Improving the Density and Properties of Nitrogen-rich Scaffolds by Introduction of a C-NO2 group

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Improving the Density and Properties of Nitrogen-rich Scaffolds by Introduction of a C-NO_2 group

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In order to understand the impact of introducing a C-NO_2 moiety into an energetic nitrogen-rich scaffold-containing material, the physical properties of compounds **1**-**3** and **10** were determined. It was found that as the C-NO_2 groups were introduced in the nitrogen-rich scaffold, the values of the density, and the detonation velocity and pressure were improved. The density of **3•**H_2O is 1.84 g/cm^3 (detonation velocity and pressure of 8608 m/s and 29.6 GPa) compared with **1'**. And **3•**H_2O exhibits excellent thermal stability with a high nitrogen content giving rise to acceptable impact and friction sensitivity. While for compound 10•H_2O, which contains C-NO_2 group is 1.79 g/cm^3 (detonation velocity and pressure of 8636m/s and 29.5 GPa) compared with **10'**.

Introduction

High-energy-density materials (HEDMs) have attracted much interest worldwide for civilian and military applications during the last decade.[1] Nitrogen-rich compounds are very important to the field of energetic materials research because these compounds improve many fundamental properties such as density and environmental greenness.[2] The tetrazole group is a desirable energetic moiety for high-energy-density materials because of the larger number of N–N bonds, higher nitrogen content, higher heat of formation, and a more enthusiastic performance.[3] When the nitrogen content increases from pyrazole to tetrazole, the heat of formation and the density increase sharply while the impact and friction sensitivity decrease (Figure 1). Introducing a nitro group into compounds of interest is an effective and widely used method to obtain higher density and better detonation properties. For example, TKX-50, that has a detonation performance similar to ε-CL-20 and a thermal stability similar to TNT, is a potential candidate as a future energetic material.[4] The introduction of oxygen atoms not only increases oxygen balance, but also enhances detonation performance.

1H,1'H-5,5'-bitetrazole (**1'**) [5] and 4,5-bis(tetrazol-5-yl)-1,2,3-triazole (**10'**) [6] are good scaffolds because of their excellent thermal stability, high nitrogen content and acceptable impact and friction sensitivities as well as being good precursors to nitrogen-rich energetic salts.[7] In order to understand the relationship of introducing the C-NO_2 group to the resulting positive properties, compounds **3** and **10** were selected as promising subjects. Now we report the ready syntheses of **3** and **10**-the members of a new family of nitrogen-rich energetic tetrazoles which, despite being nitrogen-rich, exhibit outstanding thermal stability and insensitivity (Scheme 1).

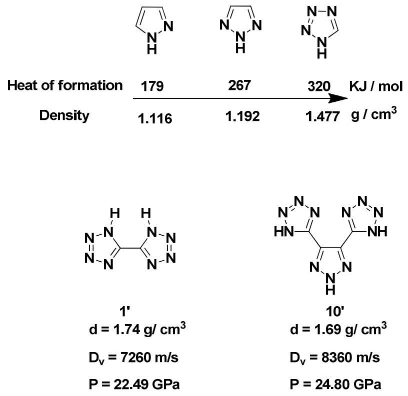
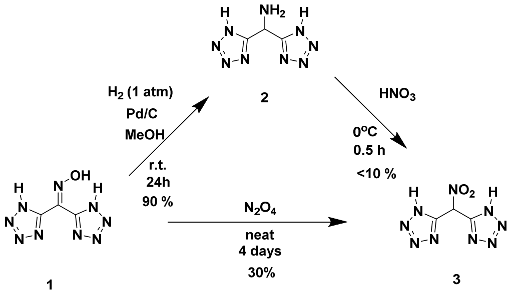


Figure 1. Calculated gas phase heats of formation (G2 atomization method) and experimental densities from pyrazole to tetrazole, and energetic performance parameters of compound **1'** and **10'**.



Scheme 1. Syntheses of **2–3**.

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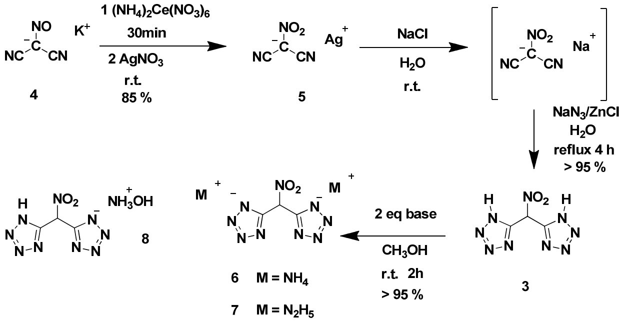
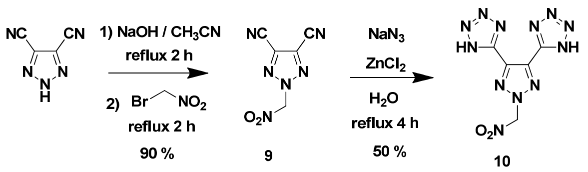
Di(1H-tetrazol-5-yl)methanone oxime (**1**),[8] was treated with hydrogen (1 atm) in the presence of catalytic amounts of palladium on activated carbon (5% Pd) in methanol at room temperature for 24 hours to obtain **2**•H_2O (Scheme 1). The latter was then oxidized with 100% nitric acid to give **3**•H_2O in ≤ 10% yield. After trying several oxidizing agents, nitrogen dioxide (N_2O_4) was found to behave effectively. Compound **1** was treated with N_2O_4 at -20 °C for 4 days to produce **3**•H_2O in about 30% yield. However, this reaction was difficult to control due to the $N_2O_4 \rightleftharpoons 2NO_2$ equilibrium and was not scaled up to larger amounts because of the toxicity of N_2O_4 and the sensitivity of mixing compound **1** and N_2O_4.

An applicable and straightforward synthetic route to **3**•H_2O was found when silver nitrodicyanomethanide, **5**, was synthesized by the oxidation of potassium nitrosodicyanomethanide, **4**, with ammonium cerium (IV) nitrate.[9] Sodium nitrosodicyanomethanide, obtained by ion exchange with sodium chloride and **5**, was used subsequently in reaction with sodium azide in the presence of zinc chloride in aqueous solution to prepare 5,5'-(nitromethylene)bis(1H-tetrazole) (**3**•H_2O) in > 95% yield (Scheme 2). Compound **3**•H_2O decomposes in DMSO or DMF after two hours. For the energetic salts of **3**, the ammonium salt (**6**) and the hydrazinium salt (**7**), are dication salts, while the hydroxylammonium salt **(8)** is mono-cation.



Scheme 2. Syntheses of **3**•H_2O and its selected nitrogen-rich salts.

On the other hand, when 4,5-dicyano-2H-1,2,3-triazole was treated with sodium hydroxide, and bromonitromethane was added, compound **9** was obtained with high yield. Compound **9** was used subsequently in reaction with sodium azide in the presence of zinc chloride in aqueous solution to prepare 5,5'-(2-(nitromethyl)-2H-1,2,3-triazole-4,5-diyl)bis(1H-tetrazole) (**10**·H_2O) in essentially quantitative yield (Scheme 3).



Scheme 3. Syntheses of **10**.

The structures of **2**•H_2O, **3**•H_2O, **6**•H_2O, **7**, **8** and **10**•H_2O are supported by IR, and ^1H and ^{13}C NMR spectral data as well as elemental analyses. In the ^1H NMR of **2**•H_2O, the signal due to amino group was observed at 6.32 ppm. For **10**•H_2O, the signal corresponding to methylene protons is at 7.50 ppm. Compound **1** exhibits three carbon resonance bands in the ^{13}C NMR spectrum due to restricted rotation around the carbon–nitrogen double bond giving a fixed geometry and thus three nonequivalent carbon atoms.[8] However, the ^{13}C NMR spectra of **2** and **3** have only two peaks since rotation around the carbon–nitrogen single bond is no longer restricted. For **2**, the signal corresponding to the amino-methylene carbon is at 42.7 ppm, while the signal corresponding to nitro-methylene carbon is at 96.8 ppm in **3.** For **10**•H_2O, the signal corresponding to the methylene carbon is at 84.63 ppm, while the signal corresponding to the triazole carbon is at 131.74 ppm in **10**•H_2O**.** In the ^{13}C NMR of all the compounds, signals corresponding to the tetrazole moiety were in the range 148.2-156.0 ppm.

The palladium complex of **2**•H_2O and the sodium salt of **3**•H_2O, were characterized based on single crystal X-ray structure analysis. The palladium complex of **2**•H_2O crystallizes in the triclinic space group P-1 with a calculated density of 1.688 g/cm^3 at 293K with two molecules and two DMSO molecules in the unit cell (Figure 2). Compound **2**•H_2O was found to be in a gauche conformation with the angles between the tetrazole rings along the C-C axis at 41.7°.

For the sodium salt of **3**•H_2O, all the atoms are coplanar due to electron delocalization of the central carbon anion. Normally the proton bonded to the tetrazole ring is more acidic than the protons on other carbons in the molecule,[3,6] but as is seen in the structure of sodium salt **3**•H_2O (Figure 3), the proton on the carbon bonded to the nitro group was displaced by the sodium ion, and not the proton of the tetrazole ring. Apparently, because of the electron-withdrawing effects of the nitro and the tetrazole groups, the carbon proton is more acidic. The sodium salt of **3**•H_2O crystallizes in the orthorhombic space group Pbcm with one water molecule in the unit cell and a calculated density of 1.952 g/cm^3 at 293K (Figure 3). It is important to note that the water molecules play an important role in forming layers of hydrogen-bonding pairs.[9]

Thermal stability, density, detonation performance as well as sensitivity properties were investigated to determine any potential applications of these compounds as energetic materials. The results are shown in Table 1. Compound **2**•H_2O melts at 139 °C prior to decomposition at 240 °C. Unexpectedly, **1** is more thermally stable with a decomposition temperature of 289 °C with an additional oxygen atom relative to **2**•H_2O. This may arise from the presence of the oxime group where restricted rotation around the carbon–nitrogen double bond limits the fixed geometry. The conjugative effect of the C-N double bond and tetrazole rings result in **1** having the highest decomposition temperature. Furthermore, the decomposition temperature of **3**•H_2O has decreased to 238 °C with C-NO_2 group than in 1' (T_d = 254 °C) [5], and the thermal stability of **3**•H_2O is comparable to RDX. Compared with compound **10'** (T_d = 277 °C),[6] after introducing the C-NO_2 group, the decomposition temperature of **10**•H_2O has changed to 281 °C.

Table 1 Energetic performance parameters of **1–3**, **6**, **7 and 10** compared with TNT and RDX.

	ρ[a] (g·cm^{-3})	*Dv* [b] (m/s)	*P*[c] (GPa)	ΔH_f[d] (kJ/mol) /(kJ/g)	T_m[e] (°C)	T_{dec}[f] (°C)	*IS*[g] (J)	*FS*[h] (N)
1	1.74	8226	27.4	590.5/ 2.9	164	289	>40	>360
2•H_2O	1.59	7371	18.4	415.8 /2.48	139	240	>40	>360
3H_2O	1.84	8608	29.6	402.3/ 2.04	116	238	15	240
6•H_2O	1.82	8592	25.0	20.7/ 0.09	191	248	11	240
7	1.64	8701	27.5	689.9/ 2.7	156	172	20	240
10·H_2O	1.79	8636	29.5	945．8/ 3.35	132	281	10	240
RDX[i]	1.80	8795	34.9	92.6/ 0.42	-	204	7.5	120
TNT	1.65	7303	21.3	-59.4/ -0.26	81	295	15	>353

[a] Density measured - gas pycnometer at 25 °C; [b] Calculated detonation velocity; [c] Calculated detonation pressure; [d] Heat of formation, $\Delta H_f(H_2O)$=241.82 kJ/mol; [e] Melting point; [f] Temperature of decomposition (onset); [g] Impact sensitivity; [h] Friction sensitivity. [i] Reference 6.

Compounds **6•**H_2O and **7** decompose at 248 and 172 °C, respectively. For **1–3**, the density was increased by introducing additional oxygen atoms. The density of **2•**H_2O is 1.59 g/cm^{-3} compared with that of **1** at 1.74 g/cm^{-3} after additional of one oxygen atom. Furthermore, the density of **3•**H_2O has been increased to 1.84 g/cm^{-3} with the presence of two oxygen atoms. Compared with **1’** (d = 1.74 g/cm^{-3}), [5] after introducing the C-NO_2 group, the density of **3•**H_2O was increased apparently. On the other hand, between the **10’** (d=1.69 g/cm^{-3})[6] and **10**(d=1.79 g/cm^{-3})**,** we also see the increase in density after introducing C-NO_2 group. Heats of formation were calculated using the Gaussian 03 (Revision E.01)[11] suite of programs. Compounds, **2•**H_2O, **3•**H_2O, **6•**H_2O, **7** and **10•**H_2O have relatively high positive heats of formation (ΔH_f) falling between 0.09 and 3.35 kJ/g, which are more positive than TNT (-0.26 kJ/mol) and RDX (0.42 kJ/mol). Compound **10•**H_2O at 3.35 kJ/g has the highest heat of formation. From the values of the heats of formation and experimental densities of these compounds, detonation velocities and pressures were calculated based on traditional Chapman–Jouget thermodynamic detonation theory by using the Explo5 program (version 6.01).[12] The energetic performance parameters of these compounds increased with the introduction of additional oxygen atoms. The detonation velocity and pressure of **2•**H_2O are 7371 m/s and 18.4 GPa, while those for **1** are 8226 m/s and 27.4 GPa, respectively, with one more oxygen atom. Furthermore, the detonation velocity and pressure of **3•**H_2O increased to 8608 m/s and 29.6 GPa, respectively, with one more oxygen atom than in **1**. Compared with **1’** (P: 22.49 GPa, Dv: 7260 m/s)[5] and **10’** (P: 34.9 GPa, Dv: 8795 m/s) and (P: 24.80 GPa, Dv: 8360 m/s)[6], the detonation velocity and pressure of **3•**H_2O (P: 29.60 GPa, Dv: 8608 m/s) and 10 (P: 29.5 GPa, Dv: 8636 m/s) have improved by introducing a C-NO_2 group. All compounds exhibit superior detonation properties relative to TNT; additionally **3•**H_2O, its ammonium salt and **10•**H_2O exhibit excellent detonation properties approaching RDX (P: 34.9 GPa, Dv: 8795 m/s). By using a BAM drop hammer apparatus and BAM friction tester,[13] the sensitivities toward impact and friction were determined, respectively. All compounds have lower impact and friction sensitivities compared to RDX. The impact and friction sensitivity of **1** and **2•**H_2O are >40 J and >360 N. However, for **3•**H_2O and **10•**H_2O, these values have decreased to 15 J: 240 N and 10 J : 240 N, respectively. Compounds **6•**H_2O and **7** also have acceptable impact sensitivities relative to RDX.

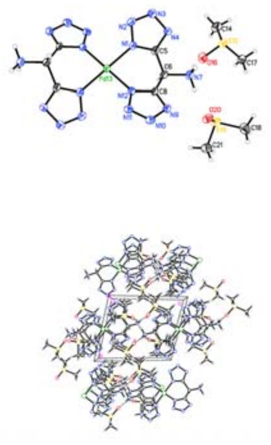


Figure 2. (a) Thermal ellipsoid plot (50%) and labeling scheme for the palladium complex of **2**. (b) Ball-and-stick packing diagram of the palladium complex of **2** viewed down the b Dashed lines indicate strong hydrogen bonding.

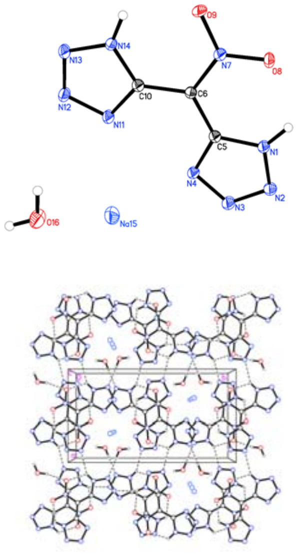


Figure 3. (a) Thermal ellipsoid plot (50%) and labeling scheme for **3•**H_2O (sodium salt). (b) Ball-and-stick packing diagram of **3•**H_2O (sodium salt) viewed down the b axis. Dashed lines indicate strong hydrogen bonding.

Conclusions

In summary, 5,5'-(nitromethylene)bis(1*H*-tetrazole) (**3**•H_2O), its energetic salts and 5,5'-(2-(nitromethyl)-2H-1,2,3-triazole-4,5-diyl)bis(1H-tetrazole) were synthesized and fully characterized. An applicable and facile synthetic route was developed, which was scalable. Because of the poor crystallinity of this series of compounds, the single crystal structures of **2**•H_2O and **3**•H_2O were not obtained. However, single crystal X-ray structures of the palladium complex of **2** and the sodium salt of **3**•H_2O were obtained which support the structures of **2** and **3**. Their physical properties, and detonation performances as well as impact and friction sensitivities were determined. Introduction of C-NO_2 group has the effect of increasing density and detonation performance. Compound **1'** has a density 1.74 g/cm^3 and the detonation velocity and pressure are 7260 m/s and 22.49 GPa; after introducing C-NO_2 group, the density of **3**•H_2O is 1.84 g/cm^3, and the detonation velocity and pressure have increased to 8608 m/s and 29.6 GPa. Furthermore, after addition of a C-NO_2 group, the density of **10**•H_2O**,** compared to **10'**, has increased to 1.79 g/cm^3, and the detonation velocity and pressure are 8636 m/s and 29.5 GPa. Particularly attractive are the impact and friction sensitivities of **3**•H_2O and **10**•H_2O at 15 J : 240 N and 10 J : 240N. These materials have the potential to compete with current explosives.

Experimental Section

Experimental Section

Caution**:** All of the compounds presented in this paper are sensitive to impact and may explode under certain conditions. Appropriate safety precautions should be taken when preparing and handling.

General Methods

Reagents were purchased from Aldrich and Acros Organics and were used as received. ^{1}H, and ^{13}C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, respectively. DMSO-d$_6$ was used as solvent and locking solvent. 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 using 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 ^{o}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.

Synthesis

Di(1H-tetrazol-5-yl)methanamine(2): Compound **1** (360 mg, 2 mmol) was dissolved in methanol (20 mL), and Pd/C (40 mg, 5%) was added under a nitrogen atmosphere. After 24 h stirring, the suspension was filtered and the filtrate was evaporated in vacuo. A white solid (300 mg), **2**, was obtained. Yield: 90%. M.p. 139 ^{o}C; T$_{d\ (onset)}$ 240 ^{o}C; ^{1}H NMR (300 MHz, [D$_6$]DMSO): 6.32 (s, 2H) ppm; ^{13}C NMR (75 MHz, [D$_6$]DMSO): d 155.5, 42.7 ppm; IR (KBr): v 3142, 3015, 2185, 1918, 1699, 1649, 1528, 1400, 1340, 1273, 1156, 1121, 1038, 1005, 936, 828, 789, 761, 733, 677 cm^{-1}; elemental analysis: calcd (%) for $C_3H_5N_9\cdot H_2O$ (185.08): C 19.41, H 3.81, N 68.09; found: C 19.18, H 4.05, N 72.74.

5,5'-(Nitromethylene)bis(1*H*-tetrazole)(3) Method A: Compound **2** (300 mg, 1.79 mmol) was added to 100% nitric acid (3 mL). After stirring 0.5h, the solution was poured into ice (50 mL). A white solid (**3,** 35mg) was obtained by filtration. Yield: 10%. Method B: compound **1** (100 mg, 0.55 mmol) was stirred into neat liquid N_2O_4 (2 mL) at -20 ^{o}C. After 96h, the mixture was evaporated in vacuo to leave a white solid (**3,** 30 mg) which was washed by ether 3 times. The reaction temperature must be carefully maintained to prevent an explosion. Yield: 30 %. M.p.116 ^{o}C; T$_{d\ (onset)}$ 238 ^{o}C; ^{1}H NMR (300 MHz, [D$_6$]DMSO): 7.24 (br, 2H), 7.17(s, 1H) ppm; ^{13}C NMR (75 MHz, [D$_6$]DMSO): 148.2, 96.8 ppm; IR (KBr): v 3557, 3462, 242, 3006, 1774, 1619, 1594, 1556, 1453, 1421, 1359, 1328, 1295, 1225, 1151, 1099, 1048, 1027, 1001, 926, 893, 777, 760 cm^{-1}; elemental analysis: calcd (%) for $C_3H_3N_9O_2\bullet H_2O$ (215.05): C 16.75, H 2.34, N 58.60; found: C 16.63, H 2.34, N 57.36.

For salts, in general, **3** (187 mg, 1 mmol) was dissolved in methanol with sonication followed by addition of aqueous ammonia (2 mmol) or hydrazine hydrate (2 mmol), followed by stirring for 10 hrs. The precipitate was filtered and dried to give a pure material.

Ammonium 5,5'-(nitromethylene)bis(tetrazol-1-ide) (**6**)
Yield: 220 mg, > 95% M.p.191^{o}C; T$_d$ = 248^{o}C; ^{1}H NMR (300 MHz, [D$_6$]DMSO): 7.94 (br, 2H), 7.20(s, 1H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): 156.0, 80.3 ppm; IR (KBr): v 3062, 2118, 1870,1741, 1726, 1700, 1499, 1466, 1429, 1396, 1342, 1225, 1220, 1135, 1196, 1121, 1084, 1040, 1010, 953. 767, 731 cm^{-1}; elemental analysis: calcd (%) for $C_3H_9N_{11}O_2\bullet H_2O$ (249.10): C 14.46, H 4.45, N 61.83; found: C 14.08, H 4.57, N 62.07.

Hydrazonium 5,5'-(nitromethylene)bis(tetrazol-1-ide) (**7**)
Yield: 249 mg, >95 %; M.p.156 ^{o}C; T$_{d\ (onset)}$ = 172 ^{o}C; ^{1}H NMR (300 MHz, [D$_6$]DMSO): 7.28 (s, 2H), 5.58(br, 1H); ^{13}C NMR (75 MHz, [D$_6$]DMSO): 155.7, 79.8 ppm; IR (KBr): v 3330, 2943, 2176, 1630, 1560, 1503, 1503, 1416, 1343, 1308, 1204, 1131, 1086, 1035, 1013, 951, 821, 763, 753, 728, 695 cm^{-1}; elemental analysis: calcd (%) for $C_3H_{11}N_{13}O_2$ (261.11): C 13.79, H 4.24, N 69.71; found: C 13.79, H 5.30, N 65.02.

Hydroxylammounium 5,5'-(nitromethylene)bis(tetrazol-1-ide) (**8**)
Yield: 130 mg, 50 %; T$_{d\ (onset)}$ = 218 ^{o}C; ^{1}H NMR (300 MHz, [D$_6$]DMSO): 9.8 (s, 4H), ^{13}C NMR (75 MHz, [D$_6$]DMSO): 150.2, 95.06 ppm; IR (KBr): v 3116, 1891, 1578, 1385, 1192, 1124, 1058, 1000, 940, 825, 753, 599 cm^{-1}; elemental analysis: calcd (%) for $C_3H_6N_{10}O_3$ (230.06): C 15.66, H 2.63, N 60.86; found: C 15.69, H 2.644, N 59.37.

2-(Nitromethyl)-2H-1,2,3-triazole-4,5-dicarbonitrile (**9**)
Yield: 130 mg, 90 %; M.p.192 ^{o}C; T$_{d\ (onset)}$ = 271 ^{o}C; ^{1}H NMR (300 MHz, [D$_6$]DMSO): 7.5 (s, 2H), ^{13}C NMR (75 MHz, [D$_6$]DMSO):

127.7, 108.7, 64.4 ppm; IR (KBr): v 3448, 3047, 2990, 2935, 2665, 1589, 1490, 1480, 1417, 1390, 1361, 1320, 1195, 996, 856, 721, 660, 620, 576, 523 cm^{-1}.

5,5'-(2-(Nitromethyl)-2H-1,2,3-triazole-4,5-diyl)bis(1H-tetrazole) (**10**)

Yield: 130 mg, 50%; T_m = 132 °C; $T_{d\,(onset)}$ = 281 °C; ^{1}H NMR (300 MHz, [D$_6$]DMSO): 9.8 (s, 4H), ^{13}C NMR (75 MHz, [D$_6$]DMSO): 150.2, 95.06 ppm; IR (KBr): v 3655, 3622, 3429, 3105, 3070, 3040, 3601, 2976, 1911, 1625, 1578, 1509, 1479, 1465, 1449, 1387, 1365, 1331, 1294, 1261, 1210, 1201, 1168, 1068, 1033, 1013, 972, 898, 835, 753, 744, 699, 657, 607, 565, 538, 513 cm^{-1}; elemental analysis calcd (%) for $C_5H_4N_{12}O_2$•H_2O (282.07): C 21.28, H 2.14, N 59.57; found: C 21.61, H 2.511, N 59.55.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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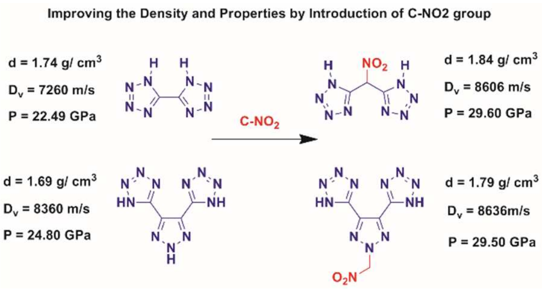

5,5'-(Nitromethylene)bis(1*H*-tetrazole) and 5,5'-(2-(nitromethyl) -2H-1,2,3-triazole -4,5-diyl) bis(1H-tetrazole) were synthesized by introducing a C-NO_2 group to increase the density and detonation performance.