Azo- and methylene-bridged mixed azoles for stable and insensitive energetic applications

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Azo- and methylene-bridged mixed azoles for stable and insensitive energetic applications

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A simple synthetic strategy for the preparation of high nitrogen content azo- and methylene bridged mixed energetic azoles was used. All new compounds were fully characterized by NMR and infrared spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). In addition, the structures of energetic salts **7** and **10** were confirmed by single-crystal X-ray diffraction analysis. Detonation performances, calculated from heats of formation and experimental densities, thermal stabilities, and impact and friction sensitivities suggest possible applications in the field of insensitive energetic materials.

Introduction

In recent times, nitrogen-rich energetic materials have received considerable attention from the materials science, physical, organic and theoretical chemistry communities due to their high density, energy content and vital applications as propellants, explosives and pyrotechnics.[1] Nitrogen-rich five membered ring heterocycles (pentazole, tetrazole, triazole, pyrazole, furazan, etc.) are the most promising compounds in the field of energetic materials research.[2] Compared to other five membered ring heterocycles, triazoles and tetrazoles possess high densities and high heats of formation which are widely used for the preparation of primary and secondary explosives.[3] Specifically, triazoles and tetrazoles which contain the amine have been used to prepare high nitrogen-rich, azo-bridged energetic materials with improved densities and heats of formation.[4] Azo-bridged bistetrazoles and bistriazoles were found to be sensitive energetic materials, whereas their nitrogen-rich energetic salts were less sensitive.[5] Additionally, insertion of an alkyl bridge between these energetic azoles was found to lead to insensitivity relative to the azoles themselves.[6]

5-Amino-3-nitro-1,2,4-triazole (ANTA) **1** is one of the most promising triazole compounds with a combination of a high nitrogen content and a high heat of formation. Structurally, ANTA contains both primary and secondary amines and it can be prepared from readily available starting materials.[7] The primary amine of ANTA was used for oxidative azo-coupling to generate 3,3'-dinitro-5,5'-azo-1H-1,2,4-triazole (DNAT), which exhibits high density and a positive heat of formation, but it is sensitive to friction.[8] As a part of alkyl bridged azoles, our group has reported excellent thermostable and high performing *N,N'*-ethylene-bridged bis(nitroimino)tetrazoles using ANTA.[9] Later in 2016, the methylene-bridged azole compounds were reported to be more energetic than the ethylene bridged analogues.[10]

During the last few years our group has synthesized various energetic compounds with *N*-methylene bridged tetrazole derivatives based on the combination of trinitro pyrazole and nitramino tetrazole.[11] Encouraged by our previous results, we now have synthesized two different compounds: (i) a combination of 5,5'-azo-3,3-dinitrotriazole and methyl tetrazole, and (ii) a combination of 5-amino-3-nitro-1,2,4-triazole or 5-nitroimino-3-nitro-1,2,4-triazole with methyl tetrazole. Additionally, both *N*-methylene bridged tetrazole compounds **3** and **8** were used for the preparation of energetic salts. All the new compounds have high nitrogen content and they are well characterized. Most of these energetic compounds have good thermal stabilities and the salts have good detonation properties approaching those of RDX.

Results and discussion

Synthesis

The synthesis of 1-((1*H*-tetrazol-5-yl)methyl)-5-nitro-1*H*-1,2,4-triazol-3-amine **3** resulted from the *N*-acetonitrilation of 3-amino-5-nitro-1*H*-1,2,4-triazole **1** followed by conversion of the nitrile with excess sodium azide. Compound **3** was reacted with potassium permanganate ($KMnO_4$) in acidic medium to obtain the azo-bridged derivative **4**. Compound **3** was further used for the preparation of energetic salts **5**–**7** by simple neutralization with nitrogen-rich bases. It was suspended in acetonitrile, the corresponding base was added, and the suspension stirred at room temperature for 2 h. The yellow solid salts **5**–**7** were collected by filtration and purified by recrystallization from methanol (Scheme 1).

Compound **3** was reacted with 100 % freshly distilled nitric acid at -5 °C for 12 hours to give the nitramine compound **8**. The energetic salts 9-11 were prepared by the simple neutralization reaction of **8** with nitrogen-rich bases. Compound **8** was suspended in ethanol, the corresponding base was added, and the suspension stirred at room temperature for 2 h. The yellow salts were collected by filtration and crystalized from ethanol (Scheme 1).

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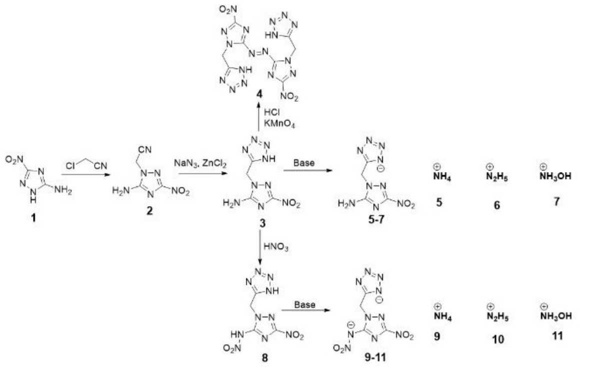

Scheme 1 Synthesis of energetic derivatives based on mixed azoles.

Compounds **2**–**11** were fully characterized by NMR and IR spectroscopy, as well as elemental analysis. Methylene bridged mixed azoles were observed between the range of 5.31-5.76 ppm in the ^1H ppm and 41.3-43.5 ppm in ^{13}C in the NMR spectra. For compounds **2**, **3**, **5**–**7**, amine signals were observed over the range of 7.12-7.44 ppm; for compound **8**, the nitramine signal was observed at 12.27 ppm and the amine proton signal had disappeared for the azo-bridged compound **4**. In the ^{13}C NMR spectra of compounds **2**–**11**, signals corresponding to the triazole and tetrazole ring carbons were observed in the range of 152.98–161.20 ppm. Further, ^{15}N NMR spectra were used to understand the structures of compound **3** and compound **4**. In case of **3**, the NH_2 signal is seen at 323.04 ppm and it has disappeared to form the azo-bridged nitrogen of 119.30 ppm in compound **4** (Fig. 1).

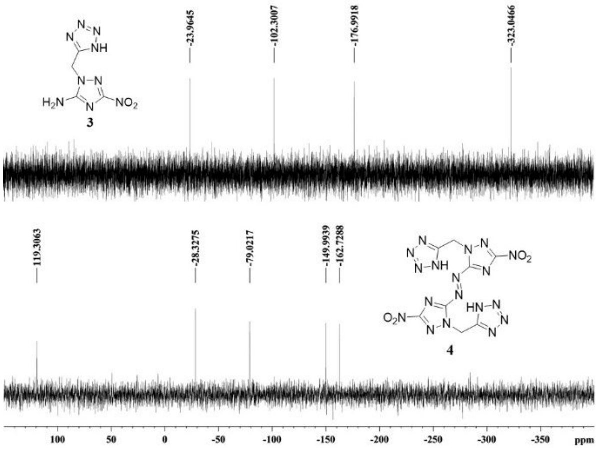

Fig. 1 ^{15}N NMR spectra of **3** and **4**.

Single crystal X-ray diffraction analysis

Suitable crystals of compounds **7** and **10** were obtained by slow evaporation of their saturated solutions in mixtures of methanol/water. Their crystal structures are given in Fig. 2 and 3. Compound **7** (CCDC 1985501) crystallizes in the triclinic space group P1 with two units in the lattice cell (Z = 2) and a density of 1.742 g cm^{-3} at 100 K. Compound **10** (CCDC 1975376) has monoclinic space group P2$_1$/c symmetry with four units in the lattice cell (Z = 4) and a crystal density of 1.709 g cm^{-3} at 173 K.

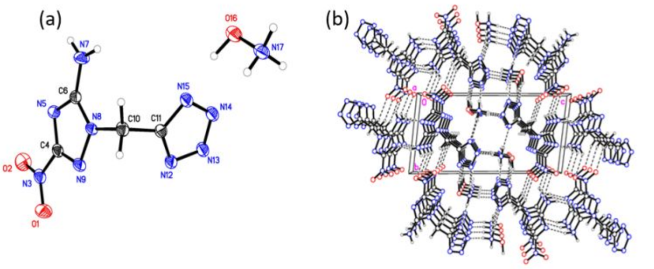

Fig. 2 (a) Thermal ellipsoid plot (50%) and labeling scheme for **7**. (b) Ball-and-stick packing diagram of **7** viewed up the b axis. Dashed lines indicate strong hydrogen bonding.

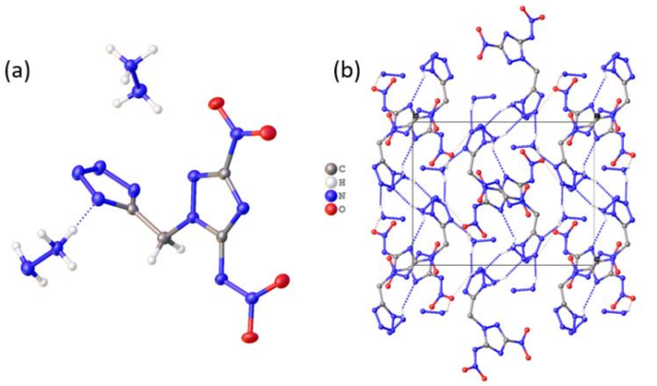

Fig. 3 (a) Thermal ellipsoid plot (50%) and labeling scheme for **10**. (b) Ball-and-stick packing diagram of **10** viewed up the b axis. Dashed lines indicate strong hydrogen bonding.

In both crystal structures, the geometry of the bridging methylene carbon is nearly tetrahedral with the *N*-methylene-C angles N(8)-C(10)-C(11) = 110.76(12)° (**7**) and N(3)–C(3)–C(4) = 111.95(12)° (**10**). The dihedral angles between the mean planes through the 5-nitro-3-amino-1,2,4-triazole and tetrazole rings were found to be in the range 77.31° (**7**) to 85.55° (**10**). The bond lengths in the 1,2,4-triazole ring and tetrazole ring are between typical single and double bonds. In **7**, the bond lengths of triazole C-NH_2, C6–N7 is 1.326(2) Å and C-NO_2, C4–N3 is 1.449(19) Å. Similarly, in **10**, the bond lengths of triazole C-NNO_2, C1–N4 is 1.373(19) Å and C-NO_2, C2–N6 is 1.448(2) Å. In both energetic salts, C-NH_2 and C-NNO_2 bond lengths are significantly changed.

In the crystal packing of compounds **7** and **10** are shown many strong intermolecular hydrogen interactions due the presence of amino groups, nitro oxygen atoms and nitrogen atoms in both the anions and cations (Fig. 2b and 3b). In compound **7**, the NH_2 and NO_2 groups of the nitrogen-rich anion participated in hydrogen bonding with adjacent nitrogen-rich anions (N(7)–H(7A)···N(5) and N(4)–H(7B)···O(2)) to form 2D layers which are further linked by hydrogen bonding with hydroxylamine to form a 3D framework. In this arrangement hydroxylamine forms five hydrogen bonds with adjacent nitrogen-rich anions (O(16)–H(16)···N(15), N(17)–H(17A)···N(13), N(17)–H(17B)···N(14) and N(17)–H(17C)···N(12)) (ESI Table S8). Similarly, in compound **10**, amine groups of the hydrazinium cation participated in hydrogen bonding with adjacent nitrogen-rich anions. In this arrangement each hydrazinium cation formed with four adjacent nitrogen-rich anions [(N(11)–H(11A)···N(8), N(11)–H(11B)···N(4), N(12)–H(12A)···O(1), N(11)–H(11C)···N(1)) and (N(14)–H(14A)···N(9), N(14)–H(14B)···N(10), N(14)–H(14C)···O(1), N(14)–H(14C)···O(3)] (ESI

Table S16). The packing coefficient is calculated by the ratio of total molecular volume and unit cell volume to understand the crystal density of compounds **7** and **10**. Based on the ratio of 75.3% for compound **7** suggests a slightly high density than for compound **10** at 74.7%.

Physicochemical and energetic properties

Thermal stabilities of **2–11** were determined using differential scanning calorimetric (DSC) measurements with a heating rate of 5 °C min^{-1}. All the nitrogen rich compounds decompose ($T_{d\ onset}$) in the range 149 (**8**) and 250 (**3**) °C. Apart from the nitramine compound **8** (T_d = 149 ℃) and the azole derivative **4** (T_d = 171 ℃), all other compounds were found to have decomposition temperatures higher than RDX (T_d = 204 ℃). The densities of all new compounds were measured using a gas pycnometer at 25 ℃ and the values range between 1.615 (**5**) and 1.770 (**8**) g·cm^3. Except for **5**, all new compounds have higher densities than TNT (1.650 g·cm^3), with **3** (1.757 g·cm^3), **4** (1.742 g·cm^3) and **8** (1.770 g·cm^3) approaching RDX (1.80 g·cm^3).

Heats of formation of **3–11** were calculated by using the Gaussian 03 suite of programs with isodesmic reactions (ESI).[12] All these high nitrogen compounds have relatively high positive heats of formation (ΔH_f) between 447.9 to 1292.8 kJ·mol^{-1}, and are significantly higher than both TNT (59.4 kJ·mol^{-1}), ANTA (21.0 kJ·mol^{-1}) and RDX (92.6 kJ·mol^{-1}). Based on the values of experimental densities and calculated heats of formation, detonation properties were determined using EXPLO5 (version 6.01).[13] The calculated detonation pressures (P) range between 23.27 and 32.87 GPa and calculated detonation velocities (Dv) between 8059 and 8995 m·s^1. All new energetic compounds have better detonation properties than TNT and few of them has better properties compared with ANTA. Compounds **6** (P: 27.10 GPa, Dv: 8564 m·s^1), **7** (P: 28.04 GPa, Dv: 8590 m·s^1), **8** (P: 32.87 GPa, Dv: 8759 m·s^1), **10** (P: 30.53 GPa, Dv: 8933 m·s^1), and **11** (P: 31.92 GPa, Dv: 8870 m·s^1) exhibit detonation properties approaching RDX (P: 34.9 GPa, Dv: 8795 m·s^1). Impact and friction sensitivity values were obtained by using BAM drop hammer and friction tester techniques.[14] All new compounds except **8** were found to be insensitive (IS > 40 J, FS > 360 N) to both impact and friction, and **8** (IS: 22 J, FS: 240 N) is less sensitive compared than RDX (IS: 7.5 J, FS: 120 N) (Table 1).

Table 1. Energetic properties of new compounds compared to TNT, ANTA and RDX.

z	$T_d{}^a$(℃)	P^b[g cm^{-3}]	$\Delta H_f{}^c$[kJ mol^{-1}/kJ g^{-1}]	$D_v{}^d$[m s^{-1}]	P^e[GPa]	IS^f[J]	FS^g[N]
3	242	1.75	651.8/3.08	8631	29.03	>40	>360
4	171	1.74	1292.8/3.09	8311	27.11	>40	>360
5	250	1.61	517.9/2.27	8059	23.27	>40	>360
6	209	1.66	681.2/2.80	8564	27.10	>40	>360
7	246	1.70/1.74^h	564.33/2.29	8590	28.04	>40	>360
8	149	1.77	706.7/2.76	8759	32.87	22	240
9	207	1.72	447.9/1.54	8662	28.55	>40	>360
10	208	1.69/1.71^i	793.81/2.47	8933	30.53	>40	>360
11	218	1.72	587.8/1.82	8870	31.92	>40	>360
TNT^j	294	1.65	-59.4/-0.26	7303	21.3	15	353
ANTA^k	238	1.82	21.0/0.16	8460	31.4	>40	>360
RDX^j	204	1.80	92.6/0.41	8795	34.9	7.5	120

[a] Decomposition temperature (onset). [b] Density – gas pycnometer at 25 °C. [c] Calculated molar enthalpy of formation. [d] Calculated detonation velocity. [e] Calculated detonation pressure. [f] Impact sensitivity. [g] Friction sensitivity, [h] Crystal density at 100 K, [i] Crystal density at 173 K, [j] Ref. 11b, [k] Ref. 7b and 7c.

Conclusion

In summary, a new high nitrogen azo- and methylene bridged mixed azole **4** was synthesized as well as its half unit of methylene bridged mixed azole **3**. The methylene bridged mixed azole **3** was used for synthesis of a nitroimino mixed azole and its energetic salts. Most of these new compounds have good thermal stabilities and sensitivities. All energetic compounds have positive heats of formation with energetic compound **8** at D_v, 8759 m·s^{-1}; P, 32.87 GPa. Other salts, **7** (D_v, 8590 m·s^{-1} ; P, 28.04 GPa), **10** (D_v, 8933 m·s^{-1}; P, 30.53 GPa) and **11** (D_v, 8870 m·s^{-1}; P, 31.92 GPa) have better detonation properties than TNT and ANTA which were comparable with RDX (D_v, 8795 m·s^{-1}; P, 34.9 GPa).

Experimental Section

Caution! Although no explosions or detonations occurred during the preparation and handling of these energetic materials, all reactions should be carried out on a small scale with appropriate safety precautions (safety glasses, face shields, ear plugs, as well as gloves).

General methods

Reagents were purchased from Aldrich and Acros Organics and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13 and 75.48 MHz, respectively, by using DMSO-d_6 as the solvent and locking solvent. ^{15}N spectra were obtained on a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz. The decomposition temperatures were obtained on a differential scanning calorimeter (TA Instruments Company, Model: Q2000) at a scan rate of 5 °C min^{-1}. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films using KBr plates. Density was measured at room temperature by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses (C, H, N) were determined using a Vario Micro cube Elementar Analyser. The impact and friction sensitivities were tested by employing a standard BAM drop hammer and BAM friction tester.

2-(5-Amino-3-nitro-1*H*-1,2,4-triazol-1-yl)acetonitrile (2). To a suspension of 3-nitro-1*H*-1,2,4-triazol-5-amine **1** (0.5 g, 3.87 mmol) in DMF (5 mL), tetraethylammonium bromide (TEAB, 0.08 g, 0.4 mmol) and KOH (0.21 g, 10 mmol) were added. The reaction was warmed to 70 °C for 0.5h. Chloroacetonitrile (0.35 g, 4.6 mmol) was added drop wise and the final orange suspension was held at 70 °C overnight. The reaction mixture was poured into cold water (20 mL) and stirred for an additional 0.5 h. The precipitate was filtered, washed with water and dried in the air to give **2** as a yellowish solid. Yield: 0.40 g, 62%. T_m (5 °C min^{-1}): 203 °C (onset). T_{dec} (5 °C min^{-1}): 225 °C (onset); ^{1}H NMR (DMSO-d_6): δ 7.44 (s, 2H, NH_2); 5.37 (s, 2H, CH_2); ^{13}C NMR (DMSO-d_6): δ 161.2, 158.0, 115.8, 37.15; IR (KBr pellet): ν 3422, 3295, 3166, 2961, 2931, 2271, 1641, 1571, 1550, 1552, 1438, 1413, 1315, 1263, 1151, 1086, 952, 878, 807, 762 cm^{-1}; Anal. Calcd for $C_4H_4N_6O_2$ (168.11): C, 28.58; H, 2.40; N, 49.99; found: C, 28.86; H, 2.75; N, 49.54.

1-((1*H*-Tetrazol-5-yl)methyl)-3-nitro-1*H*-1,2,4-triazol-5-amine (3). A solution of zinc chloride [0.95 g, 2.97 mmol in H_2O (2 mL)] was added to mixture of **2** (0.50 g, 2.97 mmol) and sodium azide (0.23 g, 3.56 mmol) in distilled water (5 mL). The resulting mixture was heated at 80 °C for 24 h. Then the reaction was cooled to room temperature and acidified with concentrated hydrochloric acid to reach pH~1. The reaction mixture was stirred for an additional 30 minutes at room temperature. The resulting precipitate was collected by filtration and washed with cold water (5 mL), and dried at room temperature by air to yield **3** as a yellow solid. Yield: 0.62 g, 99.6%. T_{dec} (5 °C min^{-1}): 242 °C (onset). ^{1}H NMR (DMSO-d_6): δ 7.31 (s, 2H, NH_2), 5.69 (s, 2H, CH2). ^{13}C NMR (DMSO-d$_6$): δ 159.8, 156.9, 153.0, 41.4. ^{15}N NMR (DMSO-d$_6$, ppm): 23.96, 102.30, 176.99, 323.04. IR (KBr pellet): **ν** 3411, 3317, 3245, 3184, 3008, 2905, 2797, 2746, 1651, 1584, 1560, 1529, 1452, 1426, 1412, 1312, 1253, 1092, 1055, 1030, 998, 862, 751, 710, 632, 504 cm^{-1}. Anal. Calcd for $C_4H_5N_9O_2$ (211.14): calcd C, 22.75; H, 2.39; N, 59.70; Found: C 22.98, H 2.52, N 58.93.

1,2-Bis(1-((1*H*-tetrazol-5-yl)methyl)-5-nitro-1*H*-1,2,4-triazol-3-yl)diazene (4). Compound **3** (0.60 g, 2.8 mmol) was dissolved in concentrated hydrochloric acid (10 mL) and distilled water (20 mL). The resulting mixture was cooled to 0 °C. Then $KMnO_4$ (0.45 g, 2.8 mmol) suspended in minimum amount of distilled water was added drop wise while maintaining the reaction temperature at < 10 °C. The resulting solution was warmed to room temperature and stirred for 24 h. A light brown precipitate was formed, and it was decolorized by addition of H_2O_2 (5%). The precipitate was collected by filtration, washed with water and dried by air to yield **4** as a yellow solid. Yield: 0.34 g, 57%. T_{dec} (5 °C min^{-1}): 171 °C (onset). ^{1}H NMR (DMSO-d$_6$): δ 6.43 (s, 4H, CH$_2$).^{13}C NMR (DMSO-d$_6$): δ 161.1, 157.4, 152.9, 44.2. IR (KBr pellet): **ν** 3496, 2984, 2897, 1646, 1562, 1510, 1484, 1425, 1389, 1364, 1316, 1233, 1144, 1086, 1054, 952, 863, 813, 712, 645. Anal. Calcd for $C_8H_{10}N_{18}O_6$ (454.10, M+2H$_2$O): calcd C 21.15, H 2.22, N 55.50%. Found: C 20.90, H 2.33, N 54.94%.

Ammonium-5-((5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)methyl)tetrazol-1-ide (5). Compound **3** (0.20 g, 0.95 mmol) was dissolved in acetonitrile (5 mL) and aqueous ammonia (28%, 2 mL) was added dropwise. The resulting solution was stirred at room temperature for 2 h. The pale-yellow precipitate was filtered, washed with acetonitrile (2 mL), and dried in the air to yield **5** as a white solid. Yield: 0.21 g, 97%. T_{dec} (5 °C min^{-1}): 250 °C (onset). ^{1}H NMR (DMSO-d$_6$): δ 7.12 (s, 2H, NH$_2$), 5.31 (s, 2H, CH$_2$), 3.49 (s, 4H, NH$_4$). ^{13}C NMR (DMSO-d$_6$): δ156.4, 156.1, 43.5. IR (KBr pellet): **ν** 3450, 1644, 1573, 1522, 1401, 1327, 1313, 1261, 1126, 866, 722, 629 cm^{-1}. Anal. Calcd for $C_4H_8N_{10}O_2$ (228.17, M+1.5H$_2$O): calcd C 18.83, H 4.34, N 54.89%. Found: C 18.93, H 4.35, N 54.91%.

Hydrazinium-5-((5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl)methyl)-tetrazol-1-ide (6). Compound **3** (0.20 g, 0.95 mmol) was dissolved in acetonitrile (5 mL) and hydrazine monohydrate (2 mL) was added dropwise to acetonitrile (2.0 mL). The resulting solution was stirred at room temperature for 2 h. The yellowish precipitate was filtered, washed with acetonitrile (2.0 mL), and dried in the air to yield **6** as yellow solid. Yield: 0.22 g, 96%. T_{dec} (5 °C min^{-1}): 209 °C (onset). ^{1}H NMR (DMSO-d$_6$): δ 7.15 (s, 2H, NH$_2$), 5.34 (s, 2H, CH$_2$), 4.57 (s, 5H, N$_2$H$_5$). ^{13}C NMR (DMSO-d$_6$): δ 159.0, 156.5, 156.2, 43.5. IR (KBr pellet): **ν** 3521, 2994, 2970, 2958, 2946, 2920, 1644, 1576, 1507, 1409, 1313, 1143, 1143, 1129, 1109, 1007, 865, 764, 720, 555 cm^{-1}. Anal. Calcd for $C_4H_9N_{11}O_2$ (243.19): calcd C 19.76, H 3.73, N 63.36%. Found: C 19.79, H 3.78, N 62.60%.

Hydroxylammonium-5-((5-amino-3-nitro-1*H*-1,2,4-triazol-1-yl) methyl)tetrazol-1-ide (7). Compound **3** (0.20 g, 0.95 mmol) was dissolved in acetonitrile (5 mL) and aqueous hydroxylamine (50%, 2 mL) was added dropwise in acetonitrile (2.0 mL). The resulting solution was stirred at room temperature for 2 h. The pale-yellow precipitate was filtered, washed with acetonitrile (2.0 mL), and dried in the air to yield **7** as a yellow solid. Yield: 0.22 g, 95%. T_{dec} (5 °C min^{-1}): 246 °C (onset). ^{1}H NMR (DMSO-d$_6$): δ 7.17 (s, 2H, NH$_2$), 5.97 (s, 4H, NH$_3$OH), 5.40 (s, 2H, CH$_2$). ^{13}C NMR (DMSO-d$_6$): δ 159.3, 156.7, 156.1, 43.2. IR (KBr pellet): **ν** 3441, 1643, 1572, 1549, 1523, 1410, 1327, 1314, 1110, 868, 719, 677 cm^{-1}. Anal. Calcd for $C_4H_8N_{10}O_3$ (244.17): calcd C 19.68, H 3.30, N 57.36%. Found: C 19.77, H 3.35, N 57.15%.

N-(1-((1*H*-tetrazol-5-yl)methyl)-3-nitro-1*H*-1,2,4-triazol-5-yl) nitramide (8). Compound **3** (0.60 g, 2.8 mmol) was dissolved in nitric acid (100% fuming, 3 mL) at -10 ℃ and stirred for 2 hours at the same temperature and followed at room temperature for overnight. The resulting mixture was poured into crushed ice (~50 grams) and the organic compound was collected after washing with brine solution in EtOAc. The organic layer was dried over Na_2SO_4 and the solvent was removed by air blower at room temperature to yield **8** as yellow solid. Yield: 0.57 g, 79%. T_{dec} (5 °C min^{-1}): 149 °C (onset). ^{1}H NMR (DMSO-d$_6$): δ 12.27 (s,b, 1H, NH), 5.72 (s, 2H, CH$_2$). ^{13}C NMR (DMSO-d$_6$): δ 160.2, 155.3, 152.8, 41.7. IR (KBr pellet): **ν** 3148, 2782, 1706, 1598, 1436, 1384, 1287, 1192, 1109, 966, 905, 843, 799. Anal. Calcd for $C_4H_4N_{10}$O4 (256.04): calcd C 18.76, H 1.57, N 54.68%. Found: C 19.05, H 1.83, N 54.44%.

Ammonium (1-((1*H*-tetrazol-5-yl)methyl)-5-nitro-1*H*-1,2,4-triazol-3-yl)(nitro)amide (9+H$_2$O). Compound **8** (0.30 g, 1.2 mmol) was dissolved in ethanol (3 mL) and aqueous ammonia (28%, 1.0 mL) was added in ethanol (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 2 hours. A yellow precipitate was formed and collected by filtration and dried by air blower at room temperature to yield **9** as a yellow solid. Yield: 0.21 g, 93%. T_{dec} (5 °C min^{-1}): 207 °C (onset). ^{1}H NMR (DMSO-d$_6$): δ 7.14 (s,b, 8H, NH), 5.37 (s, 2H, CH$_2$). ^{13}C NMR (DMSO-d$_6$): δ 159.6, 156.5, 156.2, 43.1. IR (KBr pellet): **ν** 3422, 3190, 1621, 1559, 1492, 1395, 1301, 1134, 1027, 783 cm^{-1}. Anal. Calcd for $C_4H_{12}N_{12}O_5$ (308.10): calcd C 15.59, H 3.92, N 54.53%. Found: C 15.80, H 3.78, N 54.16%.

Hydrazinium (1-((1*H*-tetrazol-5-yl)methyl)-5-nitro-1*H*-1,2,4-triazol-3-yl)(nitro)amide (10). Compound **8** (0.20 g, 0.8 mmol) was dissolved in ethanol (3 mL) and hydrazine monohydrate (0.5 mL) in ethanol (2 mL) was added at room temperature. The resulting mixture was stirred at room temperature for 2 hours. A yellow precipitate was formed and collected by filtration and dried by air blower at room temperature to yield **10** as a yellow solid. Yield: 0.22 g, 89%. T_{dec} (5 °C min^{-1}): 208 °C (onset). ^{1}H NMR (DMSO-d$_6$): δ 6.18 (s, 5H, N$_2$H$_5$), 5.40 (s, 2H, CH$_2$). ^{13}C NMR (DMSO-d$_6$): δ 159.7, 156.5, 43.2ppm. IR (KBr pellet): **ν** 3468, 3181, 2892, 1638, 1561, 1488, 1383, 1317, 1024, 1013, 824, 784 cm^{-1}. Anal. Calcd for $C_4H_{12}N_{14}O_4$ (320.11): calcd C 15.00, H 3.78, N 61.24%. Found: C 15.17, H 4.029, N 60.36%.

Hydroxylammonium (1-((1*H*-tetrazol-5-yl)methyl)-5-nitro-1*H*-1,2,4-triazol-3-yl)(nitro)amide (11+H$_2$O). Compound **8** (0.20 g, 0.8 mmol) was dissolved in ethanol (3 mL) and aqueous hydroxylamine, (50 %, 2 mL) was added in ethanol (2 mL) at room temperature. The resulting mixture was stirred at room temperature for 2 hours. A yellow precipitate formed and was collected by filtration and dried by air blower at room temperature to yield **11** as a yellow solid. Yield: 0.22 g, 86%. T_{dec} (5 °C min^{-1}): 218 °C (onset). ^{1}H NMR (acetone-d$_6$): δ 7.60 (s, 8H, NH$_3$OH), 5.87 (s, 2H, CH$_2$). ^{13}C NMR (DMSO-d$_6$): δ 160.1, 153.2, 152.6, 41.9 ppm. IR (KBr pellet): **ν** 3422, 3136, 2884, 1637, 1559, 1492, 1385, 1306, 1027, 1003, 826, 781 cm^{-1}. Anal. Calcd for $C_4H_{12}N_{12}O_7$ (340.09): calcd C 14.12, H 3.56, N 49.40%. Found: C 14.04, H 3.25, N 47.12%.

Conflicts of interest

There are no conflicts to declare.

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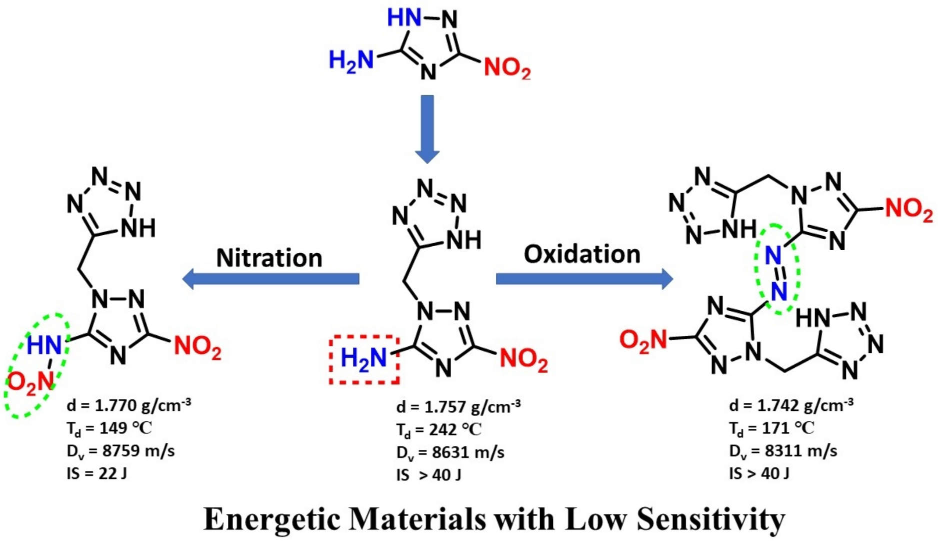

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