

# The Taming of $\text{CN}_7^-$ : The Azidotetrazolate 2-Oxide Anion

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*Dedicated to Professor Jürgen Evers on the occasion of his 70th birthday*

**Abstract:** The highly sensitive 5-azido-tetrazolate anion was oxidized to its corresponding *N*-oxide by aqueous oxidation in a buffered oxone solution to the azidotetrazolate 2-oxide anion. After acidic extraction and neutralization with ammonia, the ammonium salt was isolated. Several energetic salts of this novel anion were prepared from the ammonium salt, and in all cases

were found to be of lower sensitivity than the corresponding 5-azidotetrazolate salt while still being highly sensitive towards mechanical stimuli. Explosive performances (detonation velocity,

detonation pressure) of applicable salts were also found to be higher than the non-*N*-oxide variants. Preparation of the free acid 2-hydroxy-5-azidotetrazole was achieved by protonation of the anion and identified by NMR spectroscopy, whereas the majority of the azidotetrazolate 2-oxide salts have unequivocal crystallographic proof.

**Keywords:** azides • explosives • materials science • oxidation • tetrazoles

## Introduction

The synthesis of nitrogen-rich, energetic compounds is a longstanding tradition in the chemical sciences; it attracts scientists as a result of the technical challenges presented in their synthesis and isolation.<sup>[1–3]</sup> Such compounds are metastable with regards to their detonation products, with the energy requirement for inducing explosion ranging from as little as a gentle touch to as much as requiring another explosion for initiation. Energetic materials chemistry pushes the limits of the unique molecules that can be created while straddling the line between existence and nonexistence. Nitrogen-rich compounds are candidates for replacing currently used energetic materials (propellants, explosives, pyrotechnics) with “green” replacements because the main combustion/detonation product is harmless molecular nitrogen.<sup>[4–6]</sup>

The unique stability of dinitrogen that arises from its strong, short, triple bond means that the decomposition of high-nitrogen compounds with the formation of nitrogen gas is highly favored energetically, thus making nitrogen-rich compounds one intensely pursued strategy in the design of

energetic materials.<sup>[7–9]</sup> For a nitrogen-rich material to find practical use as a high explosive, it needs to possess high thermal and mechanical stabilities while concurrently satisfying the demand for ever higher-performing materials. As the nitrogen content of a material rises, the heat of formation also rises, and concurrently the energetic performance. Unfortunately, however, compounds with higher and higher heats of formation are increasingly unstable, both thermally and mechanically. When the five-membered azoles from pyrazole to pentazole are considered, this trend becomes obvious. Pyrazole is not used in energetic materials due to low performance, and the few pentazole derivatives known are unstable under ambient conditions.<sup>[10]</sup> With their high nitrogen content and resulting heats of formation, triazoles and especially tetrazoles are very useful heterocyclic backbones for the preparation of high-performance energetic materials.

The tetrazole ring has allowed the preparation of a wide spectrum of energetic compounds from insensitive secondary explosives<sup>[11]</sup> to exceedingly sensitive primary explosives<sup>[12]</sup> depending on substituents and anion–cation pairing. Of the 5-substituted tetrazoles, 5-azidotetrazole and its salts are comparable or only slightly less sensitive than the most sensitive tetrazoles.<sup>[13]</sup> For example, the unquestionably most sensitive tetrazole derivative, diazotetrazole,<sup>[14]</sup> explodes in aqueous solution once it crystallizes or the concentration exceeds a few percent, and the lower alkali metal salts of azidotetrazole also explode during crystallization. 1,1'-Azobis(tetrazole) often explodes when manipulated dry, whereas free 5-azidotetrazole can be manipulated dry with only relative safety, yet while still being exceedingly dangerous. 5-Azidotetrazole was first described in patents in 1939;<sup>[15–17]</sup> however, not until 2008 was a detailed study of its salts published.<sup>[13]</sup>

The oxidation of a tetrazole ring to its 2-oxide has been previously shown by our research group to be an effective

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method of reducing the sensitivity of tetrazole-based energetic materials towards mechanical stimuli.<sup>[18]</sup> The addition of the single oxygen atom to the ring simultaneously decreases the heat of formation while allowing more intermolecular interactions (as evidenced by the density), both of which are factors that reduce the sensitivity of an energetic material. The increased density relative to the unoxidized form, when combined with the increased oxygen balance makes tetrazole *N*-oxides a useful strategy for increasing energetic performance. The oxygen balance ( $\Omega$ ) is a percentage representation of the oxygen content of a compound, thereby enabling it to oxidize all of its nonoxidizing content to their respective oxides and is easily calculated by Equation (1), in which  $w$  is the number of oxygen atoms,  $x$  is the number of carbon atoms,  $y$  is the number of hydrogen atoms,  $z$  is the number of sulfur atoms, and  $M$  is the molecular weight:

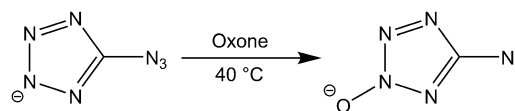
$$\Omega [\%] = (w - 2x - \frac{1}{2}y - 2z) \times 1600/M \quad (1)$$

The only downside observed in our work was the slightly lowered decomposition temperatures.<sup>[18]</sup> Unfortunately, this was in contrast to other *N*-oxide based systems in which thermal stability increases.<sup>[19–22]</sup> The high performance of azidotetrazole-based energetic materials and their unacceptable sensitivities made this system an interesting candidate for oxidation with anticipated lowered sensitivities and increased performances.

The oxidation of the 5-azidotetrazolate anion under mild aqueous conditions yielded the 5-azidotetrazolate 2*N*-oxide anion. This unique anion was isolated as the ammonium and various other nitrogen-rich and alkali metal salts were rendered by means of metathesis reactions. Characterization included X-ray diffraction, IR, NMR spectroscopy, differential scanning calorimetry (DSC), and impact, friction, and electrostatic discharge; it is as complete as possible. However, a couple of compounds exhibited extensive nonexplosive decomposition during synthesis, and as a result only crystal structures were obtained. All of the salts characterized show lower sensitivities and higher performances relative to their nonoxide analogues. Also of interest is that one prepared salt crystallized as a monohydrate and is completely insensitive towards impact, thus making for the safest compound known that contains the azidotetrazole moiety.

## Results and Discussion

**Synthesis:** The oxidation of the 5-azidotetrazolate anion in a saturated, buffered aqueous Oxone ( $2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$  triple salt) solution proceeds easily over three days at 40 °C (Scheme 1). Free acid 5-azido-2-hydroxytetrazole (HAZX, **4**) and its sodium ( $\text{NaAZX} \cdot \text{H}_2\text{O}$ , **2**· $\text{H}_2\text{O}$ ), potassium (KAZX, **3**), aminoguanidinium (AGAZX, **5**), and silver (AgAZX, **6**) salts were prepared by simple acid–base chemistry and metathesis reactions with either acid, alkali



Scheme 1. Oxidation of the azidotetrazolate anion to the azidotetrazolate 2-oxide anion.

hydroxide, silver nitrate, or aminoguanidine bicarbonate. Hydroxylammonium azidotetrazolate ( $\text{HxAzTz}$ , **7**) is a constitutional isomer of **1** and was prepared from 5-azidotetrazole and hydroxylamine in aqueous solution.

After acidification of the reaction solution, ethereal extraction, treatment with ammonia, and recrystallization from acetonitrile, ammonium azidotetrazolate 2-oxide (**1**) was obtained. The crystals produced during recrystallization were suitable for X-ray measurement. Compounds **2** and **3** were prepared by heating to reflux the ammonium salt with the corresponding alkali hydroxide. Evaporation of the solution followed by recrystallization from acetonitrile yielded the pure products. Compound **2** was isolated as a monohydrate, **2**· $\text{H}_2\text{O}$ , and was completely safe to handle, whereas anhydrous **3** was highly sensitive. Neither compound **2** nor **2**· $\text{H}_2\text{O}$  formed measurable crystals under any conditions attempted. Long, hairlike fibers were always formed; however, the methanol cocrystal **2**· $\text{MeOH}$  was crystallized by the slow diffusion into a methanolic solution of **2**, whereas **3** crystallized upon evaporation. Free acid **4** was prepared by acidification of a solution of **1**, followed by ether extraction and evaporation. Attempts to crystallize this oily material were unsuccessful; however, several times during evaporation the material decomposed nonexplosively for unknown reasons. For this reason, only the NMR spectra are reported. Aminoguanidinium salt **5** was prepared by the treatment of **1** with aminoguanidine bicarbonate in ethanol. Evaporation of the reaction liquors gave a material that was nonexplosive and had only traces of the azidotetrazolate 2-oxide anion remaining within. Diffusion of diethyl ether into a methanolic solution of this material luckily gave a few crystals of pure **5** suitable for X-ray analysis. The reaction of an aqueous solution of **1** with silver nitrate yielded **6** as a highly explosive precipitate, which dry exploded when moved onto a porcelain plate. Compound **7** was prepared by mixing an aqueous solution of hydroxylamine and 5-azidotetrazole. After careful evaporation under ambient conditions, **7** was obtained as a highly sensitive white powder. By diffusion of ether into a solution of **7** in methanol yielded crystals suitable for X-ray measurement.

**Spectroscopy:** Multinuclear NMR spectroscopy, and particularly  $^{13}\text{C}$  and  $^{15}\text{N}$  spectroscopy, proved to be a valuable tool for the characterization of the tetrazole and tetrazolates. With the exception of the free acid **4**, all NMR spectra were performed in  $[\text{D}_6]\text{DMSO}$ . We anticipated a high acidity for **4** comparable to our previously reported 2-hydroxy-5-nitrotetrazole, so NMR spectroscopic experiments were performed in  $[\text{D}_8]\text{THF}$ . The anionic azidotetrazolate 2-oxides

all show the single  $^{13}\text{C}$  peak near  $\delta = 151$  ppm, lower than the corresponding azidotetrazolate, which occurs near  $\delta = 158$  ppm. This trend is comparable to that seen when nitrotetrazolate is oxidized, and the signal shifts upfield. When the  $^{15}\text{N}$  spectrum of the azidotetrazolate 2-oxide anion is compared with azidotetrazolate, a loss of nitrogen equivalency is seen between N1 and N4 and between N2 and N3. Unfortunately for N2 and N3, the shifts show up close together at  $\delta = -39.1$  and  $-40.8$  ppm (in azidotetrazolate at  $\delta = -4.5$  ppm), and although one would rationally expect the largest shift change to belong to N2 where the oxygen has been added, a calculated (MPW1PW91/aug-cc-pVDZ, Gaussian 03<sup>[23]</sup>) spectrum says N3 is the most upfield of the two; so for such close signals, precise assignment is avoided. Protonation of the azidotetrazolate-2N-oxide anion yields highly acidic **4**, and the  $^{13}\text{C}$  NMR spectroscopic shift occurs at  $\delta = 155$  ppm. The  $^1\text{H}$  signal occurs as a broad singlet at  $\delta = 11.71$  ppm, out of range for an N–H proton because azidotetrazole has its N–H proton at  $\delta \approx 7.0$  ppm, thus indicating that, like nitrotetrazolate 2-oxide,<sup>[18]</sup> AZX also likely protonates on oxygen to form a 5-azido-2-hydroxytetrazole. Lack of N–H coupling in the  $^{15}\text{N}$  spectrum also supports this conclusion, as well as the resonances in the spectrum being similar to other 2-substituted azidotetrazoles.  $^{15}\text{N}$  signal assignments were based on a calculated spectrum performed as above and comparison with literature spectra for 2-substituted azidotetrazoles. Unfortunately, assignment for N4 and N2 are unclear as their resonances occur very near each other at  $\delta = -81.3$  and  $-82.9$  ppm, thus making precise assignment impossible. Figure 1 shows the  $^{15}\text{N}$  spectra that belong to the azidotetrazolate 2-oxide anion and to 5-azido-2-hydroxytetrazole (**4**).

The IR and Raman spectra of all compounds were recorded and assigned using frequency analysis from an optimized structure (B3LYP/cc-pVDZ using the Gaussian 03 software<sup>[23]</sup>). All calculations were performed at the DFT level of theory; the gradient-corrected hybrid three-parameter B3LYP<sup>[24,25]</sup> functional theory has been used with a correlation consistent cc-pVDZ basis set.<sup>[26–29]</sup> The anionic azidotetrazolate 2-oxides generally contain a strong, diagnostic band in the infrared that ranges from 2139 to 2169  $\text{cm}^{-1}$ . The calculated value for this band is 2252  $\text{cm}^{-1}$  and arises from the azide asymmetric stretch. Another strong band occurs at 1340–1380  $\text{cm}^{-1}$  (calcd 1452  $\text{cm}^{-1}$ ) and this is assigned to the C–N5 covalent azide stretch with minor components of N–O stretching and azide symmetric stretching. The Raman spectra of all salts of azidotetrazolate-2N-oxide all adopt a characteristic pattern of three bands. The first at 2152–2159  $\text{cm}^{-1}$  (calcd 2252) results from the azide asymmetric stretch. The second at 1493–1499  $\text{cm}^{-1}$  (calcd 1452  $\text{cm}^{-1}$ ) results from the C–N5 covalent azide stretch with minor components of N–O stretching and azide symmetric stretching. The final diagnostic Raman stretch occurs at 1019–1040  $\text{cm}^{-1}$  (calcd 1080  $\text{cm}^{-1}$ ) and is assigned to an asymmetric tetrazole deformation vibration.

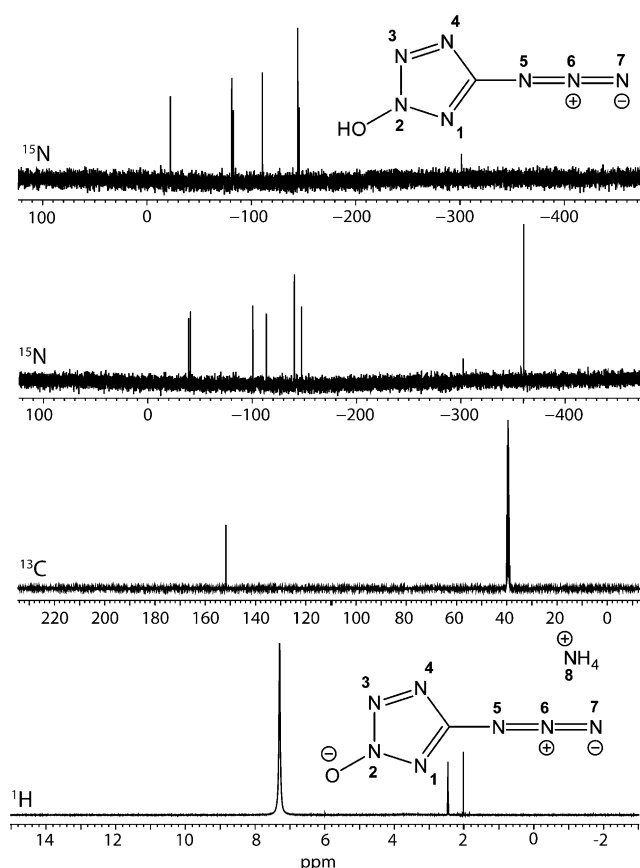


Figure 1. Multinuclear NMR spectroscopy of **1** and **4**.

**Relative energy:** To support the NMR spectroscopic data in that the azidotetrazolate 2-oxide anion is protonated on the oxygen to form 2-hydroxy-5-nitrotetrazole, the relative energies of N1–H, N3–H, and N4–H ring-protonated species were calculated. The calculations performed were in accordance with the same software, theory, and basis set as described in the vibrational spectroscopy section (Table 1). The relative energies indicate that 5-azido-2-hydroxytetrazole is the lowest-energy species formed from the protonation of the azidotetrazolate 2-oxide anion, similar to what occurred with nitrotetrazolate 2-oxides.

Table 1. Relative energies of protonation sites on the azidotetrazolate 2-oxide anion.<sup>[a]</sup>

	O–H	N1–H	N3–H	N4–H
point group	$C_1$	$C_s$	$C_s$	$C_s$
$-E$ [a.u.]	497.044145	497.031215	497.031624	497.038024
electronic state	$^1A'$	$^1A'$	$^1A'$	$^1A'$
NIMAG	0	0	0	0
zpe [kcal mol $^{-1}$ ]	33.7	33.6	33.8	33.3
$E_{\text{rel}}$ [Kcal mol $^{-1}$ ]	0	8.1	7.9	3.8

[a]  $-E$  = electronic energy; NIMAG = number of imaginary frequencies; zpe = zero point energy;  $E_{\text{rel}}$  = relative energy.

**Single-crystal X-ray structure analysis:** The low-temperature determination of the crystal structures of **1**, **2**·MeOH, **3**, **5**,

Table 2. X-ray data and parameters of azidotetrazolate 2-oxides.<sup>[a]</sup>

	1	2-MeOH	3	5	7
formula	CH <sub>4</sub> N <sub>8</sub> O	C <sub>2</sub> H <sub>4</sub> N <sub>7</sub> NaO <sub>2</sub>	CN <sub>7</sub> OK	C <sub>2</sub> H <sub>7</sub> N <sub>11</sub> O	CH <sub>4</sub> N <sub>8</sub> O
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	144.12	181.11	165.18	201.19	144.12
crystal system	orthorhombic	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> (19)	<i>P</i> 2 <sub>1</sub> / <i>m</i> (11)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (14)	<i>P</i> 1̄ (2)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (14)
color/habit	colorless block	colorless rod	colorless plate	colorless rod	colorless rod
size [mm]	0.17 × 0.21 × 0.23	0.06 × 0.12 × 0.17	0.06 × 0.40 × 0.55	0.13 × 0.17 × 0.30	0.05 × 0.10 × 0.35
<i>a</i> [Å]	7.911(5)	8.8466(8)	3.676(3)	7.7099(4)	3.677(3)
<i>b</i> [Å]	9.562(5)	6.4024(8)	20.793(5)	8.3482(4)	20.885(5)
<i>c</i> [Å]	14.981(5)	13.2145(14)	7.048(7)	13.8979(8)	7.641(7)
<i>α</i> [°]	90	90	90	73.420(5)	90
<i>β</i> [°]	90	92.546(9)	100.755(5)	82.182(4)	98.367(5)
<i>γ</i> [°]	90	90	90	76.385(4)	90
<i>V</i> [Å <sup>3</sup> ]	1133.2(10)	747.72(14)	529.3(7)	830.96(8)	580.5(7)
<i>Z</i>	8	4	4	4	4
<i>ρ</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	1.689	1.609	2.073	1.608	1.649
<i>μ</i> [mm <sup>-1</sup> ]	0.144	0.184	0.931	0.133	0.140
<i>F</i> (000)	592	368	328	416	296
<i>T</i> [K]	173	173	173	173	173
<i>θ</i> <sub>min</sub> , <i>θ</i> <sub>max</sub> [°]	4.3, 26.0	4.2, 25.0	4.2, 26.0	4.1, 26.0	4.7, 26.0
dataset	−9:9; −11:11; −18:9	−10:10; −7:4; −15:14	−3:4; −24:25; −7:8	−9:9; −10:10; −17:17	−4:4; −25:25; −9:7
reflns collected	5818	3556	2722	8398	2928
indep reflns	1293	1422	1041	3265	1132
<i>R</i> <sub>int</sub>	0.027	0.049	0.032	0.046	0.041
obsd reflns	1140	819	776	1777	700
params	214	124	91	309	107
<i>R</i> <sub>1</sub> (obsd) <sup>[b]</sup>	0.0235	0.0444	0.0277	0.0369	0.0395
<i>wR</i> <sub>2</sub> (all data) <sup>[c]</sup>	0.0589	0.1018	0.0608	0.0787	0.0857
GOF <sup>[d]</sup>	0.97	0.83	0.92	0.81	0.85
residual density [e Å <sup>-3</sup> ]	−0.13, 0.15	−0.25, 0.65	−0.20, 0.26	−0.22, 0.17	−0.18, 0.23
solution	SIR-92	SIR-92	SHELXS-97	SHELXS-97	SHELXS-97

[a] Measurements were carried out on a Oxford Xcalibur3 CCD, refined with SHELXL-97, and multiscan absorption correction.  $\lambda$  (MoK $\alpha$ ) = 0.71073 Å. [b]  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . [c]  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ ;  $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}$  and  $P = (F_o^2 + 2F_c^2)/3$ ; [d] GOF =  $[\sum [w(F_o^2 - F_c^2)^2] / (n - p)]^{1/2}$  ( $n$  = number of reflections;  $p$  = total number of parameters).

and **7** were performed using a Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection and reduction were carried out using the CrysAlisPro software.<sup>[30]</sup> The structures were solved either with SIR-92<sup>[31]</sup> or SHELXS-97,<sup>[32]</sup> refined with SHELXL-97<sup>[33]</sup> and finally checked using the Platon<sup>[34]</sup> software integrated in the WinGX<sup>[35]</sup> software suite. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were located and freely refined. The absorptions were corrected by a Scale3 Abspack multiscan method.<sup>[36]</sup> In the case of the chiral space group *P*2<sub>1</sub>2<sub>1</sub> of **1**, the Friedl pairs were merged. Selected data and parameter of the X-ray determinations are given in Table 2.

The molecular structure of ammonium azidotetrazolate 2-oxide, which crystallizes orthorhombically in the space group *P*2<sub>1</sub>2<sub>1</sub>, is shown in Figure 2. Its density of 1.689 g cm<sup>-3</sup> is the highest one of the metal-free salts discussed in this work. It is also higher relative to its isomer **7** (1.649 g cm<sup>-3</sup>), which corroborates the theory of increased density in *N*-oxide compounds.<sup>[18]</sup> The geometry of the azidotetrazolate 2-oxide anion is very similar in all compounds within this work. The *N*-oxide is bonded in a distance between 1.280 and 1.311 Å, which is between an N=O double (1.17 Å) and an N–O single bond (1.45 Å), thereby indicat-

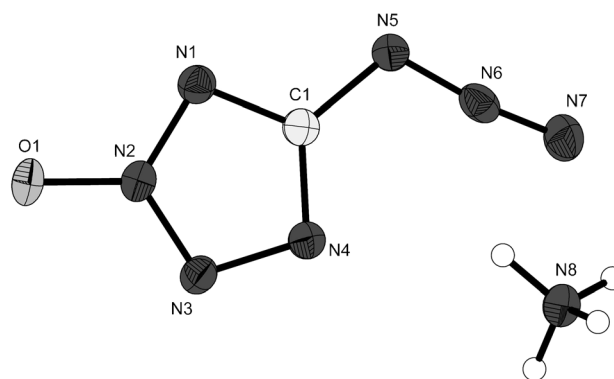


Figure 2. Molecular unit of **1**. Thermal ellipsoids represent the 50% probability level. Hydrogen atoms are drawn as small spheres of arbitrary radius.

ing significant *N*-oxide character. The oxide is also planar with the tetrazole ring, thereby indicating the sp<sup>2</sup> nature of the N2 to which it is bonded. The azide is angulated (angles 170.9–173.0°) and follows the plane of the aromatic tetrazole ring system. Exact bond lengths are given in Table 3. The structure of **1** is strongly dominated by the hydrogen bonds (Figure 3) of all ammonium hydrogen atoms, with three of

Table 3. Anion bond lengths [Å] in the azidotetrazolate 2-oxide anion.

	1	2·MeOH	3	5	7
O1–N2	1.311(2)	1.280(3)	1.294(3)	1.299(2)	
N1–N2	1.333(2)	1.3533(11)	1.340(3)	1.342(2)	1.355(3)
N1–C1	1.333(2)	1.3368(11)	1.334(3)	1.331(3)	1.322(3)
N2–N3	1.306(2)	1.3005(11)	1.319(3)	1.314(2)	1.304(3)
N3–N4	1.352(2)	1.3550(11)	1.359(3)	1.355(2)	1.345(3)
N4–C1	1.330(2)	1.3186(11)	1.332(3)	1.322(2)	1.328(3)
C1–N5	1.395(2)	1.4007(11)	1.405(3)	1.398(3)	1.391(3)
N5–N6	1.253(2)	1.2240(11)	1.252(3)	1.248(2)	1.249(3)
N6–N7	1.118(2)	1.1254(11)	1.118(3)	1.121(2)	1.125(3)

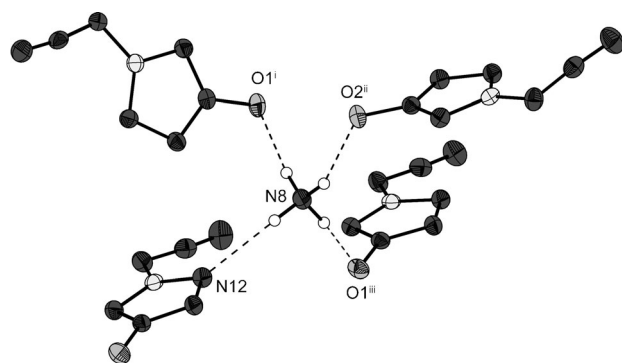


Figure 3. Hydrogen bonding of the ammonium cations. Symmetry codes: i)  $-x, 0.5+y, 0.5-z$ ; ii)  $0.5-x, 1-y, -0.5+z$ ; iii)  $0.5-x, -y, -0.5+z$ .

them interacting with the oxygen atom of the tetrazolate *N*-oxides.

Compound **2** could only be obtained crystalline as a methanol adduct shown in Figure 4. Its density of  $1.609 \text{ g cm}^{-3}$  is very low in comparison with other sodium tetrazolates in the literature,<sup>[37]</sup> which is probably a result of the inclusion of methanol.

Compound **5**, depicted in Figure 5, crystallizes with the lowest density ( $1.608 \text{ g cm}^{-3}$ ) of all compounds investigated

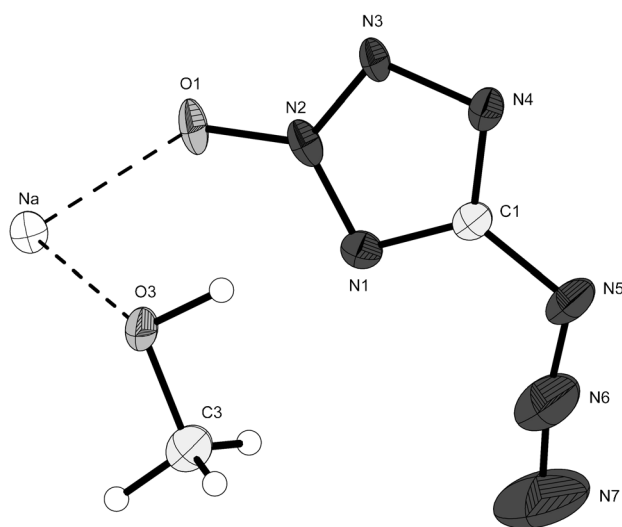


Figure 4. Molecular unit of **2·MeOH**. Thermal ellipsoids represent the 50% probability level.

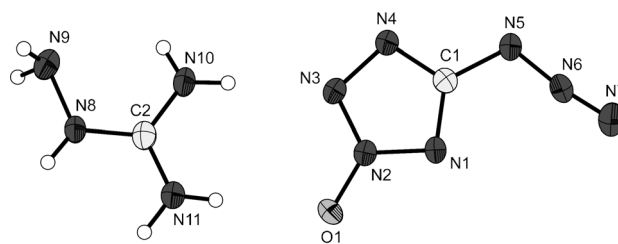


Figure 5. Molecular unit of **5**. Thermal ellipsoids represent the 50% probability level. Hydrogen atoms are drawn as small spheres of arbitrary radius.

in this work. The colorless rods are based on the triclinic crystal system, space group  $P\bar{1}$ . The structure is strongly dominated by several hydrogen bonds, illustrated in Figure 6. Typical hydrogen-bond graph sets<sup>[38]</sup> can be identified, for example, **R(2,2)8**, **R(1,2)3**, **C(2,2)7**, and **C(2,2)8**.

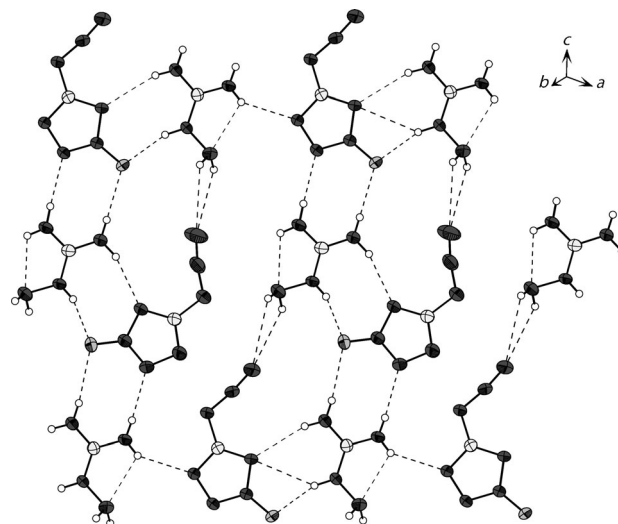


Figure 6. View of the hydrogen-bond motifs within the layers in **5**.

The potassium salt **3** crystallizes in the monoclinic space group  $P2_1/n$  with the highest density ( $2.074 \text{ g cm}^{-3}$ ) observed in this work. Within the asymmetric unit (Figure 7) the potassium cations are coordinated by the atoms N3 and O1 and show coordination distances of  $\text{N3–K} = 2.963(3) \text{ Å}$  and

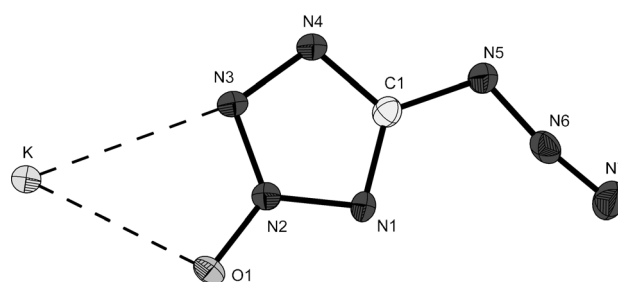


Figure 7. Asymmetric unit of **3**.



O1–K=2.849(3) Å. Within the structure two flight chains along the *a* axis are formed (Figure 8)

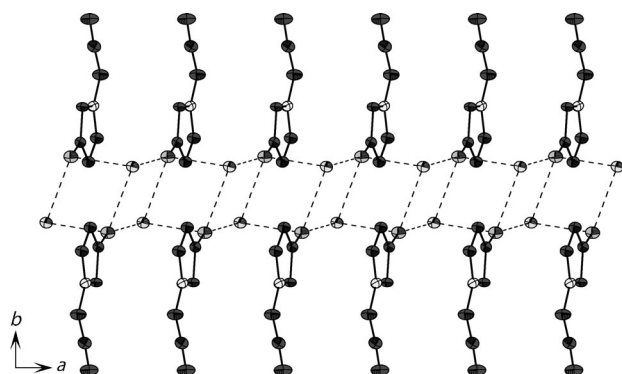


Figure 8. View on the chains along the *a* axis in the structure of **3**.

The isomer of **1**, hydroxylammonium 5-azidotetrazolate (**7**), crystallizes in the monoclinic space group  $P2_1/c$ . Its molecular structures (Figure 9) are arranged in a wavelike layer structure along the *b* axis. The layers are formed by double flight strands along the *c* axis, which is depicted in Figure 10.

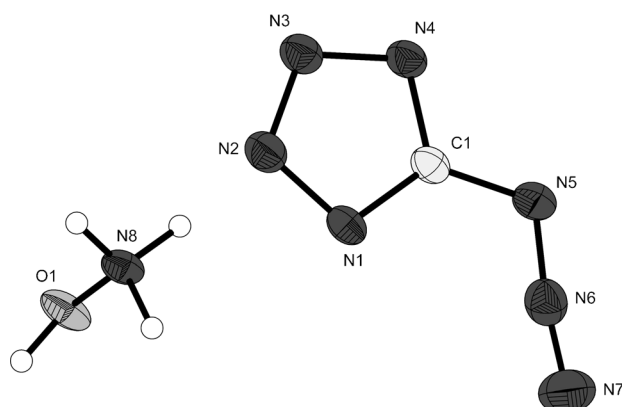


Figure 9. Asymmetric unit of **7**.

**Heats of formation:** Nitrogen-rich heterocycles, especially those that contain the azide functionality, tend to explode in bomb calorimeters, thereby resulting in insufficient combustion results. Therefore the heats of formation of the metal-free compounds **1**, **5**, and **7** were determined by quantum chemical calculations. For energetic nitrogen-rich compounds, it has been shown appropriate in recent studies<sup>[39–40]</sup> to use the atomization method [according to Eq. (2)] based on CBS-4M enthalpies:

$$\Delta_f H^\circ_{(\text{g, M, 298K})} = H_{(\text{molecule, 298K})} - \sum H^\circ_{(\text{atoms, 298K})} + \sum \Delta_f H^\circ_{(\text{atoms, 298K})} \quad (2)$$

The computations were performed with the Gaussian 09 software package.<sup>[41]</sup> The obtained gas-phase enthalpies

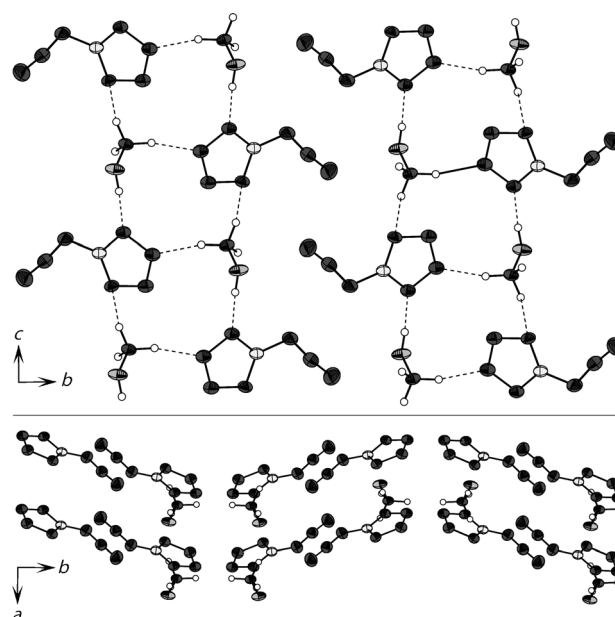


Figure 10. Views along the *a* and *c* axes in the structure of **7**.

were converted into the solid-state enthalpies with Jenkin's equations by using the total molecular volume of the anion-cation pair from the crystal structure (Table 4).

Table 4. CBS-4M calculation results and molecular volumes ( $V_M$ ) taken from X-ray structures.

M	$-H^{298}$ [a.u.]	$\Delta_f H^\circ(\text{g, M})$ [kcal mol <sup>-1</sup> ]	$V_M$ [nm <sup>3</sup> ]
AZX <sup>-</sup>	495.889863	108.7	
AzTz <sup>-</sup>	420.796001	113.5	
NH <sub>4</sub> <sup>+</sup>	56.796608	151.9	
NH <sub>2</sub> O <sup>+</sup>	131.863249	177.9	
AG <sup>+</sup>	260.701802	160.4	
<b>1</b>		260.6	0.142
<b>5</b>		269.1	0.208
<b>7</b>		277.6	0.145

When the heats of formation of the ammonium (**1**) and aminoguanidinium (**5**) salts of azidotetrazolate 2-oxide are compared to the corresponding azidotetrazolates, the solid-state heats of formation are lower by 6 and 20 kJ mol<sup>-1</sup>, respectively. This trend is comparable to that seen for nitrotetrazolate and its *N*-oxide.<sup>[18]</sup>

**Detonation parameters:** The calculation of the detonation parameters (Table 5) were performed with the program package EXPLO5<sup>[42]</sup> using version 5.04 as well as version 5.03 (values in brackets), in which several parameters have been modified. The input was made using the sum formula, energy of formation, and the experimentally determined densities (X-ray). The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker–Kistiakowsky–Wilson equation of state (BKW EOS) for gaseous detonation products and Cowan–Fickett's

Table 5. Energetic properties and detonation parameters of AZX salts.

	<b>1</b>	<b>5</b>	<b>7</b>
formula	CH <sub>4</sub> N <sub>8</sub> O	C <sub>2</sub> H <sub>7</sub> N <sub>11</sub> O	CH <sub>4</sub> N <sub>8</sub> O
<i>M<sub>r</sub></i> [g mol <sup>-1</sup> ]	144.12	201.19	144.12
IS [J] <sup>[a]</sup>	1	N.D.	< 1
FS [N] <sup>[b]</sup>	20	N.D.	< 5
ESD test [J] <sup>[c]</sup>	0.030	N.D.	0.100
<i>N</i> [%] <sup>[d]</sup>	77.76	76.60	77.76
$\Omega$ [%] <sup>[e]</sup>	-33.31	-51.70	-33.31
<i>T<sub>decomp</sub></i> [°C] <sup>[f]</sup>	151	N.D.	96
density [g cm <sup>-3</sup> ] <sup>[g]</sup>	1.689	1.608	1.649
$\Delta_f H_m^\circ$ [kJ mol <sup>-1</sup> ] <sup>[h]</sup>	534.0	623.3	608.8
$\Delta_f U^\circ$ [kJ kg <sup>-1</sup> ] <sup>[i]</sup>	3816.9	3215.1	4335.5
EXPLO 5.04 (5.03)			
$-\Delta_f U^\circ$ [kJ kg <sup>-1</sup> ] <sup>[j]</sup>	5668 (5674)	4743 (4770)	6181 (6188)
<i>T<sub>E</sub></i> [K] <sup>[k]</sup>	3960 (4129)	3277 (3396)	4267 (4428)
<i>p<sub>C-J</sub></i> [kbar] <sup>[l]</sup>	325 (330)	262 (267)	324 (330)
<i>D</i> [m s <sup>-1</sup> ] <sup>[m]</sup>	8926 (9167)	8332 (8592)	8959 (9175)
<i>V<sub>gas</sub></i> [L kg <sup>-1</sup> ] <sup>[n]</sup>	830 (842)	820 (840)	831 (844)

[a] Impact sensitivity (BAM drop hammer, 1 of 6). N.D.=not determined. [b] Friction sensitivity (BAM friction test 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] From X-ray diffraction. [h] Calculated (CBS-4M) heat of formation. [i] Energy of formation. [j] Energy of explosion. [k] Explosion temperature. [l] Detonation pressure. [m] Detonation velocity. [n] Assuming only gaseous products.

equation of state for solid carbon.<sup>[43–46]</sup> The calculation of the equilibrium composition of the detonation products is done by applying a modified version of White, Johnson, and Dantzig's free-energy minimization technique. The program is designed to enable the calculation of detonation parameters at the Chapman–Jouguet point. The BKW equation [Eq. (3)] in the following form was used with the BKWN set of parameters ( $\alpha$ ,  $\beta$ ,  $\kappa$ ,  $\theta$ ) and with  $X_i$  being the mole fraction of the  $i$ th gaseous product, and  $k_i$  being the molar volume of the  $i$ th gaseous product:

$$pV/RT = 1 + x e^{\beta x} \quad x = (\kappa \sum X_i k_i) / [V(T + \theta)]^\alpha \quad (3)$$

$$\alpha = 0.5, \beta = 0.176, \kappa = 14.71, \theta = 6620 \text{ (EXPLO 5.03)}$$

$$\alpha = 0.5, \beta = 0.96, \kappa = 17.56, \theta = 4950 \text{ (EXPLO 5.04)}$$

The detonation parameters calculated with the EXPLO5 program are summarized in Table 5.

Compound **1** has a detonation velocity 250 ms<sup>-1</sup> higher than the corresponding azidotetrazolate,<sup>[13]</sup> and that of compound **5** is 168 ms<sup>-1</sup> higher than its analogue that lacks an *N*-oxide. This again confirms that the strategy of *N*-oxide incorporation into tetrazole-based energetic materials is an effective method of increasing their performance.

Compound **7** is of interest because it is a constitutional isomer of **1**. Their performances are almost identical, thereby indicating that the decrease in heats of formation and increase in density balance each other out for compounds of identical oxygen balance. In the next sections, the thermal stabilities and sensitivities will illustrate the superiority of **1** versus **7** and as such the versatility of *N*-oxides as a strategy in energetic material design.

**Thermal behavior:** The thermal behavior of **1**, **2**, **3**, and **7** were all investigated using a Linseis PT10 differential scanning calorimeter at heating rates of 5 °C min<sup>-1</sup> with approximately 1–1.5 mg of material. The ammonium salt (**1**) is the most stable; it decomposes at 151 °C with no prior melting. Relative to its non-*N*-oxide counterpart, ammonium azidotetrazolate, **1** decomposes 6 °C lower. Sodium salt **2**·H<sub>2</sub>O loses hydration water at 100 °C, undergoes a brief melting event at 118 °C, quickly followed by decomposition at 122 °C. This decomposition temperature is 33 °C lower than its non-*N*-oxide counterpart. Potassium salt **3** decomposes at 138 °C with no prior melting, 10 °C lower than its non-*N*-oxide counterpart. The overall trend of the azidotetrazolate 2-oxide salts is that they possess slightly lowered decomposition temperatures relative to analogous azidotetrazolate salts, the same trend that was observed for nitrotetrazolate 2-oxide and nitrotetrazolate.

**Sensitivities:** For initial safety testing, the impact, friction, and electrostatic discharge (ESD) sensitivity of the prepared nitrogen-rich salts were carried out.<sup>[47,48]</sup> The impact sensitivity tests were carried out according to STANAG 4489<sup>[49]</sup> and were modified according to instruction<sup>[50]</sup> using a BAM (Bundesanstalt für Materialforschung<sup>[48]</sup>) drop hammer.<sup>[51]</sup> The friction sensitivity tests were carried out according to STANAG 2287<sup>[52]</sup> and were modified according to instruction<sup>[53]</sup> using a BAM friction tester. Electrostatic sensitivity tests were performed on all materials using a small-scale electric spark tester ESD 2010EN (OZM Research<sup>[54]</sup>) operating with the Winspark 1.15 software package.<sup>[55]</sup> The ammonium salt **1** has an impact sensitivity of 1 J, a friction sensitivity of 10 N, and an ESD sensitivity of 30 mJ. These values place the ammonium salt well within the range of highly sensitive primary explosives according to the UN Recommendations on the Transport of Dangerous Goods.<sup>[56]</sup> The electrostatic discharge sensitivity of this compound is in the vicinity of what can be developed by the human body, thus mandating properly grounded handling processes. However, when compared to the impact and friction sensitivities of ammonium azidotetrazolate (<1 J, <5 N), the ability of *N*-oxides to desensitize compounds is again illustrated. Interestingly, **2**·H<sub>2</sub>O, sodium azidotetrazolate 2-oxide is completely insensitive towards impact (>40 J) and of low friction and ESD sensitivities (120 N and 0.5 J, respectively). This is despite the fact that it explodes when contacted with a flame, which makes for a very novel, insensitive compound that contains the azidotetrazole moiety. This is in contrast to sodium azidotetrazolate monohydrate, which, despite being hydrated, still possesses very high sensitivities (<1 J impact, <5 N friction). The potassium salt (**3**) has an impact sensitivity of 1.5 J, a friction sensitivity of <5 N, and an ESD sensitivity of 1.3 mJ. Unfortunately, the sensitivities of potassium azidotetrazolate were unmeasured in the literature<sup>[13]</sup> due to explosions upon handling, so again our *N*-oxide version is less sensitive. Of interest is the exceedingly high ESD sensitivity of **3**, as 1.3 mJ is easily achieved by the human body, thus making handling exceedingly dangerous. By far

the most sensitive azidotetrazolate 2-oxide salt prepared was the silver salt **6**; this compound exploded repeatedly when attempting to handle and measure sensitivities, so one can say that the impact sensitivity is much less than 1 J, and the friction sensitivity is much less than 5 N. Hydroxylammonium azidotetrazolate (**7**) is an isomer of **1**, which makes for an interesting comparison because they both have similar performances, but **7** is of much higher sensitivity with <1 J impact, <5 N friction, and almost exploding (crackling) when pressed for infrared spectroscopy. Again the lower sensitivity of azidotetrazolate 2-oxide salts is manifested.

## Conclusion

From this combined experimental and theoretical work, the following conclusions can be drawn: 1) The  $\text{CN}_7\text{O}^-$  anion can be prepared from azidotetrazolate salts in a mild aqueous oxidation using buffered potassium acetate; 2) azidotetrazolate 2-oxide salts are generally highly sensitive energetic materials; however, while they are less sensitive than the corresponding azidotetrazolate, proper safety measures must still be observed; 3) azidotetrazolate 2-oxides show higher densities, lower heats of formation, and higher performances than the corresponding azidotetrazolates; 4) unfortunately, the thermal stability of azidotetrazolate 2-oxides are lower than the corresponding azidotetrazolate; and 5) sodium azidotetrazolate 2-oxide monohydrate is the safest known compound that contains the azidotetrazole moiety that is insensitive (>40 J) towards impact.

## Experimental Section

**General:** All reagents and solvents were used as received (Sigma–Aldrich, Fluka, Acros Organics) if not stated otherwise. Azidotetrazole was prepared according to the literature procedure. Melting and decomposition points were measured using a Linseis PT10 DSC with heating rates of  $5^\circ\text{C min}^{-1}$ , which were checked using a Büchi Melting Point B-450 apparatus.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  NMR spectra were measured using a JEOL instrument. All chemical shifts are quoted in ppm relative to TMS ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or nitromethane ( $^{15}\text{N}$ ). Infrared spectra were measured using a Perkin–Elmer Spektrum One FTIR instrument. Raman spectra were measured using a Perkin–Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). Elemental analyses were performed using a Netsch STA 429 simultaneous thermal analyser. Sensitivity data were determined using a BAM drophammer and a BAM friction tester. The electrostatic sensitivity tests were carried out using an Electric Spark Tester ESD 2010 EN (OZM Research) operating with the Winspark 1.15 software package.

**Caution!** All compounds prepared herein are highly energetic compounds highly sensitive to various stimuli. Although we only encountered accidental explosions in the handling of silver salt **6**, proper protective measures (e.g., face shield, ear protection, body armor, Kevlar gloves and earthed equipment) should be used at all times.

**Ammonium azidotetrazolate 2-oxide (1):** 5-Azidotetrazole (2.00 g, 18 mmol) (**Danger!** Weigh in small portions, dissolve in water and combine. Do not handle 2 g of dry azidotetrazole at one time.) was dissolved in distilled water (90 mL) and NaOH (2 M, 9 mL, 18 mmol) was added followed by potassium acetate (17.1 g, 174 mmol). The solution was

heated to  $40^\circ\text{C}$  and oxone (35.1 g, 57 mmol) was added slowly. The resulting suspension was stirred at  $40^\circ\text{C}$  for three days, diluted until all solids dissolved, and concentrated sulfuric acid (16.2 mL, 288 mmol) was added upon cooling. The solution was extracted with 5 portions of diethyl ether (100 mL) and  $\text{NH}_3$  solution (2 M, 28 mL, 56 mmol) was added to the extracts, followed by stirring and evaporation of the two-phase mixture under a stream of nitrogen. The resulting solid was recrystallized from acetonitrile. The first crop of crystals yielded 0.54 g, and the second yielded 0.24 g for a combined yield of 30%.  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 7.17$  ppm (s, 4H;  $\text{NH}_4$ );  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 151.0$  ppm (s, 1C;  $\text{CN}_4$ );  $^{15}\text{N}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = -39.1$  (s, 1N; N2 or N3),  $-40.8$  (s, 1N; N2 or N3),  $-100.5$  (s, 1N; N4),  $-113.4$  (s, 1N; N1);  $-140.4$  (s, 1N; N6),  $-147.3$  (s, 1N; N7),  $-302.2$  (s, 1N; N5),  $-360.2$  ppm (s, 1N; N8); IR:  $\tilde{\nu} = 3167$  (m), 3012 (m), 2852 (m), 2447 (w), 2278 (w), 2139 (s), 1650 (w), 1540 (w), 1479 (m), 1469 (m), 1432 (m), 1417 (m), 1404 (m), 1372 (m), 1342 (s), 1282 (m), 1232 (m), 1216 (m), 1195 (m), 1135 (m), 1061 (w), 1047 (w), 1020 (w), 997 (w), 970 (w), 854 (w), 830 (w), 806 (w), 791 (w), 765 (m), 743 (w), 724 (m),  $685\text{ cm}^{-1}$  (w); Raman IR (1064 nm):  $\tilde{\nu} = 3065$  (5), 2858 (1), 2152 (20), 2041 (1), 1684 (3), 1493 (66), 1435 (16), 1407 (6), 1373 (3), 1352 (4), 1234 (20), 1144 (6), 1063 (6), 1022 (100), 814 (12), 768 (2), 727 (6), 686 (1), 596 (13), 517 (7), 433 (2), 362 (14),  $280\text{ cm}^{-1}$  (8); DSC ( $5^\circ\text{C min}^{-1}$ ):  $151^\circ\text{C}$  (decomp); MS (FAB+):  $m/z$ : 18.1 ( $\text{NH}_4^+$ ); MS (FAB−):  $m/z$ : 126.0 ( $\text{CN}_7\text{O}^-$ ); elemental analysis calcd (%) for  $\text{CH}_4\text{N}_8\text{O}$  (144.10  $\text{g mol}^{-1}$ ): C 8.33, N 77.76, H 2.80; found: too sensitive for measurement; BAM impact: 1 J; BAM friction: 10 N; ESD: 30 mJ.

**Sodium azidotetrazolate 2-oxide monohydrate (2·H<sub>2</sub>O):** Compound **1** (0.240 g, 1.67 mmol) was dissolved in cold water (15 mL). NaOH solution (2 M, 0.83 mL, 1.67 mmol) was added, and the solution was boiled until no more ammonia was released. The solution was allowed to evaporate, and the resulting white powder was recrystallized from acetonitrile to yield **2·H<sub>2</sub>O** (0.15 g, 54%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 3.47$  ppm (s, 2H;  $\text{OH}_2$ );  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 151.0$  ppm (s, 1C;  $\text{CN}_4$ ); IR:  $\tilde{\nu} = 3172$  (m), 3519 (m), 3423 (m), 3361 (m), 3258 (w), 2968 (w), 2437 (w), 2365 (w), 2266 (w), 2169 (s), 1653 (w), 1641 (w), 1596 (w), 1506 (m), 1500 (m), 1440 (s), 1383 (s), 1243 (w), 1223 (m), 1156 (w), 1072 (w), 1044 (w), 904 (w), 866 (w), 819 (w), 771 (m), 751 (w), 725 (w), 688 (w),  $682\text{ cm}^{-1}$  (w); Raman IR (1064 nm):  $\tilde{\nu} = 3357$  (1), 2180 (1), 2151 (9), 1643 (1), 1500 (40), 1485 (2), 1444 (2), 1412 (2), 1394 (4), 1243 (5), 1227 (2), 1158 (4), 1069 (2), 1041 (25), 773 (1), 725 (1), 681 (1), 602 (2), 508 (3), 415 (1), 368 (7),  $272\text{ cm}^{-1}$  (3); DSC ( $5^\circ\text{C min}^{-1}$ ):  $98^\circ\text{C}$  ( $-\text{H}_2\text{O}$ ),  $118^\circ\text{C}$  (decomp); MS (FAB+):  $m/z$ : 23.0 ( $\text{Na}^+$ ); MS (FAB−):  $m/z$ : 126.0 ( $\text{CN}_7\text{O}^-$ ); elemental analysis calcd (%) for  $\text{NaCN}_7\text{O} \cdot \text{H}_2\text{O}$  (167.06  $\text{g mol}^{-1}$ ): C 7.19, N 58.69, H 1.21; found: 7.76, N 55.92, H 1.48; BAM impact: >40 J; BAM friction: 120 N; ESD: 0.500 J.

**Potassium azidotetrazolate 2-oxide (3):** Compound **1** (0.240 g, 1.67 mmol) was dissolved in cold water (15 mL) and KOH solution (2 M, 0.83 mL, 1.67 mmol) was added. The solution was boiled until no more ammonia was released. The solution was allowed to evaporate, thereby yielding **3** (0.22 g, 80%).  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 151.2$  ppm (s, 1C;  $\text{CN}_4$ ); IR:  $\tilde{\nu} = 3341$  (w), 2189 (m), 2143 (s), 1492 (m), 1468 (m), 1438 (m), 1386 (s), 1364 (s), 1237 (s), 1195 (m), 1150 (m), 1128 (m), 1056 (m), 1018 (m), 839 (m), 791 (w), 738 (m), 726 (m),  $692\text{ cm}^{-1}$  (w); Raman IR (1064 nm):  $\tilde{\nu} = 2153$  (14), 1514 (3), 1499 (100), 1440 (6), 1398 (7), 1376 (2), 1239 (17), 1193 (8), 1130 (3), 1058 (2), 1051 (13), 1020 (86), 841 (4), 740 (17), 728 (3), 577 (4), 538 (8), 424 (3), 376 (6),  $266\text{ cm}^{-1}$  (5); DSC ( $5^\circ\text{C min}^{-1}$ ):  $138^\circ\text{C}$  (decomp); MS (FAB+):  $m/z$ : 39.0 ( $\text{K}^+$ ); MS (FAB−):  $m/z$ : 126.0 ( $\text{CN}_7\text{O}^-$ ); elemental analysis calcd (%) for  $\text{KCN}_7\text{O}$  (165.16  $\text{g mol}^{-1}$ ): C 7.27, N 59.37; found: too sensitive for measurement; BAM impact: 1.5 J; BAM friction: <5 N; ESD: 1.3 mJ.

**5-Azido-2-hydroxytetrazole (4):** Compound **1** (0.20 g, 1.39 mmol) was dissolved in distilled water (10 mL) and concentrated sulfuric acid (0.5 mL) was added with stirring in an ice bath. The solution was extracted with ten portions (10 mL each) of diethyl ether, and the ether was dried over magnesium sulfate. The ether solution was filtered and transferred to a Schlenk flask in an ice bath and a stream of nitrogen was used to evaporate the ether. Evaporation using a rotary evaporator led to energetic decomposition. After evaporation, a small amount of oily light yellow liquid was obtained that was dissolved in cool deuterated THF for NMR



spectroscopy.  $^1\text{H}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 11.17$  ppm (s, 1H; OH);  $^{13}\text{C}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = 155.0$  ppm (s, 1C;  $\text{CN}_4$ );  $^{15}\text{N}$  NMR ( $[\text{D}_8]\text{THF}$ ):  $\delta = -22.4$  (s, 1N; N3),  $-81.3$  (s, 1N; N4 or N2),  $-82.9$  (s, 1N; N4 or N2),  $-110.6$  (s, 1N; N1),  $-144.6$  (s, 1N; N6),  $-145.8$  (s, 1N; N7),  $-301.4$  ppm (s, 1N; N5).

**Aminoguanidinium azidotetrazolate 2-oxide (5):** Compound **1** (0.240 g, 1.67 mmol) was dissolved in ethanol (10 mL), and aminoguanidine bicarbonate (0.227 g, 1.67 mmol) was added. The solution was heated at reflux overnight and evaporated to yield a nonexplosive, off-white precipitate.  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 8.81$  (s, 1H;  $\text{NH}-\text{NH}_2$ ), 7.35 and 6.98 (2×s, 2×2H;  $\text{CNH}_2$ ), 4.67 ppm (s, 2H;  $\text{NH}-\text{NH}_2$ );  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 164.0$ , 158.9 (s, 1C;  $\text{CN}_3\text{H}_7$ ), no AZX at  $\approx 151$  ppm. This unknown solid was dissolved in a small amount of methanol and diethyl ether was allowed to diffuse into it, thereby yielding a small number of crystals of pure **5**.

**Silver azidotetrazolate 2-oxide (6):** Compound **1** (0.200 g, 1.39 mmol) was dissolved in distilled water (10 mL), and a solution of silver nitrate (0.232 g, 1.39 mmol) in water (10 mL) was added. The solution was stirred for 10 min in the dark and filtered through a tared piece of filter paper. The light yellow precipitate was allowed to dry undisturbed in the dark on the filter paper, thereby yielding **6** (0.227 g, 71%). Further handling led to explosions of the material. IR:  $\nu = 2161$  (m), 1504 (s), 1450 (m), 1436 (m), 1383 (s), 1367 (s), 1352 (s), 1251 (m), 1233 (w), 1206 (m), 1155 (w), 1134 (m), 1093 (w), 1074 (w), 1061 (w), 1031 (m), 851 (m), 825 (w), 795 (w), 772 (m), 744 (m),  $716\text{ cm}^{-1}$  (m).

**Hydroxylammonium azidotetrazolate (7):** 5-Azidotetrazole (0.500 g, 4.5 mmol) was dissolved in distilled water (10 mL), and a 50% aqueous hydroxylamine solution (0.276 mL, 4.5 mmol) was added to this. The solution was stirred for 10 min and allowed to evaporate until crystallization, at which point filtration yielded **7** (0.39 g, 60%).  $^1\text{H}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 8.77$  ppm (s, 4H;  $\text{NH}_4\text{O}$ );  $^{13}\text{C}$  NMR ( $[\text{D}_6]\text{DMSO}$ ):  $\delta = 158.4$  ppm (s, 1C;  $\text{CN}_4$ ); IR:  $\nu = 3123$  (m), 2888 (m), 2821 (m), 2658 (m), 2444 (m), 2409 (m), 2362 (m), 2258 (m), 2139 (s), 2024 (m), 1623 (m), 1602 (m), 1576 (m), 1566 (m), 1525 (m), 1470 (s), 1462 (s), 1413 (s), 1340 (m), 1247 (m), 1233 (m), 1213 (m), 1141 (w), 1110 (w), 1080 (w), 1001 (m), 913 (m), 787 (m),  $735\text{ cm}^{-1}$  (m); Raman IR (1064 nm):  $\nu = 3160$  (1), 2907 (5), 2680 (2), 2150 (27), 1604 (2), 1578 (2), 1487 (100), 1417 (8), 1338 (2), 1249 (31), 1213 (2), 1144 (5), 1112 (35), 1082 (19), 1005 (26), 790 (13), 737 (5), 552 (32), 424 (12), 342 (16), 302 (40),  $214\text{ cm}^{-1}$  (2); DSC ( $5^\circ\text{C min}^{-1}$ ):  $96^\circ\text{C}$  (decomp); MS (FAB+):  $m/z$ : 34.0 ( $\text{NH}_4\text{O}^+$ ); MS (FAB-):  $m/z$ : 110.0 ( $\text{CN}_7^-$ ); elemental analysis calcd for  $\text{CH}_4\text{N}_8\text{O}$  (144.10  $\text{g mol}^{-1}$ ): C 8.33, N 77.76, H 2.80; found: too sensitive for measurement; BAM impact:  $< 5\text{ J}$ ; BAM friction:  $< 5\text{ N}$ ; ESD: 0.100 J.

CCDC-827211 (**1**), 827214 (**2-MeOH**), 827213 (**3**), 827215 (**5**) and 827212 (**7**) 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).

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