# Bistetrazolylamines—synthesis and characterization†

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The acid-catalyzed cyclization reaction of sodium dicyanamide and sodium azide in the ratio of 1:2afforded 5,5'-bis(1H-tetrazolyl)amine (H<sub>2</sub>bta, **2**) in high yield (88%) as the monohydrate. Dehydration of  $2 \cdot H_2O$  at elevated temperature and reduced pressure gave anhydrous 2, while recrystallization from DMSO yielded  $2 \cdot H_2O \cdot DMSO$ . 2 was converted into 5,5'-bis(2-methyltetrazolyl)methylamine (Me<sub>3</sub>bta, 6) in two steps. In the first step, 2 was twice deprotonated with sodium hydroxide and alkylated with MeI producing 5,5'-bis(2-methyltetrazolyl)amine (Me2bta, 5) in moderate yield (55%). The second step involved the alkylation of 5 with dimethyl sulfate in alkaline solution (72%). In all cases, the obtained colorless, crystalline compounds were fully characterized by vibrational (IR, Raman) spectroscopy, multinuclear NMR spectroscopy, mass spectrometry, elemental analysis, X-ray structure determination, and initial safety testing (impact, friction and electrical spark sensitivity). According to the UN Recommendations for the "Transport of Dangerous Goods", compounds  $2 \cdot H_2O$ , 5, and 6 are classified as "insensitive" while 2 is described as "sensitive". The thermal behaviors were investigated using differential scanning calorimetry (DSC). The heats of formation ( $\Delta_f H_m^{\circ}$  (2\*H<sub>2</sub>O) = 203 kJ mol<sup>-1</sup>,  $\Delta_{\rm f} H_{\rm m}^{\circ}$  (2) = 633 kJ mol<sup>-1</sup>,  $\Delta_{\rm f} H_{\rm m}^{\circ}$  (5) = 350 kJ mol<sup>-1</sup>,  $\Delta_{\rm f} H_{\rm m}^{\circ}$  (6) = 583kJ mol<sup>-1</sup>) were calculated using heats of combustion ( $\Delta_{comb}$ . H (2 ·  $H_2O$ ) = -1714 kJ mol<sup>-1</sup>,  $\Delta_{comb}$ . H (2) = -1858 kJ mol<sup>-1</sup>,  $\Delta_{comb}$ . H(5) =  $-2932 \text{ kJ mol}^{-1}$ ,  $\Delta_{\text{comb.}} H$  (6) =  $-3843 \text{ kJ mol}^{-1}$ ) obtained from oxygen bomb calorimetry. In addition, explosion parameters such as the detonation velocity ( $D(2 \cdot H_2O) = 7792 \text{ m s}^{-1}$ ,  $D(2) = 9120 \text{ m s}^{-1}$ ,  $D(5) = 7291 \text{ m s}^{-1}$ ,  $D(6) = 7851 \text{ m s}^{-1}$ ) and detonation pressure ( $P(2 \cdot H_2O) = P(2 \cdot H_2O)$ ) 220 kbar, P(2) = 343 kbar, P(5) = 172 kbar, P(6) = 205 kbar) were calculated using the program EXPLO5. "Koenen tests" were successfully performed for compound 2 using critical diameters of 8 mm and 10 mm.

# Introduction

In the continuous search for novel, green, energetic materials<sup>1</sup> with high nitrogen but low carbon content,<sup>2,3</sup> several groups around the world are currently investigating HEDMs (High Energy Dense Materials), based on tetrazoles.<sup>4</sup> These energetic materials are applicable in low-smoke producing pyrotechnic compositions,<sup>5</sup> gas generators,<sup>6</sup> propellants,<sup>7</sup> high explosives,<sup>8</sup> and primers in primer charges (PC).<sup>9</sup> Tetrazoles,<sup>10,11</sup> tetrazolate,<sup>12,13</sup> and tetrazolium<sup>14,15</sup> salts are of special interest. In particular, certain derivatives of tetrazolylamines display low sensitivities and high thermal stabilities.

The mono-substituted tetrazole 5-aminotetrazole (1, 5-at) represents a valuable building-block for the preparation of tetrazole-based high energetic materials<sup>16</sup> and was first described by Thiele in 1892.<sup>17</sup> Metal salts of 5,5'-bis(1*H*-tetrazolyl)amines (2, H<sub>2</sub>bta) were described as useful colorants in pyrotechnic compositions by Highsmith *et al.*<sup>18</sup> and Hiskey *et al.*<sup>19</sup> In addition, several nitrogen-rich salts such as ammonium,

hydrazinium, and guanidinium derivatives were recently published as energetic materials.<sup>20</sup> The parent compound has only been sparingly described in the literature.<sup>21</sup> To date, there are no reports on tris(tetrazolyl)amine (**3**,  $H_3$ tta). This may be due to the influence of electronic and/or steric factors which prohibit a viable synthesis.

Two synthesis protocols are used for the preparation of **1**: the conversion of aminoguanidinium salts with nitrous acid<sup>17</sup> and the acid-catalyzed cycloaddition of hydrazoic acid with dicyanodiamide.<sup>22</sup> The latter reaction is a general protocol for the formation of tetrazole derivatives since both neutral azides and the azide anion can undergo cycloaddition with cyano groups. In this way, a broad range of different tetrazole derivatives have been achieved.<sup>23</sup> A suitable precursor for the synthesis of **2** is the non-linear pseudohalide dicyanamide anion (N(CN)<sub>2</sub><sup>-</sup>). The first synthesis of **2**, obtained as a monohydrate, was described by Norris and Henry by refluxing sodium dicyanamide, sodium azide, and trimethylammonium chloride in water.<sup>24</sup> Currently,



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<sup>&</sup>lt;sup>b</sup>WWU Münster, IAAC, Corrensstr. 28/30, D-48149 Münster, Germany † CCDC reference numbers 299051 (2), 687771 (2 $\cdot$ H<sub>2</sub>O), 687768 (2 $\cdot$ H<sub>2</sub>O $\cdot$ DMSO), 687770 (5) and 687769 (6). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b811273h



Scheme 1 Protocols for the synthesis of 2.

there are three synthesis procedures for **2**: (1) the *in situ* reaction of hydrazoic acid (prepared from sodium azide and a weak acid like trimethylammonium chloride, boric acid, ammonium chloride) with sodium dicyanamide,<sup>25</sup> (2) the reaction of sodium dicyanamide with sodium azide in the presence of a catalyst like zinc chloride, bromide or perchlorate, followed by an acidic work-up,<sup>26</sup> and (3) the reaction of **1** with cyanogen bromide under base-catalyzed conditions forming the 5-cyaniminotetrazolinediide anion (**4**, cit<sup>2-</sup>),<sup>24,27</sup> followed by a subsequent cycloaddition of hydrazoic acid under acidic conditions (Scheme 1).

Surprisingly, 2 has only been poorly characterized and the chemistry of methyl derivatives of 2 has not been investigated. Therefore, we wish to report a modified synthesis and full characterization of 5,5'-bistetrazolylamine 2 and its monohydrate  $2 \cdot H_2O$ . Furthermore, the recrystallization of  $2 \cdot H_2O$  in DMSO resulted in the formation of  $2 \cdot H_2O \cdot DMSO$ . We are also presenting the results of the methylation reaction of 2 with MeI under basic conditions yielding 5,5'-bis(2-methyltetrazolyl)amine (5, Me<sub>2</sub>bta) as the main product.<sup>28</sup> The subsequent reaction of 5 with Me<sub>2</sub>SO<sub>4</sub> under basic conditions afforded 5,5'-bis(2-methyltetrazolyl)methylamine (6, Me3bta) in good yields. All compounds were obtained in high purities as colorless, crystalline materials. The molecular structures of all compounds were confirmed by means of X-ray investigations at low temperature. Initial safety testing and energetic properties are reported. The cheap and facile synthesis route, high thermal stability, and low sensitivities of 2 and its derivatives bode well for the application of these compounds for use in novel propellant systems, pyrotechnic formulations<sup>29</sup> and/or in high-energy-capacity transition metal complexes.30

## **Results and discussion**

#### Synthesis and characterization

In contrast to the previously reported synthesis of  $2 \cdot H_2O$  by Norris and Henry,<sup>24</sup>  $2 \cdot H_2O$  is obtained in high yields and high purity by the reaction of sodium dicyanamide with two equiv. of sodium azide and hydrochloric acid (Scheme 2). The reaction was performed in an aqueous ethanolic solution by slow addition of diluted hydrochloric acid at 80 °C over the course of 4 h and subsequent refluxing of the reaction mixture for a further 48h.<sup>31</sup> Compound  $2 \cdot H_2O$  is insoluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, diethyl ether or THF and dissolves only poorly in



Scheme 2 Preparative route to 2; i) EtOH–H<sub>2</sub>O, 2 M HCl. 80 °C; ii) 120 °C,  $10^{-3}$  Torr.



Scheme 3 Preparative route to 5 and 6; i) NaOH,  $H_2O$ , MeI–acetone, 60 °C; ii) NaOH,  $H_2O$ ,  $Me_2SO_4$ , reflux.

MeOH or EtOH when heated.  $2 \cdot H_2O$  is soluble in water or mineral acids (*e.g.* HCl or HClO<sub>4</sub>) when warmed. Anhydrous **2** is obtained when  $2 \cdot H_2O$  is dehydrated under vacuum (24 h,  $10^{-3}$  Torr) at elevated temperature (120 °C).

Our two-step synthesis of **6** starts from  $2 \cdot H_2O$  (Scheme 3). In the first step, neutralization of an aqueous solution of **2** with two equiv. sodium hydroxide at 60 °C and addition of two equiv. MeI in acetone yields the dimethylated product **5** after 12 h of refluxing and further cooling to 4 °C. The obtained precipitate was recrystallized from dilute HCl affording pure **5**. Interestingly, when the methylation was performed with dimethyl sulfate *in lieu* of MeI, a mixture of 1- and 2-methylated isomers was obtained. However, the 1,1'-, 1,2'-, and 2,2'-isomers were detected in the <sup>13</sup>C NMR spectrum of the reaction mixture. In the second step, **6** was obtained in 62% yield through methylation of **5** with an excess of dimethyl sulfate in refluxing aqueous sodium hydroxide solution. **6** is soluble in common solvents, *e.g.*, ethanol, acetone, and acetonitrile, and was recrystallized from hot water yielding colorless needles.

The 5,5'-bistetrazolylamines 2, 5, and 6 were characterized and identified by IR, Raman, and NMR spectroscopies and by elemental analysis. The <sup>1</sup>H and <sup>13</sup>C NMR experiments were measured in  $[d_6]$ -DMSO at RT. The <sup>1</sup>H NMR spectrum for 2 depicts a broad resonance (due to fast proton exchange) appearing at 11.92 ppm, a typical value for tetrazole protons.<sup>32</sup> The proton of the secondary amine is deshielded due to electronic effects of the tetrazole substituent and appears at 9.53 ppm. After methylation of 2, the proton of the secondary amine in 5 is further deshielded and appears at 10.91 ppm. The range of resonances for methyl substituents is consistent with literature data<sup>33</sup> and these protons are more deshielded for the methylazoles (4.27 (5) and 4.29 (6) ppm) than for the tertiary amine in 6 (3.60 ppm). The <sup>13</sup>C chemical shift can be used to distinguish between 1,5- and 2,5-disubstituted tetrazoles. The chemical shift for the tetrazole carbon atom in the 2,5-isomers is found at a higher frequency, typically with values greater than 160 ppm (162.7 (5) and 164.6 (6) ppm) for methyl derivatives. The resonances of C-5 for the corresponding 1,5-isomers are expected to range from 145 to 160 ppm. Similar results are observed for the methyl group shifts. Once again, the 2,5-isomers display

Table 1  ${}^{15}$ N NMR chemical shifts ( $\delta$ , ppm) and  ${}^{15}$ N ${}^{-1}$ H NMR coupling constants (Hz) for compounds 2, 5 and 6

	N-1	N-2	N-3	N-4	N-5
2 <sup><i>a</i></sup> 5 <sup><i>b</i></sup>	-123.8 -110.2 q, ${}^{3}J = 1.9$	-17.9 -111.5 q, ${}^{2}J = 2.1$	-11.3  q, ${}^{3}J = 1.9$	-109.2	-315.7 -316.4
<b>6</b> <sup><i>a</i></sup>	-104.0  q, ${}^{3}J = 1.9$	-110.5  q, ${}^{2}J = 2.2$	-5.2  q, ${}^{3}J = 1.9$	-76.2	-324.5  q ${}^{2}J = 2.2$
<sup>a</sup> In	[d <sub>6</sub> ]-DMSO. <sup>b</sup>	In CF <sub>3</sub> COOH.			

higher resonances (40.1 (5) and 40.3 (6) ppm) compared to those expected for the more shielded 1,5-isomers.<sup>34</sup>

The <sup>15</sup>N NMR shifts and the absolute values of the <sup>15</sup>N,<sup>1</sup>H NMR coupling constants are presented in Table 1. The spectra of compounds **2**, **5**, and **6** are depicted in Fig. 1. Our assignments were mainly based on the analysis of the <sup>15</sup>N–<sup>1</sup>H NMR coupling patterns and on previous investigations. In agreement with the correlations between <sup>15</sup>N NMR chemical shifts and electron densities at the nitrogen atoms, the <sup>15</sup>N NMR chemical shifts become increasingly more negative for 2,5-disubstituted tetrazoles: N-3 < N-4 < N-1 < N-2.<sup>14,16,34,35</sup> In the proton-coupled spectra of **5** and **6**, the N-1, N-2, and N-3 signals appear as quartets with <sup>15</sup>N–H coupling constants that are similar in magnitude, resulting from coupling to protons of the *N*-Me group. For **6**, the N-5 signal also appears as a quartet due to coupling to protons of the *C*-Me group.

Vibrational spectroscopy is another suitable method for identifying bistetrazolylamines. The IR and Raman spectra (Fig. 2) of the investigated compounds are characteristic for 5-aminotetrazoles.<sup>36</sup> Assignments were performed with the help of a frequency analysis after calculating (B3LYP/cc-pVDZ) the optimal geometry with the Gaussian03 software.<sup>37</sup> Compared to the characteristic bands located at 1656 and 1556 cm<sup>-1</sup>, assigned to the  $v_{asym}(C_{tet}-N-C_{tet})$  and  $v_{sym}(C_{tet}-N-C_{tet})$  stretching vibrations in  $2 \cdot H_2O$ , the corresponding bands are shifted to lower frequencies in the methylated compounds by approximately 8 to 12 cm<sup>-1</sup>. Further bands can be attributed to the stretching vibrations of the N=N (1454 cm<sup>-1</sup>), C=N (1352, 1337 cm<sup>-1</sup>), and N-N (1282, 1268 cm<sup>-1</sup>) bonds in the vibrational spectra of



Fig. 1 <sup>15</sup>N NMR spectra of compounds 2, 5 and 6.



Fig. 2 Raman spectra of compounds  $2 \cdot H_2O$ , 2, 5 and 6.

 $2 \cdot H_2O.^{38}$  The IR and Raman spectra of the investigated compounds have in common the bands for the stretching and bending modes of the C–H (2950–3150 cm<sup>-1</sup>) and N–H (3300–3450 cm<sup>-1</sup>) groups from the protons of the tetrazole ring and of the secondary amino group.

#### Molecular structures

Crystallographic and structural refinement data for compounds  $2 \cdot H_2O$ ,  $2 \cdot H_2O \cdot DMSO$ , 2, 5, and 6 are listed in Table 2 and selected bond lengths and angles are included in Table 3. Tables of atomic coordinates, thermal displacement parameters, and a complete list of bond angles and distances can be obtained from ESI<sup>†</sup>. Suitable crystals for the X-ray investigations were produced by recrystallization of  $2 \cdot H_2O$  and 5 from warm aqueous HClO<sub>4</sub> solutions (20%). X-Ray quality crystals of  $2 \cdot H_2O \cdot DMSO$  were acquired from warm DMSO solution and from water for 6. Single crystals of 2 were obtained from an organic tetranitromethane solution through a failed attempt to nitrate the secondary amine.

2. H<sub>2</sub>O (Fig. 3) crystallizes in the monoclinic space group  $P_{2_1/c}$  with four molecules in the unit cell. Interestingly, the bistetrazolylamine molecules are planar (torsion angle C1–N1–C2– N9 = -179.6(1)°). The C–N bond distances to the amine nitrogen show lengths of N1–C1 = 1.370(2) Å and N1–C2 = 1.360(2) Å and are significantly shorter than C–N single bonds (1.47 Å) suggesting that, in addition to the planar geometry, there is a delocalization of the amine lone pair. The bond distances in the tetrazole rings are in the typical range of 1.29–1.36 Å between N–N single bonds (1.45 Å) and N=N double bonds (1.25 Å)<sup>39</sup> and are given in Table 2.

**2**⋅H<sub>2</sub>O forms a layer structure involving several hydrogen bonds (Fig. 4). The strongest hydrogen bond is found between the water oxygen atom and the ring nitrogen (N2–H1…O1, D–H = 0.94(2), H–A = 1.69(2) Å, D–A = 2.623(2) Å, D–H–A = 177(2)°). Both water hydrogen atoms are directed to further bistetrazolylamine molecules with "D–A hydrogen bond distances" of about 2.8 Å. The distance between the layers is *ca.* 3.35 Å.

### Table 2 Crystallographic data and parameters

	2	<b>2</b> ⋅ H <sub>2</sub> O	$2 \cdot H_2O \cdot DMSO$	5	6
Formula	C <sub>2</sub> H <sub>3</sub> N <sub>9</sub>	C <sub>2</sub> H <sub>5</sub> N <sub>9</sub> O	C <sub>4</sub> H <sub>11</sub> N <sub>9</sub> OS	$C_4H_7N_9$	$C_5H_9N_9$
Formula weight/g mol <sup>-1</sup>	153.13	171.15	249.54	181.19	195.21
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Pbca</i> (61)	$P2_1/c$ (14)	C2/c (15)	$P2_{1}/c$ (14)	$P2_1/m$ (11)
Color/habit	colorless needles	colorless plates	colorless rods	colorless needles	colorless rods
Size/mm	$0.05 \times 0.06 \times 0.19$	$0.04 \times 0.10 \times 0.15$	$0.04 \times 0.11 \times 0.11$	$0.08 \times 0.16 \times 0.23$	$0.12 \times 0.15 \times 0.26$
a/Å	11.109(2)	9.367(2)	15.933(1)	10.279(2)	3.852(1)
b/Å	9.227(2)	10.531(2)	6.8863(6)	11.338(2)	19.395(5)
c/Å	21.327(4)	6.808(1)	19.920(2)	6.772(1)	5.769 (2)
$\alpha /^{\circ}$	90	90	90	90	90
βI°	90	90.42(3)	104.227(7)	94.74(3)	95.60(3)
$\gamma/^{\circ}$	90	90	90	90	90
$V/Å^3$	2186.1(7)	671.6(2)	2118.6(3)	786.5(3)	428.9(2)
Ζ	16	4	8	4	2
$\rho_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.861	1.693	1.563	1.530	1.512
$\mu/\text{mm}^{-1}$	0.147	0.140	0.312	0.115	0.112
F(000)	1248	352	1040	376	204
λMoKα/Å	0.71073	0.71073	0.71073	0.71073	0.71073
T/K	200	200	200	200	200
$\theta_{Min}, \theta_{Max}/^{\circ}$	3.5, 26.5	3.6, 27.4	4.3, 25.5	3.5, 27.5	4.1, 26.0
Dataset	-13:13;-11:11;	-12:12;-13:13;	-19:19;-8:8;	-13:13;-14:14;	-4:4;-17:23;
	-26:26	-8:8	-24:24	-8:8	-6:7
Reflections collected	4201	2966	9776	3457	2226
Independent reflections	2257	1529	1965	1803	862
R <sub>int</sub>	0.026	0.019	0.029	0.023	0.033
Observed reflections	1618	1257	1846	1383	724
Parameters	223	129	165	146	86
$R_1$ (obs)	0.0396	0.0367	0.0406	0.0407	0.0570
$wR_2$ (all data)	0.1022	0.0998	0.1067	0.1171	0.1353
GooF	1.06	1.08	1.11	1.14	1.18
Resd. Dens./e Å <sup>-3</sup>	-0.28, 0.25	-0.28, 0.19	-0.34, 0.34	-0.26, 0.19	-0.23, 0.22
Device type	Nonius	Nonius	Oxford	Nonius	Oxford
	Kappa CCD	Kappa CCD	Xcalibur3 CCD	Kappa CCD	Xcalibur3 CCD
Solution	SHELXS-97	SIR-92	SIR-92	SHELXS-97	SIR-92
Refinement	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97	SHELXL-97
Absorption correction	none	none	multi-scan	None	multi-scan
CCDĊ	299051	687771	687768	687770	687769

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Table 3 Bond lengths [Å] and bond angles [°] of 2, 2·H\_2O, 2·H\_2O·DMSO, 5 and 6

	2	$2 \cdot H_2O$	$2 \cdot H_2O \cdot DMSO$	5	6
N1-C1	1.365(2)	1.370(2)	1.351(2)	1.366(2)	1.381(2)
N1-C2	1.366(2)	1.360(2)	1.358(2)	1.371(2)	1.381(2)
C1–N2	1.339(2)	1.330(2)	1.326(2)	1.329(2)	1.326(3)
C1-N5	1.317(2)	1.320(2)	1.316(2)	1.354(2)	1.354(3)
N2-N3	1.350(2)	1.353(2)	1.346(2)	1.347(2)	1.342(3)
N3-N4	1.287(2)	1.290(2)	1.278(2)	1.307(2)	1.307(3)
N4-N5	1.368(2)	1.360(2)	1.360(2)	1.329(2)	1.328(3)
C2-N6	1.339(2)	1.338(2)	1.322(3)	1.327(2)	1.326(3)
C2-N9	1.319(2)	1.323(2)	1.312(2)	1.349(2)	1.354(3)
N6-N7	1.352(2)	1.358(2)	1.348(2)	1.344(2)	1.342(3)
N7–N8	1.287(2)	1.286(2)	1.284(2)	1.312(2)	1.307(3)
N8-N9	1.371(2)	1.364(2)	1.361(2)	1.327(2)	1.328(3)
N3-C3				1.457(2)	1.454(3)
N7-C4				1.451(2)	1.454(3)
N1-C5					1.468(4)
C1-N1-C2	123.3(2)	122.5(1)	123.6(2)	126.4(1)	122.5(3)
N2-C1-N1	122.5(2)	124.4(1)	127.7(2)	127.0(1)	126.6(2)
N2-C1-N5	109.5(2)	110.2(1)	108.9(2)	113.1(1)	113.1(2)
N1-C2-N6	122.1(2)	126.8(1)	124.2(2)	127.0(1)	126.6(2)
N6-C2-N9	109.3(2)	109.1(1)	110.1(2)	113.7(1)	113.1(2)



Fig. 3 Molecular structure of  $2 \cdot H_2O$ . Hydrogen atoms are shown as spheres of arbitrary radii and thermal displacements are set at 50% probability.



**Fig. 4** Hydrogen bonding of one  $H_2$ bta (**2**) molecule within the layers (i: 2 - x, -y, -z; ii: 1 - x, 0.5 + y, 0.5 - z; iii: 1 - x, -0.5 + y, 0.5 - z).

"Water-free" **2** crystallizes in the orthorhombic space group *Pbca* with 16 molecules in the unit cell. The density of 1.861 g cm<sup>-3</sup> is the highest of the investigated compounds in this work and is also higher in comparison to densities of other tetrazoles. The molecular geometry shows a significant difference to that observed in **2**  $\cdot$  H<sub>2</sub>O and can be seen in Fig. 5. In the structure of **2**, all hydrogen atoms are directed to one side of the molecule. This structure is anomalous and could not be achieved as a minimum in theoretical structure optimization. Once again, all hydrogen atoms participate in hydrogen bonds (Fig. 6) and the molecule is nearly planar (torsion angle C1–N1–C2–N9 =  $-4.4(3)^{\circ}$ . The bonds to the tetrazole carbon atoms have lengths of C1–N1 = 1.365(2) Å and N1–C2 = 1.366(2) Å.

Recrystallization of  $2 \cdot H_2O$  from dimethyl sulfoxide yields colorless crystals containing, besides the bta molecule, one crystal water and one DMSO molecule, abbreviated as



**Fig. 5** Molecular structure of **2**. For clarity, only one molecule of the asymmetric unit is shown. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as spheres of arbitrary radii.



**Fig. 6** Selected hydrogen bonds in **2**: (N1–H1–N9<sup>i</sup>, 0.90(2), 2.18(2), 2.977(2) Å, 147(2)°; N1–H1–N5<sup>i</sup>, 0.90(2), 2.39(2), 3.090(2) Å, 135(2)°; N6–H6–N14<sup>ii</sup>, 0.87(2), 2.09(2), 2.914 (2) Å, 159(2)°; N2–H2–N15<sup>iii</sup>, 0.92(2), 2.02(2), 2.871(2) Å, 152(2)°; N2–H2–N19<sup>iiii</sup>, 0.92(2), 2.48(2), 3.141(2) Å, 128(2)° (i: 1.5 - x, 0.5 + y, z; ii: 1.5 - x, 0.5 + y, z; iii: 2 - x, 0.5 + y, 0.5 - z).



Fig. 7 Molecular structure of  $2 \cdot H_2O \cdot DMSO$ . Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms are shown as spheres of arbitrary radii.

 $2 \cdot H_2O \cdot DMSO$ . This compound crystallizes in the monoclinic space group C2/c with eight molecules in the unit cell and can be seen in Fig. 7. The DMSO solvent molecule participates in a strong hydrogen bridge to the N2 atom through its oxygen atom (N2–H2–O2, 0.85(3), 1.89(3), 2.645(2) Å, 148(2)°). The distances and angles within the bistetrazolylamine are comparable to those found in the previously described H<sub>2</sub>bta structures and are given in Table 3.

**5** crystallizes in the monoclinic space group  $P2_1/c$  with four molecules in the unit cell and a lower density of 1.530 g cm<sup>-3</sup> in comparison to the structures of **2**. The molecular unit is shown in Fig. 8.

Both methyl groups are directed in the same direction. On the other side, a hydrogen bond between the nitrogen atoms N1 and N5 (N9–H7–N4<sup>i</sup>: 0.92(2), 2.03(2), 2.946(2) Å, 174(2)°; i: -x, 2 - y, 2 - z.) results in dimer formation (Fig. 9). Once again, the



**Fig. 8** Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms shown as spheres of arbitrary radii.



Fig. 9 Formation of dimers in the layer structure of  $Me_2bta$  (5).

molecules are packed in layers with a larger distance of approximately 3.65 Å in comparison to those of  $2 \cdot H_2O$ .

Me<sub>3</sub>bta (6) crystallizes in the monoclinic space group  $P2_1/m$  with 2 molecules in the unit cell. The atoms N1, C1, and H2 on x,  $\frac{3}{4}$ , z are divided by the mirror plane generating the molecular unit shown in Fig. 10.

The bond lengths and angles are in the same range as the previously discussed molecules, whereby the molecule is not observed to be planar (torsion angle N2–C2–N1–C2' =  $14.6(4)^{\circ}$ ). Me<sub>3</sub>bta crystallizes in a layer structure (Fig. 11), with only weak interactions between and within the layers. There are no hydrogen bonds since there are no N–H or O–H groups in these molecules, resulting in the lowest density of 1.51 g cm<sup>-3</sup>observed in this work.

## Differential scanning calorimetry (DSC)

DSC measurements to determine the melt and decomposition temperatures of **2**,  $2 \cdot H_2O$  **5**, and **6** were performed in covered Al containers containing a hole in the lid with a nitrogen flow of 20 mL min<sup>-1</sup> on a Perkin-Elmer Pyris 6 DSC,<sup>40</sup> calibrated by standard pure indium and zinc at a heating rate of 5 °C min<sup>-1</sup>. The DSC plots in Fig. 12 show the thermal behavior of 1.0 mg of **2**,  $2 \cdot H_2O$ , **5**, and **6** in the 50–400 °C temperature range.



Fig. 10 Molecular structure of 6. Thermal ellipsoids are drawn at the 50% probability level and hydrogen atoms shown as spheres of arbitrary radii (i: x, 1.5 – y, z).



Fig. 11 View along the *a*-axis on the Me<sub>3</sub>bta molecules in the b-c layers.

Temperatures are given as onset temperatures. The loss of water in  $2 \cdot H_2O$  starts at around 145 °C. However, 2 and  $2 \cdot H_2O$  show the same decomposition temperatures of about 250 °C. 5 is temperature-stable up to 263 °C, whereupon it melts under decomposition. 6 melts at 138 °C and starts to decompose at 236 °C.

#### **Bomb calorimetry**

The heats of combustion of compounds  $2 \cdot H_2O$ , 2, 5, and 6 were determined experimentally using a Parr 1356 bomb calorimeter (static jacket) equipped with a Parr 1108CL oxygen bomb.<sup>41</sup> To achieve better combustion, the samples (*ca.* 200 mg) were pressed with a defined amount of benzoic acid (*ca.* 800 mg) forming a tablet, and a Parr 45C10 alloy fuse wire was used for ignition.



Fig. 12 DSC thermograms of compounds  $2 \cdot H_2O$ , 2, 5, and 6 (heating rate of 5 °C min<sup>-1</sup>).

In all measurements, a correction of 2.3 cal cm<sup>-1</sup> wire burned was applied and the bomb was examined for evidence of noncombusted carbon after each run. A Parr 1755 printer was furnished with the Parr 1356 calorimeter to produce a permanent record of all activities within the calorimeter. The reported values are the average of three separate measurements. The calorimeter was calibrated by combustion of certified benzoic acid (SRM, 39i, NIST) in an oxygen atmosphere at a pressure of 3.05 MPa. The experimental results of the constant volume combustion energy  $(\Delta_{\text{comb}}, U)$  of the salts are summarized in Table 4. The standard molar enthalpy of combustion  $(\Delta_{\text{comb.}} H^{\circ})$  was derived from  $\Delta_{\text{comb.}} H^{\circ} = \Delta_{\text{comb.}} U + \Delta n R T (\Delta n = \Delta n_i \text{ (products, g)} - \Delta n_i \text{ (products, g)})$  $\Delta n_i$  (reactants, g);  $\Delta n_i$  is the total molar amount of gases in the products or reactants). The enthalpy of formation,  $\Delta_f H^\circ$ , for each of the compounds was calculated at 298.15 K using Hess' law and the combustion reactions shown in Scheme 4. All investigated tetrazoles are strongly endothermic, which was expected by comparison with the literature ( $\Delta_{\rm f} H^{\circ} \mathbf{2} \cdot \mathbf{H}_2 \mathbf{O}$ : +203, 2: +633, 5: +350, 6: +586 kJ mol<sup>-1</sup>). The influence of crystal water can be seen at the lower  $\Delta_f H^\circ$  of  $2 \cdot H_2O$ , in comparison to 2.

The enthalpies of energetic materials are governed by the molecular structures of the compounds and, therefore, heterocycles with a higher nitrogen content (*e.g.* imidazole  $(\Delta_f H^\circ_{cryst} = 14.0 \text{ kcal mol}^{-1})$ ;<sup>42</sup> 1,2,4-triazole  $(\Delta_f H^\circ_{cryst} = 26.1 \text{ kcal mol}^{-1})$ ;  $(\Delta_f H^\circ_{cryst} = 56.7 \text{ kcal mol}^{-1})$ )<sup>43</sup> show higher heats of formation. From the experimentally determined heats of formation and densities obtained from single crystal structure X-ray diffraction, various thermochemical properties have been calculated using the EXPLO5 software (see below) and are summarized in Table 4.

## Sensitivities

Since the investigated tetrazoles are energetic compounds with high nitrogen contents, the sensitivities toward friction and impact were tested.<sup>44</sup> The impact sensitivity tests were carried out according to STANAG 4489<sup>45</sup> and were modified according to instruction<sup>46</sup> using a BAM (Bundesanstalt für Materialforschung<sup>47</sup>) drophammer.<sup>48</sup> The friction sensitivity tests were carried out according to STANAG 4487<sup>49</sup> and were modified

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Table 4 Physico-chemical properties

	<b>2</b> ⋅ H <sub>2</sub> O	2	5	6
Formula	C <sub>2</sub> H <sub>5</sub> N <sub>9</sub> O	C <sub>2</sub> H <sub>3</sub> N <sub>9</sub>	C <sub>4</sub> H <sub>7</sub> N <sub>9</sub>	C <sub>5</sub> H <sub>9</sub> N <sub>9</sub>
Molecular mass/g mol <sup>-1</sup>	171.15	153.13	181.19	195.21
Impact sensitivity/J <sup>a</sup>	>100	>30	>45	>70
Friction sensitivity/N <sup>b</sup>	>360	>360	>360	>360
Electrical spark	12	7.5	10	20
discharge/J <sup>c</sup>				
$N(\%)^{d}$	73.67	82.34	69.6	64.59
$\Omega(\%)^e$	-51.42	-57.47	-101.57	-118.85
Combustion	poor	very good	good	poor
$T_{\rm dec}/{}^{\circ}{\rm C}^{f}$	250	250	263	236
Density/g cm <sup>-3g</sup>	1.693	1.861	1.530	1.512
$-\Delta_{\rm comb} U/{\rm cal} {\rm g}^{-1h}$	2392	2898	3865	4702
$-\Delta_{\rm comb} H/\rm kJ \ mol^{-1i}$	1714	1858	2932	3843
$\Delta_{\rm f} H_{\rm m}^{\circ}/{\rm kJ} {\rm mol}^{-1/j}$	203	633	350	583
Calculated values by EXI	PLO5:			
$-\Delta_{\rm E} U^{\circ}/{ m J} { m g}^{-1k}$	2985	4537	2684	3853
$T_{\rm E}/{\rm K}^l$	2555	3449	2184	2602
<i>p</i> /kbar <sup>m</sup>	220	343	172	205
$D/m  s^{-1^n}$	7792	9120	7291	7851
Gas vol./L kg <sup>-10</sup>	808	753	754	752
-				

<sup>*a*</sup> BAM methods, see ref. 46, 47. <sup>*b*</sup> BAM methods, see ref. 46, 47. <sup>*c*</sup> OZM electric spark tester, see ref. 51. <sup>*d*</sup> Nitrogen content. <sup>*e*</sup> Oxygen balance. <sup>*f*</sup> Decomposition temperature from DSC (5 °C min<sup>-1</sup>). <sup>*g*</sup> Estimated from X-ray diffraction. <sup>*h*</sup> Experimental (constant volume) combustion energy. <sup>*i*</sup> Experimental molar enthalpy of combustion. <sup>*j*</sup> Molar enthalpy of formation. <sup>*k*</sup> Energy of explosion, EXPLO5 V5.02. <sup>*l*</sup> Explosion temperature. <sup>*m*</sup> Detonation pressure. <sup>*n*</sup> Detonation velocity. <sup>*o*</sup> Assuming only gaseous products.

	Scheme 4	Combustion reactions.
6	$C_5H_9N_9$ + 29/4 $O_2$ (g)	→ 5 CO <sub>2</sub> (g) + 9/2 H <sub>2</sub> O (l) + 9/2 N <sub>2</sub> (g)
5	$C_4H_7N_9 + 23/4 O_2(g)$	→ 4 CO <sub>2</sub> (g) + 7/2 H <sub>2</sub> O (I) + 9/2 N <sub>2</sub> (g)
2	$C_2H_3N_9$ + 11/4 $O_2$ (g)	→ 2 CO <sub>2</sub> (g) + 3/2 H <sub>2</sub> O (l) + 9/2 N <sub>2</sub> (g)
<b>2</b> *H <sub>2</sub> O	C <sub>2</sub> H <sub>5</sub> N <sub>9</sub> O + 11/4 O <sub>2</sub> (g)	$\longrightarrow$ 2 CO <sub>2</sub> (g) + 5/2 H <sub>2</sub> O (l) + 9/2 N <sub>2</sub> (g)

according to instruction<sup>50</sup> using the BAM friction tester. Powdered  $2 \cdot H_2O$  and 5 are sensitive towards neither impact (<100 J) nor friction (<360 N), while 2 shows a moderate impact (30 J) and friction sensitivity (300 N). **6** is only moderately impact sensitive (30 J), but not friction sensitive. According to the UN Recommendations on the Transport of Dangerous Goods,<sup>51</sup> compounds  $2 \cdot H_2O$ , **5**, and **6** are classified as "insensitive", while **2** is described as "sensitive" and should only be handled with care and 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".<sup>52</sup> The electrical spark sensitivities were determined to be 7.5 J (2), 12 J ( $2 \cdot H_2O$ ), 10 J (5), and 20 J (6).

#### **Detonation parameters**

Some detonation parameters such as pressure, temperature, velocity, the heat of explosion, and the amount of gaseous decomposition products were calculated with the EXPLO5 V5.02 software.<sup>53,54</sup> This program is based on the steady-state model of equilibrium detonation and uses BKW E.O.S. for

gaseous detonation products and Cowan-Fickett E.O.S. for solid carbon. The calculations were performed using the BKWN set of constants, the maximum densities according to the crystal structures, the molecular masses and the experimentally determined heats of formations. The results are given in Table 4. The most useful values for classifying new explosives are the detonation pressure and detonation velocity. In comparison with common explosives such as TNT (trinitrotoluene, p = 202 kbar,  $D = 7150 \text{ m s}^{-1}$ ), compounds  $2 \cdot \text{H}_2\text{O}$ , 2, and 6 show higher detonation pressures (2·H<sub>2</sub>O: 220, 2: 343, 6: 205 kbar) while that of compound 5 is lower (172 kbar). Due to the correlation of the detonation pressure and velocity, the same trend can be found in the detonation velocities  $(2 \cdot H_2O: 7792, 2: 9120, 5: 7291,$ 6: 7851 m s<sup>-1</sup>). The calculated values of 2 are even higher than those of RDX (hexogen, p = 340 kbar, D = 8882 m s<sup>-1</sup>). Therefore, the experimental explosion performance of 2 was tested using a "Koenen" steel sleeve test.

## Koenen test

The explosion performance, under confinement of compound 2 ignited thermally, was investigated using a "Koenen test" steel sleeve apparatus.<sup>55</sup> Data obtained from the Koenen test can be related to the performance of the compound and can be used to determine the shipping classification of a substance. This information can also be used in evaluating the degree of venting required to avoid an explosion during processing operations. This test uses a non-reusable open-ended flanged steel tube, a closing device with a variable orifice of 0-10 mm (through which gases formed on decomposition are vented), an industrial propane cylinder, and four Bunsen burners. For the test, a defined volume of 25 mL of the compound is loaded into a flanged steel tube and a threaded collar is slipped onto the tube from below. The closing plate with the orifice is fitted over the flanged tube and secured with a nut. Heating is provided by four propane burners that are ignited simultaneously. The test is completed when either rupture of the tube is observed or when no reaction is observed after heating the tube for a minimum of 5 min. After each trial, the fragments of the tube, if any, are collected and weighed. The reaction is evaluated as an explosion if the tube is fragmented into three or more pieces. TNT destroys the steel tube to a hole of width 6 mm and RDX achieves this with a hole of width 8 mm. The result of the Koenen test can be seen in Fig. 13. Compound 2 destroyed the steel tube into more than 20 fragments using hole widths of 8 mm and 10 mm, and it can therefore be assumed that compound 2 offers a greater explosion performance than RDX, which is in accordance with the calculated detonation values.

# Experimental

All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics) if not stated otherwise. Melting points were measured with a Perkin-Elmer Pyris 6 DSC, using heating rates of 5 °C min<sup>-1</sup> and were checked using a Büchi Melting Point B-450 apparatus. <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N spectra were recorded with a Jeol Eclipse 270, a Jeol EX 400, or a Jeol Eclipse 400 instrument. All chemical shifts are quoted in ppm relative to TMS (<sup>1</sup>H, <sup>13</sup>C), CH<sub>3</sub>NO<sub>2</sub> (<sup>15</sup>N). For compounds **2**, **5**, and **6** the proton



**Fig. 13** "Koenen test" of compound **2** (a: filled steel sleeve; b: Koenen test setup; c: collected fragments using a hole width of 8 mm; d: collected fragments using a hole width of 10 mm).

coupled and decoupled <sup>15</sup>N NMR spectra (with full NOE) were recorded. Infrared (IR) spectra were recorded using a Perkin-Elmer Spektrum "One FT-IR" instrument. Raman spectra were measured using a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported as percentages relative to the most intense peak and are given in parentheses. Elemental analyses were performed with a Netsch STA 429 Simultaneous Thermal Analyzer. Bomb calorimetry was performed using a Parr 1356 Bomb calorimeter with a Parr 1108CL oxygen bomb. The sensitivity data were obtained using a BAM drophammer and a BAM friction tester.

# **CAUTION!**

Tetrazole derivatives are considered energetic materials and tend to explode under certain conditions. Although we have not experienced any problems during the synthesis of the reported compounds, appropriate safety precautions should be taken at all times, especially when manipulating 2. Laboratories and personnel should be properly grounded and safety equipment such as Kevlar<sup>®</sup> gloves, leather coats, face shields, and ear plugs are necessary.

#### 5,5'-Bis(1*H*-tetrazolyl)amine monohydrate (2 · H<sub>2</sub>O)

To a 2000 mL three-neck reaction flask containing a refluxing suspension of sodium dicyanamide (44.5 g, 0.5 mol), sodium azide (65.0 g, 1.0 mol), ethanol (400 mL), and water (250 mL) was added 2 M HCl (750 mL) over the course of five hours. The reaction mixture was refluxed for a further 48 h. After cooling to  $0 \,^{\circ}$ C in an ice bath and addition of conc. HCl (80 mL) **2**·H<sub>2</sub>O was

obtained as a fine colorless precipitate. The precipitate was filtered off and washed with small amounts of ethanol and diethyl ether and dried under vacuum. Yield: 75 g (0.43 mol, 88%). The product can be recrystallized from dilute acids such as HCl or HClO<sub>4</sub>. Mp 250 °C (dec.), (DSC, 5 °C min<sup>-1</sup>); IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu} = 3456$  (s), 3028 (s), 2932 (s), 2858 (s), 2671 (m), 2438 (m), 1796 (w), 1656 (vs), 1611 (s), 1556 (s), 1454 (m), 1352 (m), 1337 (m), 1282 (m), 1263 (m), 1154 (w), 1110 (m), 1072 (s), 1501 (s), 1036 (m), 1003 (m), 899 (m), 819 (m), 790 (m), 738 (m), 690 (m), 503 (m), 406 (w); Raman (200 mW, 25 °C, cm<sup>-1</sup>):  $\tilde{\nu} =$ 3328 (11), 3120 (8, br), 1649 (9), 1618 (34), 1552 (54), 1480 (22), 1455 (17), 1370 (17), 1346 (15), 1267 (25), 1226 (26), 1151 (15), 1128 (15), 1073 (100), 1039 (42), 838 (7), 794 (17), 736 (9), 670 (7), 421 (22), 409 (48), 381 (9), 348 (20), 321 (48), 172 (100), 147 (46); <sup>1</sup>H NMR ([d<sub>6</sub>]-DMSO, 25 °C) δ: 11.92 (s, br), 9.53 (s, br); <sup>13</sup>C NMR ([d<sub>6</sub>]-DMSO, 25 °C) δ: 154.7 (C); <sup>15</sup>N{<sup>1</sup>H} NMR ([d<sub>6</sub>]-DMSO, 25 °C)  $\delta$ : -17.9 (N2), -123.8 (N1), -315.7 (NH); m/z (DEI<sup>+</sup>): 153 (M<sup>+</sup> - H<sub>2</sub>O, 66), 128 (18), 127 (9), 97 (16), 96 (20), 70 (35), 69 (34), 68 (36), 57 (33), 53 (23), 43 (33), 42 (81), 41 (39), 29 (39), 28 (100); EA (C<sub>2</sub>H<sub>5</sub>N<sub>9</sub>O, 171.15) calcd: C 14.04, H 2.95, N 73.67%; found: C 14.10, H 2.61, N 73.19%; impact sensitivity: >100 J; friction sensitivity: >360 N;  $\Delta_{\text{comb}}$  U: 2392 cal g<sup>-1</sup>.

# 5,5'-Bis(1*H*-tetrazolyl)amine (2)

Compound **2**·H<sub>2</sub>O was dehydrated under vacuum (24 h,  $10^{-3}$  Torr) at elevated temperature (120 °C). Mp 250 °C (dec.); IR (KBr, cm<sup>-1</sup>)  $\tilde{\nu} = 3267$  (m), 3136 (m), 3080 (m), 2934 (m), 1654 (vs), 1618 (s), 1607 (s), 1570 (s), 1547 (m), 1481 (m), 1445 (w), 1384 (w), 1321 (w), 1288 (w), 1228 (w), 1174 (w), 1133 (m), 1078 (w), 1057 (m), 1042 (m), 1014 (w), 835 (w), 806 (w), 749 (w), 719 (w), 600 (w); Raman (200 mW, 25 °C, cm<sup>-1</sup>)  $\tilde{\nu} = 2986$  (58), 1606 (47), 1595 (48), 1568 (22), 1550 (83), 1450 (32), 1422 (20), 1381 (37), 1322 (38), 1287 (27), 1243 (17), 1186 (57), 1132 (100), 1078 (50), 1057 (53), 1014 (38), 810 (13), 397 (81), 339 (32), 312 (26), 201 (41), 167 (47); EA (C<sub>2</sub>H<sub>3</sub>N<sub>9</sub>, 181.17) calcd: C 15.69, H 1.97, N 82.34%; found: C 15.61, H 2.07, N 81.62%; impact sensitivity: >30 J; friction sensitivity: >300 N;  $\Delta_{comb}$ . *U*: -2898 cal g<sup>-1</sup>.

# 5,5'-Bis(2-methyltetrazolyl)amine (5)

In a 500 mL three neck round bottom flask,  $2 \cdot H_2O$  (17.1 g, 0.1 mol) was neutralized with an aqueous NaOH solution (8.0 g, 0.2 mol in 100 mL water) and warmed to 60 °C until a clear darkred solution was obtained. Methyl iodide (12.5 mL, 0.21 mol) in acetone (50 mL) was then added drop-wise to the reaction mixture. Afterwards the solution was heated under reflux for 12 h. After cooling the reaction mixture (4 °C) compound 5 was obtained as a colorless precipitate. The precipitate was filtered off and washed with acetone (2  $\times$  30 mL) and dried under vacuum. Yield: 9.1 g (55 mmol, 55%). The product can be recrystallized from dilute mineral acids such as HCl or HClO<sub>4</sub>. Mp 263 °C (dec.); IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu} = 3417$  (w), 3278 (m), 3194 (m), 3097 (m), 3049 (m), 2949 (w), 2890 (w), 2862 (w), 1644 (vs), 1565 (s), 1540 (s), 1465 (w), 1434 (w), 1417 (w), 1329 (w), 1202 (m), 1097 (w), 1055 (w), 1010 (w), 885 (w), 837 (w), 744 (m), 702 (w), 679 (w); Raman (200 mW, 25 °C, cm<sup>-1</sup>):  $\tilde{\nu} = 3269$  (4), 3197 (4), 3047(22), 3031(21), 2963 (81), 2821 (4), 1631 (7), 1563 (100), 1395 (8), 1455 (14), 1438 (14), 1419 (14), 1396 (33), 1381 (23),

1346 (11), 1204 (22), 1098 (14), 1084 (30), 1065 (24), 1011 (55), 748 (5), 680 (38), 446 (8), 386 (8), 348 (20), 247 (30), 222 (20); <sup>1</sup>H NMR ([d<sub>6</sub>]-DMSO, 25 °C) δ: 10.91 (s, NH), 4.27 (s, CH<sub>3</sub>); <sup>13</sup>C NMR ([d<sub>6</sub>]-DMSO, 25 °C) δ: 162.7 (CN<sub>4</sub>), 40.1 (CH<sub>3</sub>); <sup>15</sup>N NMR (CF<sub>3</sub>-COOH, 25 °C) δ: -11.3 (N3, q, <sup>3</sup>*J*<sub>NH</sub> = 1.86 Hz), -109.2 (N4, s), -110.2 (N1, q, <sup>3</sup>*J*<sub>NH</sub> = 1.9 Hz), -111.5 (N2, q, <sup>2</sup>*J*<sub>NH</sub> = 2.1 Hz), -316.4 (N5, s); *m/z* (DEI<sup>+</sup>): 181 (M<sup>+</sup>, 11) 153 (11), 96 (2), 82 (3), 67 (5), 56 (4), 53 (10), 43 (100), 42 (63), 39 (4), 28 (42), 27 (12), 15 (54); EA (C<sub>4</sub>H<sub>7</sub>N<sub>9</sub>, 181.17) calcd: C 26.52, H 3.89, N 69.59%; found: C 26.50, H 3.93, N 69.27%; impact sensitivity: >45 J; friction sensitivity: >360 N;  $\Delta_{comb}$ , *U*: -3865 cal g<sup>-1</sup>.

## 5,5'-Bis(2-methyltetrazolyl)methylamine (6)

Dimethyl sulfate (0.95 mL, 10 mmol) was slowly added to a stirred, warm (65 °C) solution of 5 (1.81 g, 10 mmol) and NaOH (0.40 g, 10 mmol) in H<sub>2</sub>O (15 mL). The colorless mixture was heated for 2 h from which after cooling to RT the product 6 separated as a colorless precipitate. After filtration, 6 was washed with cold water and recrystallized. Yield: 1.41 g (7.2 mmol, 72%). Mp 137–139 °C, 236 °C (dec.); IR (KBr, cm<sup>-1-</sup>):  $\tilde{\nu} = 3109$  (w), 3038 (w), 2957 (w), 2576 (w), 2421 (w), 1968 (w), 1585 (s), 1553 (vs), 1471 (m), 1421 (m), 1385 (w), 1364 (w), 1293 (w), 1210 (m), 1167(m), 1147 (m), 1061 (w), 1009 (m), 745 (m), 735 (s), 697 (w), 666 (w), 580 (w); Raman (200 mW, 25 °C, cm<sup>-1</sup>):  $\tilde{\nu} = 3038$  (17), 3018 (18), 2961 (67), 1614 (11), 1553 (91), 1463 (13), 1425 (14), 1383 (27), 1366 (23), 1295 (8), 1202 (19), 1148 (15), 1060 (15), 1010 (100), 736 (15), 582 (42), 390 (19), 341 (16), 250 (16), 145 (27); <sup>1</sup>H NMR ([d<sub>6</sub>]-DMSO, 25 °C) δ: 4.29 (CH<sub>3</sub>, s), 3.60 (N<sub>s</sub>CH<sub>3</sub>, s); <sup>13</sup>C NMR ([d<sub>6</sub>]-DMSO, 25 °C) δ: 164.6 (C2), 40.3 (C3), 36.8 (C1); <sup>15</sup>N NMR ([d<sub>6</sub>]-DMSO, 25 °C)  $\delta$ : -5.2 (N3, q,  ${}^{3}J_{N-HH} = 1.9$  Hz), -76.2 (N4, s), -104.0 (N1, q,  ${}^{3}J_{N-H} = 1.9$  Hz),  $-110.5 (N2, q, {}^{2}J_{N-H} = 2.2 \text{ Hz}), -324.5 (N5, q, {}^{2}J_{N-H} = 2.2 \text{ Hz};$ EA (C5H9N9, 195.22): calcd: C 30.77, H 4.65, N 64.59%; found: C 30.62, H 4.50, N 64.51%; m/z (DEI): 195 [(M<sup>+</sup>) (22)], 167 (9), 68 (8), 96 (48), 56 (21), 53 (12), 43 (100), 42 (37), 28 (34), 27 (8); impact sensitivity: >70 J; friction sensitivity: >360 N.  $\Delta_{\rm comb}$  U: -4702 cal g<sup>-1</sup>.

# X-Ray diffraction studies

Suitable single crystal of  $2 \cdot H_2O \cdot DMSO$  and 6 were picked from the crystallization mixture and mounted in Kel-F oil and transferred to the N<sub>2</sub> stream of an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collections were performed using the CrysAlis CCD software,56 the data reduction with the CrysAlis RED software.<sup>57</sup> The data for compounds 2, 2·H<sub>2</sub>O and 5 were collected on a Nonius Kappa CCD diffractometer under an N<sub>2</sub> stream as well. Data collection and reduction was done by the Bruker "Collect" and the "HKL Denzo and Scalepack" software.58 The structures were solved with SIR-92 (2·H<sub>2</sub>O, 2·H<sub>2</sub>O·DMSO and 6),<sup>59</sup> and SHELXS-97 (2 and 5),<sup>60</sup> refined with SHELXL-9761 and finally checked using the PLA-TON software.62 The non-hydrogen atoms were refined anisotropically and the hydrogen atoms were located and freely refined. The absorptions of  $2 \cdot H_2O \cdot DMSO$  and 6 were corrected by a SCALE3 ABSPACK multi-scan method.63 All relevant data

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and parameters of the X-ray measurements and refinements are given in Table 2. Further information on the crystal-structure determinations is available as ESI.†

# Conclusions

From this experimental study the following conclusions can be drawn:

-5,5'-(Bis-1*H*-tetrazolyl)amine monohydrate ( $2 \cdot H_2O$ ,  $H_2bta \cdot H_2O$ ) can be synthesized in high yield and pure quality by the reaction of sodium dicyanamide and 2 eq. sodium azide in aqueous/ethanolic solution by adding diluted hydrochloric acid. 5,5'-Bis(2-methyl-tetrazolyl)amine (Me<sub>2</sub>bta, **5**) and 5,5'-bis(2-methyltetrazolyl)methylamine (Me<sub>3</sub>bta, **6**) can be obtained by methylation of deprotonated  $H_2$ bta and Me<sub>2</sub>bta, respectively.

- H<sub>2</sub>bta·H<sub>2</sub>O can be dehydrated at 120 °C under reduced pressure yielding water-free H<sub>2</sub>bta (**2**).

- The structures of 2,  $2 \cdot H_2O$ ,  $2 \cdot H_2O \cdot DMSO$ , 5 and 6 in the crystalline state were determined using X-ray diffraction, showing monoclinic crystal systems and layer structures ( $2 \cdot H_2O$ , 5 and 6) as well as an orthorhombic structure (2) with a high density.

- The investigated compounds were fully characterized and a detailed discussion of the vibration spectroscopy as well as the heterocore NMR spectra is given in this work.

 Bistetrazolylamines are suitable energetic materials with low sensitivities and high thermal stabilities and can be used in high nitrogen composite propellants.

– Water-free 2 can also be used as a secondary explosive since these are highly endothermic compounds and show great calculated explosion pressures and explosion velocities. 2 was tested using a steel sleeve test (critical diameter of 10 mm), from which a higher explosion power than RDX was observed.

- Bistetrazolylamines can be used as chelating ligands in novel transition state metal complexes.

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