio between major and minor components. Bond lengths and angles of the minor component were restrained to corresponding values in major component. Minor component thermal displacement parameters were refined isotropically.

4,4',5,5'-Tetranitro-2'-trinitromethyl-1H,2'H-3,3'-bipyrazole

(**3**): Compound **1**^[5] (1.39 g, 4.0 mmol) was dissolved in acetone (20 mL), then a solution of sodium bicarbonate (0.74 g, 8.8 mmol) in water (10 mL) was added. After stirring 30 min at room temperature, bromoacetone (1.21 g, 8.8 mmol) was added to the solution and the reaction mixture was stirred at 24 h at room temperature. The solvent was removed by air and water (50 mL) was added, then the solution was extracted with ethyl acetate ($30\text{ mL} \times 3$). The combined organic phase was dried with anhydrous sodium sulfate and the solution was concentrated by vacuum. The residue is a dark red oil, which could be solidified as brown solid by adding dichloromethane. (The solid is quite hygroscopic, and must be used immediately.) The brown solid was dissolved in concentrated sulfuric acid (6 mL) and then 100% nitric acid (5 mL) was added at $0\text{--}5\text{ }^\circ\text{C}$. The solution was stirred at room temperature for 7 days and poured into 100 mL ice-water, the white solid was collected by filtration, washed with water (50 mL) and dried with air. The pure product (0.45 g, 24%) could be obtained by recrystallization from acetone/water. white solids. $T_{\text{d (onset)}}$: $150\text{ }^\circ\text{C}$. ^{13}C NMR (d_6 -acetone): δ 150.5, 143.5, 135.8, 130.8, 129.2, 126.5, 119.4 ppm. IR (KBr): $\tilde{\nu} = 1701, 1686, 1648, 1605, 1560, 1509, 1474, 1400, 1277, 1082, 936, 867, 845, 796\text{ cm}^{-1}$. Elemental analysis for $\text{C}_7\text{HN}_{11}\text{O}_{14}$ (463.15): Calcd: C 18.15, H 0.22, N 33.27 %. Found: C 18.02, H 0.39, N 33.00 %.

Potassium 4,4',5,5'-tetranitro-2H-3,3'-bipyrazolate

monohydrate (**5**· H_2O): To a solution of **4** (0.35 g, 1.0 mmol) in acetonitrile (10 mL) was added slowly nitronium tetrafluoroborate (0.40 g, 3.0 mmol) at $0\text{ }^\circ\text{C}$. The mixture was stirred at $0\text{ }^\circ\text{C}$ for 30 min and then stirred at room temperature for 1 h. Potassium acetate (0.65 g, 6.6 mmol) was added to the solution and the mixture was stirred for another 2 h. The precipitate was removed by filtration and the filtrate was allowed to evaporate in air to give **5** as yellow crystals (0.26 g, 70%). $T_{\text{d (onset)}}$: $228\text{ }^\circ\text{C}$. ^{13}C NMR (d_6 -DMSO): δ 150.4, 135.1, 123.8 ppm. IR (KBr): $\tilde{\nu} = 1617, 1557, 1537, 1494, 1437, 1360, 1333, 1270, 1154, 1109, 1033, 950, 886, 854, 823, 808, 768, 758, 684, 658\text{ cm}^{-1}$. Elemental analysis for $\text{C}_6\text{H}_3\text{KN}_8\text{O}_9$ (370.23):

Calcd C 19.46, H 0.82, N 30.27 %. Found: C 19.06, H 0.92, N 29.94 %.

Dipotassium 4,4',5,5'-tetranitro-3,3'-bipyrazolate (6): Compound **1** (0.35 g, 1.0 mmol) was suspended in water (5 mL), then potassium bicarbonate (0.20 g, 2.0 mmol) was added. After stirring at room temperature for 1 h, the precipitate was collected by filtration and recrystallized from water/ethanol to give **6** (0.30 g, 77%). Yellow crystals. $T_{d(\text{onset})}$: 323 °C. ^{13}C NMR (d_6 -DMSO): δ 151.6, 138.7, 124.2 ppm. IR (KBr): $\tilde{\nu}$ = 1570, 1491, 1381, 1419, 1381, 1351, 1327, 1252, 1126, 1107, 944, 849, 827, 809, 768, 754, 736, 691 cm^{-1} . Elemental analysis for $\text{C}_6\text{K}_2\text{N}_8\text{O}_8$ (390.31): Calcd C 18.46, H 0, N 28.17 %. Found: C 18.49, H 0.12, N 28.94 %.

Dihydroxylammonium 4,4',5,5'-tetranitro-3,3'-bipyrazolate (7): Compound **1** (0.35 g, 1.0 mmol) was dissolved in diethyl ether (10 mL), then 50% aqueous hydroxylamine (0.15 g, 2.2 mmol) was added. After stirring at room temperature for 30 min, the precipitate was collected by filtration to give **7** (0.32 g, 84%). Yellow solid. $T_{d(\text{onset})}$: 137 °C. ^1H NMR (d_6 -DMSO): 9.39 (br) ppm. ^{13}C NMR (d_6 -DMSO): δ 151.7, 138.8, 124.1 ppm. IR (KBr): $\tilde{\nu}$ = 3230, 1587, 1536, 1498, 1426, 1390, 1363, 1340, 1330, 1285, 1202, 1167, 1155, 1111, 1012, 965, 857, 810, 769, 753, 738, 683 cm^{-1} . Elemental analysis for $\text{C}_6\text{H}_8\text{N}_{10}\text{O}_{10}$ (380.19): Calcd C 18.95, H 2.12, N 36.84 %. Found: C 18.78, H 2.35, N 37.28 %.

Dihydrazinium 4,4',5,5'-tetranitro-3,3'-bipyrazolate monohydrate (8): Compound **1** (0.35 g, 1.0 mmol) was dissolved in diethyl ether (10 mL), and hydrazine monohydrate (0.11 g, 2.2 mmol) was added. After stirring at room temperature for 30 min, the precipitate was collected by filtration and recrystallized from water/methanol to give **8** (0.35 g, 88%). Yellow crystals. $T_{d(\text{onset})}$: 155 °C. ^1H NMR (d_6 -DMSO): 7.03 (s) ppm. ^{13}C NMR (d_6 -DMSO): δ 151.3, 141.2, 124.2 ppm. IR (KBr): $\tilde{\nu}$ = 3363, 1685, 1647, 1613, 1508, 1489, 1400, 1348, 1311, 1227, 1091, 968, 958, 847, 811, 751, 617 cm^{-1} . Elemental analysis for $\text{C}_6\text{H}_{12}\text{N}_{12}\text{O}_9$ (396.23): Calcd C 18.19, H 3.05, N 42.42 %. Found: C 18.14, H 3.09, N 42.28 %.

Diammonium 4,4',5,5'-tetranitro-3,3'-bipyrazolate (9): Compound **1** (0.35 g, 1.0 mmol) was dissolved in diethyl ether (10 mL), then ammonia gas was bubbled into the solution until a precipitate formed. The precipitate was collected by filtration and washed with diethyl ether to give **9** (0.30 g, 86%). **9:** Yellow solid. $T_{d(\text{onset})}$: 193 °C. ^1H NMR (d_6 -DMSO): 7.13 (s) ppm. ^{13}C NMR (d_6 -DMSO): δ 151.3, 141.1, 124.3 ppm. IR (KBr): $\tilde{\nu}$ = 3254, 1571, 1508, 1489, 1421, 1383, 1355, 1328, 1264, 1146, 1109, 951, 851, 827, 810, 769, 737, 691 cm^{-1} . Elemental analysis for $\text{C}_6\text{H}_8\text{N}_{10}\text{O}_8$ (348.19): Calcd C 20.70, H 2.32, N 40.23 %. Found: C 20.85, H 2.44, N 40.24 %.

Di(aminoguanidinium) 4,4',5,5'-tetranitro-3,3'-bipyrazolate (10): Compound **1** (0.35 g, 1.0 mmol) was suspended in water

(5 mL), then aminoguanidinium bicarbonate (0.27 g, 2.0 mmol) was added. After stirring at room temperature for 1 h, the precipitate was collected by filtration and washed with ice-water (5 mL) (0.40 g, 87%). Yellow solid. T_m : 194 °C. $T_{d(\text{onset})}$: 196 °C. ^1H NMR (d_6 -DMSO): 8.63 (s, 1H), 7.20 (s, 2H), 6.88 (s, 2H), 4.67 (s, 2H) ppm. ^{13}C NMR (d_6 -DMSO): δ 158.8, 151.3, 141.1, 124.2 ppm. IR (KBr): $\tilde{\nu}$ = 3488, 3368, 3339, 3241, 1665, 1567, 1525, 1497, 1481, 1384, 1350, 1327, 1255, 1213, 1133, 997, 945, 850, 826, 807, 742, 696 cm^{-1} . Elemental analysis for $\text{C}_8\text{H}_{14}\text{N}_{16}\text{O}_8$ (462.30): Calcd C 20.78, H 3.05, N 48.48 %. Found: C 20.97, H 3.11, N 48.79 %.

Di(3,4-diamino-1,2,4-triazolium) 4,4',5,5'-tetranitro-3,3'-bipyrazolate (11): Compound **1** (0.35 g, 1.0 mmol) was suspended in water (5 mL), then 3,4-diamino-1,2,4-triazole (0.20 g, 2.0 mmol) was added. After stirring at room temperature for 1 h, the precipitate was collected by filtration and washed with ice-water (5 mL) (0.42 g, 82%). Yellow solid. T_m : 185 °C. $T_{d(\text{onset})}$: 186 °C. ^1H NMR (d_6 -DMSO): 8.31 (s, 1H), 7.78 (s, 2H), 6.05 (s, 2H) ppm. ^{13}C NMR (d_6 -DMSO): δ 151.4, 150.8, 141.6, 138.0, 124.0 ppm. IR (KBr): $\tilde{\nu}$ = 3378, 3303, 3160, 1696, 1625, 1559, 1511, 1482, 1410, 1382, 1350, 1309, 1228, 1142, 1081, 1019, 955, 847, 810, 776, 755, 674, 542 cm^{-1} . Elemental analysis for $\text{C}_{10}\text{H}_{12}\text{N}_{18}\text{O}_8$ (512.32): Calcd C 23.44, H 2.36, N 49.21 %. Found: C 23.32, H 2.42, N 49.25 %.

Di(3,5-diamino-1,2,4-triazolium) 4,4',5,5'-tetranitro-3,3'-bipyrazolate (12): To **1** (0.35 g, 1.0 mmol) suspended in water (5 mL), was added 3,5-diamino-1,2,4-triazole (0.20 g, 2.0 mmol). After stirring at room temperature for 1 h, the precipitate was collected by filtration and washed with ice-water (5 mL) (0.47 g, 92%). Yellow solid. $T_{d(\text{onset})}$: 206 °C. ^1H NMR (d_6 -DMSO): 5.41 (br) ppm. ^{13}C NMR (d_6 -DMSO): δ 153.2, 150.8, 137.5, 123.9 ppm. IR (KBr): $\tilde{\nu}$ = 3450, 3263, 3168, 1694, 1669, 1544, 1510, 1488, 1457, 1420, 1311, 1228, 1149, 1111, 990, 963, 903, 850, 814, 733, 680, 660 cm^{-1} . Elemental analysis for $\text{C}_{10}\text{H}_{12}\text{N}_{18}\text{O}_8$ (512.32): Calcd C 23.44, H 2.36, N 49.21 %. Found: C 23.45, H 2.44, N 49.43 %.

Di(1,5-diaminotetrazolium) 4,4',5,5'-tetranitro-3,3'-bipyrazolate (13): To **1** (0.35 g, 1.0 mmol) suspended in water (5 mL), was added 1,5-diaminotetrazole (0.20 g, 2.0 mmol). After stirring at room temperature for 1 h, the precipitate was collected by filtration and washed with ice-water (5 mL) (0.48 g, 87%). White solid. T_m : 187 °C. $T_{d(\text{onset})}$: 193 °C. ^1H NMR (d_6 -DMSO): 4.68 (br) ppm. ^{13}C NMR (d_6 -DMSO): δ 154.1, 150.0, 133.4, 124.1 ppm. IR (KBr): $\tilde{\nu}$ = 3615, 3484, 3360, 3238, 1669, 1624, 1558, 1530, 1484, 1449, 1405, 1362, 1337, 1209, 1107, 1036, 951, 852, 823, 808, 773, 756, 712, 536 cm^{-1} . Elemental analysis for $\text{C}_8\text{H}_{10}\text{N}_{20}\text{O}_8$ (514.29): Calcd C 18.68, H 1.96, N 54.47 %. Found: C 18.76, H 1.88, N 55.03 %.

Di(3,6,7-triamino-7H-[1,2,4]triazolo[5,1-c][1,2,4]triazol-2-ium) 4,4',5,5'-tetranitro-3,3'-bipyrazolate (14): To **1** (0.35 g, 1.0 mmol) suspended in water (5 mL), was added 3,6,7-triamino-

7H-[1,2,4]triazolo[5,1-c][1,2,4]triazole (0.31 g, 2.0 mmol). After stirring at room temperature for 1 h, the precipitate was collected by filtration and washed with ice-water (5 mL) (0.56 g, 90%). **14**: Yellow solid. $T_{d(\text{onset})}$: 250 °C. $^1\text{H NMR}$ (d_6 -DMSO): 7.72 (s, 2H), 7.07 (s, 2H), 5.73 (s, 2H) ppm. $^{13}\text{C NMR}$ (d_6 -DMSO): δ 159.9, 151.0, 147.7, 141.5, 139.0, 124.1 ppm. IR (KBr): $\tilde{\nu}$ = 3437, 3374, 3307, 1686, 1655, 1523, 1485, 1421, 1385, 1351, 1310, 1220, 1141, 1110, 1031, 978, 956, 905, 846, 808, 725, 707 cm^{-1} . Elemental analysis for $\text{C}_{12}\text{H}_{14}\text{N}_4\text{O}_8$ (622.40): Calcd C 23.16, H 2.27, N 54.01%. Found: C 23.17, H 2.31, N 54.42%.

Conflicts of interest

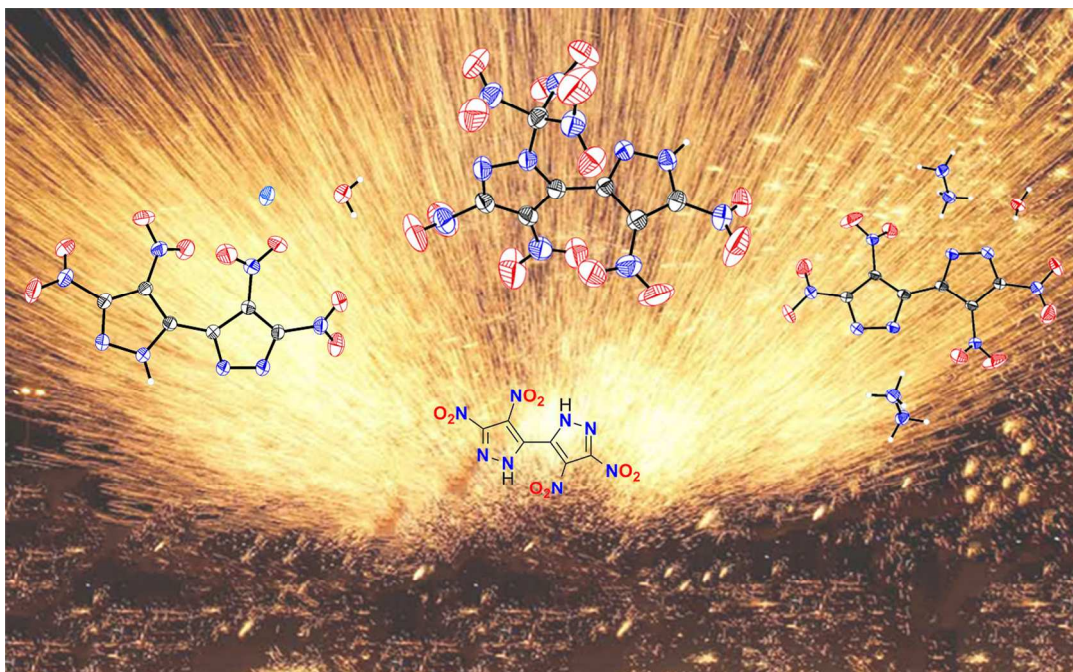
There are no conflicts to declare.

Acknowledgements

This work was supported by the Office of Naval Research (N00014-16-1-2089) and the Defense Threat Reduction Agency (HDTRA 1-15-1-0028). We are also grateful to the M. J. Murdock Charitable Trust, Reference No.: 2014120: MNL:11/20/2014 for funds supporting the purchase of a 500 MHz NMR spectrometer.

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Energetic derivatives of 4,4',5,5'-tetranitro-2H,2'H-3,3'-bipyrazole (TNBP) have been synthesized and show promise as explosives.