

5-Azido-1*H*-tetrazole – Improved Synthesis, Crystal Structure and Sensitivity DataJörg Stierstorfer<sup>a</sup>, Thomas M. Klapötke<sup>a,\*</sup>, Anton Hammerl<sup>a</sup>, and Robert D. Chapman<sup>b</sup><sup>a</sup> Munich/Germany, Ludwig-Maximilian University, Department of Chemistry and Biochemistry, Energetic Materials Research<sup>b</sup> China Lake, California/USA, Naval Air Systems Command, Chemistry Branch, Research Division, Naval Air Warfare Center Weapons DivisionReceived January 9<sup>th</sup>, 2008.

**Abstract.** Due to the highly explosive nature of 5-azido-1*H*-tetrazole (**1**), its characterization has not been fully described in the literature yet. In addition, the previously published crystal structure was of low quality, and therefore the position of the hydrogen atom was not certain. In order to resolve these problems, **1** was prepared in an improved synthesis, and the results of the subsequent detailed reinvestigation and characterization are given. The reaction of cyanogen bromide with two equivalents of sodium azide at low temperatures yielded sodium 5-azidotetrazolate, which was protonated using dilute hydrochloric acid. The product **1** was isolated and characterized using multinuclear (<sup>1</sup>H, <sup>13</sup>C, <sup>15</sup>N) NMR spectroscopy, vibrational (IR and Raman) spectroscopy and mass spectrometry. The structure of **1** in the crystalline state was determined using low-temperature single-crystal X-ray diffraction. In addition,

the optimized gas-phase structures of the 5-azido-1*H*-tetrazole and 5-azido-2*H*-tetrazole isomers were calculated (MP2/aug-cc-pVDZ) and the electronic energies were compared. The heat of formation of **1** was calculated and several detonation parameters were estimated using the EXPLO5 software. The thermal behavior was investigated using DSC (differential scanning calorimetry) and the sensitivity of this highly energetic material was tested using the BAM drophammer, ESD and friction tester. X-ray: **1**: monoclinic, *P*2<sub>1</sub>/*c*, *a* = 13.265(2) Å, *b* = 4.9693(6) Å, *c* = 16.304(3) Å, β = 127.04(1)°, *V* = 857.9(3) Å<sup>3</sup>, *Z* = 8, ρ = 1.720 g cm<sup>-3</sup>.

**Keywords:** Azidotetrazole; Crystal structure; DSC; DFT calculations; Sensitivities; Azides; Nitrogen heterocycles

## Introduction

The development of tetrazole compounds and other amine derivatives as new energetic materials [1] for military applications is an ongoing area of interest in our research groups. Tetrazoles have the outstanding property of often combining a high nitrogen content (resulting in highly endothermic compounds) with good thermal stability due to their aromatic ring system. The introduction of new explosives into technical applications is very challenging, since many requirements have to be fulfilled. The most important factors in addition to great performances are high thermal stabilities, low sensitivities towards impact and friction, and environmental compatibility of both the explosive as well as the decomposition products. Although 5-azido-1*H*-tetrazole was found to be too sensitive for applications, it is still an interesting compound, since it is the isolated tetrazole with the highest nitrogen content and also a member of the family of compounds with the highest nitrogen percentages. Chemists are particularly attracted to such nitrogen-rich

compounds, since they are on the borderline between existence and non-existence.

Except for molecular nitrogen (N<sub>2</sub>) and the cubic nitrogen modification at high temperatures and pressures described by *Eremets et al.* [2], there is no neutral polynitrogen modification known [3]. The next member in the series of compounds containing the highest nitrogen contents (Tab. 1) is hydrazoic acid (HN<sub>3</sub>, N: 97.7 %) [4] followed by [N<sub>5</sub>][P(N<sub>3</sub>)<sub>6</sub>] (N: 91.2 %) described by *Christe et al.* [5]. Unfortunately, salts containing the N<sub>5</sub><sup>+</sup> cation are often only stable at very low temperatures and require difficult preparations and are therefore unsuitable for technical use. Tetraazidomethane (C(N<sub>3</sub>)<sub>4</sub>) [6], hydrazinium azide (N<sub>2</sub>H<sub>5</sub>N<sub>3</sub>) with the empirical formula N<sub>5</sub>H<sub>5</sub> [7], ammonium azide (NH<sub>4</sub>N<sub>3</sub> or N<sub>4</sub>H<sub>4</sub>), tetrazene (N<sub>4</sub>H<sub>4</sub>) [8] as well as diazene (N<sub>2</sub>H<sub>2</sub>) [9] all have nitrogen contents of 93.3 %. Hydrazinium azide hydrazinate (N<sub>2</sub>H<sub>5</sub>N<sub>3</sub>·N<sub>2</sub>H<sub>4</sub>) [10] and [N<sub>5</sub>][P(N<sub>3</sub>)<sub>6</sub>] [5] come in eighth and ninth with 91.5 % and 91.2 %, respectively. 5-Azido-1*H*-tetrazole (CHN<sub>7</sub>) and its

**Table 1** Isolated Compounds with the highest nitrogen contents.

compound	N %	compound	N %
N <sub>2</sub> and N <sub>x</sub>	100 %	[N <sub>2</sub> H <sub>5</sub> ][N <sub>3</sub> ]*N <sub>2</sub> H <sub>4</sub>	91.5 %
HN <sub>3</sub>	97.7 %	[N <sub>5</sub> ][P(N <sub>3</sub> ) <sub>6</sub> ]	91.2 %
[N <sub>5</sub> ][B(N <sub>3</sub> ) <sub>4</sub> ]	95.7 %	CHN <sub>7</sub>	88.3 %
C(N <sub>3</sub> ) <sub>4</sub>	93.3 %	[NH <sub>4</sub> ][CN <sub>7</sub> ]	87.5 %
[N <sub>2</sub> H <sub>5</sub> ][N <sub>3</sub> ]	93.3 %	N <sub>2</sub> H <sub>4</sub>	87.4 %
[NH <sub>4</sub> ][N <sub>3</sub> ]	93.3 %	[N <sub>2</sub> H <sub>5</sub> ] <sub>2</sub> [C <sub>2</sub> N <sub>10</sub> ]*2 N <sub>2</sub> H <sub>4</sub>	85.7 %
N <sub>2</sub> H <sub>2</sub>	93.3 %	[N <sub>2</sub> H <sub>5</sub> ] <sub>2</sub> [C <sub>2</sub> N <sub>10</sub> ]	85.2 %

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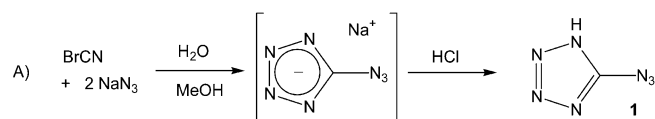
ammonium salt ( $\text{NH}_4\text{CN}_7$ ) are tenth and eleventh in this series. It is worth mentioning the next highest members of this series, which are hydrazine ( $\text{N}_2\text{H}_4$ ) [11], bishydrazinium azotetrazolate dihydrazinate ( $[\text{N}_2\text{H}_5]_2[\text{C}_2\text{N}_{10}] \cdot 2\text{N}_2\text{H}_4$ ) and bishydrazinium azotetrazolate ( $[\text{N}_2\text{H}_5]_2[\text{C}_2\text{N}_{10}]$ ) [12].

The neutral 5-azido-1*H*-tetrazole (**1**) was first described in patents in 1939 [13] and was also investigated in our research group a few years ago [14]. Due to its extremely high and unpredictable explosive character, a complete characterization was not described. In addition, the solution of the crystal structure reported previously ( $wR_2 = 39\%$ ) was poor, and the position of the hydrogen atom was uncertain. Therefore, a complete reinvestigation of **1** is given in this work.

## Results and Discussion

### Synthesis

The most facile and selective synthesis of 5-azido-1*H*-tetrazole (**1**) is the reaction of cyanogen bromide with 2 equivalents of sodium azide in aqueous solution at low temperatures followed by an acidic work up using diluted hydrochloric acid [15]. Since 5-azidotetrazolate anions are extremely sensitive, the intermediate product should not be isolated; **1** can be extracted with diethyl ether, which can be removed under reduced pressure. The product should only be handled with appropriate precautions such as safety glasses, helmet, earthened shoes, leather jacket and Kevlar<sup>®</sup> gloves. In addition, only plastic spatulas should be used; direct light should be avoided and the product must be stored in explosives containers due to possible spontaneous detonation. It is important to mention that explosive decomposition of **1** and its salts has occurred during this work without the detonation source having been identified.

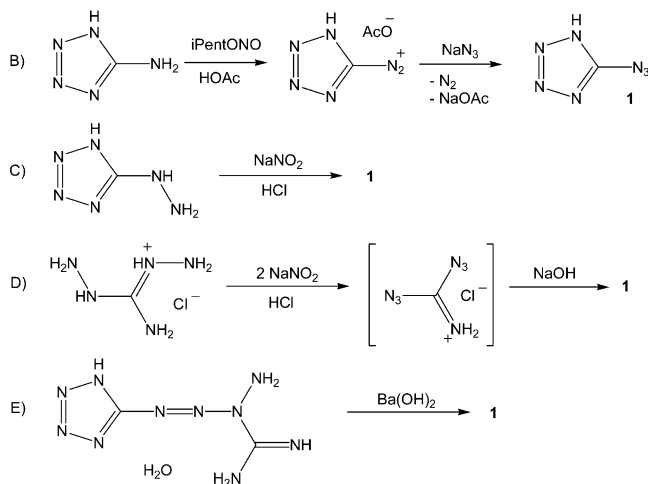


**Scheme 1** Improved synthesis of 5-azido-1*H*-tetrazole (**1**).

The synthesis of **1** can also be achieved by the diazotation of 5-amino-1*H*-tetrazole (**B**) with “ $\text{HNO}_2$ ” followed by the addition of sodium azide [14] or by the reaction (C) of 5-hydrazino-1*H*-tetrazole with one equivalent  $\text{NaNO}_2$  and  $\text{HCl}$  in aqueous solutions [16]. However, we advise against attempting this synthesis (**B**) because of the formation of highly explosive tetrazole diazonium intermediates.

The reaction (D) of diaminoguanidinium salts with two equivalents of  $\text{HNO}_2$  [17] also ends in the formation of **1**, which is also obtained as a byproduct in an advanced synthesis of 1,5-diaminotetrazole [18] by using only one equivalent of  $\text{HNO}_2$  [19].

A quite uncommon reaction (E) is the alkaline degradation of the primary explosive tetracene using  $\text{Ba}(\text{OH})_2$  [20].



**Scheme 2** Alternative reactions for synthesizing 5-azido-1*H*-tetrazole (**1**).

### Crystal Structure

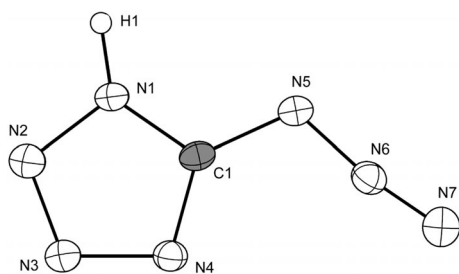
The single-crystal X-ray diffraction data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was undertaken using the CRYALIS CCD software [21], and the data reduction was performed with the CRYALIS RED software [22]. The structure was solved with SIR-92 [23] and refined with SHELXL-97 [24] implemented in the program package WinGX [25] and finally checked using PLATON [26]. Selected data and parameters from the X-ray data collection and refinement are given in Table 2. Further information regarding the crystal-structure determination (**1**) has been deposited with the Cambridge Crystallographic Data Centre [27] as supplementary publication No. 673182.

5-Azido-1*H*-tetrazole (**1**) crystallizes in the monoclinic space group  $P2_1/c$  with eight molecules in the unit cell resulting in a density of  $1.720 \text{ g cm}^{-3}$ . One molecular moiety of the asymmetric unit, containing two molecules, is shown in Figure 1. The structure of the tetrazole ring is comparable to values observed for other tetrazole derivatives, e.g., 5-aminotetrazole [28]. The N–N and C–N bond lengths are all between typical single and double bonds [29]. The constitution of the azide group is similar to those of other covalent carbon bonded azide groups, e.g., azidoformamidinium chloride [30]. The azide group is angulated ( $\text{N5–N6–N7} = 171.9(2)^\circ$ ), which is quite common for covalent azides and can be explained by hyperconjugation effects [31].

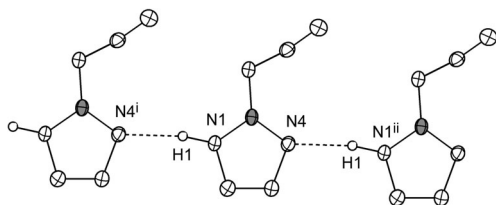
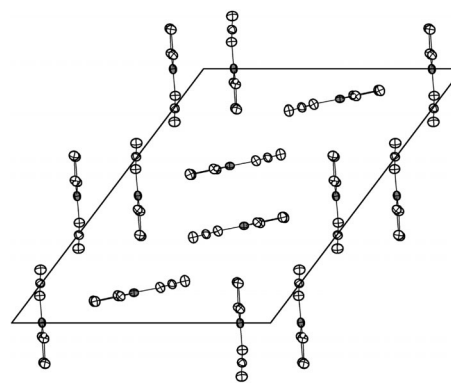
The position of the hydrogen atom at the nitrogen atom N1 can be shown best by viewing on the 1-dim chains (Fig. 2), which are arranged by a strong hydrogen bridge. This is the only structural motif that is found in the packing. These chains along the *b* axes are parallel as well as nearly orthogonal to each other and are only connected by “Van der Waals” forces, which are illustrated in Figure 2.

**Table 2** Crystallographic data

1	
Formula	CHN <sub>7</sub>
Formula weight / g mol <sup>-1</sup>	111.09
Crystal system	monoclinic
Space Group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Color / Habit	colorless needles
Size, mm	0.03 × 0.04 × 0.10
<i>a</i> / Å	13.265(2)
<i>b</i> / Å	4.9693(6)
<i>c</i> / Å	16.304(3)
$\beta$ / °	127.04(1)
<i>V</i> / Å <sup>3</sup>	857.9(3)
<i>Z</i>	8
$\rho_{\text{calc.}}$ / g cm <sup>-3</sup>	1.720
$\mu$ / mm <sup>-1</sup>	0.139
<i>F</i> (000)	448
$\lambda_{\text{MoK}\alpha}$ / Å	0.71073
<i>T</i> / K	100
Theta Min, Max / °	3.8, 26.0
Dataset	-16: 16 ; -6: 6 ; -20: 20
Reflections collected	8224
Independent reflections	1696
<i>R</i> <sub>int</sub>	0.063
Observed reflections	1154
No. parameters	153
<i>R</i> <sub>1</sub> (obs)	0.0306
<i>wR</i> <sub>2</sub> (all data)	0.0806
<i>S</i>	1.00
Resid. Dens. / e Å <sup>-3</sup>	-0.21, 0.19
Device type	Oxford Xcalibur3 CCD
Solution	SIR-92
Refinement	SHELXL-97
Absorption correction	none
CCDC	673182

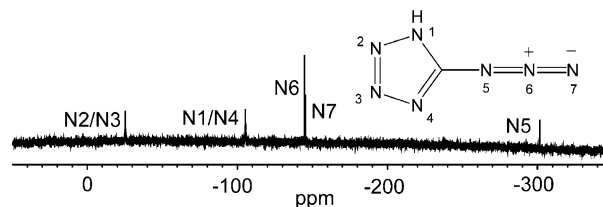
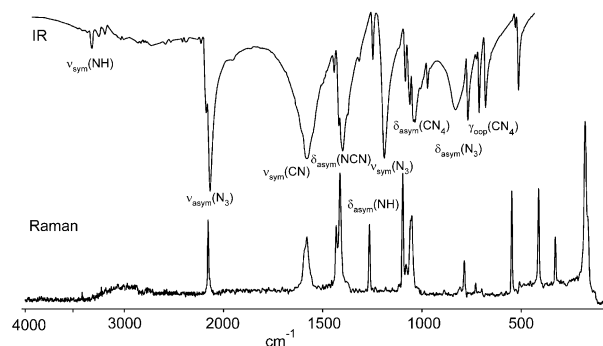
**Figure 1** Molecular unit of **1**. Thermal ellipsoids represent the 50% probability level.

Selected geometries: distances (in Å) C1–N1 = 1.327(2), N1–N2 = 1.355(2), N2–N3 = 1.295(2), N3–N4 = 1.372(2), N4–C1 = 1.321(2), C1–N5 = 1.383(2), N5–N6 = 1.267(2), N6–N7 = 1.117(2); angles (in °) C1–N1–N2 = 108.3(1), N3–N2–N1 = 106.5(1), N2–N3–N4 = 110.6(1), N1–C1–N5 = 121.0(1), C1–N4–N3 = 105.1(1), N4–C1–N5 = 129.5(2), N6–N5–C1 = 113.1(1), N5–N6–N7 = 171.9(2); torsion angles (in °) C1–N1–N2–N3 = 0.1(2), N2–N1–C1–N5 = 178.0(1), N1–C2–N5–N6 = 174.7(1).

**Figure 2** View of the 1-dim chains illustrating the hydrogen bond (N1–H1···N4<sup>i</sup>: D–H = 0.95(2), H–A = 1.87(2), D–A = 2.815(2) Å, D–H–A = 168.8(2)°; (i): x, 1+y, z, (ii): x, -1+y, z).**Figure 3** View along the *b* axes and the 1-dim chains. The unit cell is marked.

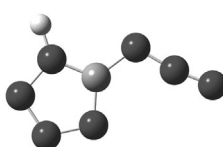
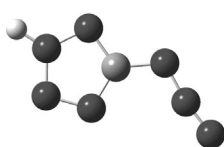
### Spectroscopy

Multinuclear NMR spectroscopy, such as <sup>1</sup>H, <sup>13</sup>C and <sup>15</sup>N NMR, is a valuable method for characterization of tetrazoles. In the <sup>1</sup>H and <sup>13</sup>C NMR spectra of **1**, only one signal can be observed at 9.20 ppm and 157.5 ppm, respectively. In the <sup>15</sup>N spectrum (Fig. 4) of **1**, measured in [D<sub>6</sub>]DMSO, five signals are observed, which were assigned by comparison with literature [32]. The identical chemical shifts of the atoms N2 and N3 as well as N1 and N4 are caused by fast proton exchange in the polar solvent. The chemical shifts are given relative to TMS (<sup>1</sup>H, <sup>13</sup>C) and CH<sub>3</sub>NO<sub>2</sub> (<sup>15</sup>N) as external standards.

**Figure 4** <sup>15</sup>N NMR spectrum of **1** ( $\delta$ : N2/N3 = -25.3, N1/N4 = -105.3, N6 = -144.7, N7 = -145.4, N5 = -301.4).**Figure 5** Vibrational spectroscopy of **1**. Top: IR spectrum; bottom: Raman spectrum.

Also, vibrational spectroscopy, such as IR and Raman spectroscopy, is adequate to identify **1** [33]. Figure 5 illustrates the IR as well as the Raman spectrum of **1**. The as-

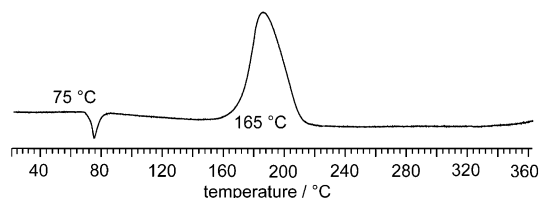
**Table 3** Physico-chemical properties

	5-azido-1 <i>H</i> -tetrazole ( <b>1</b> )	5-azido-2 <i>H</i> -tetrazole
		
−E / a.u.	420.828841	420.834983
E <sub>rel.</sub> / kcal mol <sup>−1</sup>	+3.85	0.00
point group	C <sub>s</sub>	C <sub>s</sub>
NIMAG	0	0
zpe / kcal mol <sup>−1</sup>	31.0	31.5
μ / D	4.5	2.5

signments were done using a frequency analysis after optimizing the geometry (see computational study). The most intensive vibration in the IR spectrum is the ν<sub>sym</sub> vibration of the azide group, which can also be seen in the Raman spectrum. The broad signal at 1591 cm<sup>−1</sup> can be assigned to the stretch vibration between the atoms C1 and N5. In the range of 980–1100 cm<sup>−1</sup> many deformation vibrations and combinations of the tetrazole ring can be found.

### Thermal behavior

For determining the decomposition temperature, a Linseis DSC PT 10 [34] with a heating rate of 5 K min<sup>−1</sup> and a nitrogen flow of 5 L h<sup>−1</sup> was used. The measurement with ca. 1.5 mg of **1** was performed in a pressed Al-container containing a hole (0.1 mm) for the gas release. The DSC plot in Figure 6 shows the thermal behavior of **1** in the 50–360 °C temperature range. Temperatures are given as “onset temperatures”. **1** melts at 75 °C and decomposes above 165 °C.

**Figure 6** DSC thermogram of **1** (β = 5 °C min<sup>−1</sup>).

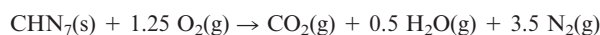
### Computational study

All calculations were carried out using the program package Gaussian03W [35]. The structure, energy and frequency calculations were performed at the Hartree–Fock level followed by a Møller–Plesset correlation energy correction, truncated at second order [36]. For all atoms H, C and N, an augmented correlation consistent polarized double-zeta basis set was used (aug-cc-pVDZ) [37]. The results of the calculations are presented in Table 3. The gas phase structure of 5-azido-2*H*-tetrazole is lower in electronic energy than that of 5-azido-1*H*-tetrazole.

The two structural isomers 5-azido-1*H*-tetrazole and 5-azido-2*H*-tetrazole (both C<sub>s</sub> symmetry) were both found to be true minima on the potential energy surface with the 5-azido-2*H*-tetrazole being more stable in the gas phase by 3.85 kcal mol<sup>−1</sup> (Table 3). The fact that 5-azido-1*H*-tetrazole was unambiguously identified in the solid state can be explained by favorable hydrogen bonding (Fig. 2) of this species. Moreover, the higher dipole moment of 5-azido-1*H*-tetrazole may also favor this species in solution in polar solvents. This situation is also found for other 5-substituted tetrazoles, e.g. 1*H*-tetrazole, in the literature [38].

With the ab initio (MP2/aug-cc-pVDZ) computed electronic energies and the estimated heat of sublimation for 5-azido-1*H*-tetrazole of +65.5 kJ mol<sup>−1</sup> (estimated as: ΔH<sub>sub</sub> / J mol<sup>−1</sup> = 188 · (T<sub>m</sub> / K) [39]) and after correction for the work term (pΔV), the vibrational correction (Δ<sub>vib</sub>U), the translational term (Δ<sub>trans</sub>U) and the rotational term (Δ<sub>rot</sub>U) [40], the enthalpy of combustion of 5-azido-1*H*-tetrazole was calculated to be:

$$\Delta H_{\text{comb.}} = -1125.8 \text{ kJ mol}^{-1}.$$



With the known enthalpies of formation of carbon dioxide (Δ<sub>f</sub>H<sup>o</sup><sub>298</sub>(CO<sub>2</sub>(g)) = −393.5 kJ mol<sup>−1</sup> [41]) and water (Δ<sub>f</sub>H<sup>o</sup><sub>298</sub>(H<sub>2</sub>O(g)) = −241.8 kJ mol<sup>−1</sup> [41]), the enthalpy of formation of **1** can now be calculated as:

$$\Delta_f H^o_{298}(\mathbf{1}(\text{s})) = +611 \text{ kJ mol}^{-1}.$$

### Detonation parameters

The detonation parameters were calculated using the program EXPLO5 V5.02 [42]. The program is based on the steady-state model of equilibrium detonation and uses Becker–Kistiakowsky–Wilson’s equation of state (BKW E.O.S.) for gaseous detonation products and Cowan–Fickett E.O.S. for solid carbon [43]. The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig’s free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation in the following form was used with the BKWN set of parameters (α, β, κ, θ) as stated below the equations and with X<sub>i</sub> being the mole-fraction of *i*-th gaseous product, and k<sub>i</sub> is the molar covolume of the *i*-th gaseous product [44]:

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

$$\alpha = 0.5, \beta = 0.176, \kappa = 14.71, \theta = 6620.$$

The calculation was performed using the maximum density (1.72 g cm<sup>−3</sup>) according to the crystal structure. **1** shows a high calculated detonation pressure of 327 kbar and a detonation velocity of 8986 m s<sup>−1</sup>, higher than those

**Table 4** Physico-chemical properties of **1**

	<b>1</b>
Formula	CHN <sub>7</sub>
Molecular Mass / g mol <sup>-1</sup>	111.07
Impact sensitivity / J <sup>a</sup>	< 1
Friction sensitivity / N <sup>b</sup>	< 5
ESD / mJ <sup>c</sup>	< 2.2
N / % <sup>d</sup>	88.28
Ω / % <sup>e</sup>	-36.0
Combustion	fulmination
T <sub>dec.</sub> / °C <sup>f</sup>	165
Density / g cm <sup>-3</sup> g	1.72
Δ <sub>f</sub> H <sub>m</sub> <sup>o</sup> / kJ mol <sup>-1</sup> h	611
Δ <sub>f</sub> U <sup>o</sup> / kJ kg <sup>-1</sup> i	5590
<b>Calculated values by EXPLO5:</b>	
-Δ <sub>E</sub> U <sub>m</sub> <sup>o</sup> / J g <sup>-1</sup> j	5721
T <sub>E</sub> / K <sup>k</sup>	4701
P / kbar <sup>l</sup>	327
D / m s <sup>-1</sup> m	8986
Gas vol. / mL g <sup>-1</sup> n	752

a) b) BAM methods, see ref. [45–52]; c) electrical spark sensitivity, see ref. [55]; d) Nitrogen content; e) Oxygen balance; f) Decomposition temperature from DSC ( $\beta = 5 \text{ }^\circ\text{C min}^{-1}$ ); g) Estimated from X-ray diffraction; h) Molar enthalpy of formation; i) Energy of formation; j) Energy of Explosion, EXPLO5 V5.02; k) Explosion temperature; l) Detonation pressure; m) Detonation velocity; n) Assuming only gaseous products.

of TNT ( $P = 202 \text{ kbar}$ ,  $D = 7150 \text{ m s}^{-1}$ ) and comparable to those observed for RDX ( $P = 340 \text{ kbar}$ ,  $D = 8882 \text{ m s}^{-1}$ ). This is atypical of compounds with very high sensitivities. These kinds of compounds, which belong to the class of primary explosives, are mostly characterized by lower detonation velocities.

### Sensitivities

For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivity were determined [45]. The impact sensitivity tests were carried out according to STANAG 4489 [46] modified according to instruction [47] using a BAM (Bundesanstalt für Materialforschung [48]) drophammer [49]. The friction sensitivity tests were carried out according to STANAG 4487 [50] modified according to instruction [51] using the BAM friction tester. Compound **1** is very sensitive towards impact (< 1 J) and friction (< 5 J) and thereby classified according to the “UN Recommendations on the transport of dangerous goods” as “extremely sensitive” in both categories [52]. Since this value is higher than that observed for lead azide [53, 54], it should be considered to be a primary explosive and should only be handled with appropriate precautions.

The electrostatic sensitivity tests were carried out using an electric spark tester ESD 2010EN (OZM Research) operating with the “Winspark 1.15 software package” [55]. The electrical spark sensitivity was determined to be 2.2 mJ, which also compares with values observed for primary explosives.

## Experimental Part

### CAUTION

*5-Azido-1H-tetrazole (1)* is a highly energetic compound with increased sensitivities toward various stimuli; therefore, proper protective measures (safety glasses, face shield, leather coat, earthened equipment and shoes, Kevlar® gloves and ear plugs) should be used.

Cyanogen bromide (530 mg, 5 mmol) was dissolved in a mixture of 15 mL cold water and 5 mL MeOH. To this a solution of NaN<sub>3</sub> (650 mg, 10 mmol) was added dropwise while cooling in an ice bath. After 2 h, 1 *n* HCl (5 mL, 5.0 mmol) was added slowly, and the solution was allowed to come to room temperature. The mixture was extracted three times with 20 mL of cold diethyl ether. The organic phases were combined and dried with MgSO<sub>4</sub>, and the solvent was removed at room temperature under reduced pressure, whereby 410 mg (yield 74 %) of colorless **1** was obtained.

### 5-Azido-1H-tetrazole (1)

**m.p.:** 75 °C, 165 °C (dec.). **IR** (KBr):  $\nu = 3343$  (w), 3022 (m), 2897 (m), 2747 (m), 2604 (m), 2298 (m), 2194 (m), 2156 (vs), 1591 (s, br), 1454 (m), 1430 (s), 1411 (s), 1260 (w), 1202 (s), 1097 (m), 1074 (m), 1048 (m), 985 (m), 845 (m, br), 783 (m), 726 (m), 694 (m), 528 (m) cm<sup>-1</sup>. **Raman** (1064 nm):  $\nu = 2155$  (40), 1579 (32), 1431 (38), 1412 (62), 1264 (38), 1096 (32), 1051 (42), 786 (20), 729 (10), 547 (54), 412 (56), 356 (32), 177 (100) cm<sup>-1</sup>. **<sup>1</sup>H NMR** ([D<sub>6</sub>]DMSO):  $\delta = 9.20$  (1H, br). **<sup>13</sup>C NMR** ([D<sub>6</sub>]DMSO):  $\delta = 157.5$  (1C). **<sup>15</sup>N NMR** ([D<sub>6</sub>]DMSO):  $\delta = -25.3$  (N2/N3),  $-105.3$  (N1/N4),  $-144.7$  (N6),  $-145.4$  (N7),  $-301.4$  (N5). **MS** (DEI): *m/z* 111 (2 %), 71 (1 %), 69 (1 %), 57 (1 %), 55 (6 %), 54 (2 %), 53 (12 %), 45 (3 %), 44 (12 %), 41 (4 %), 42 (2 %), 31 (4 %), 29 (11 %), 28 (100 %), 27 (21 %), 26 (6 %), 18 (10 %). **EA:** CHN<sub>7</sub> (111.09); not determinable (calc. C 10.81, H 0.91, N 88.28 %). **BAM drophammer:** < 1 J. **BAM friction test:** < 5 N. **ESD:** 2.2 mJ.

### Conclusion

From this experimental and theoretical study the following conclusions can be drawn:

- The most facile synthesis of preparing 5-azidotetrazole is the reaction of cyanogen bromide with two equivalents of sodium azide, followed by an acidic work up.

- The crystal structure of 5-azido-1H-tetrazole was determined by low temperature X-ray diffraction. The compound crystallizes monoclinic in the space group  $P2_1/c$  with a density of 1.72 g cm<sup>-3</sup>. The position of the hydrogen atom at the nitrogen atom N1 was confirmed by a strong hydrogen bond.

- The gas phase structures of 5-azido-1H-tetrazole and 5-azido-2H-tetrazole were compared by DFT calculations showing a lower electronic energy for the 2H-isomer.

- The heat of formation of **1** was calculated to be strongly endothermic ( $\Delta_f H^\circ_{298} = 611 \text{ kJ mol}^{-1}$ ). With this value and the density observed from the X-ray determination, several detonation parameters were calculated using the EXPLO5 software. Though **1** is a primary explosive, its detonation performance can be compared with that of RDX.

- A comprehensive analytical characterization of the chemical and thermochemical properties of **1** is given. The thermal behavior is characterized by a melting point at 75 °C and a decomposition temperature of 165 °C.

– The sensitivities of **1** were determined to be extremely high: **1** shows an impact sensitivity of < 1 J, a friction sensitivity of < 5 N and an electrical spark sensitivity of < 2.2 mJ.

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