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Energetic derivatives of 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole†‡

Dániel Izsák, Thomas M. Klapötke* and Carolin Pflüger

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This study presents the preparation of the novel nitrogen-rich compound 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**5**) from commercially available chemicals in a five step synthesis. The more energetic derivatives with azido (**6**) and nitro (**7**) groups, as well as a diazene bridge (**8**) were also successfully prepared. The energetic compounds were comprehensively characterized by various means, including vibrational (IR, Raman) and multinuclear (^{1}H, ^{13}C, ^{14}N, ^{15}N) NMR spectroscopy, mass spectrometry and differential thermal analysis. The sensitivities towards important outer stimuli (impact, friction, electrostatic discharge) were determined according to BAM standards. The enthalpies of formation were calculated on the CBS-4M level of theory, revealing highly endothermic values, and were utilized to calculate the detonation parameters using EPXLO5 (6.02).

Introduction

Poly-azole compounds have been the focus of several research groups world-wide working in the field of energetic materials in the recent years. These feature two, or even more, linked azoles (furazan, 1,2,4-triazole, tetrazole, *etc.*), which can be either directly linked,[1–6] or through energetic bridging moieties like a diazene bridge.[7–11] The detonation performance of energetic compounds depends strongly on the enthalpy of formation and the density, with higher values resulting in more powerful explosives. The high nitrogen content of azole based compounds results in high positive enthalpies of formation due to the large number of inherent N–N and C–N bonds and thereby showing high potential as explosive.[12] Furthermore, the nitrogen-rich heterocycles mainly release nontoxic dinitrogen gas upon decomposition, whereby the environmental pollution might be diminished. The design of new high explosives should consider improved thermal and mechanical sensitivities as well as an increased detonation performance, but unfortunately, these parameters often have contradictory impact to each other.[13] The combination of multiple different heterocycles is advantageous due to the vast possibilities of tailoring the energetic performances. An interesting example combining the frequently utilized tetrazole and 1,2,4-triazole moieties are the derivatives of 5-(5-amino-1*H*-1,2,4-triazol-3-yl)-tetrazole with the energetic azido, nitro and nitramino groups, which have been investigated recently.[14] This C–C linkage of the two heterocycles benefits from the energetic tetrazole ring, the higher stability of the triazole ring and the second carbon atom of the triazole which carries various energetic groups. Another option would be the utilization of a 1,2,3-triazole instead of the 1,2,4-triazole, which should result in higher enthalpies of formation and thus improved energetic performances, although potentially at the expense of thermal and mechanical stability. A suitable nitrile precursor had already been reported in 1956,[15] but no studies concerning the binary combination of a tetrazole and a 5-amino-1,2,3-triazole by means of a C–C link could be found.

The goal of this study has therefore been the synthesis of the novel 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**5**) and its derivatives with azido (**6**) and nitro (**7**) groups as well as diazene bridging (**8**), their comprehensive characterization and the comparison of the compounds with the respective 1,2,4-triazole isomers and analogues.

Results and discussion

Synthesis

There are two possible routes to the intermediate 5-amino-1-benzyl-1,2,3-triazole-4-carbonitrile (**3**). The first one is the direct synthesis from benzyl azide (**1**) and malononitrile with sodium in ethanol,[15] but this reaction suffers from low yields and the formation of 5-amino-l-benzyl-4-carbiminoethoxy-1,2,3-triazole as a byproduct, due to the presence of the second nitrile which can react with the formed ethoxide. The second

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Department of Chemistry, Ludwig–Maximilian University of Munich, Butenandtstr. 5-13 (D), 81377 Munich, Germany. E-mail: tmk@cup.uni-muenchen.de; Fax: +49-89-2180-77492

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option is the well working synthesis (80%) of 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**2**) from benzyl azide (**1**) and cyanoacetamide with sodium in ethanol,[15] which can then be further processed in two different ways. The first one would be the debenzylation to 4-amino-2*H*-1,2,3-triazole-5-carboxamide with sodium in liquid ammonia,[15] followed by the dehydration of the amide to a nitrile. Although the debenzylation is working well (96%), the dehydration did not result in a complete conversion with various reagents (phosphorus pentoxide, phosphoryl chloride, phosphorus pentachloride, thionyl chloride). Therefore, the benzyl protective group was left on the triazole and thus enabling the use of trifluoroacetic anhydride by protecting the ring from its acylation properties, resulting in a complete conversion of **2** into **3** in high yields (86%). The next step, the formation of 5-(5-amino-1-benzyl-1,2,3-triazol-4-yl)tetrazole (**4**) from **3** and sodium azide, proved to be quite difficult due to the frequent hydrolysis of the nitrile, in addition to the desired product, when zinc chloride was employed in a protic solvent (water, ethanol, methanol). Hydrochloric acid and ammonium chloride in the same solvents did not result in partial hydrolysis, but also did not yield any product, and neither did acetic acid (both as acid and as solvent). Utilization of the polar, aprotic tetrahydrofuran and zinc chloride finally yielded pure **4** (97%). Debenzylation was again carried out with sodium in liquid ammonia to obtain the title compound 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**5**) in high yield (95%). The optimized route is shown in Scheme 1.

The amine of **5** was then converted into different energetic moieties as illustrated in Scheme 1. The azido derivative **6** was obtained in high yield (87%) by diazotation with sodium nitrite in sulfuric acid, followed by a diazo azide exchange with sodium azide. The nitro derivative **7** could not be obtained by the common reaction with an excess of sodium nitrite in sulfuric acid, a method which works well with 5-(5-amino-1*H*-1,2,4-triazol-3-yl)tetrazole for example,[14] but it was obtained by oxidation of the amine with potassium superoxide in tetrahydrofuran in a fair yield (68%). Azo coupling with potassium permanganate in water yielded 1,2-bis(4-(1*H*-tetrazol-5-yl)-2*H*-1,2,3-triazol-5-yl)diazene (**8**) also only in a fair yield (48%) as a dihydrate.

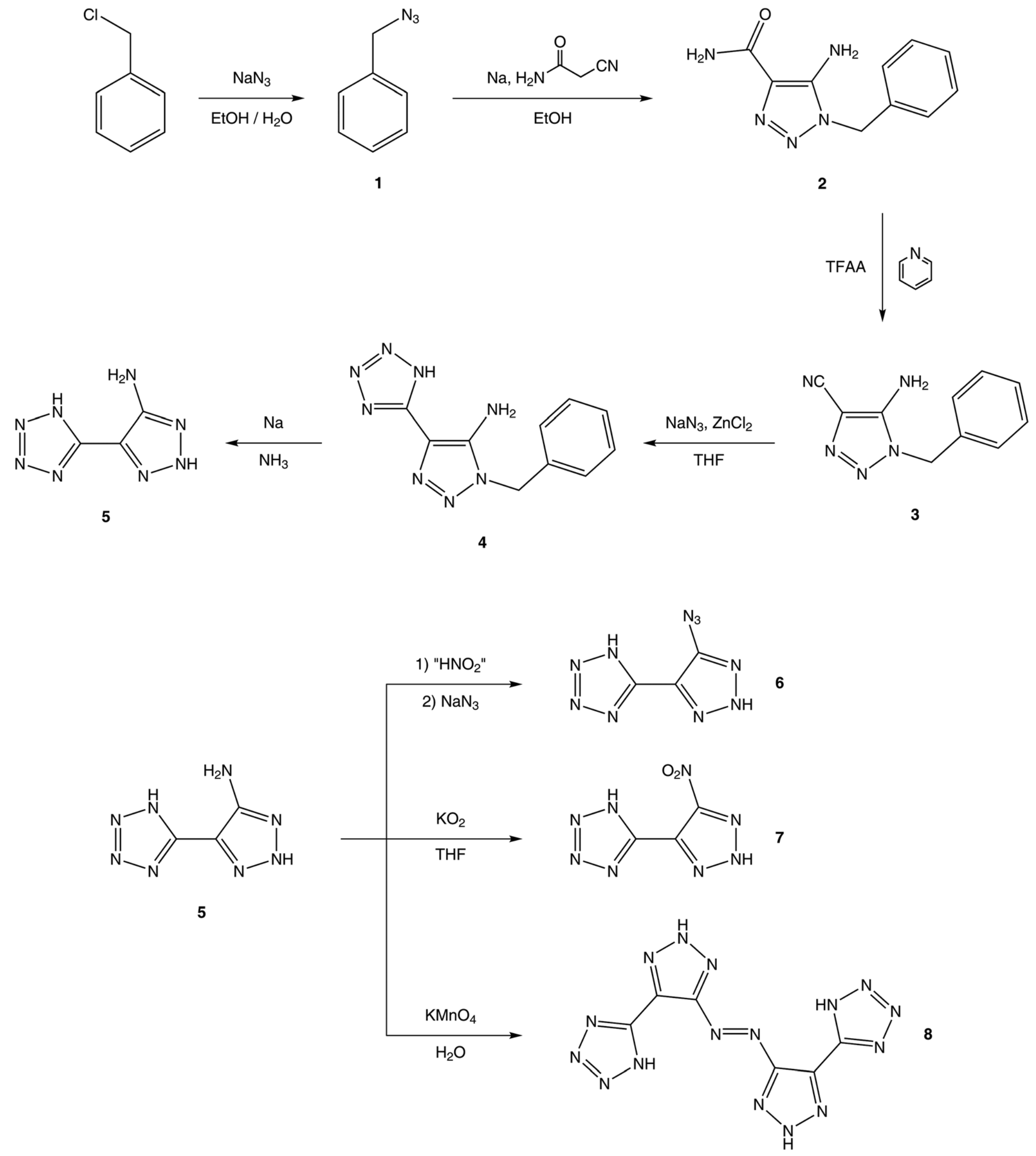
Crystal structures

The precursor molecule 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**2**) crystallized in the monoclinic space group $P2_1/c$ with four formula units per unit cell. The molecular unit is depicted in Fig. 1. The bond lengths of the 1,2,3-triazole ring are between the length of the corresponding single and double bonds,[16] with the N1–N2 bond being significantly longer (1.376(1) Å) than the N2–N3 bond (1.304(1) Å), which is quite common for 1,4,5-substituted 1,2,3-triazoles.[17] The bond lengths of the amino group attached to the triazole (1.351(2) Å), as well as the amide N4–C3 bond (1.346(2) Å) are considerably shorter than the corresponding single bonds, caused by an involvement of the non-bonding electron pair of the nitrogen atoms, with both groups being almost planar. The amide group and the triazole ring are practically in plane (C2–C1–C3–O1: 1.66(2)°). The molecule features one weak and undirected intramolecular hydrogen bond between the ring amine and the amide oxygen as N5–H3···O1 (D···A: 2.956(1) Å; D–H···A: 125(1)°), and a long but directed intermolecular hydrogen bond N4–H2···O1^{i} (D···A: 3.070(2) Å; D–H···A: 171(2)°) resulting in dimers (see Fig. 2 for both). The dimers are connected by undulated ribbons through a π–π stacking interaction of the phenyl groups, depicted in Fig. 2. The distance between the two aromatic moieties is 3.531(2) Å, which is characteristic for these interactions.[18] The second intermolecular interaction which connects the ribbons is formed by a very long but directed hydrogen bond N5–H4···N2^{ii} between the amino moiety and a nitrogen atom of a neighboring triazole (D···A: 3.128(2) Å; D–H···A: 164(1)°), slightly above the sum of the van der Waals radii ($\sum r_w(N,N)$ = 3.10 Å).[19] The resulting crystal structure, presented in Fig. 3, has two areas which are either dominated by polar hydrogen bonds or by nonpolar π–π stacking interactions. The parameters of the described hydrogen bonds are summarized in Table 1. Further information regarding the crystal structure determination has been compiled in the ESI (Table S1†).

The title compound 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**5**) crystallized in the monoclinic space group $P2_1/n$ with four formula units per unit cell and a calculated density of 1.705 g cm^{-3} at 100 K. The molecular unit is depicted in Fig. 4. The bond lengths are again between formal single and double bonds. The triazole ring is more symmetrical than that of **2** with N1–N2 and N2–N3 bond lengths of 1.350(2) and 1.311(2) Å, respectively. The length of the C1–C3 bond (1.442(2) Å) is comparable to similar bisazole compounds.[14] Both rings form an almost planar system with a N3–C1–C3–N4 torsion angle of −1.1(2)°. The amino group is similar to that of **2** and is also in plane with both rings, leading to the assumption of a conjugated π-system across the whole molecule. Additionally, the molecule features an intramolecular N8–H4···N7 hydrogen bond between the amino group and the tetrazole ring. The structure is dominated by an extensive hydrogen bonding network involving all eight nitrogen atoms, which is illustrated in Fig. 5. The strong and quite directed N2–H1···N6^{i} hydrogen bond (D···A: 2.875(2) Å; D–H···A: 163(1)°) results in the formation of a chain (A), which is connected to the anti-parallel chain (B) through the N4–H2···N1^{ii}, N8–H3···N3^{iii} and N8–H4···N5^{iv} contacts (see Fig. 5 and Table 2). The arrangement of the anti-parallel chains overall results in a layer structure with no special interactions between the layers.

Multinuclear NMR spectroscopy

All compounds prepared herein were investigated by multinuclear NMR spectroscopy (^{1}H and ^{13}C, some additionally ^{14}N and ^{15}N). ^{13}C NMR spectroscopy is well suited to differentiate between the precursor molecules **2–4**, the title compound **5** and its further derivatives **6–8**. While **2–4** all show the signals of the benzyl group (phenyl: 135.2–136.0, 128.7, 127.8–127.9, 127.4–127.5 ppm; methylene: 48.4–48.8 ppm), those are completely gone in the spectrum of **5**. The signal of the triazole carbon atom attached to the exocyclic carbon is at 121.8 (**2**),



Scheme 1 Synthetic route towards 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**5**) from commercially available benzyl chloride, and its energetic derivatives 5-(5-azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**6**), 5-(5-nitro-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**7**) and 1,2-bis(4-(1*H*-tetrazol-5-yl)-2*H*-1,2,3-triazol-5-yl)diazene (**8**).

113.7 (**3**) and 114.4 ppm (**4**). The carbon atom carrying the amine shows a signal at 144.9 (**2**), 148.0 (**3**) and 148.6 ppm (**4**). While the spectrum of **2** shows a signal at 164.5 ppm, stemming from the amide, **3** has the signal of the nitrile at 101.3 ppm and shows no signs of the former. Pure **4** finally exhibits a new signal at 142.9 ppm, belonging to the newly formed tetrazole. The signals of compounds **5–8** (^{1}H, ^{13}C and ^{14}N) are compiled in Table 3. While **6–8** show three sharp signals for the two triazole and one tetrazole carbon atoms in their corresponding ^{13}C NMR spectra, **5** shows only one sharp signal at 149.0 ppm, attributed to the tetrazole, and two small and broad signals at 147.6 and 111.6 ppm, attributed to the triazole. The carbon resonances of the rings are assigned due to their signal shapes and intensities, and in comparison to

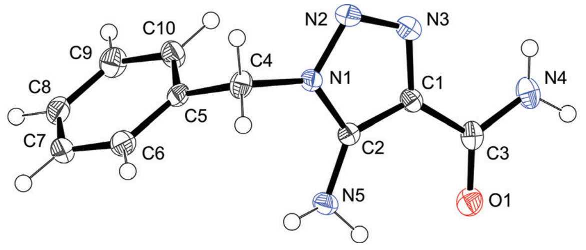


Fig. 1 Molecular structure of 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**2**). Thermal ellipsoids at 50% probability.

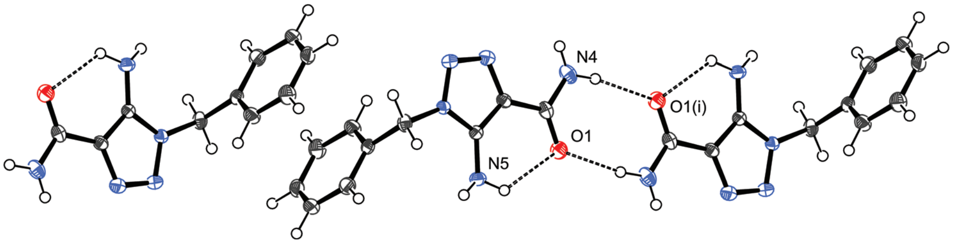


Fig. 2 Hydrogen bonds and π–π stacking interactions of **2**. Thermal ellipsoids at 50% probability. Symmetry code: (i) $-x + 1, -y + 3, -z + 1$.

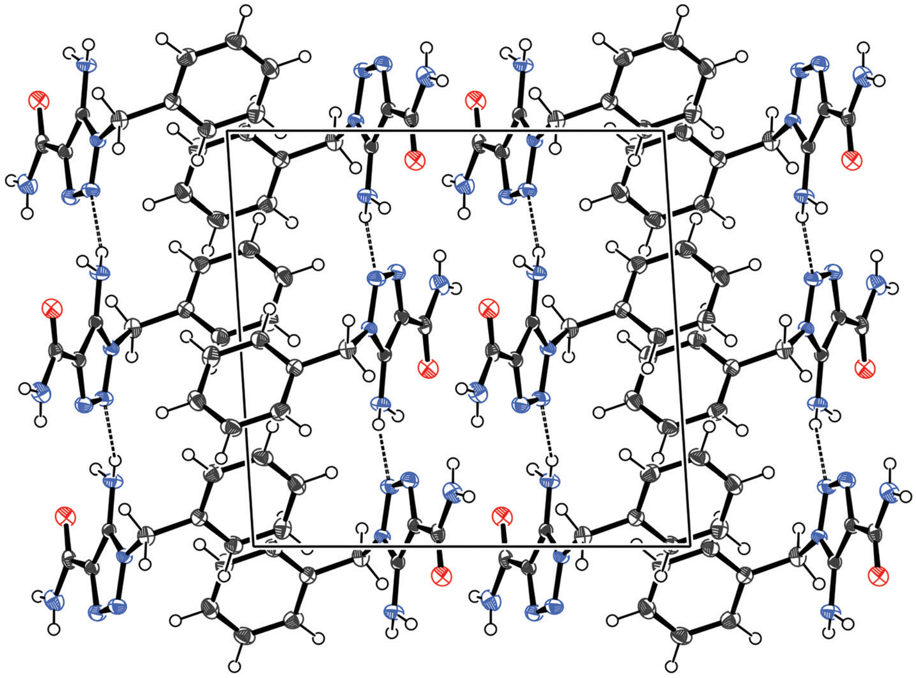


Fig. 3 Unit cell of **2** along the (010) axis, illustrating the intermolecular N5–H4⋯N2^{ii} hydrogen bond. Thermal ellipsoids at 50% probability.

Table 1 Hydrogen bonds present in **2**

D–H⋯A	D–H/Å	H⋯A/Å	D⋯A/Å	D–H⋯A/°
N5–H3⋯O1	0.88(2)	2.36(1)	2.956(1)	125(1)
N4–H2⋯O1^{i}	0.90(2)	2.17(2)	3.070(2)	171(2)
N5–H4⋯N2^{ii}	0.91(2)	2.24(2)	3.128(2)	164(1)

Symmetry codes: (i) $-x + 1, -y + 3, -z + 1$; (ii) $x, -y + 1.5, z - 0.5$.

^{13}C NMR spectra of corresponding salts. The corresponding ^{14}N NMR spectra show the signals of the central azide nitrogen atom (N_{β}) of **6** at −138 ppm as a broad signal and the nitro group of **7** at −21 ppm. Compounds **6** and **7** were further investigated by ^{15}N and ^{15}N{^{1}H} NMR spectroscopy. The proton coupled ^{15}N NMR spectra are depicted in Fig. 6. The proton decoupled ^{15}N NMR spectra can be found in the ESI (Fig. S1†). All nitrogen atoms display clearly visible resonances in the ^{15}N NMR spectra of both **6** (eight signals) and **7** (six signals). The tetrazole emits only two signals due to the enabled proton exchange in DMSO-d_6, equalizing the four nitrogen atoms to one protonated (−101.9 ppm in **6**, −65.4 ppm in **7**) and one non-protonated (−11.1 ppm in **6**, −14.4 ppm in **7**), similar to 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole and 5-(3-nitro-1*H*-1,2,4-triazol-5-yl)-2*H*-tetrazole for example.[14] The triazole shows three signals in both compounds, with one being strong and sharp (−74.1 ppm in **6**, −51.1 ppm in **7**) and the other two being weaker and broad (−55.7 and −126.3 ppm in **6**, −65.4 and −97.2 ppm in **7**). The ^{15}N{^{1}H} NMR spectra confirm that the signals at −126.3 and −97.2 ppm carry the proton, in addition to their high field shift. The signal of the protonated nitrogen atom of the tetrazole ring is in all spectra broader than that of the triazole. The remaining signals are belonging to the azide (−143.2, −148.6 and −303.3 ppm) of **6** and the nitro group (−27.5 ppm) of **7**. While the signal at −303.3 ppm in the spectrum of **6** can be clearly attributed to the alpha nitrogen atom of the azide, the signals at −143.2 and −148.6 ppm have nearly identical intensities and are thus preventing an unambiguous assignment to the beta and gamma nitrogen atoms.

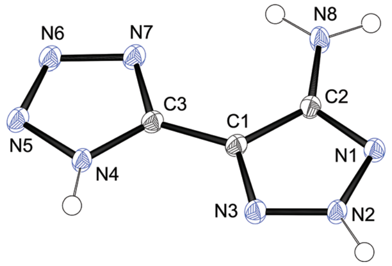


Fig. 4 Molecular structure of 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**5**). Thermal ellipsoids at 50% probability.

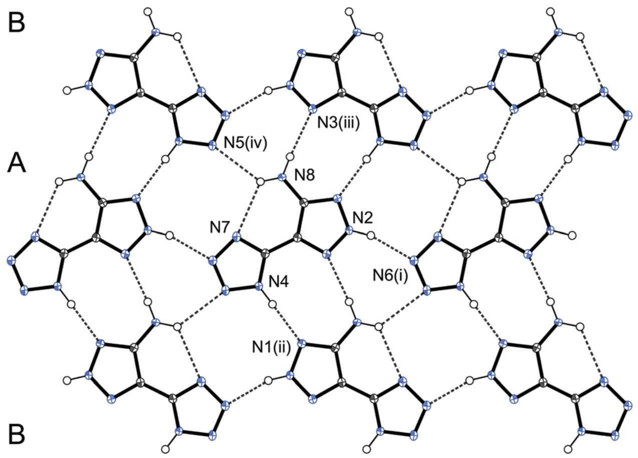


Fig. 5 Hydrogen bonds of **5**, illustrating the two anti-parallel chains (A) and (B). Thermal ellipsoids at 50% probability. Symmetry codes: (i) *x*, *y*, *z* + 1; (ii) −*x* + 0.5, *y* + 0.5, −*z* + 0.5; (iii) −*x* + 0.5, *y* − 0.5, −*z* + 0.5; (iv) −*x* + 0.5, *y* − 0.5, −*z* − 0.5.

Table 2 Hydrogen bonds present in **5**

D–H⋯A	D–H/Å	H⋯A/Å	D⋯A/Å	D–H⋯A/°
N2–H1⋯N6^{i}	0.90(2)	2.00(2)	2.875(2)	163(1)
N4–H2⋯N1^{ii}	0.91(2)	1.98(2)	2.891(2)	178(2)
N8–H3⋯N3^{iii}	0.89(2)	2.12(2)	3.011(2)	175(2)
N8–H4⋯N7	0.88(3)	2.41(2)	3.004(2)	125(2)
N8–H4⋯N5^{iv}	0.88(3)	2.42(2)	3.081(2)	131(2)

Symmetry codes: (i) *x*, *y*, *z* + 1; (ii) −*x* + 0.5, *y* + 0.5, −*z* + 0.5; (iii) −*x* + 0.5, *y* − 0.5, −*z* + 0.5; (iv) −*x* + 0.5, *y* − 0.5, −*z* − 0.5.

Table 3 NMR signals of **5**–**8** in DMSO-d_6 at room temperature

δ				
	^{1}H	^{13}C{^{1}H} (triazole)	^{13}C{^{1}H} (tetrazole)	^{14}N
5	16.19, 14.64, 6.03	147.6, 111.6	149.0	—
6	15.81	147.7, 123.0	143.1	−138
7	9.93	151.1, 127.7	147.7	−21
8	10.09	153.7, 126.6	147.2	—

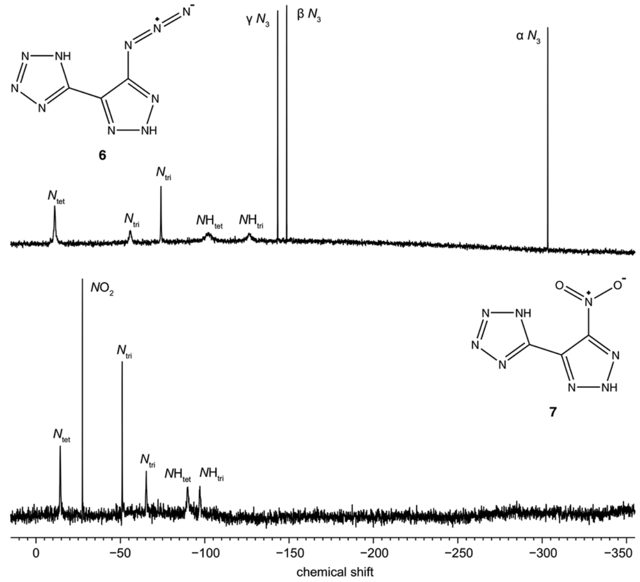


Fig. 6 ^{15}N NMR spectra of 5-(5-azido-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**6**) and 5-(5-nitro-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**7**) in DMSO-d_6 at room temperature.

Theoretical calculations, performances and stabilities

The thermal behaviors of the synthesized compounds were investigated by differential thermal analysis (DTA). The amino derivative **5** displays, as expected, the highest thermal stability of the neutral compounds (241 °C), while the nitro derivative **7** (188 °C), azido derivative **6** (152 °C) and especially the diazene bridged derivative **8** (128 °C) are significantly less thermally stable. It is interesting to note that, while the isomer 5-(5-amino-1*H*-1,2,4-triazol-3-yl)tetrazole (347 °C) and its nitro derivative (211 °C) display higher thermal stabilities than **5** and **7**,[14] respectively, due to the 1,2,4-triazole, the azido derivative exhibits the same decomposition temperature as **6**, as does the third isomer 1-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole.[20] The azo bridged 1,2-bis(4-(1*H*-tetrazol-5-yl)-2*H*-1,2,3-triazol-5-yl)diazene (**8**), which was obtained as a dihydrate according to elemental analysis, shows no sign of water loss before decomposition at 128 °C. Dehydration thus proved to be unsuccessful at 100 °C and high vacuum for two days. Higher temperatures were not desirable due to the low decomposition point.

For initial safety testing the impact and friction sensitivities as well as the electrostatic discharge sensitivities were determined and assigned according to the UN recommendations on the transport of dangerous goods.[21] The parent compound **5** is the least sensitive of the neutral compounds, although it is still sensitive to impact (10 J), but insensitive to friction (360 N). While the azido derivative **6** is very sensitive to impact (3 J) and to friction (10 N), the nitro derivative **7** is only sensitive to impact (4 J) and to friction (108 N). Interestingly, the diazene **8** is very sensitive to both impact (2 J) and friction (28 N), although it is a dihydrate. 5-(5-Amino-1*H*-1,2,4-triazol-3-yl)-tetrazole and its derivatives show the same trends, although the amine itself is additionally insensitive to impact, while its nitro derivative displays likewise lower sensitivities (25 J, 288 N) than its isomer **7**.[14]

The enthalpies and energies of formation were calculated on the CBS-4M level of theory as implemented in Gaussian 09,[22,23] using the atomization energy method and utilizing experimental data.[24,25] Gas phase enthalpies were transformed to solid state enthalpies by using Trouton's rule for neutral compounds.[26] The complete method is extensively described in the literature.[27] Calculations with the various isomers regarding the position of the proton revealed the 1*H*-tetrazole to be the most stable, albeit the difference to the 2*H*-tetrazole is only marginally. Detonation parameters of the neutral compounds were calculated with EXPLO5 6.02.[28] The program is based on the steady-state model of equilibrium and uses the Becker–Kistiakowsky–Wilson equation of state (BKW EOS) for gaseous detonation products and the Murnaghan EOS for both solid and liquid products. The parameters of the BKW EOS in EXPLO5 6.02 are calibrated particularly for the formation of nitrogen gas, which is the main detonation product for compounds with a high nitrogen content. It is designed to enable the calculation of detonation parameters at the Chapman–Jouguet point. The calculations were performed using the maximum densities at room temperature, measured with a helium pycnometer. The calculated detonation performances of **5–7** and RDX are summarized in Table 4. The calculated detonation velocities range from 7963 m s^{-1} (**6**) up to 8397 m s^{-1} (**5**). The calculated detonation pressures are in the range of 237 to 263 kbar and the volume of gaseous reaction products amounts up to 772 L kg^{-1} (**5**). The detonation temperature of **7** (3816 K) is similar to RDX. The parameters of compound **8** were not calculated due to the unsuccessful dehydration.

Table 4 Energetic properties and detonation parameters of **5–7** and RDX

	5	6	7	RDX
Formula	$C_3H_4N_8$	$C_3H_2N_{10}$	$C_3H_2N_8O_2$	$C_6H_5N_7O_4$
FW/g mol^{-1}	152.13	178.13	182.11	222.12
N^a/%	73.66	78.64	61.53	37.84
IS^b/J	10	3	4	7.4
FS^c/N	>360	10	108	120
ESD^d/mJ	800	250	250	200
$T_m{}^e$/°C	—	—	180	—
$T_d{}^f$/°C	241	152	188	204
Ω^g/%	−84.1	−60.0	−43.9	−21.6
ρ^h/g cm^{-3}	1.66	1.56	1.69	1.80
$\Delta_f H^{\circ\, i}$/kJ mol^{-1}	460	846	516	85
$\Delta_f U^{\circ\, j}$/kJ kg^{-1}	3120	4833	2915	481
Calculated detonation parameters (EXPLO5 6.02)				
$-\Delta_{ex}U^k$/kJ kg^{-1}	3481	4929	5064	5903
$T_{det}{}^l$/K	2479	3678	3816	3849
$p_{CJ}{}^m$/kbar	237	220	263	347
D^n/m s^{-1}	8397	7963	8251	8854
$V_0{}^o$/L kg^{-1}	772	758	753	785

[a] Nitrogen content. [b] Impact sensitivity (BAM drophammer, 1 of 6). [c] Friction sensitivity (BAM friction tester, 1 of 6). [d] Sensitivity to electrostatic discharge. [e] Melting point. [f] Decomposition temperature. [g] Oxygen balance (CO_2). [h] Density at room temperature. [i] Calculated enthalpy of formation. [j] Calculated energy of formation. [k] Heat of explosion. [l] Explosion temperature. [m] Detonation pressure. [n] Detonation velocity. [o] Volume of gaseous detonation products.

Conclusions

The goal of this study has been the preparation and thorough characterization of the novel nitrogen-rich compound 5-(5-amino-2*H*-1,2,3-triazol-4-yl)-1*H*-tetrazole (**5**) and the further derivatization of the amino moiety into the more energetic azido (**6**) and nitro (**7**) groups, as well as the connection by means of a diazene bridge (**8**). Low temperature single crystal X-ray diffraction revealed the position of the benzyl group of the precursor molecule 5-amino-1-benzyl-1,2,3-triazole-4-carboxamide (**2**), and likewise the position of the protons of the title compound **5**. The compounds were comprehensively characterized by multinuclear NMR (including ^{15}N for **6** and **7**) as well as vibrational spectroscopy and mass spectrometry. While the amino derivate exhibits a very good thermal stability (241 °C), as evidenced by DTA, the more energetic derivatives **6–8** are less thermally stable (128 to 188 °C). With the exception of the friction insensitive **5**, the main compounds **5–8** all have to be classified as sensitive to both impact and friction, as determined by BAM standards. Although, compounds **5–7** are superior to the commonly used TNT regarding their calculated detonation parameters (EPXLO5, 6.02), the performance of RDX is not reached. On the other hand, taking into account the high nitrogen contents of 73.66 (**5**), 78.64 (**6**) and 61.53% (7) and high enthalpies of formation the compounds might be of interest as anions for primary as well as secondary explosives, or gun propellants in combination with metal (**6**) or nitrogen-rich cations (**5** and **7**), respectively.[29]

Experimental section

All chemicals were used as supplied (ABCR, Acros Organics, AppliChem, Sigma-Aldrich, VWR), if not stated otherwise.

NMR spectra were recorded using the spectrometers JEOL Eclipse 270, JEOL Eclipse 400, JEOL ECX 400 and Bruker Avance III 400. The measurements were conducted in regular glass NMR tubes (Ø 5 mm) and, if not stated otherwise, at 25 °C. Tetramethylsilane (^1H, ^{13}C) and nitromethane ($^{14/15}N$) were used as external standards. As additional internal standard the reference values of the partially deuterated solvent impurity (^1H) and the fully deuterated solvent (^{13}C) were used.[30] $^{13}C\{^1H\}$ and $^{14}N\{^1H\}$ NMR spectra are simplified as ^{13}C and ^{14}N NMR spectra, respectively. The routinely performed ^1H broad band decoupling is not mentioned explicitly. Infrared (IR) spectra were recorded on a PerkinElmer BX FT IR spectrometer equipped with a Smiths DuraSamplIR II diamond ATR unit with pure samples. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m) and "weak" (w). Raman spectra were recorded on a Bruker RAM II spectrometer equipped with a Nd:YAG laser operating at 1064 nm and a reflection angle of 180°. The intensities are reported as percentages of the most intense peak and are given in parentheses. Low resolution mass spectra were recorded on a JEOL MStation JMS-700. Determination of the carbon, hydrogen and nitrogen contents was carried out by combustion analysis using an Elementar Vario EL (the determined nitrogen values are often lower than the calculated ones, which is common with nitrogen-rich compounds and cannot be avoided). Differential thermal analysis was conducted with an OZM Research DTA 552-Ex in open glass tubes (diameter 4 mm, length about 47 mm) at a heating rate of 5 °C min^{-1}. The temperatures are given as onset temperatures. Melting points were checked with a Büchi Melting Point B-540 in open glass capillaries.

Sensitivities to impact (IS) and friction (FS) were determined according to BAM standards,[31] using a BAM drop hammer and a BAM friction apparatus.[32] The compounds were classified in compliance with UN guidelines.[21] Impact: insensitive >40 J, less sensitive ≥35 J, sensitive ≥4 J, very sensitive ≤3 J; Friction: insensitive >360 N, less sensitive = 360 N, sensitive <360 N and >80 N, very sensitive ≤80 N, extremely sensitive ≤10 N. Sensitivities to electrostatic discharge (ESD) were determined with an OZM Research ESD 2010 EN. The compounds were sieved to determine the grain size (<100 µm, 100 to 500 µm, >500 µm).

The crystal structures of **2** and **5** were determined by single crystal X-ray diffraction on an Oxford Diffraction Xcalibur 3 or a Bruker D8 Venture diffractometer. Both devices work with graphite-monochromated molybdenum K$_\alpha$ radiation (λ = 71.073 pm). Data collection and reduction were performed with CrysAlisPro,[33] or SAINT.[34] The structures were solved with SIR97,[35] refined with SHELXL-97,[36] or SHELXL-2013,[37] and finally checked with PLATON,[38] all integrated into the WinGX software suite.[39] The finalized CIF files were checked with checkCIF,[40] and deposited at the Cambridge Crystallographic Data Centre as supplementary publications 1406925 (**2**) and 1413469 (**5**).[41] Intra- and intermolecular contacts were analyzed with Mercury.[42] The illustrations of molecular structures were drawn with ORTEP-3.[43]

Caution! Most compounds prepared herein are energetic compounds sensitive to impact, friction and electrostatic discharge. Although there were no problems in handling the compounds, proper protective measures (ear protection, Kevlar® gloves, face shield, body armor and earthed equipment) should be used.

Benzyl azide (1)

Benzyl chloride (106 g, 840 mmol) and sodium azide (82.0 g, 1.26 mol) were stirred in a mixture of ethanol (400 mL) and water (50 mL) for 20 hours at 95 °C. The suspension was afterwards poured in water (2 L), divided into four portions and each was extracted with diethyl ether (2 × 200 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure at 50 °C to obtain a clear, yellow liquid (106 g, 796 mmol, 95%). **^{1}H NMR** (DMSO-d_6): δ = 7.44–7.34 (m, 5H, CH), 4.44 (s, 2H, CH$_2$). **^{13}C NMR** (DMSO-d_6): δ = 135.6, 128.7, 128.4, 128.1, 53.6 (CH$_2$). **^{14}N NMR** (DMSO-d_6): δ = −127, −164, −300.

5-Amino-1-benzyl-1,2,3-triazole-4-carboxamide (2)

Cyanoacetamide (16.8 g, 200 mmol) and **1** (26.6 g, 200 mmol) were added to sodium (4.60 g, 200 mmol) in ethanol (500 mL) and the mixture was refluxed for one hour. The precipitate was filtered off and washed with water and ethanol, then suspended in ethanol/water (4 : 1, 500 mL) and heated for half an hour. The precipitate was filtered off again, washed with water, ethanol and diethyl ether to yield a colorless solid (34.5 g, 159 mmol, 80%). **^{1}H NMR** (DMSO-d_6): δ = 7.50 (br, 2H, NH$_2$), 7.39–7.20 (m, 5H, CH), 5.45 (s, 2H, CH$_2$). **^{13}C NMR** (DMSO-d_6): δ = 164.5 (CONH$_2$), 144.9 (C$_{\text{tri}}$), 136.0, 128.7, 127.8, 127.4, 121.8 (C$_{\text{tri}}$), 48.4 (CH$_2$). **MS** (DEI+): m/z = 217.2 ([M]$^+$). **EA** ($C_{10}H_{11}N_5O$): calcd C 55.29, H 5.10, N 32.24%; found C 55.17, H 4.93, N 32.11%.

5-Amino-1-benzyl-1,2,3-triazole-4-carbonitrile (3)

Trifluoroacetic anhydride (26.0 mL, 184 mmol) was carefully added to a suspension of **2** (20.0 g, 92.1 mmol) in dry pyridine (210 mL), while cooled with an ice/water bath. The flask was sealed and the deep red solution was stirred for 16 hours without removing or refreshing the cooling bath. The reaction mixture was poured on ice (250 g) and stirred for about 24 hours at room temperature. Concentrated hydrochloric acid (220 mL) was added dropwise, then stirred for about 48 hours at room temperature until a completely homogenized, light brown suspension was obtained. The precipitate was filtered off, washed with diluted hydrochloric acid and water, then suspended in toluene and stirred for one hour. The solvent was removed under reduced pressure and the residue was suspended in *n*-pentane, filtered off and washed with *n*-pentane to yield a pale brownish powder (15.7 g, 78.8 mmol, 86%). **^{1}H NMR** (DMSO-d_6): δ = 7.40–7.30 (m, 3H, CH), 7.25–7.23 (m, 2H, CH), 7.18 (s, 2H, NH$_2$), 5.43 (s, 2H, CH$_2$). **^{13}C NMR** (DMSO-d_6): δ = 148.0 (C$_{\text{tri}}$), 135.2, 128.7, 127.9, 127.5, 113.7 (C$_{\text{tri}}$), 101.3 (CN), 48.8 (CH$_2$). **MS** (DEI+): m/z = 199.1 ([M]$^+$). **EA** ($C_{10}H_9N_5$): calcd C 60.29, H 4.55, N 35.16%; found C 60.29, H 4.47, N 34.97%.

5-(5-Amino-1-benzyl-1,2,3-triazol-4-yl)tetrazole (4)

A suspension of **3** (15.9 g, 80.0 mmol), sodium azide (10.4 g, 160 mmol) and zinc chloride (13.6 g, 100 mmol) in dry tetrahydrofuran (250 mL) was stirred for 16 hours at 70 °C. Concentrated hydrochloric acid (14 mL) was added to the cooled down solution, which was then stirred for half an hour. The solvent was removed under reduced pressure and the residue was suspended in half concentrated hydrochloric acid (300 mL) and stirred for several hours. The precipitate was filtered off and washed with diluted hydrochloric acid and water to yield a pale yellow powder (18.8 g, 77.6 mmol, 97%). **^{1}H NMR** (DMSO-d_6): δ = 7.37–7.26 (m, 5H, CH), 6.61 (s, 2H, NH$_2$), 5.55 (s, 2H, CH$_2$). **^{13}C NMR** (DMSO-d_6): δ = 148.6 (C$_{\text{tri}}$), 142.9 (C$_{\text{tet}}$), 135.8, 128.7, 127.9, 127.5, 114.4 (C$_{\text{tri}}$), 48.8 (CH$_2$). **MS** (DEI+):

m/z = 242.2 ([M]$^+$). **EA** ($C_{10}H_{10}N_8$): calcd C 49.58, H 4.16, N 46.26%; found C 48.95, H 4.05, N 45.32%.

5-(5-Amino-2*H*-1,2,3-triazol-4-yl)tetrazole (5)

Sodium was added in small pieces to a clear red solution of **4** (37.6 g, 155 mmol) in liquid ammonia (about 150 mL) until a deep blue suspension was obtained, carefully followed by ammonium chloride until the blue color was completely gone. The solvent was allowed to slowly evaporate and the residue was dissolved in water (about 200 mL), then filtered. The filtrate was evaporated under reduced pressure and the residue was dissolved again in water (200 mL), then acidified with concentrated hydrochloric acid (40 mL). The precipitate was filtered off and washed with water to yield a yellow powder (22.5 g, 148 mmol, 95%). **^{1}H NMR** (DMSO-d_6): δ = 16.19 and 14.64 (br, 2H, NH), 6.03 (br, 2H, NH$_2$). **^{13}C NMR** (DMSO-d_6): δ = 149.0 (C_{tet}), 147.6 (br, C_{tri}), 111.6 (br, C_{tri}). **IR** (ATR): ν = 3437 (m), 3317 (m), 3227 (w), 3138 (m), 3036 (m), 2976 (m), 2895 (m), 2796 (m), 2700 (m), 2553 (m), 1624 (vs), 1564 (s), 1503 (m), 1467 (m), 1404 (w), 1372 (m), 1332 (w), 1250 (w), 1240 (s), 1214 (m), 1185 (m), 1145 (m), 1090 (s), 1019 (m), 1003 (s), 971 (vs), 866 (vs), 764 (m), 749 (vs), 691 (m) cm^{-1}. **Raman** (300 mW): ν = 1646 (24), 1627 (100), 1571 (8), 1474 (5), 1406 (21), 1250 (8), 1178 (6), 1151 (9), 1104 (13), 1020 (23), 747 (9), 421 (12), 334 (15), 172 (14), 140 (24), 121 (31), 63 (10) cm^{-1}. **MS** (DEI+): m/z = 152.1 ([M]$^+$). **EA** ($C_3H_4N_8$): calcd C 23.69, H 2.65, N 73.66%; found C 24.07, H 2.76, N 73.29%. **DTA** (5 °C min^{-1}): T_d = 241 °C. **Sensitivities** (grain size <100 μm): IS 10 J, FS 360 N, ESD 800 mJ.

5-(5-Azido-2*H*-1,2,3-triazol-4-yl)tetrazole (6)

Sodium nitrite (2.07 g, 30.0 mmol) was added to a suspension of **5** (3.04 g, 20.0 mmol) in sulfuric acid (20%, 200 mL) at 0 °C. The cooling was removed and the yellow reaction mixture was stirred for three hours at room temperature. Sodium azide (2.60 g, 40.0 mmol) was then added in small portions and stirred for 30 minutes at room temperature. The resulting colorless foamy suspension was refluxed until a clear solution was obtained. The resulting suspension after cooling down was extracted with ethyl acetate (4 × 150 mL). The combined organic phases were dried over magnesium sulfate and evaporated under reduced pressure. The residue was suspended in toluene, evaporated again and washed with *n*-pentane to yield a colorless solid (3.08 g, 17.3 mmol, 87%). **^{1}H NMR** (DMSO-d_6): δ = 15.81 (br, NH). **^{13}C NMR** (DMSO-d_6): δ = 147.7 (C_{tri}), 143.1 (C_{tet}), 123.0 (C_{tri}). **^{14}N NMR** (DMSO-d_6): δ = −138 (N_β). **^{15}N NMR** (DMSO-d_6): δ = −11.1 (N_{tet}), −55.7 (N_{tri}), −74.1 (N_{tri}), −101.9 (NH_{tet}), −126.3 (NH_{tri}), −143.2 (N_γ), −148.6 (N_β), −303.3 (N_α). **^{15}N{^{1}H} NMR** (DMSO-d_6): δ = −11.1 (N_{tet}), −55.4 (N_{tri}), −74.0 (N_{tri}), −102.1 (NH_{tet}), −126.1 (NH_{tri}), −143.2 (N_γ), −148.6 (N_β), −303.3 (N_α). **IR** (ATR): ν = 3524 (w), 3227 (w), 3132 (w), 2923 (w), 2800 (w), 2677 (w), 2426 (w), 2331 (w), 2147 (vs), 1915 (w), 1628 (s), 1525 (vs), 1407 (w), 1356 (w), 1345 (w), 1322 (m), 1308 (w), 1295 (w), 1250 (w), 1209 (s), 1160 (w), 1121 (w), 1103 (w), 1067 (m), 1019 (s), 1006 (m), 977 (s), 835 (m), 795 (m), 769 (m), 757 (s), 717 (w), 703 (w), 694 (w) cm^{-1}. **Raman** (300 mW): 2163 (12), 1631 (100), 1534 (22), 1445 (5), 1409 (17), 1357 (18), 1326 (9), 1299 (5), 1252 (8), 1219 (11), 1168 (17), 1126 (5), 1022 (16), 978 (9), 797 (6), 760 (11) cm^{-1}. **MS** (DEI+): m/z = 178.1 ([M]$^+$). **EA** ($C_3H_2N_{10}$): calcd C 20.23, H 1.13, N 78.64%; found C 19.83, H 1.89, N 73.11%. **DTA** (5 °C min^{-1}): T_d = 152 °C. **Sensitivities** (grain size <100 μm): IS 3 J, FS 10 N, ESD 250 mJ.

5-(5-Nitro-2*H*-1,2,3-triazol-4-yl)tetrazole (7)

Potassium superoxide (4.75 g, 66.9 mmol) and **5** (1.00 g, 6.57 mmol) were stirred in tetrahydrofuran (50 mL) for 72 hours at 60 °C. The solvent was removed under reduced pressure and ice (80 g) was added to the dry residue, followed by sulfuric acid (11 mL). The resulting yellow suspension was stirred for one hour, then extracted with methyl ethyl ketone (5 × 75 mL). The combined organic phases were washed with a saturated sodium chloride solution (2 × 50 mL), dried over magnesium sulfate and removed under reduced pressure. The resulting green solid was dried in fine vacuum overnight, pestled, resuspended in dichloromethane, sonicated for a few minutes and filtered off to yield a pale green solid (814 mg, 4.47 mmol, 68%). **^{1}H NMR** (DMSO-d_6): δ = 9.93 (br, NH). **^{13}C NMR** (DMSO-d_6): δ = 151.1 (C_{tri}), 147.7 (C_{tet}), 127.7 (C_{tri}). **^{14}N NMR** (DMSO-d_6): δ = −21 (NO_2). **^{15}N NMR** (DMSO-d_6): −14.4 (N_{tet}), −27.5 (NO_2), −51.1 (N_{tri}), −65.4 (N_{tri}), −89.6 (NH_{tet}), −97.2 (NH_{tri}). **^{15}N{^{1}H} NMR** (DMSO-d_6): −14.8 (N_{tet}), −27.9 (NO_2), −51.5 (N_{tri}), −65.8 (N_{tri}), −90.2 (NH_{tet}), −97.4 (NH_{tri}). **IR** (ATR): ν = 3221 (w), 3113 (w), 3055 (w), 2908 (w), 1630 (w), 1547 (vs), 1500 (vw), 1472 (w), 1383 (s), 1350 (m), 1244 (w), 1197 (vw), 1138 (m), 1097 (m), 1065 (s), 1021 (w), 1008 (s), 991 (m) 845 (m), 835 (vs), 744 (m), 726 (m), 707 (m) cm^{-1}. **Raman** (300 mW): ν = 1652 (12), 1630 (100), 1546 (6), 1470 (16), 1414 (7), 1387 (23), 1340 (23), 1284 (8), 1244 (6), 1201 (7), 1014 (11), 987 (8), 833 (5), 504 (7), 383 (5), 166 (5), 137 (9), 92 (40), 79 (24) cm^{-1}. **MS** (DEI+): m/z = 182.2 (12%, [M$^+$]), 30.1 (100%, [NO$^+$]). **EA** ($C_3H_2N_8O_2$): calcd C 19.79, H 1.11, N 61.53%; found C 19.88, H 1.63, N 59.98%. **DTA** (5 °C min^{-1}): T_{melt} = 180 °C, T_d = 188 °C. **Sensitivities** (grain size <100 μm): IS 4 J, FS 108 N, ESD 250 mJ.

1,2-Bis(4-(tetrazol-5-yl)-1,2,3-triazol-5-yl)diazene dihydrate (8)

Potassium permanganate (1.05 g, 6.67 mmol) was added in small portions to **5** (1.52 g, 10.0 mmol) in aqueous sodium hydroxide (10%, 40 mL) at 70 °C. After stirring for two hours at 100 °C, ethanol (10 mL) was added and stirred for further 15 minutes. The suspension was filtered through kieselgur and washed until the filtrate was colorless. The combined filtrates were evaporated under reduced pressure, the residue was suspended in hydrochloric acid (2 M, 100 mL) and stirred for several hours. The precipitate was filtered off and washed with diluted hydrochloric acid and water to yield a yellow solid (700 mg, 2.08 mmol, 42%). **^{1}H NMR** (DMSO-d_6): δ = 10.09 (br, NH). **^{13}C NMR** (DMSO-d_6): δ = 153.7, 147.2, 126.6. **IR** (ATR): ν = 3522 (w), 3422 (w), 3232 (s), 2824 (w), 2748 (w), 2613 (w), 2501 (m), 2360 (m), 2000 (vw), 1877 (w), 1637 (m), 1611 (m), 1498 (m), 1428 (vw), 1406 (m), 1369 (s), 1344 (m), 1298 (vw), 1245(w), 1220 (w), 1207 (w), 1178 (w), 1143 (w), 1125 (vs), 1076 (vs), 1030 (vs), 1004 (s), 977 (s), 960 (s), 903 (m), 822 (vs), 772 (w), 726 (m), 672 (vw) cm^{-1}. **Raman** (300 mW): ν = 1638 (37), 1613 (16), 1503 (16), 1492 (17), 1469 (100), 1432 (21), 1404 (8), 1369 (56), 1344 (69), 1329 (31), 1298 (10), 1245 (7), 1200 (14), 1182 (5), 1151 (4), 1125 (6), 980 (14), 903 (8), 621 (7), 353 (4) cm^{-1}. **MS** (FAB−): m/z = 299.1 ($[M]^+$). **EA** ($C_3H_4N_8\cdot 2H_2O$): calcd C 21.43, H 2.40, N 66.65%; found C 22.68, H 2.32, N 66.07%. **DTA** (5 °C min^{-1}): T_d = 128 °C. **Sensitivities** (grain size <100 μm): IS 2 J, FS 28 N, ESD 700 mJ.

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