

# Synthesis of 5-(1*H*-Tetrazolyl)-1-hydroxy-tetrazole and Energetically Relevant Nitrogen-Rich Ionic Derivatives

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**Abstract:** Sodium 5-cyanotetrazolate sesquihydrate (**1**) was prepared from sodium azide and two equivalents of sodium cyanide under acidic conditions. Sodium 5-cyanotetrazolate sesquihydrate (**1**) reacts with hydroxylammonium chloride to form 5-aminohydroximoyl tetrazole (**2**). 5-Aminohydroximoyl tetrazole (**2**) is treated with sodium nitrite and hydrochloric acid to form 5-chlorohydroximoyl-tetrazole (**3**). The chloride azide exchange yields 5-azidohydroximoyl-tetrazole monohydrate (**4**). When compound **4** is treated with hydrochloric acid, 5-(1*H*-tetrazolyl)-1-hydroxy-tetrazole (**5**) is obtained in good yield. Compound **5** can be deprotonated twice by various bases. Different ionic derivatives such as bis(hydroxylammonium) (**6**), bis(hydrazinium) (**7**), bis(guanidinium) (**8**), bis(aminoguanidinium) (**9**), bis(ammonium) (**10**), and diaminouronium (**11**) 5-(1-oxidote-

tetrazolyl)-tetrazolate were synthesized and characterized. With respect to energetic use salts **6** and **7** are most relevant. Compounds **3–9** and **11** were characterized using low temperature single-crystal X-ray diffraction. All compounds were investigated by NMR and vibrational (IR, Raman) spectroscopy, mass spectrometry and elemental analysis. The thermal properties were determined by differential scanning calorimetry (DSC). The sensitivities towards impact (**4**: 4 J, **5**: 40 J, **6**: 12 J, **7**: 40 J), friction (**4**: 60 N, **5**: 240 N, **6**: 216 N, **7**: 240 N), and electrical discharge (**5**: 0.40 J, **6**: 0.75 J, **7**: 0.75 J), were investigated using BAM standards and a small scale electrostatic discharge tester. The detonation parameters of **5–7** were calculated using the EXPLO5.06 code and calculated (CBS-4 M) enthalpy of formation values.

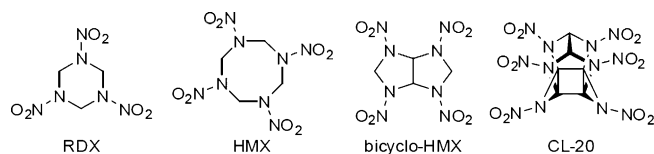
**Keywords:** Energetic materials • Tetrazoles • *N*-Oxides • Crystal structures • Nitrogen-rich

## 1 Introduction

The research of new secondary explosives in the 20th century was focused on cyclic and caged nitramines such as RDX [1], HMX [2], bicyclo-HMX [3], and CL-20 [4]. In our days, these compounds are the most prevalent in civil and military applications [5] (Figure 1). In recent years concerns about the environmental impact of energetic materials have grown, demanding new green energetic materials, which are based on a high nitrogen content that releases mainly environmentally friendly N<sub>2</sub> after decomposition [6].

Generally compounds based on azoles [6a] can be considered as basic structures for new environmentally friendly, nitrogen-rich, strained compounds. Unfortunately, tetra-

zoles without oxygen-rich groups such as nitro mostly lack in high densities. Although being interesting energetic materials with respect to propellant applications their use as explosives is very limited. Recently it has been observed that the introduction of *N*-oxides in tetrazoles results in superior energetic performance [7]. This strategy can even be increased by using bistetrazoles, which show high densities and moderate sensitivities [8]. With this knowledge in hand, the highly energetic bis(hydroxylammonium) bistetrazole-1,1'-di-*N*-oxide [9] and other nitrogen-rich bistetra-

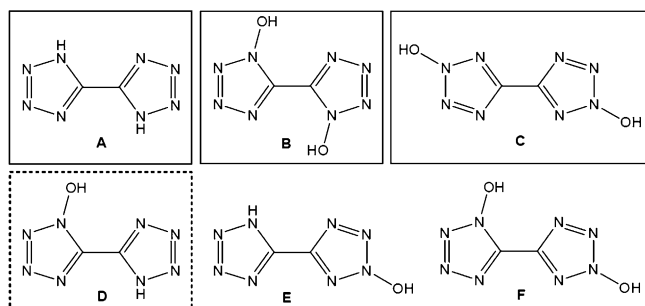


**Figure 1.** The cyclic or caged high explosives 1,3,5-trinitro-1,3,5-triazinane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX), *cis*-1,3,4,6-tetranitrooctahydroimidazo[4,5-*d*]imidazole (bicyclo-HMX), and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20).

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**Figure 2.** 5,5'-Bistetrazole and potential hydroxy-derivatives. (A) 5,5'-Bistetrazole, (B) bis(1-hydroxytetrazole), (C) bis(2-hydroxytetrazole), (D) 5-(1*H*-tetrazolyl)-1-hydroxytetrazole, (E) 5-(1*H*-tetrazolyl)-2-hydroxytetrazole, (F) 5-(2-hydroxytetrazolyl)-1-hydroxytetrazole. Continuous box: known compounds. Dashed box: investigated in this work. No box: unknown yet.

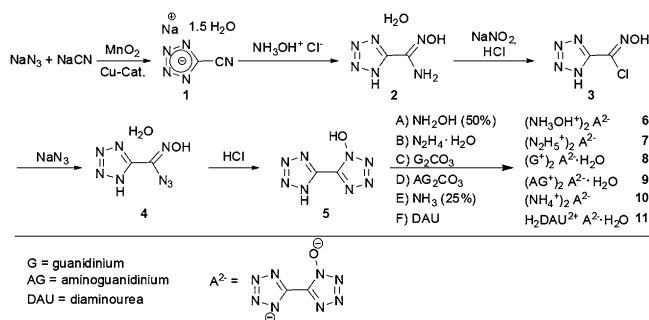
zole-1,1'-di-*N*-oxide salts [10], as well as bistetrazole-2,2'-di-*N*-oxide salts [11] have been synthesized by our group. They show much better energetic properties than the corresponding oxygen-free bistetrazoles, latter one also being described as a useful ligand in metal complexes [12]. The bis(hydroxylammonium) salt of 5,5'-bistetrazole has a low temperature (173 K) density of only 1.742 g cm<sup>-3</sup> [8a]. Bis(hydroxylammonium bistetrazole-1,1'-*N*-oxide has a density of 1.915 g cm<sup>-3</sup> at this temperature, which results in much higher calculated detonation parameters (e.g.  $V_{\text{det}} = 8854 \text{ ms}^{-1}$  vs.  $9698 \text{ ms}^{-1}$ ). So far, bistetrazole-*N*1-monoxide, which will be referred to as 5-(1*H*-tetrazolyl)-1-hydroxytetrazole is missing in the literature. We would like to investigate whether there is a density or performance increment in the introduction of *N*-oxide to the bis(tetrazole) system (Figure 2).

Herein we report the synthesis and characterization of the first anionic bistetrazole 1*N*-monoxide 5-(1*H*-tetrazolyl)-1-hydroxytetrazole, as well as its bis(hydroxylammonium) and bis(hydrazinium) salts. We further characterized two new intermediates, 5-chlorohydroximoyl-tetrazole and 5-azidohydroximoyl-tetrazole monohydrate, that were precursors of the target molecule.

## 2 Results and Discussion

## 2.1 Synthesis

Sodium 5-cyanotetrazolate sesquihydrate (**1**) and 5-amino-hydroximoyl tetrazole (**2**) were synthesized as described in the literature [14] in a two step synthetic protocol according to Scheme 1. In the first step  $\text{NaN}_3$ ,  $\text{NaCN}$ , and  $\text{MnO}_2$  are reacted to give sodium 5-cyanotetrazolate sesquihydrate, which is then converted to compound **2** by reaction with aqueous hydroxylamine solution. The 5-chlorohydroximoyl tetrazole **3** is obtained by diazotization of compound **2**, using sodium nitrite and concentrated hydrochloric acid. The mixture has to be cooled to  $0^\circ\text{C}$  and the addition of the sodium nitrite should be carried out slowly to ensure



**Scheme 1.** Synthetic route towards compounds **4–11**.

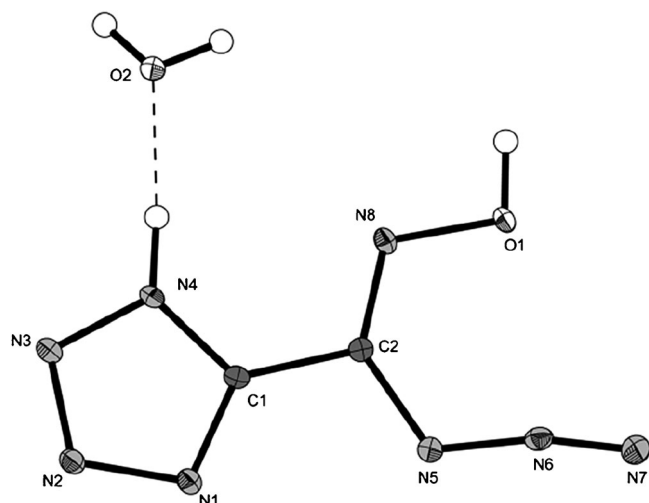
a clean reaction and complete conversion. 5-Azidohydroxymoyl-tetrazole monohydrate **4** is prepared via a chlorine-azide exchange by dissolving **3** in ice-cooled ethanol and adding an aqueous solution of sodium azide. Azide **4** is the most sensitive compound and should be handled with care (impact sensitivity: 4 J, friction sensitivity: 60 N). This can be attributed to the highly energetic covalent azide group. In the last step an acid-catalyzed (HCl) cyclization of **4** could be accomplished in good yields. The product was extracted and recrystallized with ethyl acetate to yield colorless crystals of 5-(1*H*-tetrazolyl)-1-hydroxytetrazole **5**. Mono-*N*-oxidation of 5,5'-bistetrazole by oxone as an alternative reaction to this selective process yielded a mixture of different products. Addition of aqueous hydroxylamine or hydrazine solution to the acid **5** yielded bis(hydroxylammonium) 5-(1-oxido-tetrazolyl)-tetrazolate (**6**) and bis(hydrazinium) 5-(1-oxido-tetrazolyl)-tetrazolate (**7**), respectively. All compounds can easily be identified by NMR and vibrational spectroscopy, which is shown in the Supporting Information.

## 2.2 Crystal Structures

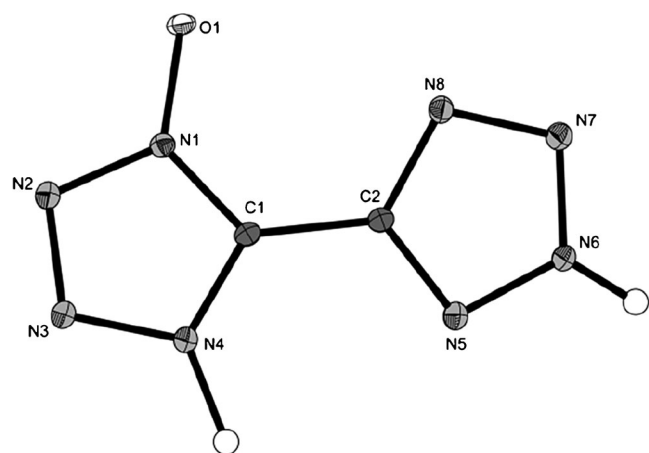
During this work the crystal structures of compounds **3–9** and **11** were determined. Selected data and parameter of the X-ray determinations for compounds **3–9** and **11** are given in Table S1 (Supporting Information). The X-ray structures of **3**, **8**, **9**, and **11** are described in the Supporting Information as well.

5-Azidohydroximoyl-tetrazole monohydrate (**4**) crystallizes from water in the orthorhombic space group  $P2_12_12_1$  with a density of  $1.745 \text{ g cm}^{-3}$  and with four molecules per unit cell. The molecular unit of **4** is illustrated in Figure 3.

5-(1*H*-Tetrazolyl)-1-hydroxytetrazole (**5**) crystallizes with and without inclusion of crystal water. The water free structure was solved in the orthorhombic space group *Pbca* with eight molecular moieties in the unit cell. Its density of 1.814 g cm<sup>-3</sup> is lower to that of 5,5'-bis(1-hydroxy)tetrazole dihydrate (1.881 g cm<sup>-3</sup>) [9] and higher than that of salts **6** and **7**. However, in comparison to 5,5-bistetrazole (1.738 g cm<sup>-3</sup>) [13] the density is significantly higher. These values insistently demonstrate the influence of introducing *N*-oxides towards tetrazoles. The tetrazole and tetrazole-1-



**Figure 3.** Molecular unit of **4**, showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

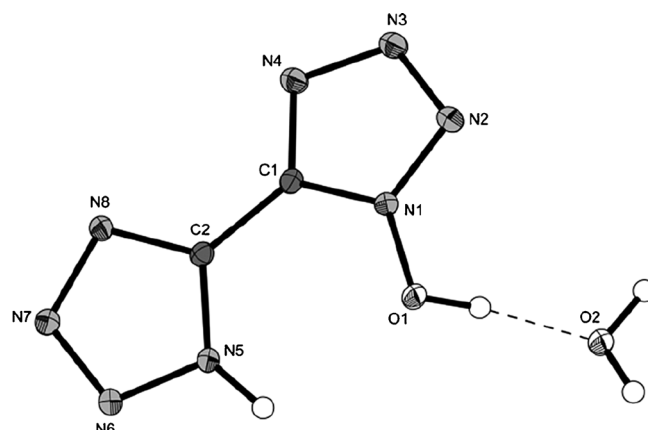


**Figure 4.** Molecular moiety of 5-(2*H*-tetrazolyl)-4*H*-tetrazole-1-oxide (**5**). Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.

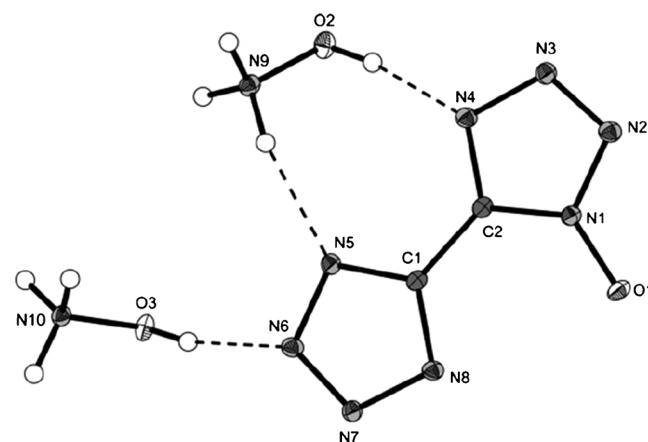
oxide ring planes are tilted against each other by a torsion angle N4–C1–C2–N5 of 14.3(2)°. The molecular unit is shown in Figure 4.

Interestingly, the two hydrogen atoms are located at the nitrogen atoms N4 and N6. The oxidized ring should be described as a zwitterionic system. This is in contrast to the structure of the corresponding monohydrate (Figure 5). There the protons are located at oxygen atom O1 as well as at nitrogen atom N5.

5-(1*H*-Tetrazolyl)-1-hydroxytetrazole monohydrate (**5**·H<sub>2</sub>O) crystallizes in the monoclinic space group *P*2<sub>1</sub>/*n* with a lower density of 1.756 g cm<sup>−3</sup>. Eight molecules are found per unit cell. With a torsion angle N1–C1–C2–N5 of 15.5(2)°, the two heterocyclic ring systems are only slightly



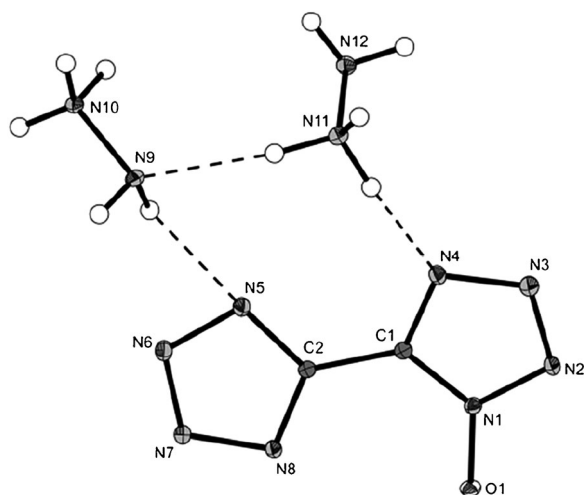
**Figure 5.** Molecular unit of 5-(1*H*-tetrazolyl)-1-hydroxytetrazole monohydrate (**5**·H<sub>2</sub>O), showing the atom-labeling scheme. Thermal ellipsoids represent the 50% probability level and hydrogen atoms are shown as small spheres of arbitrary radius.



**Figure 6.** Molecular moiety of **6**. Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths /pm: O1–N1 132.84(18), N1–C2 134.4(2), N1–N2 134.6(2), N2–N3 130.5(2), N3–N4 134.9(2), N4–C2 134.0(2).

stronger tilted against each other in comparison to those of the anhydrous structure. The molecular unit of **5**·H<sub>2</sub>O is shown in Figure 5.

The bis(hydroxylammonium) salt **6** crystallizes anhydrously from water in the triclinic space group *P*1̄ with two molecular moieties in the unit cell. Its density of 1.782 g cm<sup>−3</sup> is lower than that of **5** and also of bis(hydroxylammonium) bis(tetrazolyl-1-oxide) (1.918 g cm<sup>−3</sup>) [9] but higher than that of bis(hydroxylammonium) 5,5'-bistetrazolate (1.742 g cm<sup>−3</sup>) [8a]. This is a lower value than the expected average value of 1.85 g cm<sup>−3</sup>. The two aromatic ring systems are perfectly planar (torsion angle N8–C1–C2–N1 = 0.12(27)°). The molecular unit of **6** is shown in Figure 6.



**Figure 7.** Molecular moiety of **7**. Ellipsoids of non-hydrogen atoms are drawn at the 50% probability level. Selected bond lengths /pm: O1–N1 132.56(16), N1–C1 134.24(19), N1–N2 134.46(18), N2–N3 131.92(18), N3–N4 134.89(18), N4–C1 133.78(19).

The bis(hydrazinium) salt **7** crystallizes anhydrously from water in the triclinic space group  $P\bar{1}$  with two molecular moieties in the unit cell and a density of  $1.704 \text{ g cm}^{-3}$ . With a torsion angle N1–C1–C2–N8 of  $7.7(2)^\circ$ , the two aromatic ring systems are tilted against each other. The molecular unit of **7** is shown in Figure 7.

## 2.3 Thermal Analysis

Differential scanning calorimetry (DSC) measurements to determine the melt- and decomposition temperatures of compound **4–7** (about 1.5 mg of each energetic material) were performed in covered Al-containers with a hole (0.1 mm) in the lid for gas release and a nitrogen flow of  $20 \text{ mL min}^{-1}$  on a Linseis PT 10 DSC [15] calibrated by standard pure indium and zinc at a heating rate of  $5^\circ \text{C min}^{-1}$ .

Azide **4** decomposes without melting at  $126^\circ \text{C}$ . In contrast **5** features a higher decomposition temperature of  $192^\circ \text{C}$ . Bis(tetrazolyl-1-oxide) dihydrate ( $T_{\text{dec.}} = 214^\circ \text{C}$ ) [10] decomposes at slightly higher temperature. Moreover, its hydroxylammonium salt **6** has a decomposition temperature of  $200^\circ \text{C}$  that interestingly is slightly lower than both bis(hydroxylammonium) 5,5'-bistetrazolate ( $T_{\text{dec.}} = 205^\circ \text{C}$ ) [8a], and bis(hydroxylammonium) bis(tetrazolyl-1-oxide) ( $T_{\text{dec.}} = 221^\circ \text{C}$ ) [9]. Compound **7** shows the highest decomposition temperature of  $208^\circ \text{C}$ . Compared to commonly used RDX ( $T_{\text{dec.}} = 210^\circ \text{C}$ ) [16] compound **5–7** show similar decomposition temperatures.

## 2.4 Physiochemical and Energetic Properties

The heats and energies of formation are given in Table 1. The values were calculated by the atomization method using electronic energies (CBS-4M method). Details are

**Table 1.** Energetic properties, detonation parameters, and toxicity.

	<b>5</b>	<b>6</b>	<b>7</b>	TKX-50 [9]	RDX
Formula	$\text{C}_2\text{H}_2\text{N}_8\text{O}$	$\text{C}_2\text{H}_8\text{N}_{10}\text{O}_3$	$\text{C}_2\text{H}_{10}\text{N}_{12}\text{O}$	$\text{C}_2\text{H}_8\text{N}_{10}\text{O}_4$	$\text{C}_3\text{H}_6\text{N}_6\text{O}_6$
FW [ $\text{g mol}^{-1}$ ]	154.09	220.15	218.18	236.15	222.12
$IS^a$ [J]	40	12	40	20	7.5 [16]
$FS^b$ [N]	240	216	240	120	120 [16]
$ESD^c$ [J]	0.40	0.75	0.75	0.10	0.20
$N^d$ [%]	72.27	63.62	77.04	59.30	37.84
$\Omega^e$ [%]	−41.53	−36.33	−58.67	−27.10	−21.61
$T_{\text{dec.}}^f$ [ $^\circ \text{C}$ ]	192	200	208	221	210 [17]
$\rho^g$ [ $\text{g cm}^{-3}$ ] (298 K)	1.762	1.731	1.655	1.877	1.806 [18]
$\Delta_f H^h$ [ $\text{kJ mol}^{-1}$ ]	636.6	469.0	662.6	458.7	70.3
$\Delta_f U^i$ [ $\text{kJ kg}^{-1}$ ]	4219.6	2248.5	3167.4	2057.8	417.0
EXPLO V6.01 values:					
$-\Delta_f U^j$ [ $\text{kJ kg}^{-1}$ ]	5611	5546	4755	5939	5734
$T_E^k$ [K]	4043	3490	2903	3642	3800
$\rho_{C-J}^l$ [GPa]	31.4	32.3	29.0	40.1	35.2
$D^m$ [ $\text{m s}^{-1}$ ]	8843	9117	8979	9781	8815
$V_0^n$ [ $\text{L kg}^{-1}$ ]	797	924	939	913	792
SSRT:					
Weight [mg]	–	474	–	509	504
Dent [mg $\text{SiO}_2$ ]	–	723	–	857	858
Toxicity assessment:					
$EC_{50}$ (15 min) [ $\text{g L}^{-1}$ ]	–	1.634	–	1.172	0.327
$EC_{50}$ (30 min) [ $\text{g L}^{-1}$ ]	–	0.330	–	0.580	0.239

a) Impact sensitivity (BAM drophammer, 1 of 6). b) Friction sensitivity (BAM friction tester, 1 of 6). c) Electrostatic discharge device (OZM). d) Nitrogen content. e) Oxygen balance. f) Decomposition temperature from DSC ( $\beta = 5^\circ \text{C}$ ). g) Recalculated from low temperature X-ray densities ( $\rho_{298\text{K}} = \rho_T / (1 + \alpha_V(298 - T_0))$ ;  $\alpha_V = 1.5 \cdot 10^{-4} \text{ K}^{-1}$ ). h) Calculated (CBS-4 M) heat of formation. i) Calculated energy of formation. j) Energy of explosion. k) Explosion temperature. l) Detonation pressure. m) Detonation velocity. n) Assuming only gaseous products.

given in the Supporting Information. Compounds **5–7** have a large positive heat of formation. The highest value of  $663 \text{ kJ mol}^{-1}$  was calculated for the hydrazinium salt **7**.

The calculation of the detonation parameters was performed with the program package EXPLO5 (version 6.01) [19]. The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon.

The EXPLO5 detonation parameters calculated of compounds **5–7** using the room temperature recalculated X-ray densities [20] are summarized in Table 1 and compared to the values calculated for TKX-50 and RDX.

The detonation velocities ( $D=8843$  (**5**),  $9117$  (**6**),  $8979$  (**7**)  $\text{ms}^{-1}$ ) of the two salts are slightly higher than that of the acid **5**. All of them are higher than the detonation velocity of RDX, ( $D=8815 \text{ ms}^{-1}$ ). However, the detonation pressure of compounds **5–7** ( $p_{\text{CJ}}=31.4$  (**5**),  $32.3$  (**6**),  $29.0$  (**7**) GPa) is lower than that of RDX ( $p_{\text{CJ}}=35.2$  GPa). Both trends fit to the equations of Kamlet and Jacob [21].

A small-scale reactivity test (SSRT) was carried out to assess the explosive performance of **6** in comparison to the previous measured TKX-50, CL-20 and RDX (for a detailed set up description, see reference [9]). From measuring the volumes of the dents (Table 1), it can be concluded that the small scale explosive performance of **6** is slightly lower than the performance of commonly used RDX.

## 2.5 Sensitivities

The impact and friction sensitivities were explored by BAM methods (method 1 of 6). The CHNO-based energetic compounds **4–7** reveal strong differences regarding their impact and friction sensitivity. The azido-based compound **4** has to be classified as very sensitive towards impact (4 J) and sensitive towards friction (60 N). The free acid **5** and its hydrazinium salt **7** can both be considered as insensitive as each reveals a value of 240 N for the friction test and 40 J for the impact test. The hydroxylammonium salt **6** exhibits a friction sensitivity of 216 N and an impact sensitivity of 12 J. Therefore it has to be classified as sensitive, however compound **5–7** are still less sensitive than commonly used RDX ( $IS=7.5 \text{ J}$ ,  $FS=120 \text{ N}$ ).

## 2.6 Toxicity Assessment

The toxicity to aquatic life was investigated using the luminescent marine bacterium *Vibrio fischeri* using the commercially available bioassay system LUMISTox®. *Vibrio fischeri* is a representative species for other aquatic life and therefore a useful indicator when it comes to groundwater pollution. Being the most important toxicological parameter, the  $\text{EC}_{50}$  value of the sample was determined.  $\text{EC}_{50}$  is the effective concentration of the examined compound, at which the bioluminescence of the strain *Vibrio fischeri* is decreased by

50% after a defined period of exposure as compared to the original bioluminescence of the sample before being treated with the differently diluted solutions of the test compound. For the bis(hydroxylammonium) salt **6** we observed an  $\text{EC}_{50}$  value of  $1.634 \text{ g L}^{-1}$  after an incubation time of 15 min as well as an  $\text{EC}_{50}$  value of  $0.330 \text{ g L}^{-1}$  after an incubation time of 30 min. The toxicity test demonstrates the low toxicity of compound **6** compared to RDX (Table 1).

## 3 Experimental Section

The analytical methods and general procedures are described in the Supporting Information.

Sodium cyanotetrazole sesquihydrate **1** and 5-aminohydroxymoyl tetrazole **2** were synthesized according to the literature [14].

### 3.1 Synthesis of 5-Chlorohydroxymoyl-tetrazole (**3**)

5-Aminohydroxymoyl tetrazole (1.80 g, 12.3 mmol) was dissolved in fuming hydrochloric acid (33.4 mL, 404 mmol). The solution was cooled with an ice bath and additionally 50 g of ice were added. An aqueous solution of sodium nitrite (2.42 g, 35.1 mmol) was added dropwise over 1 h, while the temperature was kept below  $0^\circ\text{C}$ . Afterwards the solution was allowed to warm to ambient temperature and diluted by addition of 100 mL of ice water. The product was extracted three-times with diethyl ether (50 mL) and after removal of the solvent 5-chlorohydroxymoyl-tetrazole precipitated to give 1.65 g (11.2 mmol, 91%) of a white powder.  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta=152.4$  ( $\text{CN}_4$ ), 124.9 ppm ( $\text{CCINOH}$ ).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta=13.39$  (s, 1 H,  $-\text{NOH}$ ), 7.78 ppm (br. s, 1 H, NH). MS:  $m/z$  ( $\text{DEI}^+$ ): 147.0 [ $\text{M}^+$ ].  $\text{C}_2\text{H}_2\text{ClN}_5\text{O}\cdot\text{H}_2\text{O}$  (172.11): calcd. C 14.51, H 2.44, N 42.31%; found: C 14.59, H 2.41, N 41.88%.

### 3.2 Synthesis of 5-Azidohydroxymoyl-tetrazole monohydrate (**4**)

5-Chlorohydroxymoyl-tetrazole (1.48 g, 10 mmol) was dissolved in ethanol (50 mL) and cooled with an ice bath. An aqueous solution of sodium azide (1.30 g, 20 mmol) was added dropwise over 1 h, while the temperature was kept below  $5^\circ\text{C}$ . Afterwards, an aqueous solution of sodium hydrogen carbonate (840 mg, 10 mmol) was added slowly, the reaction mixture was stirred for 1 h and diluted with water (175 mL). The solution was adjusted to pH 1 by addition of conc. hydrochloric acid and the product was extracted three-times with diethyl ether (50 mL). During removal of the solvent, 5-azidohydroxymoyl-tetrazole monohydrate crystallized to give colorless rods. Yield: 1.27 g, 7.4 mmol, 74%. DSC ( $5^\circ\text{C min}^{-1}$ ):  $126^\circ\text{C}$  (dec.). IR (ATR):  $\tilde{\nu}=3546$  (w), 3223 (w), 3173 (m), 3020 (w), 2876 (w), 2470 (w), 2175 (m), 2116 (m), 1890 (w), 1614 (m), 1581 (m), 1421 (m), 1293 (s), 1256 (m), 1152 (w), 1129 (w), 1086 (w), 1060 (w), 1021 (vs),

948 (s), 863 (s), 760 (m), 696 (s), 609 (m)  $\text{cm}^{-1}$ . **Raman** (1064 nm, 300 mW, 25 °C):  $\tilde{\nu}$  = 2180(8), 2120(7), 1617(100), 1583(76), 1473(25), 1437(17), 1294(13), 1259(23), 1132(8), 1088(9), 1062(5), 1024(19), 960(9), 866(13), 750(6), 603(4), 575(3), 465(7), 404(9), 631(10), 315(15), 230(23), 194(9), 146(84), 125(45), 110(38), 69(45)  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR** ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 12.54 (s, 1 H, –NOH), 6.39 ppm (br. s, 1 H, NH).  **$^{13}\text{C}$  NMR** ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 150.0 ( $\text{CN}_4$ ), 133.3 ppm [ $\text{C}(\text{N}_3)\text{NOH}$ ]. **MS**:  $m/z$  ( $\text{DEI}^+$ ): 154.0 [ $\text{M}^+$ ].  $\text{C}_2\text{H}_4\text{N}_8\text{O}_2$  (172.11): calcd. C 13.96, H 2.34, N 65.11%; found: C 14.61, H 2.33, N 64.29%. Impact sensitivity: 4 J, friction sensitivity: 60 N (at grain size < 100  $\mu\text{m}$ ).

### 3.3 Synthesis of 5-(1*H*-Tetrazolyl)-1-hydroxytetrazole (5)

5-Azidohydroxymoyl-tetrazole monohydrate (5.15 g, 29.9 mmol) was dissolved in hydrochloric acid (100 mL, 37%) and stirred at ambient temperature for 24 h. The mixture is diluted with water and the product was extracted with ethyl acetate. The solution was left for crystallization to yield colorless crystals. Yield: 4.19 g, 27.2 mmol 91%. DSC (5 °C  $\text{min}^{-1}$ ): 192 °C (dec.). **IR** (ATR):  $\tilde{\nu}$  = 3046 (s), 2775 (s), 2122 (w), 1993 (w), 1731 (m), 1637 (m), 1535 (m), 1527 (m), 1470 (m), 1453 (m), 1424 (m), 1398 (m), 1389 (m), 1316 (s), 1243 (s), 1208 (s), 1184 (s), 1174 (vs), 1137 (vs), 1120 (vs), 1080 (s), 1048 (vs), 1033 (s), 1033 (s), 1008 (m), 882 (s), 757 (m), 717 (m), 708 (m), 700 (m), 693 (m), 672 (w)  $\text{cm}^{-1}$ . **Raman** (1064 nm, 300 mW, 25 °C):  $\tilde{\nu}$  = 1638(63), 1413(5), 1275(19), 1253(9), 1197(14), 1185(16), 1178(13), 1137(41), 1123(13), 1085(13), 1047(6), 1036(5), 1023(5), 1009(8), 882(3), 760(11), 682(4), 584(3), 407(22), 325(17), 220(10), 174(31), 149(30), 149(30), 133(80), 103(61), 89(44), 71(100)  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR** ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 7.87 ppm (s, 1 H, OH).  **$^{13}\text{C}$  NMR** ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 146.2 (s,  $\text{CN}_4$ ), 138.1 ppm (s,  $\text{CN}_4\text{O}$ ). **MS**:  $m/z$  ( $\text{DEI}^+$ ): 155.1 ( $\text{M}^+$ ).  $\text{C}_2\text{H}_2\text{N}_8\text{O}$  (154.09): calcd. C 15.59, H 1.31, N 72.72%; found: C 16.29, H 1.37, N 71.99%. Impact sensitivity: 40 J, friction sensitivity: 240 N, ESD: 750 mJ (at grain size 100–500  $\mu\text{m}$ ).

### 3.4 Synthesis of Bis(hydroxylammonium) 5-(1-oxidotetrazolyl)-tetrazolate (6)

5-(1*H*-Tetrazolyl)-1-hydroxytetrazole (500 mg, 3.24 mmol) was dissolved in water (20 mL). Hydroxylamine (428 mg of a 50% w/v solution in  $\text{H}_2\text{O}$ , 6.48 mmol) was added. The solution was left for crystallization and bis(hydroxylammonium) 5-(1-oxidotetrazolyl)-tetrazolate precipitated as colorless needles. Yield: 614 mg, 2.79 mmol, 86%. DSC (5 °C  $\text{min}^{-1}$ ): 200 °C (dec.). **IR** (ATR):  $\tilde{\nu}$  = 3090 (m), 2922 (m), 2860 (m), 2660 (s), 2186 (m), 2112 (m), 2062 (m), 2050 (m), 1648 (m), 1622 (m), 1600 (m), 1562 (m), 1532 (s), 1510 (s), 1458 (s), 1386 (m), 1334 (s), 1248 (s), 1228 (vs), 1190 (s), 1156 (s), 1114 (m), 1082 (m), 1082 (m), 1050 (m), 1038 (m), 1014 (m), 1000 (s), 760 (m), 726 (s), 712 (s), 682 (vs)  $\text{cm}^{-1}$ . **Raman** (1064 nm, 300 mW, 25 °C):  $\tilde{\nu}$  = 3085(4), 2923(5), 2727(5), 1617(9), 1602(100), 1586(9), 1574(5), 1526(6),

1461(5), 1389(4), 1336(4), 1242(17), 1225(5), 1192(9), 1158(7), 1140(11), 1115(14), 1082(5), 1053(8), 1039(10), 1003(18), 761(7), 587(4), 587(4), 422(10), 368(6), 325(6), 284(5), 253(6), 171(8), 154(9), 139(9), 123(35), 102(38), 79(27), 66(13)  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR** ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 9.38 ppm (br. s,  $\text{NH}_3\text{OH}^+$ ).  **$^{13}\text{C}$  NMR** ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 149.3 (s,  $\text{CN}_4$ ); 138.2 ppm (s,  $\text{CN}_4\text{O}$ ). **MS**:  $m/z$  ( $\text{FAB}^-$ ): 153.1 ( $\text{C}_2\text{HN}_8\text{O}^-$ ),  $m/z$  ( $\text{FAB}^+$ ): 33.1 ( $\text{NH}_3\text{O}^+$ ).  $\text{C}_2\text{H}_8\text{N}_{10}\text{O}_3$  (220.15): calcd. C 10.91, H 3.66, N 63.62%; found: C 11.37, H 3.59, N 63.42%. Impact sensitivity: 12 J, friction sensitivity: 216 N, ESD: 750 mJ (at grain sizes 100–500  $\mu\text{m}$ ).

### 3.5 Synthesis of Bis(hydrazinium) 5-(1-oxidotetrazolyl)-tetrazolate (7)

5-(1*H*-Tetrazolyl)-1-hydroxytetrazole (770 mg, 5.0 mmol) was dissolved in ethanol (10 mL). A solution of hydrazine (10.0 mmol, 501 mg) in water was added and a white solid precipitated instantaneously. The solution was stirred for 5 min at ambient temperature, the white precipitate was filtered off, and the filtrate was rinsed with ethanol and ether. The crude product was recrystallized from about 5 mL of water to give bis(hydrazinium) 5-(1-oxidotetrazolyl)-tetrazolate as colorless needles. Yield: 1.01 mg, 4.6 mmol, 93%. DSC (5 °C  $\text{min}^{-1}$ ): 208 °C (dec.). **IR** (ATR):  $\tilde{\nu}$  = 3310 (s), 3263 (s), 3185 (m), 2961 (s), 2944 (s), 2920 (s), 2769 (s), 2615 (s), 2505 (s), 2168 (m), 2164 (m), 2131 (m), 1948 (w), 1800 (w), 1668 (w), 1630 (s), 1624 (s), 1597 (s), 1585 (s), 1564 (s), 1528 (s), 1497 (m), 1455 (vs), 1455 (vs), 1439 (s), 1415 (m), 1374 (s), 1332 (s), 1234 (vs), 1216 (s), 1176 (s), 1134 (m), 1093 (vs), 1033 (s), 999 (s), 975 (vs), 957 (vs), 754 (s), 720 (m)  $\text{cm}^{-1}$ . **Raman** (1064 nm, 300 mW, 25 °C):  $\tilde{\nu}$  = 3310(2), 3268(3), 1599(100), 1527(4), 1456(3), 1333(4), 1235(15), 1217(13), 1175(5), 1130(12), 1112(12), 1099(9), 1071(3), 1035(11), 977(7), 959(5), 764(7), 758(4), 579(2), 421(9), 361(5), 332(4), 243(3), 243(3), 159(7), 135(9), 118(9), 98(60), 79(20), 65(11)  $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR** ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 6.66 ppm (br. s,  $\text{N}_2\text{H}_5^+$ ).  **$^{13}\text{C}$  NMR** ( $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 150.5 (s,  $\text{CN}_4$ ); 138.2 ppm (s,  $\text{CN}_4\text{O}$ ). **MS**:  $m/z$  ( $\text{FAB}^-$ ): 153.1 ( $\text{C}_2\text{HN}_8\text{O}^-$ );  $m/z$  ( $\text{FAB}^+$ ): 33.1 ( $\text{N}_2\text{H}_5^+$ ).  $\text{C}_2\text{H}_{10}\text{N}_{12}\text{O}$  (218.18): calcd. C 11.01, H 4.62, N 77.04%; found: C 11.57, H 4.55, N 75.71%. Impact sensitivity: 40 J; friction sensitivity: 240 N; ESD: 750 mJ (at grain sizes 100–500  $\mu\text{m}$ ).

**Supporting Information** (see footnote on the first page of this article): Details on the syntheses of compounds **1**, **2**, **8–11** as well as the X-ray diffraction analyses of compounds **3–9** and **11**, molecular structures of compounds **3**, **5**, **8**, **9**, and **11**. Details on the spectroscopy measurement, the explosive performance, and the toxicity assessment of the title compounds.

## 4 Conclusions

5-(1*H*-Tetrazolyl)-1-hydroxytetrazole (**5**) and various nitrogen-rich ionic derivatives (e.g. bis(hydroxylammonium) salt

**6**, bis(hydrazinium) salt **7**) were synthesized in five steps, starting from commercially available starting materials sodium azide, sodium cyanide and  $\text{MnO}_2$ .

The crystal structures of **3–7** were determined by low temperature single-crystal X-ray diffraction. The compounds crystallize in the space groups  $P2_1/n$  (**3**),  $P2_12_12_1$  (**4**),  $Pbca$  (**5**),  $P\bar{1}$  (**6**, **7**) with densities of 1.449 (**3**), 1.745 (**4**), 1.814 (**5**), and 1.782 (**6**), 1.704  $\text{g cm}^{-3}$  (**7**), respectively. Additionally all compounds were fully characterized by vibrational spectroscopy (IR and Raman),  $^1\text{H}$  and  $^{13}\text{C}$  NMR, mass spectroscopy, and elemental analysis. Furthermore, a  $^{15}\text{N}$  NMR was obtained of compound **5** and **6** and all resonances were assigned. Thermal stabilities of compounds **4–7** were investigated by DSC. They decompose at 126 °C (**4**), 192 °C (**5**), 200 °C (**6**), and 208 °C (**7**), respectively.

The sensitivities towards friction impact and electrostatic discharge were investigated by BAM methods. Compounds **4–7** were found to have impact sensitivities of 4 J (very sensitive) (**4**), 40 J (insensitive) (**5**, **7**), and 12 J (sensitive) (**6**), friction sensitivities of 60 N (sensitive) (**4**), 240 N (insensitive) (**5**, **7**), and 216 N (sensitive) (**6**), and ESD sensitivities of 0.40 J (**5**), 0.75 J (**6**), and 0.75 J (**7**).

Using calculated heats of formation and experimentally obtained crystal densities, the detonation parameters (heat of explosion, explosion temperature, detonation pressure, and velocity) were calculated for compounds **5–7** [ $D = 8843 \text{ m s}^{-1}$  (**5**),  $9117 \text{ m s}^{-1}$  (**6**),  $8979 \text{ m s}^{-1}$  (**7**)]. The sensitivities and detonation velocity of the newly synthesized 5-(1*H*-tetrazolyl)-1-hydroxytetrazole (**5**) and its salts outperform commonly used RDX ( $IS = 7.5 \text{ J}$ ,  $FS = 120 \text{ N}$ ,  $ESD = 0.2 \text{ J}$ ,  $D = 8815 \text{ m s}^{-1}$ ). The low toxicity of compound **6** was determined, which makes compound **6** a potential “green” RDX replacement.

## Symbols and Abbreviations

BAM	Bundesanstalt für Materialforschung und -prüfung
CCDC	Cambridge crystallographic data centre
DSC	Differential scanning calorimetry
FW	Formula weight [ $\text{g mol}^{-1}$ ]
IS	Impact sensitivity [J]
FS	Friction sensitivity [N]
ESD	Electrostatic discharge [J]
S	Goodness of fit
IR	Infrared
$\lambda(\text{Mo-K}\alpha)$	X-ray laser wavelength
MS	Mass spectrometry
N	Nitrogen content [%]
NMR	Nuclear magnetic resonance
$\rho$	Density [ $\text{g cm}^{-3}$ ]
STANAG	Standardization agreement
$T_{\text{dec}}$	Decomposition temperature [°C]

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