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Tetrazolyl and dinitromethyl groups with 1,2,3-triazole lead to polyazole energetic materials

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A class of polyazole energetic compounds (combination of tetrazolyl, dinitromethyl and triazole) was obtained from 4,5-dicyanotriazole. All the new compounds were fully characterized by IR, NMR [^{1}H, ^{13}C{^{1}H}], elemental analysis, and differential scanning calorimetry (DSC). Compounds **5, 6** and **8** were further characterized with single-crystal X-ray diffraction studies. Heats of formation and detonation performances were determined using Gaussian 03 and EXPLO5 v6.01 programs, which show that **5** is a promising green primary explosive and **7** as a secondary explosive has a detonation velocity superior to 1,3,5-trinitrotriazacyclohexane (RDX).

Introduction

Polyazole compounds are an interesting class of high energy density materials (HEDMs) which can be used as propellants, explosives or pyrotechnics in military and civilian applications.[1] Over many years, many polyazole groups that are linked directly or through energetic bridges have been reported.[2] The designers of modern polyazole compounds should consider combining properties such as high density, high detonation performance including detonation pressure and velocity, good thermal and mechanical stability, and low sensitivity.[3] The decomposition of polyazole compounds mainly releases nontoxic dinitrogen gas; however, the negative oxygen balance (OB) of energetic compounds usually gives rise to toxic gases due to incomplete combustion.[4] It is difficult to synthesize polyazole compounds with good comprehensive properties because of parameters with contradicting properties.[5]

Modern polyazole compounds derive their energy mainly from the high positive enthalpies of formation and additionally from the oxidation of their carbon backbones.[6] The enthalpy of formation of azoles increases as the number of catenated nitrogen atoms increases. Presently, pentazole and alkylated pentazoles have not been used routinely because of their poor thermal stabilities or
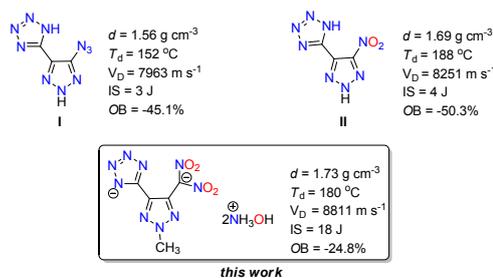
Fig. 1 Selected polyazole compounds from previous studies and this work.

sensitivities to external stimuli.[7] The combination of tetrazole and/or triazole rings could be an effective way to obtain energetic compounds with good detonation performance and safety.[8] Some similar compounds have been reported already as high performance primary[9] and secondary explosives.[10]

Earlier work showed that introduction of energetic moieties such as an azide, nitro, nitroamino, dinitromethyl or trinitromethyl group into the target molecule improves the detonation performance. Due to the higher heat of formation of 1,2,3-triazole (240 kJ mol^{-1}) compared with 1,2,4-triazole (182 kJ mol^{-1}), a large number of polyazole energetic materials which are based on the 1,2,3-triazole moiety linked with one tetrazole ring and azido/nitro group have been investigated.[11] Among them, two energetic compounds show good detonation velocities (I: V_D = 7963 m s^{-1}; II: V_D = 8251 m s^{-1}), but the density, impact sensitivity and oxygen balance of these compounds are still marginal (density < 1.7 g cm^{-3}; IS < 5J; OB < -45%) (Figure 1). Additionally, these two polyazole compounds contain highly acidic protons on the triazole ring which could cause compatibility problems in explosive charges.[12] The planarity of the dinitromethyl group not only gives rise to a more stabilizing influence than the trinitromethyl group [–C(NO$_2$)$_3$], but also it has

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an ability to enhance oxygen balance and density.[13] Now we report the synthesis, characterization and detonation properties of methylated polyazole energetic compounds resulting from the combination of tetrazolyl and dinitromethyl groups with 1,2,3-triazole (Fig. 1).

Results and discussion

Synthesis

The synthetic route to the new energetic polyazole compounds **5 9** is shown in Scheme 1. The starting material, 2-methyl-4,5-dicyano-1,2,3-triazole, **1,** was readily synthesized according to the literature.[14] Hydroximoylamine, **2,** was prepared via selectively reacting one cyano group of **1** with an equivalent amount of aqueous hydroxylamine. Aqueous sodium nitrite solution was dropped slowly into an aqueous hydrochloric acid solution containing **2** at -10 0 °C, and the amine group of **2** was diazotized to give the hydroximoyl chloride, **3**.The nitration of **3** with a mixture of trifluoroacetic acid anhydride (TFAA) and 100% HNO_3 gave a colorless oil, which was immediately treated with KI in methanol to give the yellow solid potassium salt, **5.** Subsequently, via a click reaction with sodium azide and acidification with 2 M HCl, the corresponding neutral compound was obtained as a yellow oil which decomposes slowly upon standing. The reaction of the yellow oil with a nitrogen-containing base in ethanol leads to the formation of energetic salts **6 8**. The triaminoguanidinium salt **9** was synthesized via a metathesis reaction with **6**. The structures of **5**, **6** and **8** were confirmed by single crystal X-ray diffraction analysis.

Spectral studies of compounds

All the new compounds were fully characterized by ^1H and ^{13}C {^1H} NMR and IR spectral analysis as well as elemental analysis. A signal was observed at 111.7 ppm for the carbon of the cyano group in **5**. In the ^{13}C{^1H} NMR spectra of compounds **6-9**, the carbon signals of tetrazole rings were found between 153.0-154.7 ppm. The carbon signals for the triazole rings are found in the range of 138.1-139.3 ppm for C4 and 138.3-140.5 ppm for C5. The carbon resonance of the dinitromethyl group was detected at 125.5–127.1 ppm. A signal was observed at 159.1 ppm for the carbon atoms of the triaminoguanidinium cation in **9**.

The ^{15}N NMR spectra of **6** and **9** are shown in Fig 2. They were assigned based on GIAO NMR calculations by using the Gaussian 03

program[15] and the literature values of resonance peaks in similar compounds.[16] Due to the symmetric tetrazole and dinitromethyl groups, compounds **6** and **9** give seven and eight signals, respectively. Signals of the dinitromethyl groups in **6** and **9** were observed near -21.8 ppm. The signals of N2 linked to the methyl group appear at -137.3 ppm for **6** and -138.5 ppm for **9**. The ammonium cation (δ -330.89 ppm) in **6** and triaminoguanidinium cation (δ -288.09, -328.48 ppm) in **9** were observed at high field.
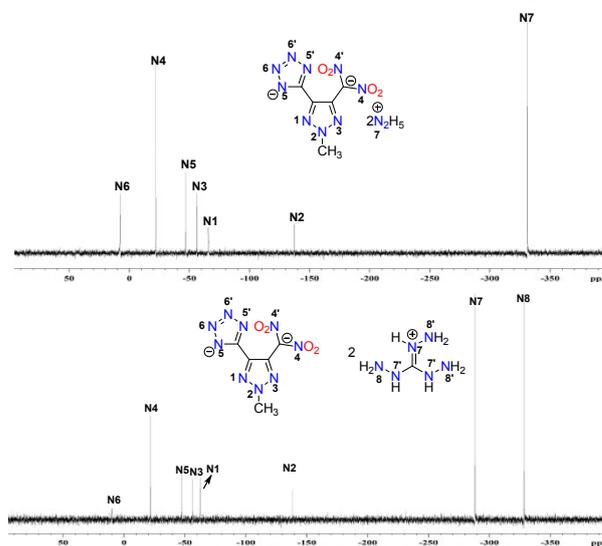
Fig. 2 ^{15}N NMR spectra of **6** and **9**.
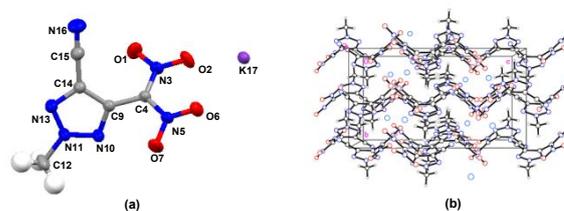
Fig. 3 (a) Molecular structure of **5**. (b) Packing diagram of **5**.
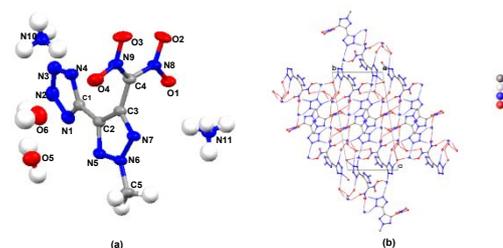
Fig. 4 (a) Molecular structure of **6**. (b) Packing diagram of **6**.
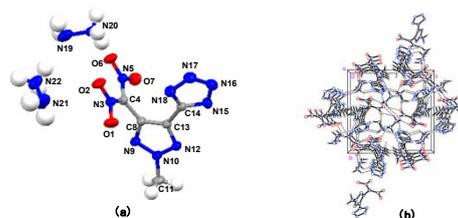
Fig. 5 (a) Molecular structure of **8**. (b) Packing diagram of **8**.
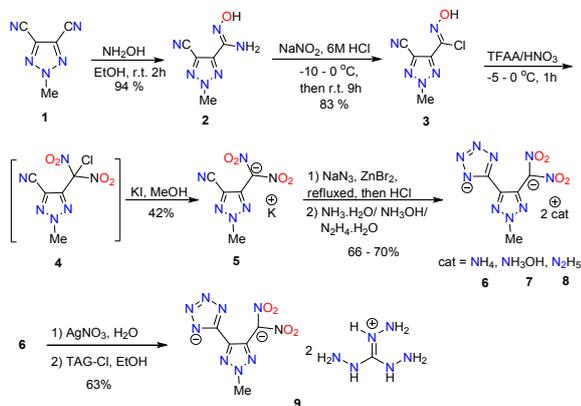
Scheme 1 Synthesis of polyazole energetic compounds **5 9**.

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Table 1 Energetic properties of compounds **5** **9**.

Comp.	r^a (g cm^{-3})	$T_m{}^e$ (°C)	$T_{dec}{}^f$ (°C)	$\triangle H_f{}^d$ (kJ mol^{-1})	$V_D{}^b$ (m s^{-1})	p^c (GPa)	IS^g (J)	FS^h (N)	OB^i (%)
5	1.79	-	194.2	201.1	7001	19.6	3	240	-19.2
6	1.63	-	153.0	402.8	8178	24.4	19	>360	-35.9
7	1.73	-	180.6	509.9	8811	30.9	18	>360	-22.4
8	1.65	-	209.5	724.0	8640	27.7	16	>360	-37.6
9	1.61	161.2	176.0	1144.9	8516	25.9	28	>360	-39.7
TNT	1.65	81.0	295	-59.4	7303	21.3	15	>353	-24.7
RDX	1.80	-	204	70.3	8795	34.9	7.4	120	0
Pb(N$_3$)$_2$	4.8	-	315	450.1	5877	33.4	2.5-4.0	0.1-1.0	0

^{a} Density measured by gas pycnometer at 25 °C. ^{b} Calculated detonation velocity. ^{c} Calculated detonation pressure. ^{d} Calculated molar enthalpy of formation in solid state. ^{e} Melting point. ^{f} Temperature of decomposition (onset). ^{g} Impact sensitivity. ^{h} Friction sensitivity. ^{i} Oxygen balance (based on CO).

Single crystal X-ray diffraction studies

Slow evaporation of an aqueous solution of **5** or of ethyl alcohol solutions (**6** and **8**) at room temperature gave yellow crystals of **5** and **6** and colorless crystals **8** for X-ray diffraction studies. Their crystal structures and unit cells are shown in Figures 3 - 6. The detailed crystallographic refinement parameters and structural data for these compounds can be found in the ESI. Compound **5** crystallizes in the orthorhombic space group *Pbca* with a density of 1.792 g cm^{-3} at 20 °C (Figure 3). The dinitromethyl and triazole rings are not planar, which is shown by a torsion angle N(5)-C(4)-C(9)-C(14) = 122.94(16)°. The lengths of the N–C bonds in the triazole ring (C14 N13: 1.345 Å; C9–N10: 1.336 Å) are slightly different because there are different substituents at C9 and C14. The packing of **5** is built up by coordinate bond interactions. The K(17) is chelated by O1, O2, O6, O7, N10, N13, N16 and the bond distances are 2.88 Å, 2.79 Å, 2.72 Å, 3.25 Å, 2.91 Å, 3.14 Å and 2.92 Å, respectively.

Ammonium salt **6** crystallizes as a dihydrate in the triclinic *P-1* space group with four formula units per cell and a crystal density of 1.573 g cm^{-3} at 173 K (Figure 4). The triazole and tetrazole rings are slightly distorted with a dihedral angle N(1)-C(1)-C(2)-N(5) = -10.36°. The C-C bond length (1.40 Å) of the triazole ring and the N-C (1.32-1.35 Å) and N-N (1.30-1.34 Å) bond lengths of both the triazole and the tetrazole rings are in the range of normal single and double bonds because of their aromaticity. The hydrazinium salt **8** is in the monoclinic *P2$_1$/n* space group with four molecules in the unit cell and a crystal density of 1.651 g cm^{-3} at 20 °C (Figure 5). The planes of the dinitromethyl group and triazole ring are almost vertical with a dihedral angel N(5)-C(4)-C(8)-N(9) = -92.26(19)°. The O2 and O6 atoms of the dinitromethyl group interact with the hydrazinium cation by forming strong hydrogen bonds [N20-H20...O1, H...A 2.31 Å, D...A 2.956(2) Å, <(DHA) 129.5°; N20-H20...O6, H...A 2.10 Å, D...A 2.912(2) Å, <(DHA) 151.1°]. Unexpectedly, there is also hydrogen bonding [N22-H22C...N19, H...A 2.05 Å, D...A 2.893(3) Å, <(DHA) 158.8°] between the two hydrazinium cations.

Physicochemical and energetic properties

The onset decomposition temperatures and thermal stabilities of compounds **5** **9** were determined using differential scanning calorimetric (DSC) measurements at a heating rate of 5 °C min^{-1} (Table 1). Although the triaminoguanidinum salt **9** melts at 161 °C, the other salts exhibit only sharp decomposition peaks with

decomposition temperatures ranging from 153 209 °C. Compound **6** has the lowest onset decomposition temperature at 153 °C, while **8** has the highest at 209 °C.

The experimental density of potassium salt **5** is 1.79 g cm^{-3}. The values of the other salts ranged between 1.61 and 1.73 g cm^{-3}. The densities of **7** (1.73 g cm^{-3}) and **8** (1.65 g cm^{-3}) equal or exceed that of the common explosive TNT (1.65 g cm^{-3}). Heats of formation of **5** **9** were calculated with Gaussian 03 software[16] based on isodesmic reactions (SI). All compounds have relatively high positive heats of formation. Based on the measured densities and calculated heats of formation, detonation performances were calculated using EXPLO5 (v 6.01).[17] Compared to the commonly used primary explosive lead azide[18] (V$_D$: 5877 m s^{-1}, P: 33.4 GPa), the potassium salt **5** has a superior detonation velocity (V$_D$: 7001 m s^{-1}) and moderate detonation pressure (19.6 GPa). Compound **7** exhibits the highest detonation velocity (8811 m s^{-1}) exceeding those of RDX (Table 1), **I** and **II** (Figure 1). The detonation pressure (30.9 GPa) approaches RDX (34.9 GPa). The other energetic compounds also exhibit good detonation velocities (8178 m s^{-1} to 8640 m s^{-1}) and detonation pressures (24.4 GPa to 27.7 GPa). These values fall in the range of well-known explosives such as RDX and TNT. Sensitivities toward impact and friction were obtained using BAM technology.[19] The potassium salt **5** is a sensitive energetic compound with an impact sensitivity of 3 J. The other polyazole compounds are less sensitive than RDX (IS: 7.4 J, 120 N), compound **I** and **II** (Figure 1). In addition, the oxygen balance (OB) values for **5** and **7** (-19.2% and 22.4%, respectively) are higher than the values of TNT, **I** and **II** (Figure 1).

Conclusion

In conclusion, a series of polyazole energetic materials combined from tetrazolyl and dinitromethyl with triazole were synthesized. All of the energetic compounds were characterized by multinuclear NMR, infrared spectra and elemental analysis. The structures of **5**, **6**, and **8** were further confirmed by X-ray diffraction. The good density, thermal stability, detonation properties, and high impact sensitivity of potassium salt **5** makes it a competitive candidate as a green primary explosive for the replacement of lead azide. Compound **7** exhibits good density and excellent calculated detonation velocity and pressure, which are close to the current secondary-explosive benchmark, RDX.

Experimental section

Caution!

Although no explosions were observed during the syntheses and handing of these compounds in this study, all manipulations should be carried out in a hood and behind a safety shield. Mechanical actions involving scratching or scraping must be avoided. Eye protection and leather gloves should be worn. All of the energetic compounds must be synthesized on a small scale.

General methods

All reagents were purchased from AKSci, VWR or Alfa Aesar in analytical grade and were used as supplied. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer or 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer. Chemical shifts for ^{1}H, and ^{13}C NMR spectra are reported relative to $(CH_3)_4Si$. [D$_6$]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 °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 Fall hammer 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. For energetic salts **5** **9**, the solid-phase enthalpy of formation was obtained using a Born–Haber energy cycle.[20]

X-ray crystallography data

A clear yellow block crystal (**5**) of dimensions 0.160 x 0.093 x 0.040 mm^{-3}, a yellow plate-shaped crystal (**6**) of dimensions 0.23 x 0.15 x 10 mm^{-3}, or a clear colorless block crystal (**8**) of dimensions 0.243 x 0.155 x 0.106 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 **5, 6** and **8** were irradiated using graphite monochromated MoK$_\alpha$ radiation (λ= 0.71073). Data of **5** was collected at 173(2) K and the data of **6** and **8** were collected at room temperature (20 °C).

Data collection was performed and the unit cell was initially refined using *APEX3* [v2015.5-2].[21] Data reduction was performed using *SAINT* [v8.34A][22] and *XPREP* [v2014/2].[23] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2014/2].[24] The structure was solved and refined with the aid of the program SHELXL-2014/7.[25] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were located from the difference electron-density maps and added using a riding model.

5-Cyano-N'-hydroxy-2-methyl-2H-1,2,3-triazole-4 carboximidamide (2). Compound **1** [(2.26 g 20 mmol)] was dissolved in ethanol (30 mL) and added over 20 min to 50% hydroxylamine solution [1.58 g (24 mmol)]. The solvent was removed under reduced pressure over 2 h. Upon filtering, **2** [3.32 g (94%)] was obtained as a yellow solid. T$_m$: 127 °C. T$_{d(onset)}$: 183 °C; ^{1}H NMR (d_6-DMSO) δ 10.30 (s, 1H), 5.91 (s, 2H), 4.27(s, 3H) ppm. ^{13}C NMR (d_6-DMSO) δ 144.9, 142.9, 116.7, 111.9, 42.9 ppm. IR (KBr): ṽ 3458, 3351, 2254, 1661, 1600, 1414, 1376, 1611, 941, 829, 737, 703 cm^{-1}; Elemental analysis (%) for C$_5$H$_6$N$_6$O (166.06): Calcd C 36.15, H 3.64, N 50.58%. Found: C 36.12, H 3.61, N 50.45%.

5-Cyano-N-hydroxy-2-methyl-2H-1,2,3-triazole-4-carbimidoyl chloride (3). Compound **2** (5.0 g, 30.1 mmol)] was dissolved in HCl (35 mL, 12 N). A solution of sodium nitrite (5.2 g, 75.3 mmol)] in water (24 mL) was added dropwise while maintaining the temperature below 0 °C and stirred for 0.5 h; then the flask was allowed to remain at ambient temperature for 6 h. Upon filtering, **3** [4.6 g (83%)] was obtained as a white solid. T$_{d(onset)}$: 150 °C; ^{1}H NMR (d_6-DMSO) δ 13.2 (s, 1H), 4.3 (s, 3H) ppm. ^{13}C NMR (d_6-DMSO) δ 144.4, 125.8, 117.3, 111.3, 43.3 ppm. IR (KBr): ṽ 3430, 3279, 2264, 1625, 1416, 1172, 1031, 914, 755 cm^{-1}; Elemental analysis (%) for C$_5$H$_4$ClN$_5$O (185.01): Calcd C 32.36, H 2.17, N 37.74%. Found: C 32.01, H 2.21, N 36.57%.

Potassium (5-cyano-2-methyl-2H-1,2,3-triazol-4-yl)dinitro methanide (5). Compound **3** (2.22 g, 12 mmol) in CHCl$_3$ (20 mL) was added dropwise to a stirred mixture of trifluoroacetic anhydride (8.4 mL) and 100% HNO$_3$ (4.8 mL), while maintaining the reaction temperature between -5 and 0 °C. After the addition was complete, the ice bath was removed, and the mixture was allowed to warm slowly to room temperature. It was stirred for another 2 h, and then poured into ice water (50 mL) and extracted with CHCl$_3$ (3 × 15 mL). The organic phases were combined, washed with water and brine, dried over sodium sulfate, and then concentrated under vacuum to provide the intermediate as a colorless oil, **4**. Then **4** was dissolved in methanol (15 mL), potassium iodide (2.39 g, 14.4 mmol) in methanol (15 mL) was added dropwise, and the mixture was stirred overnight at room temperature. The precipitate was collected by filtration and washed with cold water (3 mL), then methanol (3 mL) and ethyl ether (10 mL) to give **5** (1.42 g, 47.0%) as a yellow solid. T$_{d(onset)}$: 194 °C; ^{13}C NMR (d_6-DMSO) δ145.3, 122.6, 120.8, 111.7, 42.9 ppm. IR (KBr): ṽ 3455, 2257, 1538, 1474, 1396, 1352, 1209, 1132, 1048, 1020, 832, 749 cm^{-1}; Elemental analysis (%) for C$_5$H$_3$KN$_6$O$_4$ (249.99): Calcd C 24.00, H 1.21, N 33.59%. Found: C 24.00, H 1.25, N 34.02%.

General procedures for salts 6 8: Compound **5** (0.63 g, 2.5 mmol) was dissolved in water (25 mL) and sodium azide (0.16 g, 2.5 mmol), and zinc bromide (0.68 g, 3.0 mmol) were added. The clear solution was heated at reflux for 7 h. After several minutes, a colorless precipitate was formed. The solution was cooled to ambient temperature and 2 N HCl (10 mL) was added. The mixture was extracted with ethyl acetate (3 × 15 mL). The organic phases were combined, washed with water and brine, dried over sodium sulfate, and concentrated under vacuum to provide the intermediate as a yellow oil (560 mg). The intermediate was dissolved in ethanol (5 mL). Then 28% aqueous ammonium hydroxide (375 mg, 5.0 mmol), 50% aqueous hydroxylamine (330 mg, 5.0 mmol), or hydrazine hydrate (250 mg, 5.0 mmol) was added. After stirring 2 h at room

temperature, the product was obtained by filtration to give **6**, **7** or **8**.

Diammonium 5-(5-(dinitromethyl)-2-methyl-2H-1,2,3-triazol-4-yl)-tetrazol-1-ide (6). Yellow solid (67%). $T_{d(onset)}$: 153 °C; ^{1}H NMR (d_6-DMSO) δ 7.29 (s, 8H), 4.16 (s, 3H) ppm. ^{13}C NMR (d_6-DMSO) δ 154.7, 140.5, 139.4, 127.2, 42.8 ppm. IR (KBr): ṽ 3205, 3104, 1535, 1465, 1213, 1124, 986, 816 cm^{-1}; Elemental analysis (%) for $C_5H_{11}N_{11}O_4$ (289.10): Calcd C 20.76, H 3.83, N 53.27%. Found: C 20.63, H 3.80, N 52.43%.

Dihydroxylammonium 5-(5-(dinitromethyl)-2-methyl-2H-1,2,3-triazol-4-yl)-tetrazol-1-ide (7). Yellow solid (70%). $T_{d(onset)}$: 180 °C; ^{1}H NMR (d_6-DMSO) δ 9.16 (s, 8H), 4.22 (s, 3H) ppm. ^{13}C NMR (d_6-DMSO) δ 153.0, 138.4, 138.2, 125.5, 41.6 ppm. IR (KBr): ṽ 3518, 3112, 2362, 1628, 1538, 1459, 1398, 1246, 1127, 992, 822, 739 cm^{-1}; Elemental analysis (%) for $C_5H_{11}N_{11}O_6$ (321.09): Calcd C 18.70, H 3.45, N 47.97%. Found: C 18.62, H 3.92, N 47.34%.

Dihydrazinium 5-(5-(dinitromethyl)-2-methyl-2H-1,2,3-triazol-4-yl)-tetrazol-1-ide (8). Yellow solid (66%). $T_{d(onset)}$: 205 °C; ^{1}H NMR (d_6-DMSO) δ 7.09 (s, 10H), 4.17 (s, 3H) ppm. ^{13}C NMR (d_6-DMSO) δ 153.7, 139.4, 138.1, 126.0, 41.6 ppm. IR (KBr): ṽ 3339, 3157, 1599, 1531, 1454, 1359, 1208, 1131, 1089, 980, 938, 823, 745 cm^{-1}; Elemental analysis (%) for $C_5H_{13}N_{13}O_4$ (319.12): Calcd C 18.83, H 4.04, N 56.88%. Found: C 18.81, H 4.10, N 57.04%.

General procedure for salt 9: Silver nitrate (0.34 g, 2 mmol) was dissolved in water (5 mL) and added carefully to a solution of **6** (0.29 g, 1.0 mmol) in water (5 mL). The mixture was stirred for 2 h. After filtration, the product was obtained as a yellow solid (0.38 g). This solid was added to the methanol solution (10 mL) of triaminoguanidinium hydrochloride (228 mg, 1.62 mmol). After stirring for 2 h at room temperature, the silver chloride was removed by filtration and washed with a small amount of methanol. The filtrate was concentrated under reduced pressure and dried in vacuum to yield **9**.

Ditriaminoguanidinium 5-(5-(dinitromethyl)-2-methyl-2H-1,2,3-triazol-4-yl)-tetrazol-1-ide (9). Yellow solid (63%). T_m: 161 °C. $T_{d(onset)}$: 176 °C; ^{1}H NMR (d_6-DMSO) δ 8.59 (s, 6H), 4.50 (s, 12H)，4.14(s, 3H) ppm. ^{13}C NMR (d_6-DMSO) δ 159.1, 153.4, 140.1, 138.1, 126.0, 41.3 ppm. IR (KBr): ṽ 3580, 3331, 1684, 1599, 1530, 1455, 1364, 1219, 1115, 995, 739, 666, 608 cm^{-1}; Elemental analysis (%) for $C_6H_{13}N_{15}O_4$ (359.13): Calcd C 18.14, H 4.57, N 63.48%. Found: C 18.20, H 5.12, N 62.05%.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

1. (a) A. K. Sikder and N. Sikder, *J. Hazard. Mater.,* **2004**, A112, 1-15; (b) H. Gao and J. M. Shreeve, *Chem. Rev.* **2011**, 111, 7377-7436.
2. (a) D. E. Chavez, M. A. Hiskey and D. L. Naud, *J. Pyrotech.,* **1999**, 10, 17-36; (b) R. Wang, H. Xu, Y. Guo, R. Sa and J. M. Shreeve, *J. Am. Chem. Soc.,* **2010**, 132, 11904-11905; (c) A. A. Dippold and T. M. Klapötke, *Chem. -Eur. J.,* **2012**, 18, 16742-16753; (d) A. A. Dippold and T. M. Klapötke, *J. Am. Chem. Soc.,* **2013**, 135, 9931-9938; (e) P. Yin, D. A. Parrish and J. M. Shreeve, *Chem. - Eur. J.,* **2014**, 20, 6707-6712; (f) C. He and J. M. Shreeve, *Angew. Chem., Int. Ed.,* **2015**, 54, 6260-6264; (g) C. Bian, M. Zhang, C. Lia and Z. Zhou, *J. Mater. Chem. A,* **2015**, *3*, 163-169; (h) C. He, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A,* **2018**, 6, 16833-16837.
3. (a) H. Wei, J. Zhang., C. He and J. M. Shreeve, *Chem. -Eur. J.,* **2015**, 21, 8607-8612; (b) Y.-T. Gao, L.-M. Zhao, F.-Q. Pang, X.-J. Qi, J.-L. Huang and F.-X. Chen, *Chin. Chem. Lett.,* **2016**, 27, 433-436; (c) P. Yin, C. He and J. M. Shreeve, *Chem.- Eur. J.,* **2016**, *22*, 2108-2113.
4. J. P. Agrawal, *High Energy Materials: Propellants, Explosives and Pyrotechnics*, Wiley, 2010.
5. (a) J. P. Agrawal, High Energy Materials, Wiley-VCH, Weinheim, 2010; (b) D. Izsák, T. M. Klapötke, F. H. Lutter and C. Pflüger, *Eur. J. Inorg. Chem.,* **2016**, *2016*, 1720-1729; (c) C. Bian, X. Dong, X. Zhang, Z. Zhou, M. Zhang and C. Li, *J. Mater. Chem. A,* **2015**, 3, 3594-3601; (d) Y. Tang, C. He, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A,* **2015**, 3, 23143-23148.
6. R. Huisgen and I. Ugi, *Angew. Chem.,* **1956**, 68, 705-706.
7. R. Wang, Y. Guo, Z. Zeng, B. Twamley and J. M. Shreeve, *Chem. -Eur. J.,* **2009**, 15, 2625-2634.
8. A. A. Dippold and T. M. Klapötke, *Chem. -Asian J.* **2013**, 8, 1463-1471.
9. M. H. V. Huynh, M. A. Hiskey, T. J. Meyer and M. Wetzler, *Proc. Natl. Acad. Sci. USA,* **2006**, 103, 5409-5412.
10. (a) T. M. Klapötke and J. Stierstorfer, *Helv. Chim. Acta* **2007**, 90, 2132 -2150; (b) T. M. Klapötke, C. M. Sabate and J. Stierstorfer, *New J. Chem.,* **2009**, 33, 136-147; (c) A. Dippold, T. M. Klapötke and F. A. Martin, *Z. Anorg. Allg. Chem.,* **2011**, 637, 1181-1193.
11. (a) D. Izsák, T. M. Klapötke and C. Pflüger, *Dalton Trans.,* **2015**, 44, 17054-17063; (b) D. Izsák, T. M. Klapötke F. H. Lutter and C. Pflüger, *Eur. J. Inorg. Chem.,* **2016**, 1720-1729.
12. P. F. Pagoria, G. S. Lee, A. R. Mitchell and R. D. Schmidt, *Thermochim. Acta,* **2002**, 384, 187-204.
13. (a) Z. Zeng, H. Gao, B. Twamley and J. M. Shreeve, *J. Mater. Chem.,* **2007**, 17, 3819-3826; (b) L. Zhai, X. Fan, B. Wang, F. Bi, Y. Li and Y. Zhu, *RSC Adv.,* **2015**, 5, 57833-57841; (c) J. Zhang, S. Dharavath, L. A. Mitchell, D. A. Parrish and J. M. Shreeve, *J. Am. Chem. Soc.,* **2016**, 138, 7500-7503; (d) X. X. Zhao, S. H. Li, Y. Wang, Y. C. Li, F. Q. Zhao and S. P. Pang, *J. Mater. Chem. A,* **2016**, *4*, 5495-5504; (e) H. Li, F.-Q. Zhao, B.-Z.Wang, L.-J. Zhai, W.-P. Lai and N. Liu, *RSC Adv.,* **2015**, 5, 21422-21429; (f) L. Zhai, B. Wang, K. Xu, H. Huo, N. Liu, Y. Li, H. Li, P. Lian and X. Fan, *J. Energ. Mater.,* **2016**, 34, 92-102; (g) H. Huang, Y. Li, J. Yang, R. Pan and X. Lin. *New J. Chem.,* **2017**, 41, 7697-7704.
14. R. Walter and L. Joannis, *Chemiker-Zeitung,* **1989**, 113, 384-385;
15. (a) D. Kumar, G. H. Imler, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A,* **2017**, 5, 16767-16775; (b) Q. Yu, G. H. Imler, D. A. Parrish and J. M. Shreeve, *Chem.- Eur.J.*, **2017**, 23,17682 – 17686.
16. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y.

Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Rabuck, K. Raghavachari, J. B. Foesman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, A. Lo. G. Liu, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. Wong, C. Gonzalez and J. A. Pople, Gaussian 03 (*Revision E.01*), Gaussian, Inc, Wallingford CT, 2004.

17. M. Sucéska, EXPLO5, *Version 6.01*, Brodarski Institute, Zagreb, Croatia, 2013.

18. D. Fischer, T. M. Klapötke and J. Stierstorfer, *Angew. Chem., Int. Ed.,* **2014**, 53, 8172-8175.

19. (a) www. bam. de; (b) U. M. Regulations,, *UN Recommendations on the Transport of Dangerous Goods, Manual of Tests and Criteria*, 5th edn, United Nations Publication, New York, 2009; (c) 13.4.2 Test 3 (a)(ii) BAM Fallhammer, p. 75; d) 13.5.1 Test 3 (b)(i): BAM friction apparatus, p. 104.

20. H. Gao, C. Ye, C. M. Piekarski and J. M. Shreeve, *J. Phys. Chem. C*, **2007**, 111, 10718-10731.

21. Bruker (2015). *APEX3 v2015.5-2*. Bruker AXS Inc., Madison, Wisconsin, USA, 2015.

22. Bruker (2013). *SAINT v8.34A*. Bruker AXS Inc., Madison, Wisconsin, USA, 2013.

23. Bruker (2014). *XPREP v2014/2*. Bruker AXS Inc., Madison, Wisconsin, USA, 2014.

24. Bruker (2014). *SADABS v2014/5*, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.

25. Sheldrick, G. M. *(2014). SHELXL-2014/7*. University of Göttingen, Germany., 2014

I
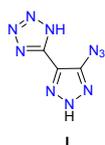
d = 1.56 g cm^{-3}
T_d = 152 °C
V_D = 7963 m s^{-1}
IS = 3 J
OB = -45.1%

II

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T_d = 188 °C
V_D = 8251 m s^{-1}
IS = 4 J
OB = -50.3%
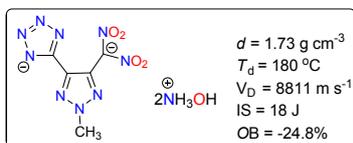
d = 1.73 g cm^{-3}
T_d = 180 °C
V_D = 8811 m s^{-1}
IS = 18 J
OB = -24.8%

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