

**Kapow!** The synthesis and full structural as well as spectroscopic characterization of three energetic C–C bonded 5-(1,2,4-triazoly)tetrazol-1-ols are presented (see figure). The potential application of the synthesized com-

pounds as energetic materials was assessed by measurement of thermal stability, sensitivity to external stimuli, and the calculated performance characteristics.

**Energetic Heterocycles**

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**A Study of 5-(1,2,4-Triazol-C-yl)tetrazol-1-ols: Combining the Benefits of Different Heterocycles for the Design of Energetic Materials**



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# A Study of 5-(1,2,4-Triazol-C-yl)tetrazol-1-ols: Combining the Benefits of Different Heterocycles for the Design of Energetic Materials

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**Abstract:** The synthesis and full structural and spectroscopic characterization of three 5-(1,2,4-triazol-C-yl)tetrazol-1-ol compounds with selected energetic moieties including nitrimino (**5**), nitro (**6**) and azido (**7**) groups are reported. The influence of those energetic moieties as well as the C–C connection of a tetrazol-1-ol and a 1,2,4-triazole on structural and energetic properties has been investigated. All com-

pounds were well characterized by various means, including IR and multinuclear NMR spectroscopy, mass spectrometry, and DSC. The molecular structures of **5–8** were determined in the solid state by single-crystal X-ray

**Keywords:** energetic materials • nitrogen heterocycles • NMR spectroscopy • X-ray diffraction

diffraction. The standard heats of formation were calculated on the CBS-4M level of theory utilizing the atomization energy method, revealing highly positive values for all compounds. The detonation parameters were calculated with the EXPLO5 program and compared to the common secondary explosive RDX. Additionally, sensitivities towards impact, friction and electrostatic discharge were determined.

## Introduction

The chemistry of explosives, their development and application are as old as 220 BC, when black powder was discovered accidentally by the Chinese. Nowadays, not only military applications are studied, but energetic materials are studied for civilian use in mining, construction, demolition and safety equipment such as airbags, signal flares and fire extinguishing systems has been extensively studied. Academic research in the area focuses mainly on the aspects of novel energetic systems affecting stability and performance and new strategies for the design of energetic materials.<sup>[1,2]</sup> Compared to typical explosives in current use, like 2,4,6-trinitrotoluene (TNT) or 1,3,5-trinitro-1,3,5-triazinane (RDX), modern energetic materials derive their energy not from the oxidation of a carbon backbone but rather from their high heats of formation. This is the result of the conversion of large numbers of nitrogen–nitrogen single and double bonds to triply bonded molecular nitrogen.<sup>[3]</sup> A prominent family of novel high-energy-density materials (HEDMs) are azole-based compounds, because they are generally highly endothermic, have high densities and low sensitivities towards external stimuli. Owing to the high positive heats of formation and the high level of environmental compatibility, these compounds have been studied in numerous research groups over the last couple of years with growing interest.

Triazoles and tetrazoles have been used for the preparation of high-performance primary<sup>[4]</sup> and secondary<sup>[5]</sup> explosives, because energetic materials based on those heterocycles show a desirable compromise between a high nitrogen content and excellent kinetic and thermal stabilities due to the aromaticity of nitrogen heterocycles. Much research has been done on the combination of heterocycles to bistetrazoles<sup>[6]</sup> and bistriazoles,<sup>[7]</sup> resulting in numerous compounds with outstanding energetic properties. The recently published C–C connection of a tetrazole and a 1,2,4-triazole leads to energetic materials with variable properties.<sup>[8]</sup>

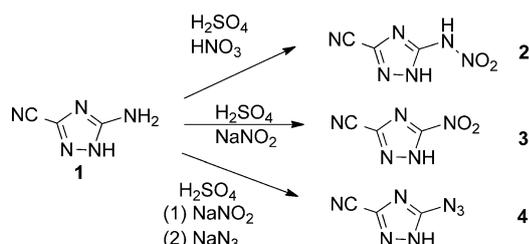
The introduction of *N*-oxides is a recently reintroduced method to raise the densities of energetic compounds to increase energy density.<sup>[9]</sup> One method for the oxidation of nitrogen-rich heterocycles uses oxidizing agents like trifluoroacetic acid,<sup>[10]</sup> potassium peroxomonosulfate (Oxone),<sup>[11]</sup> or hypofluorous acid.<sup>[12]</sup> The often low selectivity and high oxidation potential of those compounds can lead to several isomers or even a complete decomposition of the starting material, especially in compounds with several oxidizable nitrogen atoms. 1-Hydroxytetrazoles are an appropriate alternative, owing to the fact that the oxygen atom may be introduced during the synthesis of the tetrazole ring instead of subsequent oxidation.<sup>[13]</sup>

## Results and Discussion

**Syntheses:** The synthesis of the starting material 5-amino-1*H*-1,2,4-triazole-3-carbonitrile (**1**) was accomplished by dehydration of the corresponding carboxamide with phosphorus pentoxide in acetonitrile as published recently.<sup>[8]</sup> The energetic moieties were introduced by modification of the amine group of compound **1** as shown in Scheme 1. The

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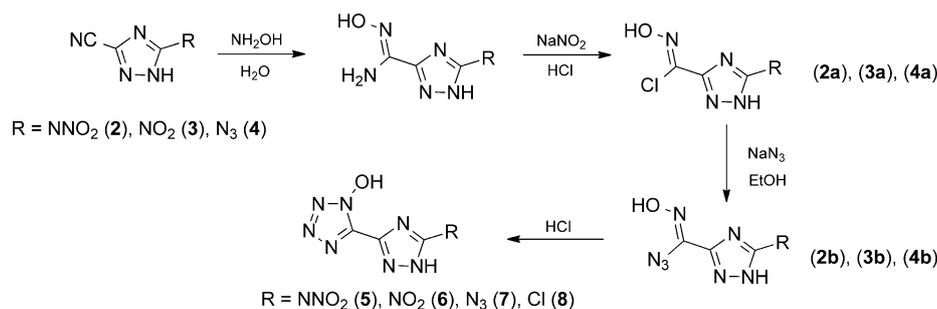
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/chem.201301339>.



Scheme 1. Synthesis of 5-nitramino-1H-1,2,4-triazole-3-carbonitrile (**2**), 5-nitro-1H-1,2,4-triazole-3-carbonitrile (**3**) and 5-azido-1H-1,2,4-triazole-3-carbonitrile (**4**).

treatment of 5-amino-1H-1,2,4-triazole-3-carbonitrile with a mixture of sulfuric acid and nitric acids (6:1) leads to 5-nitramino-1H-1,2,4-triazole-3-carbonitrile (**2**). 5-Nitro-1H-1,2,4-triazole-3-carbonitrile (**3**) was obtained by diazotization with sulfuric acid and excess sodium nitrite. The azido compound (**4**) was also synthesized by diazotization in sulfuric acid and subsequent reaction with excess sodium azide.

The synthesis of the 1-hydroxytetrazole moiety was accomplished by literature methods.<sup>[13]</sup> As shown in Scheme 2, the reaction of hydroxylamine with the nitrile moiety of **2–4**



Scheme 2. Synthesis of 5-(5-nitrimino-1,4H-1,2,4-triazol-3-yl)tetrazol-1-ol (NATTO, **5**), 5-(3-nitro-1H-1,2,4-triazol-5-yl)tetrazol-1-ol (NTTO, **6**), 5-(5-azido-1H-1,2,4-triazol-3-yl)tetrazol-1-ol (AzTTO, **7**) and 5-(5-chloro-1H-1,2,4-triazol-3-yl)tetrazol-1-ol (**8**).

leads to the formation of the corresponding amidoxime. Those intermediate compounds were not isolated but subsequently reacted with sodium nitrite after addition of hydrochloric acid. The diazotization in hydrochloric acid causes the formation of the chloroxime compounds **2a–4a**, which were collected by filtration to remove traces of unreacted nitrile. The following chlorine to azide exchange readily takes place in ethanol and leads to the azidoxime compounds **2b–4b**. The final cyclization is accomplished for compounds **2b** and **3b** in concentrated hydrochloric acid within 12 h and the energetic 1-hydroxytetrazole compounds **5–6** were isolated in excellent yields.

Due to the high sensitivity of compound **4b**, a different cyclization method was applied. The extraction of the azidoxime with diethyl ether after the chlorine to azide exchange without evaporation of the ether avoids isolation of the pure and highly sensitive compound. Subsequent saturation of the ether solution with HCl gas and stirring for two days also leads to the formation of compound **7**. After re-

moval of the ether and the excess of HCl gas, **7** could also be isolated nearly quantitatively.

Surprisingly, in the case of the azidoxime **3b**, the utilization of this method selectively leads to the chlorine compound **8**. Apparently, a nitro to chlorine exchange occurs when stirring **3b** in a saturated solution of HCl in ether and leads to the formation of the less-energetic, undesired chlorine compound.

All three energetic 5-(1,2,4-triazol-C-yl)tetrazole-1-ol compounds **5–7** were fully characterized by IR and Raman as well as multinuclear NMR spectroscopy and mass spectrometry. The molecular structures of **5–8** in the solid state were determined by single-crystal X-ray diffraction.

**Crystal structures:** Single-crystal X-ray measurements were performed for compounds **5–8** and are discussed below. The crystal structure of compound **8** can be found in the Supporting Information. The bond lengths and torsion angles within the azole ring of compounds **5–8** are all in the expected range as compared to similar triazole and tetrazole compounds.<sup>[6a,14]</sup> The bond lengths within the triazole and the tetrazole ring in the crystal structures are all between the

length of formal C–N and N–N single and double bonds (C–N: 1.47 and 1.22 Å; N–N: 1.48 and 1.20 Å).<sup>[15]</sup> As expected,<sup>[7,16]</sup> the bistriazole moiety is completely planar due to extensive delocalization of electrons in the molecule. The nitrimino moiety points towards the nitrogen atom N1 and participates in an intramolecular hydrogen bond N1–H1...O3 with a D...A length of 2.555(2) Å and a D–H...A angle of 111.7(17)° (Figure 1).

In comparison to the recently published 5-(5-nitrimino-1,4H-1,2,4-triazol-3-yl)-1H-tetrazole, the density is increased from 1.618 to 1.741 g cm<sup>-3</sup> by introduction of the 1-hydroxytetra-

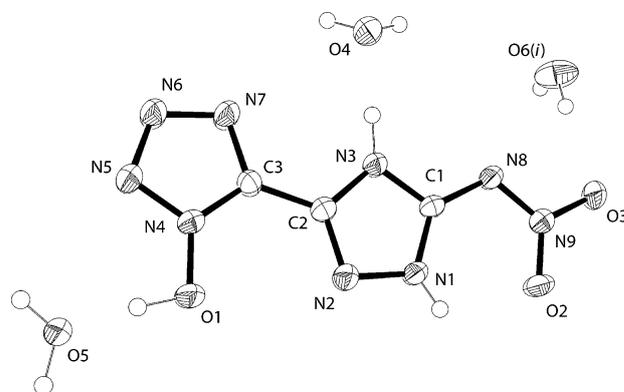


Figure 1. Molecular structure of 5-(5-nitrimino-1,4H-1,2,4-triazol-3-yl)tetrazol-1-ol (NATTO, **5**). Thermal ellipsoids are set to 50% probability. Symmetry code: *i*)  $-x, y, \frac{3}{2}-z$ .

Table 1. Hydrogen bonds present in the crystal structure of **5**.

D–H...A	<i>d</i> (D–H) [Å]	<i>d</i> (H...A) [Å]	<i>d</i> (D–H...A) [Å]	<(D–H...A) [°]
N1–H1...O2	0.82(2)	2.14(2)	2.555(2)	112(2)
N1–H1...O2 <sup>iii</sup>	0.82(2)	2.10(2)	2.890(2)	162(2)
N3–H3...O4	0.96(2)	1.62(2)	2.576(2)	179(5)
O1–H1...O5	1.12(3)	1.31(3)	2.422(2)	173(2)
O4 <sup>i</sup> –H4B...N6	0.83(2)	1.95(2)	2.752(2)	165(2)
O5 <sup>ii</sup> –H5B...N2	0.95(3)	1.87(3)	2.813(2)	173(2)
O5 <sup>iv</sup> –H5A...O3	0.86(3)	1.90(3)	2.750(2)	177(3)
O6 <sup>i</sup> –H6A...O3	0.85(2)	1.98(2)	2.796(4)	160(5)
O6 <sup>i</sup> –H6B...O4	0.84(2)	2.36(4)	3.018(5)	136(4)

Symmetry codes: *i*) 1–*x*, *y*, 3/2–*z*; *ii*) 1–*x*, –*y*, 1–*z*; *iii*) –*x*, –*y*, 1–*z*; *iv*) –1+*x*, *y*, *z*.

zole. The molecular structure of **5** together with the atom labeling is presented in Figure 1.

The structure is dominated by chains along the *a* axis, established by the threefold hydrogen bonding of the oxygen atom O5 acting both as acceptor and donor. Four further nitrogen atoms N1, N2, N3 and N6 are involved in additional hydrogen bonds (Table 1), resulting in strong interactions with surrounding molecules within the chains. The water molecule O4 at the edge acts as linker between two chains, which are arranged in a zigzag row with an angle of 141°. The rows are stacked along the *b* axis with an interlayer distance *d* = 3.31 Å and are stabilized by the intermolecular hydrogen bonds O6<sup>i</sup>–H6A...O3 and O6<sup>i</sup>–H6B...O4 (see Figure 2).

5-(3-Nitro-1*H*-1,2,4-triazol-5-yl)tetrazol-1-ol (NTTO, **6**) crystallizes as dihydrate in the triclinic space group *P* $\bar{1}$  with

a cell volume of 429.8(1) Å<sup>3</sup> and two molecular moieties in the unit cell. As expected, the torsion angle between the two heterocycles is very small (7.5(3)°) and the nitro group is also only slightly twisted out of the triazole plane (–2.4(3)°). As is also the case for the nitrmino compound **5**, the density is increased from 1.661 to 1.809 g cm<sup>–3</sup> in comparison to 5-(3-nitro-1*H*-1,2,4-triazol-5-yl)-2*H*-tetrazole. The formula unit of **6** together with the atom labeling is presented in Figure 3.

In the crystal structure of **6**, the NTTO molecules are arranged in planes and are joined by several threefold hydro-

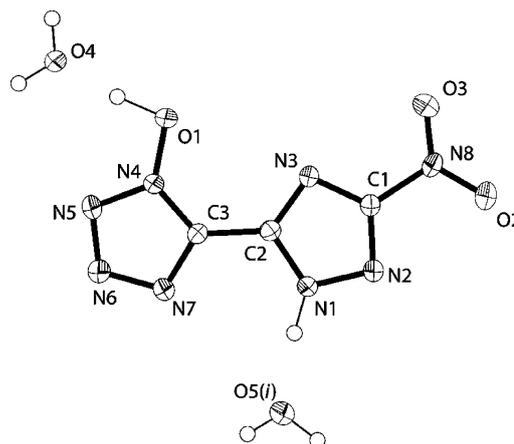


Figure 3. Molecular structure of 5-(3-nitro-1*H*-1,2,4-triazol-5-yl)tetrazol-1-ol (NTTO, **6**). Thermal ellipsoids are set to 50% probability. Symmetry code: *i*) 1–*x*, –*y*, 1–*z*.

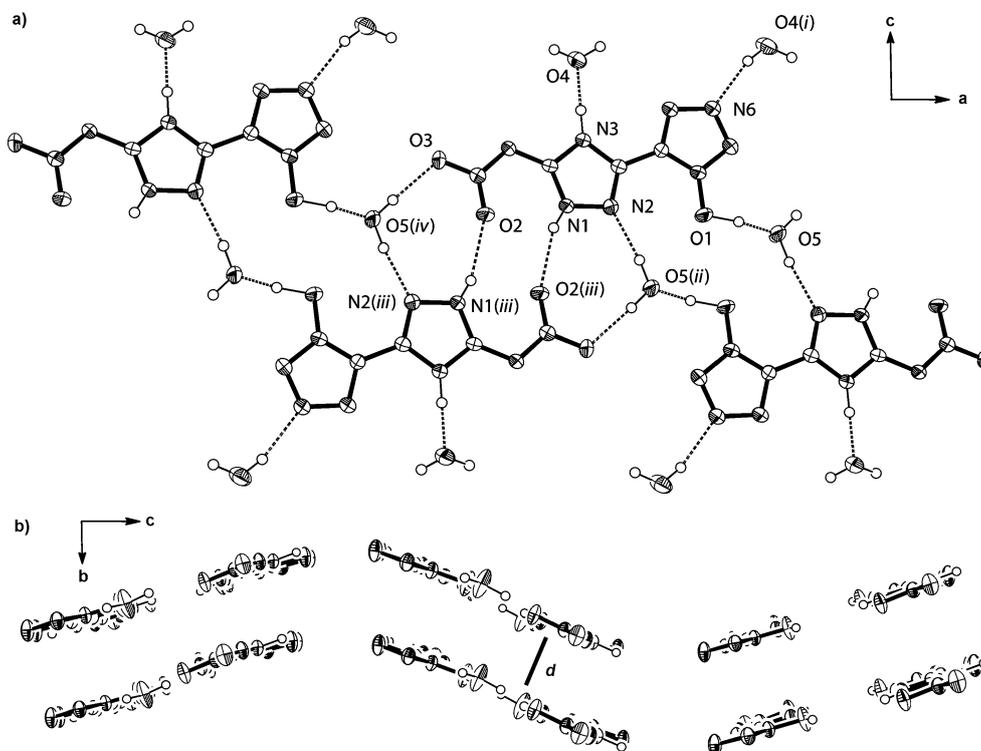


Figure 2. a) Formation of chains along the *a* axis in the crystal structure of **5**; b) zigzag arrangement of chains (layer distance *d* = 3.31 Å, water molecules are omitted for clarity). Thermal ellipsoids are set to 50% probability. Symmetry codes: *i*) 1–*x*, *y*, 3/2–*z*; *ii*) 1–*x*, –*y*, 1–*z*; *iii*) –*x*, –*y*, 1–*z*; *iv*) –1+*x*, *y*, *z*.

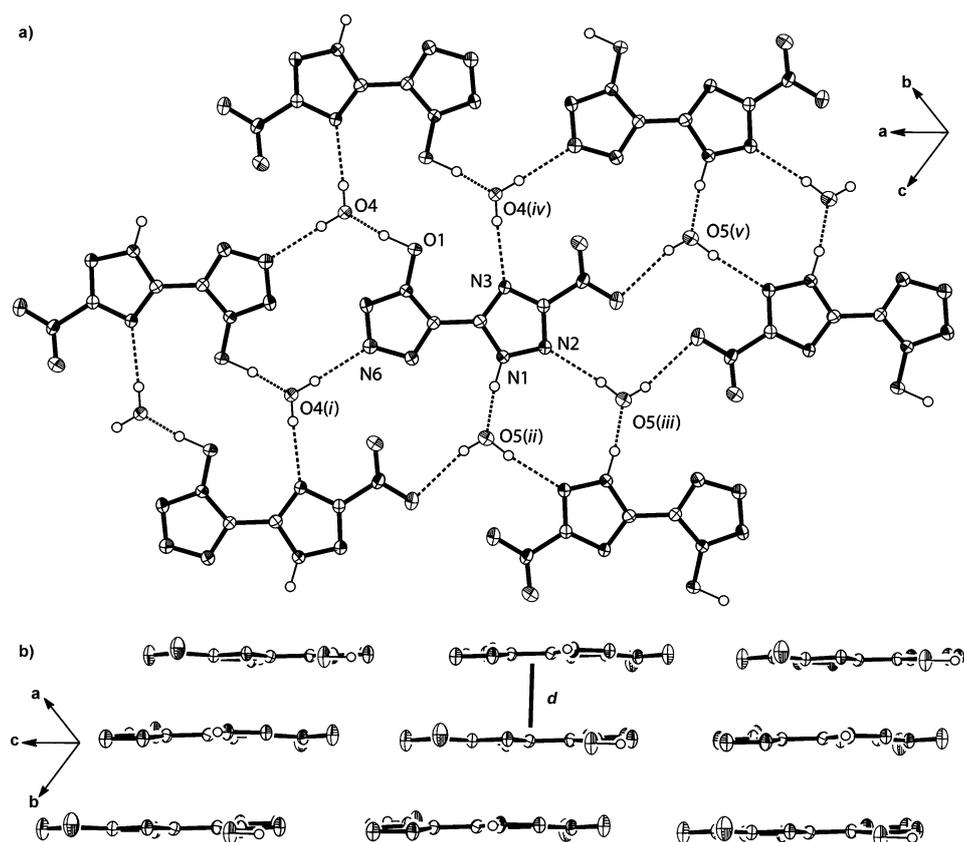


Figure 4. a) Formation of planes in the crystal structure of **6**; b) stacking of layers (layer distance  $d = 2.99$  Å, water molecules are omitted for clarity). Thermal ellipsoids are set to 50% probability. Symmetry codes: *i*)  $2-x, 1-y, 1-z$ ; *ii*)  $1-x, -y, 1-z$ ; *iii*)  $x, -1+y, z$ ; *iv*)  $2-x, 1-y, -z$ ; *v*)  $1-x, -y, -z$ .

gen bonds to the water molecules (Figure 4a and Table 2). A direct interaction between two NTTO molecules could not be observed, in contrast to the crystal structure of compound **5**. A strong network of hydrogen bonds is built up by the Oxygen atoms O4 and O5, which act both as donor and

Table 2. Hydrogen bonds present in the crystal structure of **6**.

D-H...A	$d(\text{D-H})$ [Å]	$d(\text{H...A})$ [Å]	$d(\text{D-H...A})$ [Å]	$\angle(\text{D-H...A})$ [°]
N1-H1...O5 <sup>ii</sup>	0.97(3)	1.70(3)	2.663(2)	170(2)
O1-H1...O4	1.06(3)	1.42(3)	2.471(2)	173(3)
O4 <sup>iv</sup> -H4A...N3	0.85(3)	2.11(3)	2.948(2)	170(3)
O4 <sup>i</sup> -H4B...N6	0.86(3)	2.07(3)	2.922(3)	176(3)
O5 <sup>v</sup> -H5A...O2	0.82(3)	2.28(3)	3.065(2)	160(3)
O5 <sup>iii</sup> -H5B...N2	0.89(3)	2.09(3)	2.971(3)	171(2)

Symmetry codes: *i*)  $2-x, 1-y, 1-z$ ; *ii*)  $1-x, -y, 1-z$ ; *iii*)  $x, -1+y, z$ ; *iv*)  $2-x, 1-y, -z$ ; *v*)  $1-x, -y, -z$ .

acceptor. The layers are are connected by a short contact  $\text{O}_1 \cdots \text{N}_8$  ( $d(\text{O} \cdots \text{N}) = 3.03$  Å) between the hydroxy group and the nitrogen atom of the nitro group and stacked above each other with an interlayer distance of  $d = 2.99$  Å. The stacking of the layers is displayed in Figure 4b together with the distance  $d$  between the layers.

Finally, 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (AzTTO, **7**) crystallizes as a monohydrate in the triclinic

space group  $P\bar{1}$  with two molecules in the unit cell and a cell volume of  $416.35(9)$  Å<sup>3</sup>. The formula unit of **7** together with the atom labeling is presented in Figure 5. The structure of the 5-azido-1,2,4-triazole moiety is similar to that of the recently published 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole.<sup>[8]</sup> The molecule shows a nearly planar assembly with a torsion angle between the two heterocycles of  $2.9(2)^\circ$ . The azide group is bent with an angle of  $172.1(2)^\circ$  and slightly twisted out of the triazole plane by  $-7.3(2)^\circ$ . In contrast to the nitro derivative **6** the proton is located at the nitrogen atom next to the C-N bond, similar to **5** and **4**. The oxygen and the azide are pointing into the same direction, similarly to the chloroxime precursor **4a**.<sup>[17]</sup>

The molecules form dimers between two triazole rings with a very weak and mostly electrostatic  $\text{N1-H1} \cdots \text{N2}^i$  hydrogen bond ( $d(\text{N1} \cdots \text{N2}^i) = 3.175(2)$  Å). This is similar to the precursor

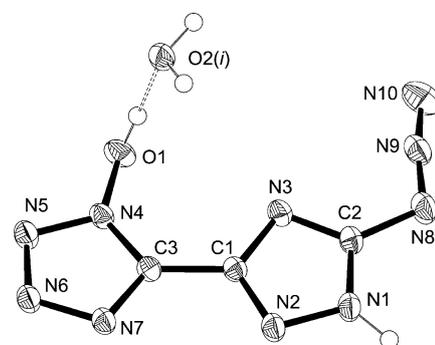


Figure 5. Molecular structure of 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (AzTTO, **7**). Thermal ellipsoids are set to 50% probability. Symmetry code: *i*)  $x, y, 1+z$ .

**4**, but there the bond is much stronger ( $d(\text{N1} \cdots \text{N2}^i) = 2.993(2)$  Å).<sup>[17]</sup> The dimers, in turn, form infinite parallel chains utilizing the water molecule and with N6 and N7 of the tetrazole ring as additional acceptors. The connection between the chains is established by a directed  $\text{N}_7 \cdots \text{O}$  interaction between the terminal nitrogen atom of the azide and the hydroxyl group ( $d(\text{N10} \cdots \text{O1}^v) = 2.879(2)$  Å;  $d(\text{N9-N10} \cdots \text{O1}^v) = 166.7(1)^\circ$ ) well below the sum of the van der Waals radii. The primary hydrogen bonding network and

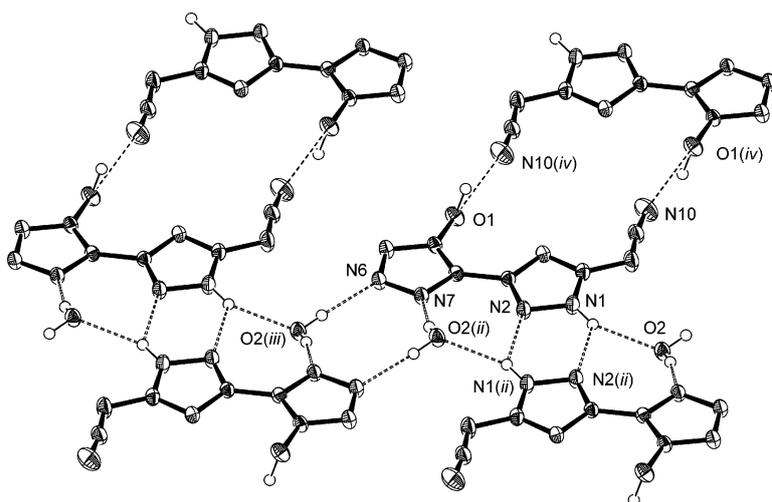


Figure 6. Formation of planes in the crystal structure of **7**, made up from infinite parallel chains. Thermal ellipsoids at 50% probability. Symmetry codes: *ii*)  $-x, 1-y, 1-z$ ; *iii*)  $x, 1+y, 1+z$ ; *iv*)  $1-x, -y, 2-z$ .

the short contact are illustrated in Figure 6 and the parameters are compiled in Table 3. Finally, the planes are connected by a strong hydrogen bond  $O1-H1O \cdots O2^i$  between the hydroxyl proton and the water molecule.

Table 3. Hydrogen bonds present in the crystal structure of **7**.

D–H...A	<i>d</i> (D–H) [Å]	<i>d</i> (H...A) [Å]	<i>d</i> (D–H...A) [Å]	$\angle$ (D–H...A) [°]
N1–H1...O2	0.91(2)	2.07(2)	2.824(2)	140(2)
N1–H1...N2 <sup>ii</sup>	0.91(2)	2.51(2)	3.175(2)	130(2)
O1–H1O...O2 <sup>i</sup>	0.97(3)	1.61(3)	2.574(2)	175(3)
O2–H2A...N7 <sup>iii</sup>	0.87(2)	1.94(2)	2.805(2)	170(2)
O2–H2B...N6 <sup>v</sup>	0.85(2)	1.99(2)	2.838(2)	177(2)

Symmetry code: *i*)  $x, y, 1+z$ ; *ii*)  $-x, 1-y, 1-z$ ; *iii*)  $x, 1+y, 1+z$ ; *v*)  $x, -1+y, -1+z$ .

**Multinuclear NMR spectroscopy:** All of the title compounds were investigated by  $^1H$ ,  $^{13}C$  and  $^{14}N$  NMR spectroscopy. Due to the low solubility of compound **5**  $^{15}N$  NMR spectra could only be obtained for compounds **6** and **7**.

Compounds **5–8** show two singlets for the carbon atoms of the C–C bridge in the expected range.<sup>[5c,14b]</sup> The signal of the carbon atom connected to the energetic moieties is observed at lower field in the range of  $\delta = 148.9$  ppm (**8**) to  $\delta = 163.2$  ppm (**6**). While the nitro group of compounds **5** and **6** can be identified by a sharp singlet at  $\delta = -24$  ppm (**6**) and  $\delta = -25$  ppm (**5**) in the  $^{14}N$  NMR spectra, the azido moiety of compound **7** shows a broad singlet at  $\delta = -136$  ppm. The NMR signals of all compounds are summarized in Table 4.

Due to the poor solubility of compound **5**,  $^{15}N$  NMR spectra could only be obtained for compounds **6** and **7**, as illustrated in Figure 7. Eight well resolved resonances are observed in the  $^{15}N$  NMR spectrum of the nitro-compound **6**. The assignments were based on comparison with theoretical calculations with Gaussian 09 (MPW1PW91/aug-cc-pVDZ).<sup>[18]</sup> The signals of the triazole nitrogen atoms as well as the nitro group can be found in the expected range simi-

lar to the recently published 5-(3-nitro-1*H*-1,2,4-triazol-5-yl)-2*H*-tetrazole,<sup>[8]</sup> at shifts of  $\delta = -157.7$  (N1),  $-91.2$  (N2),  $-139.9$  (N3), and  $-28.5$  ppm (NO<sub>2</sub>). In contrast to this, the azido-compound **7** shows only eight well resolved resonances instead of the expected ten, similar to 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazole.<sup>[8]</sup> The two missing signals are the triazole nitrogen atoms N1 and N2, probably resulting from a fast proton exchange. The remaining signals are observed at shifts of  $\delta = -150.8$  (N3),  $-295.3$  (N8),  $-145.6$  (N9), and

Table 4. NMR signals of compounds **4–8** in [D<sub>6</sub>]DMSO.

Compound	$\delta$ [ppm]			
	$^{13}C\{^1H\}$ C <sub>Triazole</sub>	$^{13}C\{^1H\}$ C <sub>Tetrazole</sub>	$^{14}N$	$^1H$
<b>5</b>	152.5, 140.5	138.7	-25	7.10
<b>6</b>	163.2, 143.3	138.0	-24	8.09
<b>7</b>	155.2, 144.6	139.7	-136	9.51
<b>8</b>	148.9, 144.8	139.0	-	9.62

$-144.0$  ppm (N10). The signals of the tetrazol-1-ol are similar for both compounds and to 5,5'-bis(tetrazol-1-ol),<sup>[19]</sup> and found at  $\delta = -112.8$  (N4),  $-17.2$  (N5),  $-4.2$  (N6), and  $-54.8$  ppm (N7) for **6** and at  $\delta = -117.8$  (N4),  $-18.1$  (N5),  $-4.1$  (N6), and  $-55.3$  ppm (N7) for **7**, respectively.

#### Theoretical calculations, performance characteristics and stabilities:

The heats of formation of **5–7** and RDX have been calculated on the CBS-4M level of theory by the atomization energy method and utilizing experimental data (for further details and results refer to the Supporting Information). The results are summarized in Table 5. All compounds show highly endothermic enthalpies of formation with 446 (**6**), 515 (**5**) and 795 kJ mol<sup>-1</sup> (**7**), all of which outperform RDX (85 kJ mol<sup>-1</sup>).

To estimate the detonation performances of the compounds prepared selected key parameters were calculated with EXPLO5 (version 5.05),<sup>[20]</sup> and compared to RDX. The calculated detonation parameters from experimentally determined densities (gas pycnometry at 25 °C with dried compounds) and above mentioned heats of formation are summarized in Table 5. All three compounds **5–7** show lower detonation velocities and pressures than RDX, although all have (much) higher heats of formation and comparable densities.

The thermal stabilities of the title compounds **5–7** were analyzed by differential scanning calorimetry with a heating rate of 5 °C min<sup>-1</sup> (Figure 8). The compounds were dried at 60 (**5**, **7**) or 110 °C (**6**), respectively, prior to sample prepara-

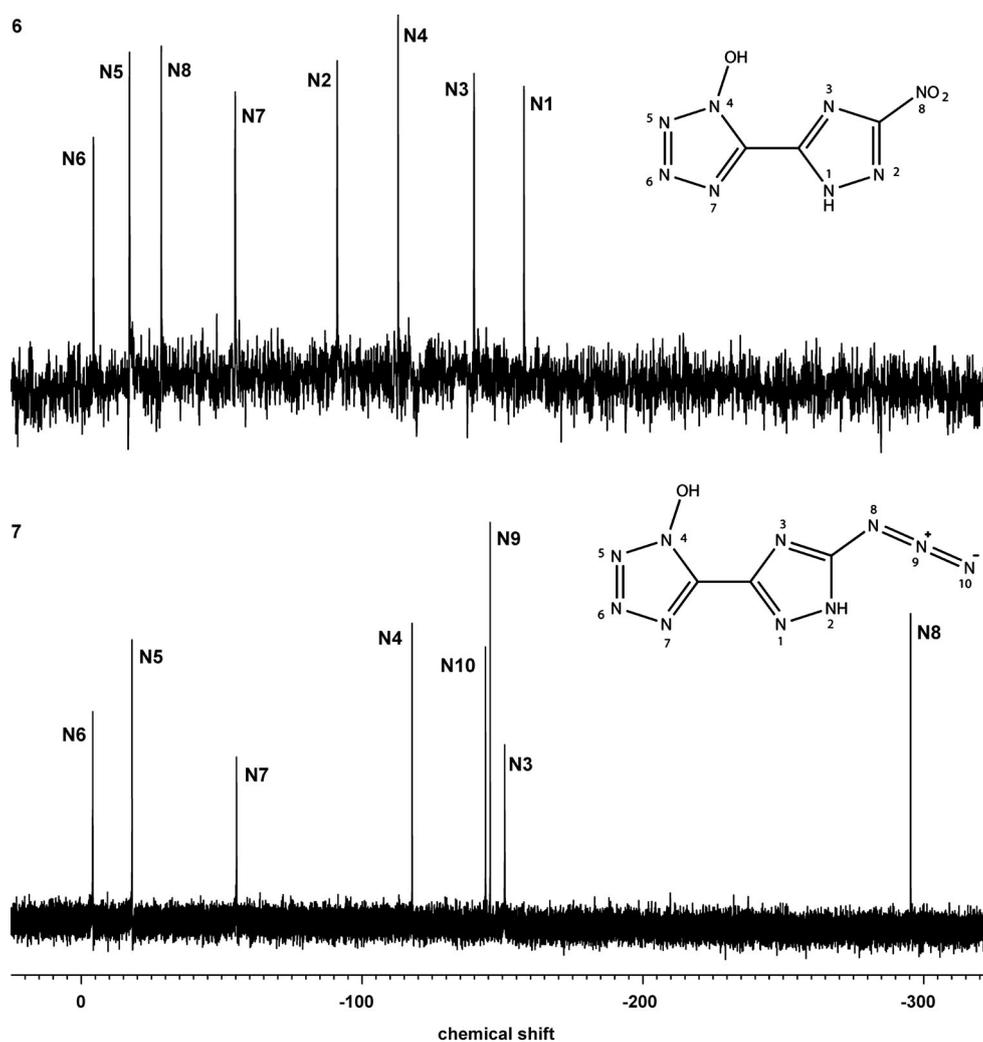


Figure 7.  $^{15}\text{N}$  NMR spectra of 5-(3-nitro-1*H*-1,2,4-triazol-5-yl)tetrazol-1-ol (**6**) and 5-(5-azido-1*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (**7**) recorded in  $[\text{D}_6]\text{DMSO}$ . The  $x$  axis represents the chemical shift  $\delta$  in ppm.

tion to remove moisture and crystal water. The thermal stabilities determined are rather low with decomposition beginning at 116 (**5**), 144 (**7**) and 152°C (**6**). The azide derivative **7** is the only compound to feature a melting point, starting at 83°C. The decomposition point of **7** is almost identical to the derivative lacking the nitrogen bound hydroxyl group, except for the missing melting point of the latter, but **6** and especially **5** are much less thermally stable (NTT: 211°C; NATT: 215°C).<sup>[8]</sup> This trend is similar to those reported for 5-nitro-2*H*-tetrazole vs. 5-nitrotetrazol-2-ol,<sup>[21]</sup> and 5,5'-bis(tetrazole) vs. 5,5'-bis(tetrazol-1-ol) and 5,5'-bis(tetrazol-2-ol).<sup>[22]</sup> As with the bistetrazoles, deprotonation of the hydroxyl group should clearly raise the thermal stabilities if paired with the right cation. For example whereas neutral 5,5'-bis(tetrazol-2-ol) decomposes at 165°C its ammonium salt is stable up to 265°C and the guanidinium salt even until 331°C.<sup>[22]</sup>

The impact and friction sensitivities as well as the sensitivity towards electrostatic discharge of compounds **5–7** were

determined and assigned according to the UN recommendations on the transport of dangerous goods.<sup>[23]</sup> All compounds were dried beforehand (temperatures as above). Interestingly, the nitrimino derivative **5** is the most sensitive of the three compounds and has to be classified as very sensitive to both impact (<1 J) and friction (60 N). The azido derivative **7** is sensitive against both impact (4 J) and friction (120 N) and the nitro derivative is almost insensitive (35 J, 360 N). Concerning the sensitivities towards electrostatic discharge both nitro substituted compounds **5** and **6** are more sensitive than **7**, with 130 (**5** and **6**) and 260 mJ (**7**), respectively.

The calculated detonation velocities are 8776 (**5**), 8655 (**6**) and 8239  $\text{ms}^{-1}$  (**7**). In comparison to the corresponding compounds bearing no hydroxyl group at the tetrazole ring,<sup>[8]</sup> a marked performance increase is seen. The detonation velocities increase by 350 (**7**) to 650  $\text{ms}^{-1}$  (**5** and **6**). The introduction of the *N*-oxide also positively influences other detonation parameters like the detonation pressure or the energy of explosion, which are also a markedly increased.

Table 5. Physicochemical properties of compounds **5–7** and hexogen (RDX).

	NATTO ( <b>5</b> )	NTTO ( <b>6</b> )	AzTTO ( <b>7</b> )	RDX <sup>[o]</sup>
formula	C <sub>3</sub> H <sub>3</sub> N <sub>3</sub> O <sub>3</sub>	C <sub>3</sub> H <sub>2</sub> N <sub>8</sub> O <sub>3</sub>	C <sub>3</sub> H <sub>2</sub> N <sub>10</sub> O	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	213.11	198.10	194.11	222.10
IS [J] <sup>[a]</sup>	<1	35	4	7.4
FS [N] <sup>[b]</sup>	60	360	120	120
ESD [mJ] <sup>[c]</sup>	130	130	260	200
<i>N</i> [%] <sup>[d]</sup>	59.2	56.6	72.2	37.8
<i>Ω</i> [%] <sup>[e]</sup>	-33.8	-32.3	-49.4	-21.6
<i>T<sub>dec</sub></i> [°C] <sup>[f]</sup>	116	152	144	204
<i>ρ</i> [g cm <sup>-3</sup> ] <sup>[g]</sup>	1.85	1.86	1.69	1.80
$\Delta_f H^\circ$ [kJ mol <sup>-1</sup> ] <sup>[h]</sup>	515	446	795	85
$\Delta_f U^\circ$ [kJ kg <sup>-1</sup> ] <sup>[i]</sup>	2502	2335	4180	481
calculated detonation parameters (EXPLO5 V5.05)				
- <i>Q<sub>v</sub></i> [kJ kg <sup>-1</sup> ] <sup>[j]</sup>	5470	5407	5360	6186
<i>T<sub>ex</sub></i> [°C] <sup>[k]</sup>	4126	4217	4207	4260
<i>P<sub>C-J</sub></i> [kbar] <sup>[l]</sup>	342	337	275	353
<i>D</i> [m s <sup>-1</sup> ] <sup>[m]</sup>	8776	8655	8239	8787
<i>V<sub>0</sub></i> [L mol <sup>-1</sup> ] <sup>[n]</sup>	708	677	693	738

[a] Impact sensitivity. [b] Friction sensitivity. [c] Sensitivity to electrostatic discharge. [d] Nitrogen content. [e] Oxygen balance. [f] Decomposition temperature (DSC, 5°C min<sup>-1</sup>). [g] Density (25°C). [h] Calculated solid state enthalpy of formation. [i] Calculated solid state energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Volume of gaseous detonation products. [o] Taken from the literature.<sup>[24]</sup>

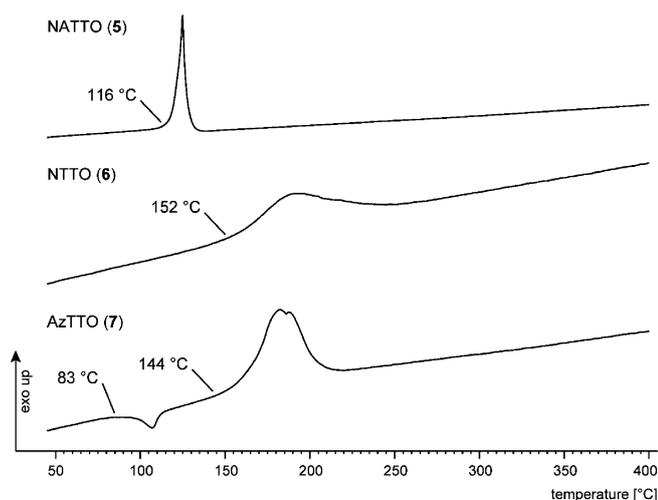


Figure 8. DSC plots for NATTO (**5**), NTTO (**6**) and AzTTO (**7**) with a heating rate of 5°C min<sup>-1</sup>.

## Conclusion

The recently introduced 5-amino-1*H*-1,2,4-triazole-3-carbonitrile (**1**) was further derivatized forming the nitrimino (**2**), nitro (**3**) and azido (**4**) compounds, which in turn were cyclized to the respective tetrazol-1-ols **5–7** via amidoxime, chloroxime and azidoxime intermediates, utilizing adapted literature methods. This innovative synthesis leads to the previously unknown C–C connection of a triazole ring with a tetrazol-1-ol ring.

Those different energetic groups containing oxygen or nitrogen and the concept of combining the benefits of two dif-

ferent azoles lead to variable energetic properties. In general, the combination of a triazole ring with its opportunity to introduce a large variety of energetic moieties and a 1-hydroxytetrazole ring implying a large energy content leads to the selective synthesis of precursors for nitrogen-rich ionic primary and secondary explosives. All energetic compounds have been fully characterized by means of vibrational and multinuclear NMR spectroscopy, mass spectrometry and differential scanning calorimetry. Single-crystal X-ray structures for compounds **5–8** were determined and deliver insight into the structural characteristics as well as inter- and intramolecular interactions found in these substances.

As expected, the nitrimino (**5**) as well as the azido-compound (**7**) are the most sensitive derivatives with an impact sensitivities of less than 1 and 4 J, respectively, and friction sensitivities of 60 (**5**) and 120 N (**7**), respectively. In contrast, the nitro-derivative (**6**) shows moderate sensitivities towards friction (360 N) and impact (35 J). Compounds **5–7** are similar to TNT with regard to their detonation parameters, however, the performance of RDX is not reached. But, taking into account the high nitrogen contents of 59.2 (**5**), 56.6 (**6**) and 72.2% (**7**) and high heats of formation, those compounds could be considered as nitrogen-rich environmentally-friendly primary explosives with proper metal cations (**7**), or be of interest as secondary explosive or propellant ingredient in combination with nitrogen-rich cations (**5** and **6**), respectively.

## Experimental Section

**Caution!** Due to the fact that energetic triazole- and tetrazole compounds are to some extent rather unstable toward external stimuli, proper safety precautions should be taken when handling the dry materials. Especially derivatives of azido- and nitrimino-triazoles are energetic primary materials and tend to explode under the influence of impact or friction. Lab personnel and the equipment should be properly grounded and protective equipment like earthed shoes, leather coat, Kevlar gloves, ear protection and face shield are recommended for the handling of any energetic material.

**General:** All chemical reagents and solvents were obtained from Sigma-Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied without further purification. <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>14</sup>N and <sup>15</sup>N NMR spectra were recorded on a JEOL Eclipse 400 instrument in [D<sub>6</sub>]DMSO at 25°C. The chemical shifts are given relative to tetramethylsilane (<sup>1</sup>H, <sup>13</sup>C) or nitro methane (<sup>14</sup>N, <sup>15</sup>N) as external standards and coupling constants are given in Hertz (Hz). Infrared (IR) spectra were recorded on a PerkinElmer BX FT IR spectrometer equipped with a Smiths DuraSAMPLIR II diamond ATR unit. Transmittance values are qualitatively described as very strong (vs), strong (s), medium (m), weak (w) and very weak (vw). Raman spectra were recorded on a Bruker RAM II spectrometer equipped with a Nd:YAG laser (200 mW) 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 with 4-nitrobenzyl alcohol as matrix for FAB measurements. Elemental analyses (CHN) were performed with an Elementar Vario EL. Melting and decomposition points were determined by differential scanning calorimetry (Linseis DSC-PT10, calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of 5°C min<sup>-1</sup> in closed aluminum sample pans with a 0.1 mm hole in the lid for gas release to avoid an unsafe increase in pressure under a nitrogen flow of 20 mL min<sup>-1</sup> with an

empty identical aluminum sample pan as a reference. Melting points were verified with a Büchi Melting Point B-540 in open glass capillaries. For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivities were determined. The impact sensitivity tests were carried out according to STANAG 4489,<sup>[25]</sup> modified according to WIWeB instruction 4-5.1.02<sup>[26]</sup> with a BAM<sup>[27]</sup> drop hammer. The friction sensitivity tests were carried out according to STANAG 4487<sup>[28]</sup> and modified according to WIWeB instruction 4-5.1.03<sup>[29]</sup> with the BAM friction tester. The electrostatic sensitivity tests were accomplished according to STANAG 4490<sup>[30]</sup> with an electric spark testing device ESD 2010 EN (OZM Research).

**Crystallographic measurements:** The single-crystal X-ray diffraction data for **5-8** were collected on an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA), Enhance MoK $\alpha$  radiation source ( $\lambda = 71.073$  pm), Oxford Cryosystems Cryostream cooling unit, four circle kappa platform and a Sapphire CCD detector. Data collection and reduction were performed with CrysAlisPro.<sup>[31]</sup> The structures were solved with SIR97,<sup>[32]</sup> refined with SHELXL-97,<sup>[33]</sup> and checked with PLATON,<sup>[34]</sup> as integrated into the WinGX software suite.<sup>[35]</sup> The finalized CIF files were checked with checkCIF.<sup>[36]</sup> Intra- and intermolecular contacts were analyzed with Mercury.<sup>[37]</sup> CCDC-926336 (**5**), CCDC-926337 (**6**), CCDC-926338 (**7**, 173 K), CCDC-926339 (**7**, 298 K) and CCDC-926340 (**8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

5-Amino-1*H*-1,2,4-triazole-3-carbonitrile (**1**),<sup>[8]</sup> 5-azido-1*H*-1,2,4-triazole-3-carbonitrile (**4**) and 5-azido-1*H*-1,2,4-triazole-3-chloroxime (**4a**) were prepared according to the literature.<sup>[17]</sup>

**5-Nitramino-1*H*-1,2,4-triazole-3-carbonitrile (2):** Nitric acid (100%, 3.3 mL) was added slowly to a solution of 5-amino-1*H*-1,2,4-triazole-3-carbonitrile (**1**, 2.2 g, 20 mmol) in concentrated sulfuric acid (20 mL) at 0°C. The mixture was stirred at 0°C for 1 h, poured on ice (250 g) and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuum to yield a colorless powder (2.7 g, 18 mmol, 87%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 14.40$  ppm (s, H<sub>triazole</sub>); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 151.1$  (C–NNO<sub>2</sub>), 135.7 (C–CN), 112.9 ppm (CN); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -32$  ppm (NNO<sub>2</sub>); IR (rel. int.):  $\tilde{\nu} = 3137$ (w), 2797(w), 2265(vw), 1716(w), 1614(m), 1569(m), 1516(m), 1468(w), 1354(w), 1323(s), 1263(vs), 1185(w), 1144(m), 1099(s), 1032(w), 1015(w), 1005(m), 868(m), 864(m), 838(w), 769(m), 758(m), 733(vs), 733(vs), 721(s), 679 cm<sup>-1</sup> (s); Raman (200 mW, rel. int.):  $\tilde{\nu} = 2266$ (43), 1722(1), 1641(2), 1565(20), 1535(9), 1473(15), 1367(6), 1324(4), 1268(4), 1147(4), 1116(2), 1094(2), 1041(12), 1017(3), 1005(6), 847(1), 758(2), 684(1), 625(2), 567(1), 487(6), 432(4), 362(3), 362(3), 220 cm<sup>-1</sup>(3); elemental analysis calcd (%) for C<sub>3</sub>H<sub>2</sub>N<sub>6</sub>O<sub>2</sub> (154.1): C 23.38, H 1.31, N 54.54; found: C 23.17, H 1.49, N 51.78; MS (DEI+):  $m/z$ : 154.1 [C<sub>3</sub>H<sub>2</sub>N<sub>6</sub>O<sub>2</sub>]<sup>+</sup>; sensitivities (grain size < 100  $\mu$ m): friction: 360 N; impact: 6 J; ESD: 0.2 J; DSC (5°C min<sup>-1</sup>): T<sub>dec</sub> = 130°C.

**5-Nitramino-1*H*-1,2,4-triazole-3-chloroxime (2a):** Hydroxylamine (50 wt % in water, 1.2 equiv, 1.4 mL) was added to a solution of **2** (2.7 g, 18 mmol) in water (30 mL). The clear solution was stirred at 70°C for 30 min. The mixture was acidified with hydrochloric acid (37%, 30 mL) and cooled to 0°C. A solution of sodium nitrite (1.5 equiv, 1.9 g, 27 mmol) in water (15 mL) was added dropwise and the solution was subsequently stirred for 2 h at room temperature. The precipitate was collected by filtration, washed with cold water and dried in air to yield a pale yellow powder (3.1 g, 15 mmol, 83%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 14.44$  (s, 1H, H<sub>triazole</sub>), 13.31 (s, 1H, NHNO<sub>2</sub>), 6.16 ppm (s, 1H, NOH); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 153.5$  (C–NNO<sub>2</sub>), 144.5 (C–CNOHCl), 125.4 ppm (CNOHCl); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -19$  ppm (NNO<sub>2</sub>); IR (rel. int.):  $\tilde{\nu} = 3430$ (w), 3336(w), 2987(w), 2836(w), 2604(w), 1616(m), 1585(m), 1547(m), 1503(w), 1451(w), 1420(w), 1289(s), 1220(vs), 1131(m), 1089(w), 1049(w), 1024(m), 1015(m), 998(s), 925(s), 853(m), 777(m), 759(w), 759(w), 745(w), 729(m), 669 cm<sup>-1</sup>(m); Raman (200 mW, rel. int.):  $\tilde{\nu} = 1614$ (47), 1586(48), 1557(100), 1507(9), 1463(3), 1297(5), 1219(8), 1137(11), 1118(6), 1057(4), 993(37), 922(3), 875(4), 857(11), 759(25),

673(6), 518(3), 489(3), 430(2), 407(2), 318(4), 246(5), 226(5), 226(5), 219 cm<sup>-1</sup>(5); MS (FAB–):  $m/z$ : 205.2 [C<sub>3</sub>H<sub>2</sub>N<sub>6</sub>O<sub>3</sub>Cl]<sup>–</sup>; sensitivities (grain size < 100  $\mu$ m): friction: 240 N; impact: 5 J; DSC (5°C min<sup>-1</sup>): T<sub>dec</sub> = 126°C.

**5-Nitramino-1*H*-1,2,4-triazole-3-azidoxime (2b):** A solution of sodium azide (1.3 g, 20 mmol) in water (8 mL) was added dropwise to a solution of **2a** (3.1 g, 15 mmol) in ethanol (100 mL). The suspension was stirred at room temperature for 12 h and subsequently poured into 2 M HCl (400 mL). The clear solution was extracted with ethyl acetate (3 × 100 mL), the combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuum to yield a colorless powder (3.0 g, 14 mmol, 93%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 14.23$  (s, 1H, H<sub>triazole</sub>), 12.46 (s, 1H, NHNO<sub>2</sub>), 10.00 ppm (s, 1H, NOH); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 153.6$  (C–NNO<sub>2</sub>), 143.3 (C–CNOHN<sub>3</sub>), 133.6 ppm (CNOHN<sub>3</sub>); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -18$  (NO<sub>2</sub>), -147 ppm (N<sub>3</sub>); IR (rel. int.):  $\tilde{\nu} = 3426$ (w), 3199(w), 2153(m), 2102(w), 1695(w), 1621(m), 1595(m), 1557(s), 1512(m), 1462(m), 1388(w), 1305(s), 1266(m), 1253(m), 1218(vs), 1131(m), 1094(w), 1044(m), 1007(s), 996(s), 987(m), 940(w), 924(m), 924(m), 862(m), 773(w), 730(w), 688(w), 667 cm<sup>-1</sup>(w); Raman (200 mW, rel. int.):  $\tilde{\nu} = 2263$ (3), 2157(4), 2107(2), 1622(59), 1600(16), 1559(100), 1514(9), 1473(5), 1308(7), 1222(5), 1134(8), 1076(6), 1058(3), 1052(2), 998(13), 985(18), 943(2), 864(12), 761(15), 520(2), 486(3), 419(3), 332(4), 332(4), 280(4), 236 cm<sup>-1</sup>(6); MS (FAB–):  $m/z$ : 212.1 [C<sub>3</sub>H<sub>2</sub>N<sub>9</sub>O<sub>3</sub>]<sup>–</sup>; sensitivities (grain size < 100  $\mu$ m): friction: 80 N; impact: 4 J; ESD: 0.13 J; DSC (5°C min<sup>-1</sup>): T<sub>dec</sub> = 66°C.

**5-(5-Nitrimino-1,4*H*-1,2,4-triazol-3-yl)tetrazol-1-ol (NATTO, 5):** A solution of **2b** (3.0 g, 14 mmol) in concentrated hydrochloric acid (50 mL) was stirred at room temperature for 10 h. The clear solution was poured on ice and extracted with ethyl acetate (3 × 100 mL). The combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuum to yield a colorless solid (2.8 g, 13 mmol, 94%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 7.10$  ppm (s, H<sub>triazole</sub>); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 152.5$  (C–NNO<sub>2</sub>), 140.5 (C<sub>triazole</sub>), 138.7 ppm (C<sub>tetrazole</sub>); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -25$  ppm (NNO<sub>2</sub>); IR (rel. int.):  $\tilde{\nu} = 3607$ (w), 3398(w), 3186(w), 1650(w), 1605(m), 1583(m), 1550(w), 1519(m), 1469(m), 1407(w), 1317(s), 1243(vs), 1202(s), 1138(w), 1089(w), 1061(w), 999(w), 958(m), 923(w), 868(w), 799(w), 774(m), 717(m), 717(m), 684 cm<sup>-1</sup>(m); Raman (200 mW, rel. int.):  $\tilde{\nu} = 1648$ (100), 1596(48), 1579(47), 1532(11), 1521(12), 1481(3), 1420(2), 1336(2), 1267(7), 1154(4), 1129(15), 1115(16), 1012(28), 973(4), 877(5), 775(2), 762(7), 746(4), 738(7), 499(2), 446(2), 423(3), 292(2), 292(2), 257 cm<sup>-1</sup>(8); elemental analysis calcd (%) for C<sub>3</sub>H<sub>3</sub>N<sub>9</sub>O<sub>3</sub> (213.1): C 16.91, H 1.42, N 59.15; found: C 17.32, H 1.59, N 56.77; MS (FAB–):  $m/z$ : 212.2 [C<sub>3</sub>H<sub>2</sub>N<sub>9</sub>O<sub>3</sub>]<sup>–</sup>; sensitivities (grain size < 100  $\mu$ m): friction: 60 N; impact: < 1 J; ESD: 0.13 J; DSC (5°C min<sup>-1</sup>): T<sub>dec</sub> = 116°C.

**3-Nitro-1*H*-1,2,4-triazole-5-carbonitrile (3):** A solution of 5-amino-1*H*-1,2,4-triazole-3-carbonitrile (**1**, 2.2 g, 20 mmol) in 20% sulfuric acid (40 mL) was added dropwise to a solution of sodium nitrite (10 equiv, 14 g, 22 mmol) in water (40 mL) at 0°C. The mixture was subsequently stirred at 40°C for 30 min. After cooling down to room temperature the mixture was acidified with sulfuric acid (20%) until no evolution of nitrogen dioxide could be observed. The aqueous solution was extracted with ethyl acetate (3 × 50 mL), the combined organic phases were dried over magnesium sulfate and the solvent was removed in vacuum to yield an orange solid (2.6 g, 18 mmol, 92%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO):  $\delta = 15.56$  ppm (s, 1H, H<sub>triazole</sub>); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO):  $\delta = 161.3$  (C–NO<sub>2</sub>), 135.2 (C–CN), 111.6 ppm (CN); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO):  $\delta = -29$  ppm (NO<sub>2</sub>); IR (rel. int.):  $\tilde{\nu} = 3141$ (w), 2263(vw), 1692(w), 1561(vs), 1530(m), 1484(w), 1427(s), 1374(m), 1314(vs), 1258(w), 1176(w), 1048(m), 1013(m), 838(vs), 708 cm<sup>-1</sup>(m). Raman (200 mW, rel. int.):  $\tilde{\nu} = 2266$ (100), 2212(1), 1577(5), 1566(5), 1527(3), 1486(3), 1451(81), 1419(13), 1380(19), 1319(13), 1188(14), 1059(15), 1017(4), 841(4), 775(3), 712(5), 639(1), 569(1), 504(3), 472(7), 406(5), 264(3), 255(4), 255 cm<sup>-1</sup>(4); elemental analysis calcd (%) for C<sub>3</sub>HN<sub>5</sub>O<sub>2</sub>: C 25.91, H 0.72, N 50.36; found: C 26.40, H 0.88, N 49.86; MS (DEI+):  $m/z$ : 139.0 [C<sub>3</sub>HN<sub>5</sub>O<sub>2</sub>]<sup>+</sup>; sensitivities (grain size < 100  $\mu$ m): friction: 360 N; impact: 40 J; DSC (5°C min<sup>-1</sup>): T<sub>dec</sub> = 196°C.

**3-Nitro-1H-1,2,4-triazole-5-chloroxime (3a):** Hydroxylamine (50 wt % in water, 1.2 equiv, 1.4 mL) was added to a solution of **3** (2.6 g, 18 mmol) in water (20 mL). The clear solution was stirred at 70 °C for 30 min. The mixture was acidified with hydrochloric acid (37%, 20 mL) and cooled to 0 °C. A solution of sodium nitrite (1.5 equiv, 1.9 g, 27 mmol) in water (10 mL) was added dropwise and the solution was subsequently stirred for 2 h at room temperature. The precipitate was collected by filtration, washed with cold water and dried in air to yield a pale yellow powder (2.8 g, 15 mmol, 82%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ = 13.39 (s, 1H, H<sub>triazole</sub>), 6.04 ppm (s, 1H, NOH); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ = 162.3 (C–NO<sub>2</sub>), 149.9 (C–CNOHCl), 125.3 ppm (CNOHCl); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO): δ = –27 ppm (NO<sub>2</sub>); IR (rel. int.):  $\tilde{\nu}$  = 3575(w), 3358(w), 3215(w), 2454(w), 1845(w), 1578(w), 1555(m), 1482(s), 1400(m), 1336(w), 1322(m), 1178(w), 1100(s), 1040(m), 1023(vs), 920(s), 844(m), 751(m), 728 m), 662 cm<sup>–1</sup>(w); Raman (200 mW, rel. int.):  $\tilde{\nu}$  = 1609(76), 1587(26), 1556(22), 1506(14), 1485(100), 1468(55), 1425(46), 1403(28), 1339(15), 1324(27), 1179(24), 1104(3), 1041(35), 1025(14), 924(12), 848(8), 775(6), 731(7), 662(12), 580(5), 544(8), 455(14), 373(5), 373(5), 349(10), 270(7), 251(12), 225 cm<sup>–1</sup>(28); MS (DEI+): *m/z*: 191.1 [C<sub>3</sub>H<sub>2</sub>N<sub>5</sub>O<sub>3</sub>Cl]<sup>+</sup>; sensitivities (grain size < 100 μm): friction: 360 N; impact: 40 J; ESD: 0.2 J. DSC (5 °C min<sup>–1</sup>): *T*<sub>dec</sub> = 195 °C.

**3-Nitro-1H-1,2,4-triazole-5-azidoxime (3b):** A solution of sodium azide (1.3 g, 20 mmol) in water (8 mL) was added dropwise to a solution of **3a** (2.8 g, 15 mmol) in ethanol (50 mL). The suspension was stirred at room temperature for 2 h and subsequently poured into 2 M HCl (200 mL). The clear solution was extracted with ethyl acetate (3 × 80 mL), the combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuum to yield a colorless powder (2.8 g, 14 mmol, 93%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ = 12.61 ppm (s, H<sub>triazole</sub>); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ = 162.5 (C–NO<sub>2</sub>), 148.7 (C–CNOHN<sub>3</sub>), 133.4 ppm (CNOHN<sub>3</sub>); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO): δ = –26 (NO<sub>2</sub>), –146 ppm (N<sub>3</sub>); IR (rel. int.):  $\tilde{\nu}$  = 3391(w), 3192(w), 2568(w), 2488(w), 2162(m), 2115(m), 1886(w), 1684(m), 1620(m), 1587(w), 1556(s), 1478(m), 1401(m), 1378(m), 1339(m), 1317(m), 1292(s), 1275(s), 1178(m), 1120(s), 1038(m), 1013(m), 938(vs), 938(vs), 861(m), 834(m), 777(w), 749(w), 733 cm<sup>–1</sup>(m); Raman (200 mW, rel. int.):  $\tilde{\nu}$  = 2988(8), 2977(7), 2946(18), 2170(9), 2122(7), 1689(7), 1623(84), 1591(33), 1567(25), 1514(8), 1489(99), 1415(31), 1320(23), 1280(16), 1185(17), 1116(5), 1040(23), 1008(14), 943(13), 864(8), 852(5), 841(7), 777(4), 777(4), 739(5), 637(4), 458(12), 383(5), 369(9), 361(9), 293(18), 253(10), 207 cm<sup>–1</sup>(3); MS (DEI+): *m/z*: 198.1 [C<sub>3</sub>H<sub>2</sub>N<sub>8</sub>O<sub>3</sub>]<sup>+</sup>; sensitivities (grain size < 100 μm): friction: 240 N; impact: 20 J; DSC (5 °C min<sup>–1</sup>): *T*<sub>dec</sub> = 124 °C.

**5-(3-Nitro-1,2,4-1H-triazol-5-yl)tetrazol-1-ol (NTTO, 6):** A solution of **3b** (2.8 g, 14 mmol) in concentrated hydrochloric acid (50 mL) was stirred at room temperature for 10 h. The clear solution was poured on ice and extracted with ethyl acetate (3 × 100 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed in vacuum to yield a colorless solid (2.6 g, 13 mmol, 94%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ = 14.15 (s, 1H, H<sub>triazole</sub>), 8.30 ppm (s, 1H, OH); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ = 163.2 (C–NO<sub>2</sub>), 143.3 (C<sub>triazole</sub>), 138.0 ppm (C<sub>tetrazole</sub>); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO): δ = –24 ppm (NO<sub>2</sub>); <sup>15</sup>N NMR ([D<sub>6</sub>]DMSO): δ = –4.2 (N<sub>6</sub>), –17.2 (N<sub>5</sub>), –28.5 (N<sub>8</sub>), –54.8 (N<sub>7</sub>), –91.2 (N<sub>2</sub>), –112.8 (N<sub>4</sub>), –139.9 (N<sub>3</sub>), –157.7 ppm (N<sub>1</sub>); IR (rel. int.):  $\tilde{\nu}$  = 3585(w), 3144(w), 2916(w), 2848(w), 2608(w), 1908(vw), 1691(m), 1620(w), 1555(s), 1520(m), 1472(m), 1411(s), 1309(vs), 1239(m), 1188(m), 1092(w), 1028(w), 1011(w), 983(s), 931(m), 836(s), 737(w), 709(w), 709(w), 666 cm<sup>–1</sup>(w); Raman (200 mW, rel. int.):  $\tilde{\nu}$  = 1674(41), 1622(100), 1610(92), 1556(19), 1521(33), 1513(38), 1488(29), 1477(29), 1442(61), 1414(76), 1359(27), 1338(10), 1312(15), 1292(8), 1277(12), 1246(44), 1202(23), 1191(59), 1161(5), 1147(21), 1098(38), 1031(12), 1015(34), 1015(34), 984(8), 847(4), 773(7), 747(20), 739(18), 563(5), 503(3), 398(12), 337(6), 303(5), 247(4), 230(6), 216 cm<sup>–1</sup>(4); elemental analysis calcd (%) for C<sub>3</sub>H<sub>2</sub>N<sub>8</sub>O<sub>3</sub> × H<sub>2</sub>O (216.1): C 16.67, H 1.87, N 51.58; found: C 19.47, H 1.87, N 50.13; MS (FAB<sup>–</sup>): *m/z*: 197.3 [C<sub>3</sub>HN<sub>8</sub>O<sub>3</sub>]<sup>–</sup>; sensitivities (anhydrous, grain size < 100 μm): friction: 360 N; impact: 35 J; ESD: 0.13 J; DSC (5 °C min<sup>–1</sup>): *T*<sub>dec</sub> = 152 °C.

**5-(5-Azido-1H-1,2,4-triazol-3-yl)tetrazol-1-ol (AzTTO, 7):** Sodium azide (1.95 g, 30.0 mmol) was dissolved in water (27 mL) and added to a solu-

tion of **4b** (3.75 g, 20.0 mmol) in ethanol (33 mL) at 0 °C. The solution was stirred for 15 min at that temperature, then for 2 h at room temperature. The suspension was acidified with hydrochloric acid (2 M, 20 mL), stirred for 30 min, extracted with diethyl ether (5 × 300 mL) and the combined organic phases were dried over magnesium sulfate. Hydrogen chloride gas was passed into the stirred solution at 0 °C for 75 min, whereby the temperature rose to 19 °C (it should not rise higher!). The flask was stoppered and the resulting solution was stirred for 2 d at room temperature under a hydrogen chloride overpressure. After evaporation of the solvent to almost complete dryness water was added and completely evaporated at ambient conditions to yield a colorless solid (3.71 g, 17.5 mmol, 80%). <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO): δ = 9.51 ppm (br); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO): δ = 155.2 (C<sub>triazole</sub>), 144.6 (C–N<sub>3</sub>), 139.7 ppm (C<sub>tetrazole</sub>); <sup>14</sup>N NMR ([D<sub>6</sub>]DMSO): δ = –136 ppm (N<sub>9</sub>); <sup>15</sup>N NMR ([D<sub>6</sub>]DMSO): δ = –4.1 (N<sub>6</sub>), –18.1 (N<sub>5</sub>), –55.3 (N<sub>7</sub>), –117.8 (N<sub>4</sub>), –144.0 (N<sub>10</sub>), –145.6 (N<sub>9</sub>), –150.8 (N<sub>3</sub>), –295.3 ppm (N<sub>8</sub>); IR (rel. int.):  $\tilde{\nu}$  = 3233(s), 2477(w), 2375(w), 2232(w), 2154(vs), 1604(m), 1535(vs), 1479(s), 1336(s) 1296(m), 1275(m), 1223(m), 1190(m), 1152(w), 1129(m), 1071(w), 1046(w), 1014(w), 982(m), 855(w), 781(m), 753(w), 712(w), 696(w), 658 cm<sup>–1</sup>(w); Raman (200 mW, rel. int.):  $\tilde{\nu}$  = 2154(8), 1605(100), 1537(20), 1485(10), 1422(8), 1397(4), 1336(12), 1276(17), 1191(2), 1130(5), 1062(2), 1045(6), 1015(5), 980(7), 805(3), 757 cm<sup>–1</sup>(3); MS (FAB<sup>–</sup>): *m/z*: 193.3 [C<sub>3</sub>HN<sub>10</sub>O]<sup>–</sup>; elemental analysis calcd (%) for C<sub>3</sub>H<sub>4</sub>N<sub>10</sub>O<sub>2</sub> (212.1): C 16.99, H 1.90, N 66.03; found: C 17.53, H 1.87, N 65.16%; sensitivities (anhydrous, grain size < 100 μm): friction: 120 N; impact: 4 J; ESD: > 260 mJ; DSC (5 °C min<sup>–1</sup>): *T*<sub>meat</sub> = 83 °C, *T*<sub>dec</sub> = 144 °C.

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