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Nitrogen-Rich Bis-1,2,4-triazoles—A Comparative Study of Structural and Energetic Properties

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Abstract: In this contribution, the synthesis and full structural and spectroscopic characterization of five bis-1,2,4-triazoles in combination with different energetic moieties like amino, nitro, nitrimino, azido, and dinitromethylene groups is presented. The main goal is a comparative study on the influence of those energetic moieties on the structural and energetic properties. A complete characterization including IR, Raman, and multinuclear NMR spectroscopy of all compounds is presented.

Additionally, X-ray crystallographic measurements were performed and deliver insight into structural characteristics as well as inter- and intramolecular interactions. The standard enthalpies of formation were calculated for all compounds at the CBS-4M level of theory, the detonation parameters were calcu-

lated by using the EXPLO5.05 program. Additionally, the impact as well as the friction sensitivities and the sensitivity against electrostatic discharge were determined. The potential application of the synthesized compounds as energetic material will be studied and evaluated by using the experimentally obtained values for the thermal decomposition, the sensitivity data, and the calculated performance characteristics.

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

Introduction

The synthesis of energetic materials that combine high performance and low sensitivities has attracted worldwide research groups over the last decades.^[1] Nitrogen-rich heterocycles are promising compounds that fulfill many requirements in the challenging field of energetic-materials research.^[1,2] A prominent family of novel high energy density materials (HEDMs) are azole-based compounds, because they are generally highly endothermic with high densities and low sensitivities towards outer stimuli. Owing to the high positive heats of formation resulting from the large number of N–N and C–N bonds^[3] and the high level of environmental compatibility, those compounds have been studied in our group over the last couple of years with growing interest. Especially 1,2,4-triazoles show a perfect balance between thermal stability and high positive heats of formation, required for applications as prospective HEDMs.

Many energetic compounds that combine the 1,2,4-triazole backbone with energetic moieties have been synthesized over the last decades. Examples for these kind of molecules are 5-amino-3-nitro-1,2,4-triazole (ANTA),^[4] 2-azido-5-nitramino-1,2,4-triazole,^[5] or trinitromethyl-substituted

1,2,4-triazoles.^[6] Bridged compounds like 5,5'-dinitro-3,3'-azo-1,2,4-triazole (DNAT)^[7] or the analogue nitrimino compound (DNAAT)^[8] have already been investigated and show remarkably high decomposition temperatures and excellent energetic properties.

Bis-1,2,4-triazoles connected through a C–C bond are expected to show similar energetic properties in comparison to azo-bridged 1,2,4-triazole compounds and with regard to the outstanding properties of 5,5'-bistetrazoles.^[9] Different synthetic pathways towards 5,5'-dinitrimino-3,3'-bis-1,2,4-triazole have been intensively investigated by Russian scientists,^[10] the sensitivities (time to explosion delay, impact sensitivity) were first investigated by Astachov et al.^[11] Shreeve and co-workers determined the energetic properties of nitrogen-rich salts and the crystal structure of the neutral compound.^[12] 3,3'-Dinitro-5,5'-bis-1,2,4-triazole has been mentioned in literature before, but was only characterized by means of ultraviolet absorption and infrared spectroscopy.^[13]

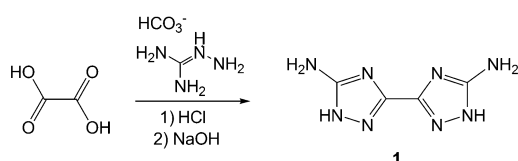
The focus of this contribution is on the full structural and spectroscopic characterization of five different bis-1,2,4-triazoles carrying energetic moieties like amino, nitro, nitramino, azido, and dinitromethyl groups. We present a comparative study on the influence of those energetic moieties on the structural and energetic properties. The potential application of the synthesized compounds as energetic material will be studied and evaluated by using the experimentally obtained values for the thermal decomposition and the sensitivity data, as well as the calculated performance characteristics.

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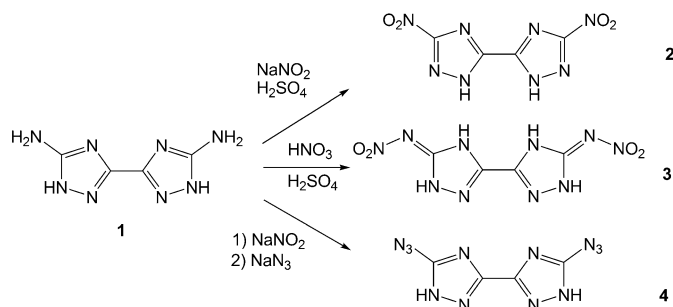
Results and Discussion

Synthesis: The starting material 3,3'-diamino-5,5'-bis(1*H*-1,2,4-triazole) (DABT, **1**) was first synthesized with a moderate yield of 56% by Shreve and Charlesworth.^[14] We developed a straightforward synthetic procedure yielding DABT as elemental analysis pure compound in yields of up to 70%. The modified procedure starts with the reaction of oxalic acid and aminoguanidinium bicarbonate in concentrated hydrochloric acid at 70°C, followed by isolation of the intermediate product by filtration. While heating to reflux in basic media, the molecule undergoes cyclization, which leads to the formation of DABT (Scheme 1).



Scheme 1. Synthesis of DABT (**1**).

As shown in Scheme 2, oxidation of DABT (**1**) was achieved by the well-known Sandmeyer reaction through diazotization in sulfuric acid and subsequent reaction with



Scheme 2. Synthesis of the energetic bis-1,2,4-triazole derivatives **2–4** based on DABT (**1**).

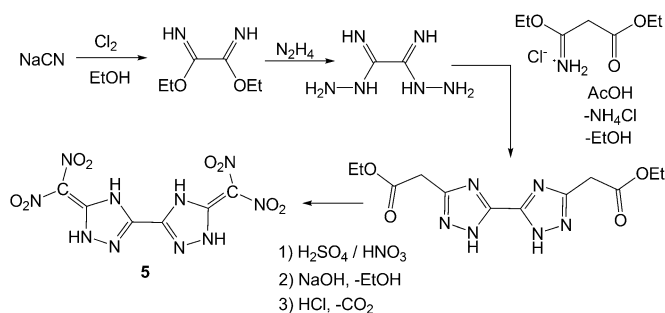
sodium nitrite.^[15] The formation of 3,3'-dinitro-5,5'-bis(1*H*-1,2,4-triazole) (DNBT, **2**) was first mentioned by Russian scientists with a low yield of 31%.^[13b] We were able to optimize the process by adding a suspension of DABT in aqueous sulfuric acid (20%) to a solution of sodium nitrite in water at 40°C, which leads to a remarkable increase of the yield up to 82%.

The nitrimino compound **3** was first synthesized by Metelkina et al. by using oxalic acid dihydrazide and 2-nitroguanidine,^[10a] by using 1-amino-2-nitroguanidine with oxalic acid,^[10b] or by using 1-methyl-2-nitro-1-nitrosoguanidine and oxalic acid dihydrazide.^[10c] We followed the most efficient method first mentioned by Astachov et al.^[11] starting from the amino compound **1**. The nitration was optimized by

using concentrated sulfuric and nitric acid in a ratio of 3:1 resulting in a yield of 77%.

The azido compound **4** was synthesized through diazotization in sulfuric acid and subsequent reaction with an excess of sodium azide. After recrystallisation from water, compound **4** can be isolated as the insensitive dihydrate.

The synthesis of the dinitromethyl-bis(1,2,4-triazole) **5** (DNMBT) was achieved through a completely different synthetic pathway (Scheme 3). The chlorination of sodium cyano-



Scheme 3. Synthetic pathway towards DNMBT (**5**).

nide in ethanol and subsequent reaction with hydrazine leads to the formation of the oxalimidohydrazide.^[16] This intermediate product was reacted with the commercially available 3-ethoxy-3-iminopropionic acid ethyl ester hydrochloride to form the 3,3'-(diethyl acetate)-5,5'-bis-1,2,4-triazole. Introduction of the NO₂ moieties was accomplished by nitration with nitric acid in a mixture of sulfuric acid and oleum (1:1). The ethyl ester hydrolyses rapidly, whereas stirring the nitrated intermediate product in basic media and subsequent acidification with concentrated hydrochloric acid leads to the release of CO₂ and the formation of 3,3'-dinitromethyl-5,5'-bis-1,2,4-triazole (**5**).

All nitrogen-rich bis-1,2,4-triazoles, that is, compounds **1–5** were fully characterized by IR and Raman spectroscopy as well as multinuclear NMR spectroscopy, mass spectrometry, and differential scanning calorimetry (DSC). Additional X-ray crystallographic measurements deliver insight into inter- and intramolecular interactions.

Crystal structures: Single-crystal X-ray measurements were accomplished for compounds **1**, **2**, **4**, and **5** and are discussed in detail. The crystal structure of the nitrimino compound **3** has already been described in literature.^[12] All compounds could only be recrystallized from water resulting in the formation of the dihydrate as crystalline species, only compound **2** could be obtained water free.

By detailed examination of the crystal structures of all compounds, no difference is observed for the 1,2,4-triazole system in comparison to other triazole ring systems.^[7,17] The bond lengths within the 1,2,4-triazole ring in the molecular structures are all in between the length of formal C–N and N–N single and double bonds (C–N: 1.47, 1.22 Å; N–N: 1.48, 1.20 Å).^[18]

Due to the very low solubility in any solvent, crystals of 5,5'-diamino-3,3'-bis-(1*H*-1,2,4-triazole) (**1**) could only be obtained by recrystallisation from DMSO. Compound **1** crystallizes as DMSO adduct in the monoclinic space group $P2_1/c$ with a cell volume of 750.55(14) Å³ and two molecular moieties in the unit cell, the crystal structure together with the labeling scheme is displayed in Figure 1.

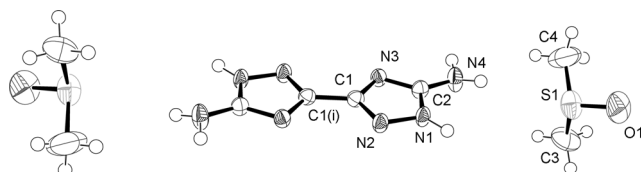


Figure 1. Crystal structure of DABT (**1**), only one orientation of the disordered DMSO molecules is shown. Thermal ellipsoids are set to 50% probability. Symmetry: i) $2-x, -y, 1-z$.

As expected, the bis-triazole moiety shows a completely planar assembly. In relation to the planar 1,2,4-triazole ring, the protons of the amine groups are twisted out of plane by only 26.1°. The angles surrounding the N4 atom are larger than expected for a sp^3 atom in the range of 116(1) (C2-N4-H5a) to 118(1)° (C2-N4-H5b), which could be a reason for the low nucleophilicity observed in reactions with compound **1**.

It is remarkable to note that all nitrogen atoms of the 1,2,4-triazole ring as well as the amine group participate in hydrogen bonds. All contacts are short with a $D\cdots A$ length of 2.890(2) and 3.055(2) Å (D =donor, A =acceptor), but only the hydrogen bond N1-H1 \cdots N3 is strongly directed with a $D-H\cdots A$ angle of 170.8(17)° (Table 1).

Table 1. Hydrogen bonds present in compound **1**.

D-H \cdots A	$d(D-H)$ [Å]	$d(H\cdots A)$ [Å]	$d(D-H\cdots A)$ [Å]	$\angle(D-H\cdots A)$ [°]
N1-H1 \cdots N3(i) ^[a]	0.881(18)	2.017(19)	2.890(2)	170.8(17)
N4-H5a \cdots N2(ii) ^[a]	0.867(19)	2.25(2)	3.055(2)	154.9(18)

[a] Symmetry operators: i) $x, 3/2-y, 1/2+z$; ii) $-x, 1/2+y, 1/2-z$.

All hydrogen-bond lengths lie well within the sum of the van der Waals radii ($r_w(N)+r_w(N)=3.20$ Å),^[18a] resulting in a strong network of hydrogen bonds in the bc plane (Figure 2). The DMSO molecules do not participate in hydrogen bonds within this plane, but connect the layers through interaction with the free hydrogen atoms of the amine groups.

3,3'-Dinitro-5,5'-bis-(1*H*-1,2,4-triazole) (**2**) crystallizes in the monoclinic space group $P2_1/n$ with a cell volume of 394.73(8) Å³ and one molecular moiety in the unit cell. The calculated density at 173 K is 1.902 g cm⁻³ and hence above the density of the dihydrate (1.764 g cm⁻³).^[17c] Again, the molecule shows a completely planar assembly with a torsion angle of the nitro group towards the triazole ring of 2.9(2)°.

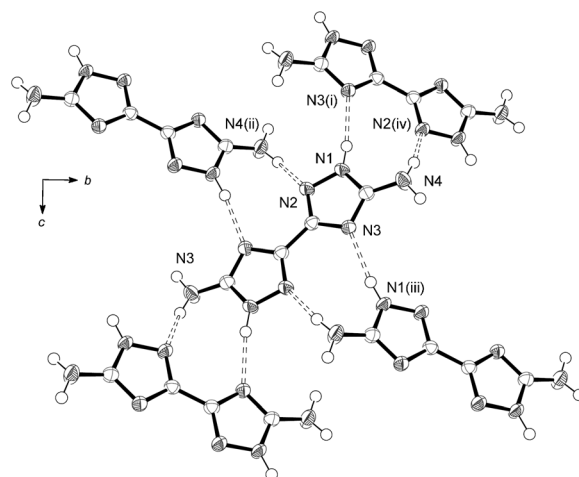


Figure 2. Hydrogen bonding within the crystal structure of DABT (**1**). DMSO molecules are omitted for clarity because they do not participate in hydrogen bonds in the bc plane. Thermal ellipsoids are set to 50% probability. Symmetry: i) $x, 1/2-y, -1/2+z$; ii) $2-x, -1/2+y, 1/2-z$; iii) $x, 1/2-y, 1/2+z$; iv) $2-x, 1/2+y, 1/2-z$.

The formula unit of compound **2** together with the atom labeling is presented in Figure 3.

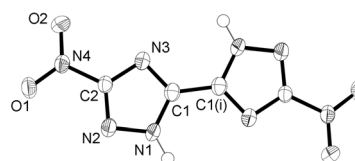


Figure 3. Crystal structure of compound **2**. Thermal ellipsoids are set to 50% probability. Symmetry operators: i) $-x, 1-y, 2-z$.

In contrast to compound **1**, the structure is built up by only one individual hydrogen bond N1-H1 \cdots O1. The $D-H\cdots A$ angle is close to 180° with 171.9(2)° and the $D\cdots A$ length is shorter than the sum of the van der Waals radii ($r_w(O)+r_w(N)=3.07$ Å)^[18a] with 2.902(2) Å (Figure 4a). In contrast to compound **1**, the nitrogen atoms N2 and N3 do not participate as acceptor in any hydrogen bond. As shown in Figure 4, the crystal structure of compound **2** consists of infinite zigzag rows along the b axis including an angle of 60.5°. The layers are stacked above each other with a layer distance of $d=2.96$ Å. The layers are connected by two short contacts, N2 \cdots N4(ii) and C1 \cdots O1(iii) (symmetry operators: ii) $3/2-x, 1/2+y, 1/2-z$; iii) $3/2-x, -1/2+y, 1/2-z$). Both contacts are shorter than the sum of the van der Waals radii,^[18a] with N2 \cdots N4 being the shortest (2.922(2) Å) and C1 \cdots O1 being the longest (3.051(2) Å) contact. The stacking of the layers is displayed in Figure 4b together with the distance d between the layers.

The azido compound **4** crystallizes in the triclinic space group $P\bar{1}$ with a cell volume of 256.34(9) Å³ and one molecular moiety in the unit cell, the calculated density for the dihydrate is 1.646 g cm⁻³. As shown in Figure 5, the proton is located at the N1 atom next to the azido group and not next

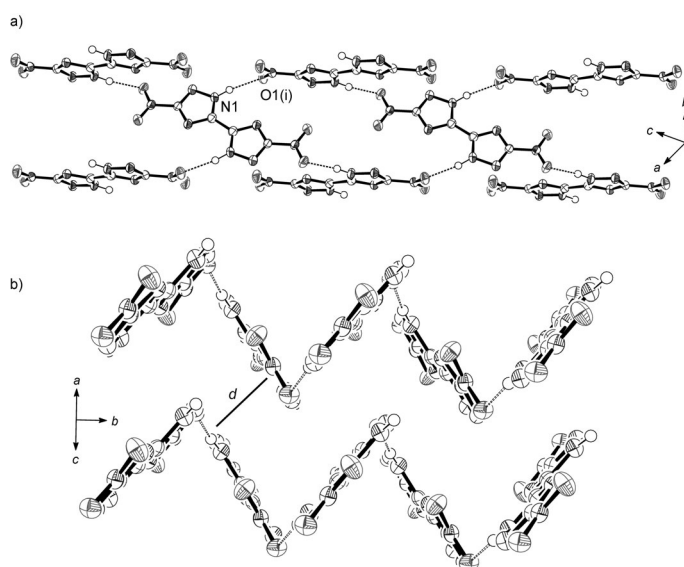


Figure 4. a) Hydrogen-bonding scheme in the crystal structure of compound **2**. b) Wave-like arrangement of the infinite rows in the crystal structure of compound **2** (layer distance $d=2.96$ Å). Thermal ellipsoids are set to 50% probability. Symmetry operators: i) $1/2+x, 1/2-y, 1/2+z$.

to the C–C bond as it is the case for the nitro compound **2**. The three nitrogen atoms of the azido group exhibit a slightly bent arrangement with a N4–N5–N6 angle of $172.34(17)^\circ$. Both azido moieties are assembled parallel and point in the opposite direction.

The crystal structure of compound **4** is build up by two individual hydrogen bonds including the nitrogen atoms N1 and N2 as well as two water molecules (Figure 6). Two molecules of compound **4** form pairs through the strong hydrogen bond N1–H1 \cdots O1(i). As shown in Table 2, the D–H \cdots A angle is close to 180° with $174(2)^\circ$ and the D \cdots A length is considerably shorter than the sum of the van der Waals radii ($r_w(\text{O})+r_w(\text{N})=3.07$ Å).^[18a]

The individual pairs are assembled coplanar, which results in the formation of a layered structure within the bc plane. The azido moieties do not participate in any hydrogen bond but are connected through a short contact N6 \cdots N6(i) with a distance of $3.067(2)$ Å (symmetry code: i) $1-x, -y, 1-z$).

3,3'-Dinitromethyl-5,5'-bis-1,2,4-triazole (**5**) crystallizes as a dihydrate in the monoclinic space group $P2_1/c$. The formula unit of compound **5** together with the atom labeling is presented in Figure 7. In compari-

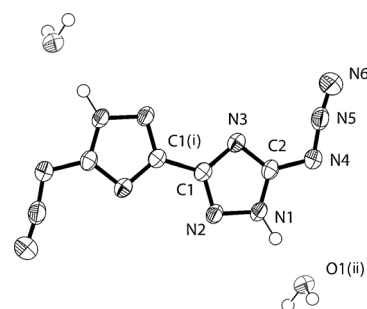


Figure 5. Crystal structure of compound **4**. Thermal ellipsoids are set to 50% probability. Symmetry operators: i) $1-x, 1-y, 2-z$; ii) $-x, 1-y, 1-z$.

Table 2. Hydrogen bonds present in compound **4**.

D–H \cdots A	$d(\text{D–H})$ [Å]	$d(\text{H}\cdots\text{A})$ [Å]	$d(\text{D–H}\cdots\text{A})$ [Å]	$\angle(\text{D–H}\cdots\text{A})$ [$^\circ$]
N1–H1 \cdots O1(i) ^[a]	0.98(2)	1.70(2)	2.676(2)	174(2)
O1–H1b \cdots N2(ii) ^[a]	0.92(2)	1.98(2)	2.892(2)	174(2)

[a] Symmetry operators: i) $x, 1+y, z$; ii) $2-x, 1-y, -z$.

son to all other bis-1,2,4-triazoles, the density of compound **5** is remarkably high with 1.951 g cm $^{-3}$.

In contrast to the previously described 3,3'-bis(dinitromethyl)-5,5'-azo-1*H*-1,2,4-triazole,^[19] the proton of the dinitromethyl moiety is not located at the C3 atom but at the N3 atom within the triazole ring. This leads to a completely planar assembly typical for sp^2 carbon atoms and a C2–C3 distance in the range of a C=C double bond ($1.440(2)$ Å).^[18a] For comparison, the C–C bond length in the similar 5-dinitromethylene-4,5-dihydro-1*H*-tetrazole is $1.418(2)$ Å.^[20] The nitro groups are twisted out of the triazole plane by only $6.5(2)$ (O1–N4–C3–C2) and $0.9(2)^\circ$ (O3–N5–C3–C2), respec-

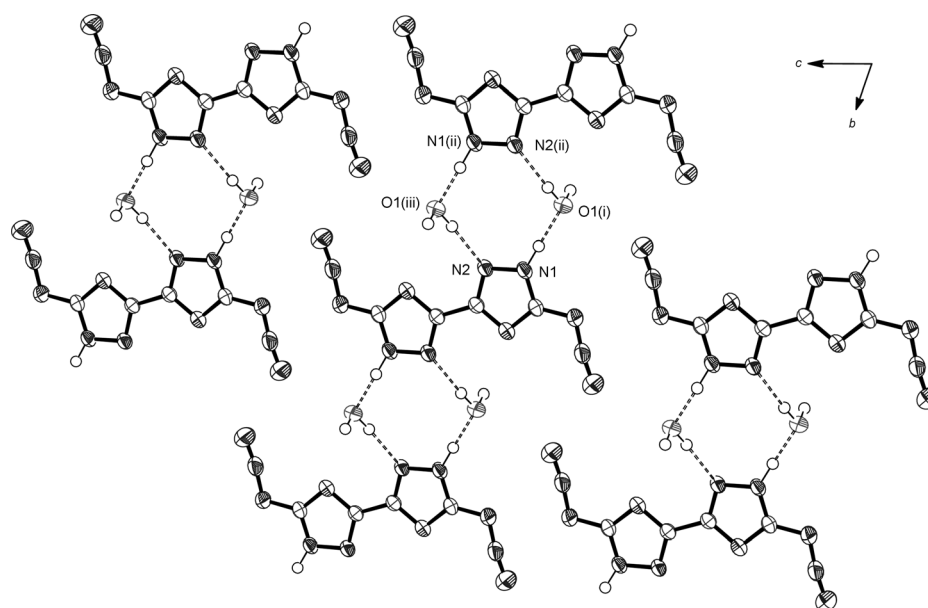


Figure 6. Hydrogen-bonding scheme in the crystal structure of compound **4**. Thermal ellipsoids are set to 50% probability. Symmetry operators: i) $-x, 1-y, 1-z$; ii) $-x, -y, 2-z$; iii) $x, -1+y, 1+z$.

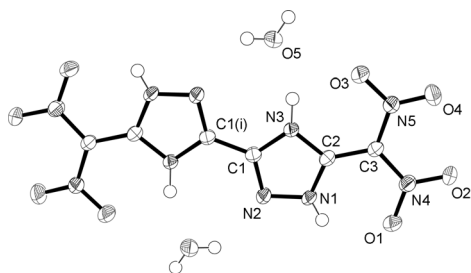


Figure 7. Crystal structure of compound **5**. Thermal ellipsoids are set to 50% probability. Symmetry operators: i) $1-x, 1-y, -z$.

tively. The planar assembly is encouraged by the formation of two intramolecular hydrogen bonds, that is, $N1-H1\cdots O1$ and $N3-H3\cdots O3$. Both interactions show rather small $D-H\cdots A$ angles of $117.9(16)$ and $113(2)^\circ$, respectively, but considerably short $D-H\cdots A$ distances of $2.558(2)$ and $2.603(2)$ Å, respectively.

The hydrogen bonds within the crystal structure of compound **5** are summarized in Table 3.

Table 3. Hydrogen bonds present in compound **5**.

D-H...A	$d(D-H)$ [Å]	$d(H\cdots A)$ [Å]	$d(D-H\cdots A)$ [Å]	$\angle(D-H\cdots A)$ [°]
$N1-H1\cdots O1$	0.79(2)	2.090(18)	2.558(2)	117.9(16)
$N1-H1\cdots O2(i)^{[a]}$	0.79(2)	2.11(2)	2.839(2)	152.6(18)
$N3-H3\cdots O3$	0.92(3)	2.10(3)	2.603(2)	113(2)
$N3-H3\cdots O5(ii)^{[a]}$	0.92(3)	1.83(3)	2.711(2)	160(2)
$O5-H5b\cdots O3(iii)^{[a]}$	0.80(3)	2.09(3)	2.883(2)	173(3)

[a] Symmetry operators: i) $-x, 1/2+y, 1/2-z$; ii) $1-x, 1-y, -z$; iii) $-1+x, 1+y, z$.

In addition to the intramolecular hydrogen bonds, three intermolecular interactions including the crystal water as well as the oxygen atoms O2 and O3 of the nitro groups could be observed. Both nitrogen atoms N1 and N3 are in-

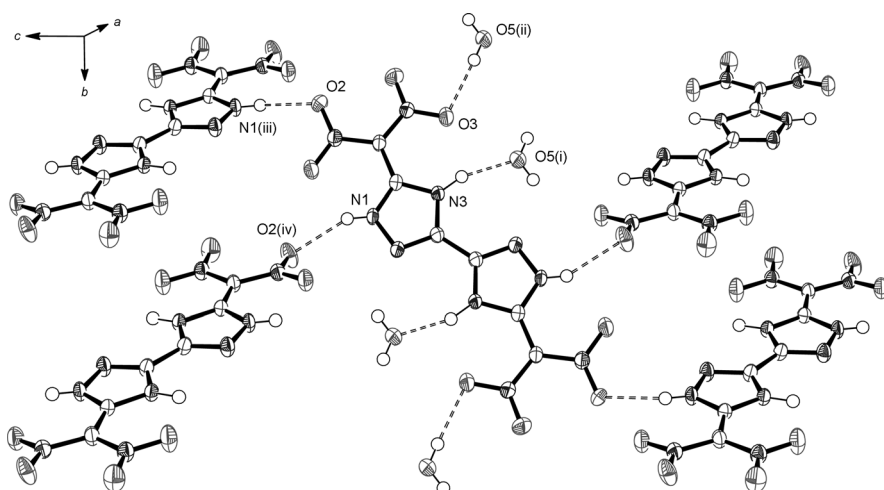


Figure 8. Surroundings and hydrogen bonds of a DNMBT molecule in the crystal structure of compound **5**. Thermal ellipsoids are set to 50% probability. Symmetry operators: i) $1-x, 1-y, -z$; ii) $1+x, -1+y, z$; iii) $-x, -1/2+y, 1/2-z$; iv) $-x, 1/2+y, 1/2-z$.

volved as donor atoms in further hydrogen bonds, that is, $N1-H1\cdots O2$ and $N3-H3\cdots O5$, resulting in strong interactions with the surrounding molecules (Figure 8).

Spectroscopic data

Vibrational spectroscopy: The IR and Raman spectra of all compounds were recorded and the frequencies were assigned according to the literature.^[21] The Raman spectrum of compound **1** is dominated by the deformation mode of the amino groups at $\tilde{\nu}=1579$ cm^{-1} . The valence stretching mode of the N-H bond is observed in the range of $\tilde{\nu}=3116$ to 3107 cm^{-1} . The nitro groups of compounds **2** and **5** are observed with both, their symmetric and asymmetric stretching modes. The vibrational frequencies for the asymmetric stretching mode of the nitro group are observed in the range of $\tilde{\nu}=1550$ (**2**) to 1568 cm^{-1} (**5**). The symmetric stretching modes are located at lower energy at $\tilde{\nu}=1410$ (**2**) and 1403 cm^{-1} (**5**). The signals of the nitrino moiety of compound **3** can be observed at $\tilde{\nu}=1565$ (ν_{asym}) and 1298 cm^{-1} (ν_{sym}). The valence stretching mode of the N-H bond of the 1,2,4-triazole ring can be observed for all compounds in the range of $\tilde{\nu}=3154$ (**3**) to 3190 cm^{-1} (**2**). In addition, as for any heterocyclic compound, many combined stretching and deformation as well as torsion stretching modes can be observed in the fingerprint region between $\tilde{\nu}=1500$ and 600 cm^{-1} .^[21b]

As shown in Figure 9, the Raman as well as the IR spectrum of the azido compound **4** exhibits two signals for the individual asymmetric stretching modes of the azide groups in the expected range.^[21c] The bands for the different “in-phase” and “out-of-phase” stretching vibrations can be observed at $\tilde{\nu}=2171$ and 2142 cm^{-1} in the Raman spectrum and at $\tilde{\nu}=2156$ and 2137 cm^{-1} in the IR spectrum.

Multinuclear NMR spectroscopy: All compounds were investigated by using ^1H , ^{13}C and ^{14}N NMR spectroscopy. Additional $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra of compound **5** were recorded at elevated temperatures to give insight into the equilibrium between both possible isomers and will be discussed in the following paragraph. Due to insufficient solubility of compounds **1**, **3**, and **5** in DMSO or any other solvent, the ^{15}N NMR spectra could only be obtained for compounds **2** and **4**.

All compounds show two signals for the 1,2,4-triazole carbon atoms in the expected range.^[7-8] One singlet for the bridging carbon atom can be found at chemical shifts of $\delta=142.1$ (**3**) to 149.3 ppm (**1**). The

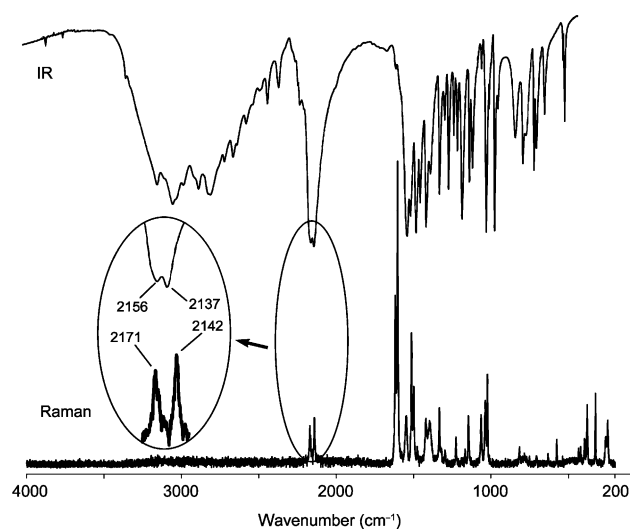


Figure 9. Comparison of the IR and Raman spectra of compound **4**. The individual stretching modes for the azide groups are expanded in the ellipse.

signal of the carbon atom connected to the energetic moieties is shifted in all cases to lower field and is observed in the range of $\delta = 151.1$ (**5**) to 162.7 ppm (**2**). In the $^{14}\text{N}\{^1\text{H}\}$ NMR spectra, the nitro group of compounds **2**, **3**, and **5** can be identified as a broad singlet at $\delta = -21$ (**3**) to -26 ppm (**2**). The azido moiety in compound **4** can be observed as a broad singlet at $\delta = -145$ ppm in the ^{14}N NMR spectrum, well-resolved resonances could only be observed in the ^{15}N NMR spectrum (as discussed below). The NMR signals of all compounds are summarized in Table 4.

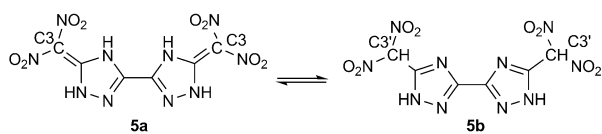
Table 4. NMR signals of compounds **1–5** in $[\text{D}_6]\text{DMSO}$.

	$^{13}\text{C}\{^1\text{H}\}$	δ [ppm] $^{14}\text{N}\{^1\text{H}\}$	^1H
1	157.3, 149.3	–	6.46
2	162.7, 145.6	–26	9.68
3	153.1, 142.1	–21	5.19
4	157.7, 145.9	–145	14.86
5	151.1, 149.3 ^[a]	–23	13.45, 8.91, 3.90

[a] Recorded at 60 °C, $\text{C}(\text{NO}_2)_2$: $\delta = 124.3$ (**5a**), 106.5 ppm (**5b**).

As mentioned before, the existence of different isomers of compound **5** (see Scheme 4) could be demonstrated by recording the $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectra at elevated temperatures. Additionally, quantum chemical calculations at the B3LYP/aug-cc-pVDZ level of theory were performed.

Because isomer **5a** is obtained in the solid state (as discussed in the previous section), in this case a sp^2 carbon



Scheme 4. Equilibrium between the two isomers **5a** and **5b**.

atom (C3) is the thermodynamically most stable configuration. However, the signals of both isomers could be observed in both the $^{13}\text{C}\{^1\text{H}\}$ and ^1H NMR spectrum at room temperature, indicating a small energy difference between both isomers. Of course there is another possible isomer in which one ring is a 1,2,4-triazole and the other is a 1,2,4-triazoline. This isomer could not be detected in any spectra at any temperature. Apparently, this transition state is not an energetic minimum and could therefore not be observed experimentally. Figure 10 shows a comparison of the experimentally obtained ^1H NMR spectra at different temperatures.

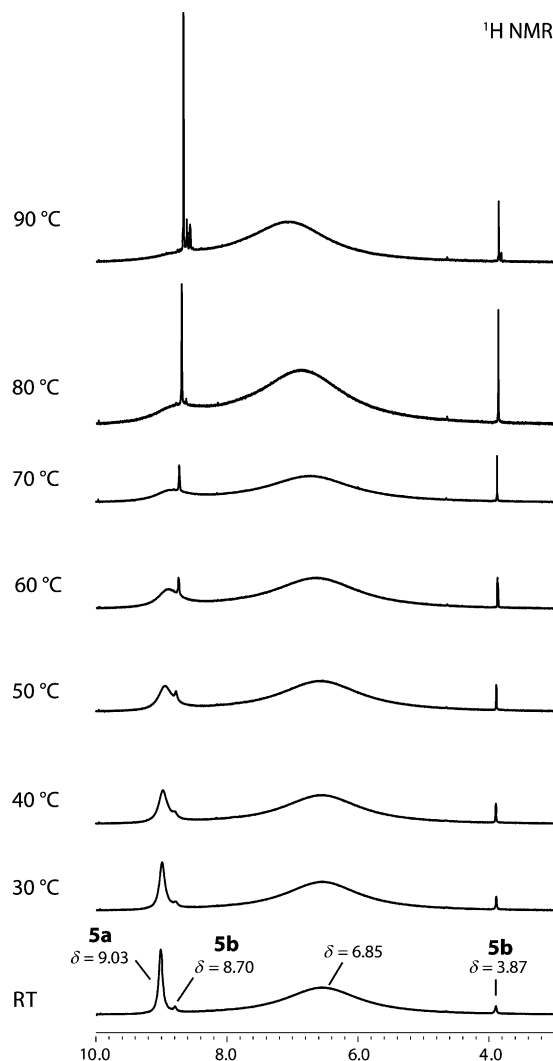


Figure 10. Comparison of ^1H NMR spectra of DNMBT (**5**) at room temperature and at elevated temperatures in $[\text{D}_6]\text{DMSO}$.

At room temperature, isomer **5a** is the dominant species resulting in a broad signal for both protons at $\delta = 9.03$ ppm (for comparison: protons of the similar 5-dinitromethylene-4,5-dihydro-1H-tetrazole appear at $\delta = 11.09$ ppm).^[20] The signals of the bis-1,2,4-triazoline isomer **5b** can also be obtained at room temperature at $\delta = 8.70$ ($\text{N}_{\text{triazole}}\text{-H}$) and

3.87 ppm (C_{sp^3-H}). Owing to the fact that compound **5** is very acidic and was used as dihydrate (as obtained after recrystallisation), the constant signal at $\delta=6.85$ ppm was assigned to the protons of the water molecules.

With raising temperature, the signal of isomer **5a** decreases and the two signals of isomer **5b** gain intensity. The conversion is completed at about 90°C, the signal of **5a** has disappeared completely. Simultaneously, the compound starts to decompose, resulting in small signals at about $\delta=8.60$ –8.70 ppm.

As shown in Figure 11, the signals of the carbon atoms of the 1,2,4-triazole in the $^{13}C\{^1H\}$ NMR spectrum at room temperature interfere with each other resulting in a broad

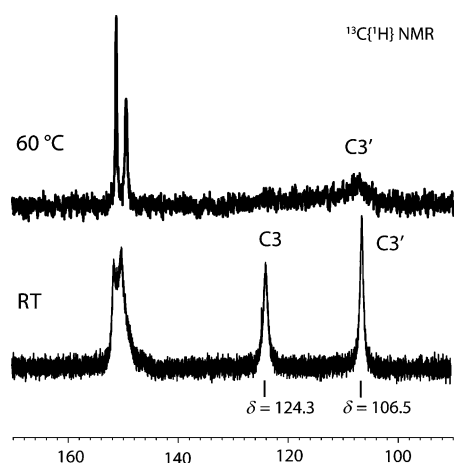


Figure 11. Comparison of the $^{13}C\{^1H\}$ NMR spectra of DNMBT (**5**) at room temperature and at elevated temperatures in $[D_6]DMSO$.

multiplet at $\delta=150.0$ ppm. The sp^2 carbon atom of isomer **5a** (C3) appears at $\delta=124.3$ ppm, the sp^3 carbon atom of isomer **5b** (C3') could be found at $\delta=106.5$ ppm. For comparison, similar sp^2 carbon atoms appear at $\delta=124.9$ (3,3'-bis(dinitromethylene)-5,5'-azo-1*H*-1,2,4-triazole)^[19] and at 121.5 ppm (5-dinitromethylene-4,5-dihydro-1*H*-tetrazole)^[20].

At 60°C, only the signals of isomer **5b** could be observed. The triazole carbon atoms now show two well-resolved resonances at $\delta=151.1$ and 149.3 ppm, the sp^3 carbon atom C3' can be found at the identical chemical shift of $\delta=106.5$ ppm (in comparison to the RT measurement) as a broad singlet.

Quantum chemical calculations at the B3LYP/aug-cc-pVDZ level of theory reveal an energy difference between both isomers of 30.4 kJ mol⁻¹ (Table 5). The calculated values go well with the experimentally obtained 1H NMR

Table 5. Calculations on the isomers of DNMBT (**5**) at the B3LYP/aug-cc-pVDZ level of theory.

	Isomer 5a	Isomer 5b
point group	C_{2h}	C_1
$-E$ [Hartree]	1380.136812	1380.125222
E_{rel} [kcal mol ⁻¹]	0.0	+7.3
E_{rel} [kJ mol ⁻¹]	0.0	+30.4

spectra, especially with the exclusive appearance of isomer **5b** in the NMR spectrum above 90°C.

The calculated optimized gas-phase structure of isomer **5a** is in good agreement with the experimentally obtained crystal structure of compound **5** (Figure 12). The planar assem-

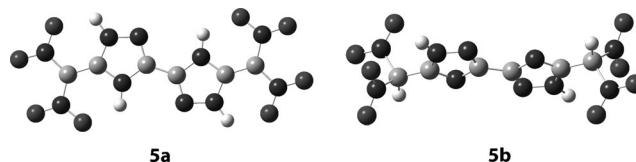


Figure 12. Comparison of the calculated gas-phase structures of the isomers **5a** and **5b**.

bly of the dinitromethylene moiety is the thermodynamically most stable configuration. In addition, the C3' atom of isomer **5b** shows the expected tetrahedral coordination as it is the case for the sp^3 carbon atoms in the similar bis(dinitromethylene)-5,5'-azo-1*H*-1,2,4-triazole.^[19]

Due to insufficient solubility, ^{15}N NMR spectra could only be obtained for compounds **2** and **4**. Four well-resolved resonances are observed in the ^{15}N NMR spectrum for the four nitrogen atoms of the dinitro compound **2** (Figure 13). The

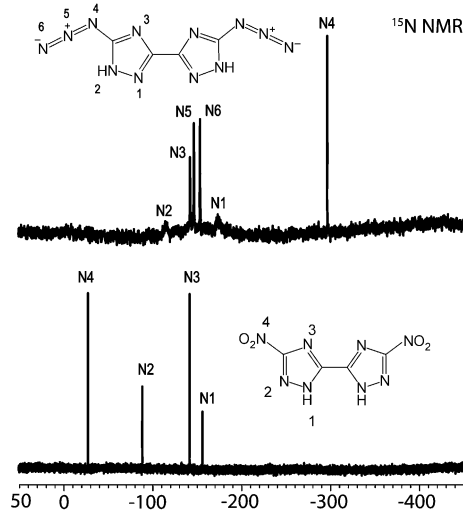


Figure 13. ^{15}N NMR spectra of 5,5'-diazo-3,3'-bis-1*H*-1,2,4-triazole (**4**, top) and 3,3'-dinitro-5,5'-bis-1*H*-1,2,4-triazole (**2**, bottom) recorded in $[D_6]DMSO$.

signals were assigned by comparison to literature values.^[21a,22] The signals of the nitrogen atoms N1 and N2 of the diazido compound **4** appear in the same range as for compound **2**, but are rather broad in comparison to the sharp signals of compound **2**. The three signals of the azido moiety are well resolved and can be found in the expected range with the signal of N4 being shifted to highest field with a chemical shift of $\Delta\delta = -295.2$ ppm.

Theoretical calculations, performance characteristics, and stabilities: All calculations regarding energies of formation were carried out by using the Gaussian G09W Version 7.0 program package.^[23] Because very detailed descriptions of the calculation process have been published earlier^[8] and can be found in specialized books,^[1b] only a short summary of the computational methods will be given. The enthalpies (H) and Gibbs free energies (G) were calculated by using the complete basis set method (CBS) of Petersson et al. in order to obtain very accurate energies. In this contribution, we used the modified CBS-4M method with M referring to the use of minimal population localization, which is a reparameterized version of the original CBS-4 computational method and also includes additional empirical calculations.^[24] The enthalpies of formation for the gas-phase species were computed according to the atomization energy method, by using NIST^[25] values as standardized values for the atoms standard heats of formation ($\Delta_f H^0$) according to Equation (1).^[26]

$$\Delta_f H^0_{(\text{g, Molecule } 298)} = H_{(\text{Molecule})} - \sum H^0_{(\text{Atoms})} + \sum \Delta_f H^0_{(\text{Atoms, NIST})} \quad (1)$$

The solid-state enthalpy of formation for neutral compounds is estimated from the computational results by using the rule of Trouton,^[27] where T_m was taken equal to the decomposition temperatures [Eq. (2)].

$$\begin{aligned} \Delta H_m &= \Delta_f H^0_{(\text{g, Molecule, } 298)} - \Delta H_{\text{sub}} \\ &= \Delta_f H^0_{(\text{g, Molecule, } 298)} - ((188 \text{ J mol}^{-1} \text{ K}^{-1}) T_m) \end{aligned} \quad (2)$$

The solid-state enthalpies of formation for the ionic compounds are derived from the calculation of the corresponding lattice energies (U_L) and the lattice enthalpies (H_L), calculated from the corresponding molecular volumes, by using the equations provided by Jenkins et al.^[28] The derived molar standard enthalpies of formation for the solid state (ΔH_m) were used to calculate the solid-state energies of formation (ΔU_m) according to Equation (3), with Δn being the change of moles of the gaseous components.^[1b]

$$\Delta U_m = \Delta H_m - \Delta n RT \quad (3)$$

The calculated standard energies of formation were used to perform predictions of the detonation parameters with the program package EXPLO5, Version 5.05.^[29] 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 together with the Cowan–Fickett equation of state for solid carbon.^[30] The calculation of the equilibrium composition of the detonation products is performed by applying a modified White, Johnson, and Dantzig free energy minimization technique. The program was designed to enable calculations of detonation parameter at the Chapman–Jouguet point. The BKW equation as implemented in the EXPLO5.05 program was used with the BKW-G set of parameters (α , β , κ , θ) given below in Equation (4), in which X_i is the mol fraction of the i th gaseous detonation product, whereas k_i is the molar co-volume of the i th gaseous detonation product.^[29,30]

$$\begin{aligned} pV/RT &= 1 + x e^{\beta x} \\ x &= (\kappa \sum X_i k_i) / [V(T + \theta)]^\alpha \\ \alpha &= 0.5, \beta = 0.096, \kappa = 17.56, \theta = 4950 \end{aligned} \quad (4)$$

The results of the detonation runs, together with the calculated energies of formation and the corresponding sensitivities, are compiled in Table 6.

As shown in Table 6, the physicochemical properties were calculated for the energetic compounds **2–5**. For the starting material 3,3'-diamino-5,5'-bis(1H-1,2,4-triazole) (DABT, **1**), only the sensitivities and the decomposition temperature was determined. Compound **1** is insensitive towards friction and impact and shows no decomposition below 450 °C.

Compound **2** as well shows a remarkably high thermal stability of 251 °C together with an insensitivity towards friction and a moderate sensitivity towards impact (10 J). The beneficial detonation parameters of DNBT with $v_{\text{det}} = 8413 \text{ ms}^{-1}$

Table 6. Physicochemical properties of compounds **2–5** in comparison to hexogen (RDX).

	DNBT (2)	DNABT (3)	DAzBT (4)	DNMBT (5)	RDX ^[n]
formula	C ₄ H ₂ N ₈ O ₄	C ₄ H ₄ N ₁₀ O ₄	C ₄ H ₂ N ₁₂	C ₆ H ₄ N ₁₀ O ₈	C ₃ H ₆ N ₆ O ₆
molecular mass [g mol ⁻¹]	226.1	256.1	218.2	344.2	222.1
impact sensitivity [J] ^[a]	10	3	3	20	7
friction sensitivity [N] ^[b]	360	108	48	360	120
ESD test [J]	0.1	0.5	0.04	0.2	–
N [%] ^[c]	49.45	54.68	77.05	40.70	37.8
Ω [%] ^[d]	–35.4	–37.5	–66.0	–27.9	–21.6
T_{decomp} [°C] ^[e]	251	194	201	121	210
ρ [g cm ⁻³] ^[f]	1.90	1.80	1.70	1.95	1.80
$\Delta_f H_m^0$ [kJ mol ⁻¹] ^[g]	285	405	971	298	70
$\Delta_f U^0$ [kJ kg ⁻¹] ^[h]	1338	1667	4532	946	417
Expos5 values					
$-\Delta_E U^0$ [kJ kg ⁻¹] ^[i]	4888	4973	4639	4977	6125
T_E [K] ^[j]	3890	3814	3670	3862	4236
p_{C-J} [kbar] ^[k]	320	300	250	341	349
$V_{\text{Det.}}$ [m s ⁻¹] ^[l]	8413	8355	7944	8499	8748
gas volume [L kg ⁻¹] ^[m]	642	670	653	641	739

[a] Bundesanstalt für Materialforschung (BAM) drop hammer. [b] BAM friction tester. [c] Nitrogen content. [d] Oxygen balance. [e] Temperature of decomposition by DSC ($\beta = 5$ °C, onset values). [f] Derived from the X-ray structure. [g] Molar enthalpy of formation. [h] Energy of formation. [i] Energy of explosion. [j] Explosion temperature. [k] Detonation pressure. [l] Detonation velocity. [m] Assuming only gaseous products. [n] Values based on reference [31] and the EXPLO5.05 database. The density values of compounds **3**, **4**, and **5** are based on the X-ray densities of the dihydrate species and additional pycnometer measurements of the anhydrous compounds.

mainly stem from the high positive heat of formation (285 kJ mol⁻¹) and the remarkably high density of 1.902 g cm⁻³ (X-ray measurement).

As it is characteristically for nitramino- and nitrimino-1,2,4-triazoles,^[8,32] the nitrimino compound **3** is very sensitive towards impact (3 J) and sensitive towards friction (108 N). As expected, the decomposition temperature (194 °C) is lower in comparison to the nitro-derivative **2**. However, the decomposition temperature was found to be repeatable higher in comparison to the value determined by Shreeve and co-workers (165 °C^[12] at a heating rate of 10 °C min⁻¹). The calculated detonation parameters are well below the commonly used explosive RDX and in the same range compared to compound **2**.

The azido compound **4** is the most sensitive compound with a friction sensitivity of 48 N, an impact sensitivity of 3 J, and a sensitivity towards electrical discharge of 40 mJ. The compound can, therefore, be classified as primary explosive and shows outstanding energetic properties for this class of energetic materials.

Compound **5** shows the best performance of all compounds with a detonation velocity of 8499 ms⁻¹, a detonation pressure of 341 kbar, and an oxygen balance of -27.9%, which is in the range of RDX. Unfortunately, the introduction of the dinitromethyl group leads to a decrease of the decomposition temperature to 121 °C in comparison to the nitro compound **2** (251 °C). 3,3'-Dinitromethyl-5,5'-bistriazole could therefore only be of interest for ionic derivatives in combination with nitrogen-rich cations, because the deprotonation increases the thermal stability as it is known for the previously described 3,3'-bis(dinitromethyl)-5,5'-azo-1*H*-1,2,4-triazole.^[19] The thermal stabilities of all compounds are illustrated in Figure 14.

Conclusion

The starting material DABT (**1**) was synthesized following a modified literature-known procedure^[14] resulting in an increase of the yield from 56 up to 70%. The optimization of the reaction conditions for the formation of 3,3'-dinitro-5,5'-bis(1*H*-1,2,4-triazole)^[13] (DNBT, **2**) and 5,5'-dinitrimino-3,3'-bis(1*H*-1,2,4-triazole)^[12] (DNABT, **3**) resulted in excellent yields and high purities. The previously unknown syntheses of 3,3'-diazido-5,5'-bis(1*H*-1,2,4-triazole) (DAzBT, **4**) as well as 3,3'-dinitromethyl-5,5'-bis(1*H*-1,2,4-triazole) (DNMBT, **5**) are presented and reveal synthetic pathways towards numerous novel energetic 1,2,4-triazole derivatives. All compounds have been fully characterized by means of vibrational and multinuclear NMR spectroscopy, mass spectrometry, and differential scanning calorimetry. Single-crystal X-ray measurements were accomplished for compounds **1**, **2**, **4**, and **5** and deliver insight into structural characteristics as well as inter- and intramolecular interactions.

Regarding the stability values and the energetic parameters, compound **2** shows the highest thermal stability of 251 °C together with an insensitivity towards friction and a

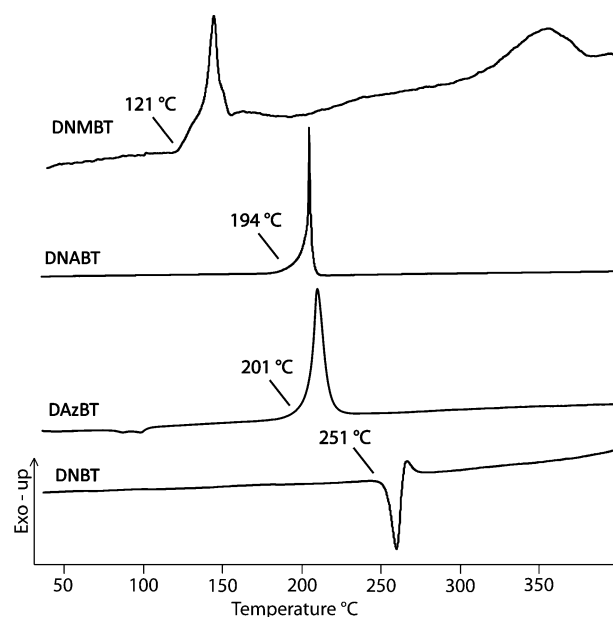


Figure 14. DSC plots of DNBT (**2**), DAzBT (**4**), DNABT (**3**), and DNMBT (**5**) in order of the decreasing decomposition temperature (onset). The DSC plots were recorded with a heating rate of 5 °C min⁻¹.

moderate sensitivity towards impact (10 J). As expected, the nitrimino compound **3** as well as the azido compound **4** are the most sensitive derivatives with an impact sensitivity of 3 J and friction sensitivities of 108 (compound **3**) and 48 N (compound **4**) and can therefore be classified as primary explosives.

The introduction of the dinitromethyl group in compound **5** leads to the best detonation parameters with a detonation velocity of 8499 ms⁻¹, a detonation pressure of 341 kbar, and an oxygen balance of -27.9%. Unfortunately, the thermal stability is decreased to 121 °C, which limits the potential applications to ionic derivatives in combination with nitrogen-rich cations. In summary, compounds **2**, **3**, and **5** are able to compete with commonly used trinitrotoluene (TNT), however, the performance data for RDX are not reached. Those three compounds can be considered as nitrogen-rich starting materials for new energetic ionic derivatives in combination with nitrogen-rich cations, as it has already been shown by Shreeve and co-workers.^[12] Because nitrogen-rich salts of energetic compounds tend to be more stable compared to the uncharged compounds and often show performance characteristics in the range of modern secondary explosives, those ionic derivatives could find application as high-nitrogen energetic materials.

Experimental Section

Caution: Although all presented bis-1,2,4-triazoles are rather stable against outer stimuli, proper safety precautions should be taken, when handling the dry materials. Especially derivatives of 3,3'-diazido-5,5'-bis(1*H*-1,2,4-triazole) (DAzBT, **4**) are energetic primary materials and tend to explode under the influence of impact or friction. Lab personnel and the equipment should be properly grounded and protective equip-

ment like earthed shoes, leather coat, Kevlar gloves, ear protection, and face shield is recommended for the handling of any energetic material.

General: All chemical reagents and solvents were obtained from Sigma-Aldrich or Acros Organics (analytical grade) and were used as supplied without further purification. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{14}\text{N}\{^1\text{H}\}$, and ^{15}N NMR spectra were recorded on a JEOL Eclipse 400 instrument in $[\text{D}_6]\text{DMSO}$ at 25 °C. The chemical shifts are given relative to tetramethylsilane (^1H , ^{13}C) or nitromethane (^{14}N , ^{15}N) as external standards and coupling constants are given in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Transmittance values are qualitatively described as “very strong” (vs), “strong” (s), “medium” (m), “weak” (w), and “very weak” (vw). Raman spectra were recorded on a Bruker RAM II spectrometer equipped with a Nd:YAG laser (200 mW) operating at $\lambda = 1064$ nm and a reflection angle of 180°. The intensities are reported as percentages of the most intense peak and are given in parentheses. Elemental analyses (CHNO) were performed with a Netzsch Simultaneous Thermal Analyzer STA 429. Melting and decomposition points were determined by differential scanning calorimetry (Linseis PT 10 DSC, calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of $5^\circ\text{C}\text{min}^{-1}$ in closed aluminum sample pans with a 1 μm hole in the lid for gas release to avoid an unsafe increase in pressure under a nitrogen flow of $20\text{ mL}\text{min}^{-1}$ with an empty identical aluminum sample pan as a reference.

For initial safety testing, the impact and friction sensitivities as well as the electrostatic sensitivities were determined. The impact sensitivity tests were carried out according to STANAG 4489,^[33] modified according to the WIWEB instruction 4-5.1.02^[34] by using a BAM^[35] drop hammer. The friction sensitivity tests were carried out according to STANAG 4487^[36] and modified according to the WIWEB instruction 4-5.1.03^[37] by using the BAM^[35] friction tester. The electrostatic sensitivity tests were accomplished according to STANAG 4490^[38] by using an electric spark testing device ESD 2010EN (OZM Research).

Crystallographic measurements: The single-crystal X-ray diffraction data of compounds **1**, **2**, **4**, and **5** were collected by using an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage = 50 kV, current = 40 mA) and a Kappa CCD detector. The data collection was undertaken by using the Crystalis CCD software,^[39] whereas the data reduction was performed with the Crystalis Red software.^[40] Crystals of compound **3c** were investigated by using a Bruker-Nonius Kappa CCD diffractometer equipped with a rotating molybdenum anode and Montel-graded multilayered X-ray optics. The structures were solved with SIR-92^[41] or SHELXS-97^[42] and refined with SHELXL-97^[43] implemented in the program package WinGX^[44] and finally checked by using PLATON.^[45] CCDC-887530 (**1**), 864398 (**2**), 887531 (**4**), and 887532 (**5**) 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.

3,3'-Diamino-5,5'-bis(1H-1,2,4-triazole) (DABT, 1): Hydrochloric acid (60 mL) was added to a stirred mixture of oxalic acid (20.0 g, 159 mmol) and aminoguanidinium bicarbonate (45.4 g, 332 mmol). The reaction was stirred at 70 °C for one hour and the precipitate was collected by filtration. The colorless solid was dissolved in water (240 mL) and alkalinized with sodium hydroxide to pH 14. The reaction mixture was heated to reflux for one hour and subsequently acidified with acetic acid to pH 4. The resulting precipitate was collected by filtration, washed with water (≈ 200 mL) and dried in air to yield **1** (18.6 g, 112 mmol, 70 %) as a colorless solid. ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 6.46$ ppm (s, 2H; NH_2); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 157.3$, 149.3 ppm; IR: $\tilde{\nu} = 3325$ (m), 3116 (m), 2863 (m), 2784 (m), 1706 (s), 1668 (s), 1654 (s), 1618 (m), 1606 (m), 1484 (m), 1457 (m), 1267 (m), 1104 (vs), 1061 (s), 987 (w), 956 (w), 769 (w), 721 cm^{-1} (s); Raman (200 mW): $\tilde{\nu}$ (rel. intensity) = 1636 (62), 1614 (100), 1591 (67), 1575 (57), 1495 (13), 1439 (21), 1432 (21), 1361 (9), 1152 (24), 1143 (23), 1059 (23), 1042 (34), 1022 (22), 980 (27), 772 (18), 554 (7), 413 (11), 328 (12), 249 cm^{-1} (16); MS (DEI+): m/z : 166.1 $[\text{C}_4\text{H}_7\text{N}_8]^+$; elemental analysis (%) calcd for $\text{C}_4\text{H}_6\text{N}_{10}$: C 28.92, H 3.64, N 67.44; found: C 28.72, H 3.58, N 66.11.

3,3'-Dinitro-5,5'-bis(1H-1,2,4-triazole) (DNBT, 2): A solution of **1** (11.9 g, 72 mmol) in 20 % sulfuric acid (140 mL) was added dropwise to a solution of sodium nitrite (98.8 g, 1.4 mol, 10 equiv) in water (140 mL) at 40 °C. The mixture was stirred at 50 °C for one hour. After cooling down to room temperature the mixture was acidified with sulfuric acid (20 %) until no evolution of nitrogen dioxide could be observed. The precipitate was collected by filtration and dissolved in boiling water. The hot solution was filtrated and allowed to cool to room temperature. Collection of the pale green precipitate affords **2**·2H₂O (15.5 g, 59 mmol, 82 %) as a crystalline solid. ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 9.68$ ppm (s, 2H; $\text{H}_{\text{Triazole}}$); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 162.7$, 145.6 ppm; ^{14}N NMR (28.9 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = -26$ ppm ($-\text{NO}_2$); ^{15}N NMR (40.5 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = -27.8$ (N4), -88.8 (N2), -141.7 (N3), -156.1 ppm (N1); IR: $\tilde{\nu} = 3599$ (m), 3499 (m), 3052 (w), 2849 (w), 2747 (w), 2670 (m), 2621 (m), 2574 (m), 2530 (m), 2488 (m), 2419 (m), 1844 (w), 1609 (m), 1532 (vs), 1466 (w), 1416 (vs), 1314 (vs), 1245 (m), 1183 (m), 1024 (m), 953 (s), 837 (s), 690 (w), 690 cm^{-1} (w); Raman (200 mW): $\tilde{\nu}$ (rel. intensity) = 3192 (3), 1641 (100), 1546 (28), 1519 (5), 1485 (75), 1468 (43), 1458 (95), 1413 (18), 1393 (97), 1365 (6), 1362 (6), 1345 (13), 1325 (27), 1306 (35), 1172 (58), 1062 (67), 1015 (31), 855 (4), 774 (8), 744 (5), 619 (4), 511 (4), 452 (5), 452 (5), 399 (9), 297 (9), 203 cm^{-1} (6); MS (FAB-): m/z : 225.1 $[\text{C}_4\text{H}_6\text{N}_8\text{O}_4]^-$; elemental analysis (%) calcd for $\text{C}_4\text{H}_2\text{N}_8\text{O}_4$: C 21.25, H 0.89, N 49.56; found: C 21.44, H 0.95, N 49.19; sensitivities (grain size < 100 μm): friction = 360 N, impact = 10 J, ESD = 0.1 J; DSC (onset, $5^\circ\text{C}\text{min}^{-1}$): $T_{\text{decomp}} = 251^\circ\text{C}$.

3,3'-Dinitrimino-5,5'-bis(1H-1,2,4-triazole) (DNABT, 3): Compound **3** was synthesized according to a modified literature-known procedure.^[12] Nitric acid (100 %, 3.0 mL) was added slowly to a solution of **1** (1.0 g, 6.0 mmol) in concentrated sulfuric acid (9.0 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred for one hour. The clear solution was poured on ice, the precipitate was collected by filtration and recrystallized from boiling water to yield **3**·2H₂O (1.35 g, 4.6 mmol, 77 %) as yellow crystalline solid. ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 5.52$ ppm (s, 2H; $\text{H}_{\text{Triazole}}$); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 153.1$, 142.1 ppm; ^{14}N NMR (28.9 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = -21$ ppm ($-\text{NO}_2$); IR: $\tilde{\nu} = 3165$ (m), 3154 (m), 1565 (vs), 1508 (s), 1463 (s), 1446 (s), 1380 (m), 1298 (vs), 1229 (vs), 1140 (m), 1085 (m), 1054 (s), 989 (m), 947 (s), 849 (m), 778 (s), 766 (s), 751 (s), 708 cm^{-1} (vs); Raman (200 mW): $\tilde{\nu}$ (rel. intensity) = 1655 (100), 1592 (60), 1568 (81), 1527 (14), 1288 (2), 1224 (7), 1123 (26), 1072 (2), 1019 (25), 992 (35), 851 (11), 764 (26), 691 (2), 558 (6), 520 (2), 440 (2), 417 (3), 407 (3), 226 cm^{-1} (6); elemental analysis (%) calcd for $\text{C}_4\text{H}_2\text{N}_8\text{O}_4$: C 16.44, H 2.76, N 47.94; found: C 16.73, H 2.69, N 47.73; sensitivities (water-free compound, grain size < 100 μm): friction = 108 N, impact = 3 J, ESD = 0.5 J; DSC (onset, $5^\circ\text{C}\text{min}^{-1}$): $T_{\text{decomp}} = 194^\circ\text{C}$.

3,3'-Diazido-5,5'-bis(1H-1,2,4-triazole) (DAzBT, 4): A solution of sodium nitrite (0.37 g, 5.4 mol, 3 equiv) in water (2.0 mL) was added dropwise to a suspension of **1** (0.3 g, 1.8 mmol) in 20 % sulfuric acid (20 mL) at 0 °C. The mixture was allowed to warm to room temperature and subsequently stirred at 40 °C for one hour. After cooling down to room temperature, a solution of sodium azide (5.9 g, 9.0 mmol, 5 equiv) in water (2.0 mL) was added dropwise. (DANGER: EVOLUTION OF HN_3 !). The suspension was stirred over night at room temperature to remove the excess of sodium azide and extracted with ethyl acetate (3×20 mL). The solvent was evaporated and the resulting solid was recrystallized from water. Collection of the colorless precipitate affords **4**·2H₂O (0.25 g, 1.0 mmol, 56 %) as crystalline needles. ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 14.86$ ppm (s, 2H; $\text{H}_{\text{Triazole}}$); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = 157.7$, 145.9 ppm ($\text{C}-\text{N}_3$); ^{14}N NMR (28.9 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = -145$ ppm ($-\text{N}_3$); ^{15}N NMR (40.5 MHz, $[\text{D}_6]\text{DMSO}$): $\delta = -115.3$ (N2), -141.9 (N3), -146.2 (N5), -153.0 (N6), -173.2 (N1), -295.2 ppm (N4); IR: $\tilde{\nu} = 3141$ (s), 3042 (s), 2876 (s), 2710 (s), 2655 (s), 2630 (m), 2571 (m), 2435 (m), 2362 (m), 2240 (m), 2228 (m), 2156 (vs), 2138 (vs), 2137 (vs), 1541 (vs), 1518 (s), 1483 (vs), 1457 (s), 1420 (vs), 1418 (vs), 1391 (s), 1333 (s), 1299 (m), 1299 (m), 1275 (s), 1241 (m), 1218 (m), 1188 (s), 1142 (s), 1122 (s), 1033 (vs), 1014 (m), 980 (vs), 958 (m), 846 (m), 799 (s), 780 (m), 729 (s), 714 (m), 661 (m), 532 cm^{-1} (m); Raman (200 mW): $\tilde{\nu}$ (rel. intensity) = 2171 (14), 2142 (17), 1620 (56), 1605 (100), 1551 (17), 1551 (16), 1549 (17), 1548 (17), 1547 (17), 1515 (44), 1503 (24), 1501 (26), 1500 (27), 1423

(16), 1422 (16), 1421 (15), 1399 (15), 1335 (20), 1298 (5), 1228 (10), 1168 (6), 1148 (17), 1147 (17), 1147 (17), 1066 (16), 1065 (17), 1039 (22), 1038 (22), 1024 (31), 817 (7), 705 (3), 629 (3), 577 (9), 436 (6), 423 (7), 397 (9), 380 (21), 326 (24), 262 (9), 247 cm⁻¹ (16); MS: (DEI+): *m/z*: 218.1 [C₈H₈N₁₂]⁺; elemental analysis (%) calcd for C₈H₈N₁₂O₂: C 18.90, H 2.38, N 66.13; found: C 19.41, H 2.14, N 65.75; sensitivities (grain size < 100 μm): friction = 48 N, impact = 3 J, ESD = 0.04 J; DSC (onset, 5 °C min⁻¹): *T*_{decomp} = 202 °C.

3,3'-Dinitromethyl-5,5'-bis(1*H*-1,2,4-triazole) (DNMBT, 5): The precursors were synthesized according to references [16a] and [16b]. 3,3'-Diethyl-acetate-5,5'-bis(1*H*-1,2,4-triazole) (0.5 g, 1.62 mmol) was dissolved in concentrated sulfuric acid (6 mL) and cooled to 0 °C. Subsequently, concentrated nitric acid (4 mL) and 60% oleum (SO₃, 2 mL) were added slowly, the mixture was allowed to warm to room temperature and stirred at for 2 h. The mixture was poured on ice, alkalinized with sodium hydroxide, and stirred until all solids were dissolved. The solution was acidified with concentrated sulfuric acid until pH 1. The precipitate was isolated by filtration and recrystallized from water. Compound **5** was obtained as a yellow solid (0.27 g, 0.79 mmol, 49%). ¹H NMR (400 MHz, [D₆]DMSO, 60 °C): δ = 8.94 (s, 2H; NH), 3.91 ppm (s, 2H; CH); ¹³C NMR (100 MHz, [D₆]DMSO, 60 °C): δ = 151.1, 149.3, 106.5 ppm (C-C); ¹⁴N NMR (28.9 MHz, [D₆]DMSO, 60 °C): δ = -23 ppm (NO₂); IR: $\tilde{\nu}$ = 3544 (m), 3467 (m), 3319 (m), 2360 (vw), 2094 (vw), 1643 (w), 1511 (s), 1484 (m), 1467 (m), 1436 (s), 1388 (m), 1364 (m), 1300 (m), 1286 (m), 1271 (s), 1200 (vs), 1146 (m), 1128 (s), 1085 (vs), 987 (vs), 976 (vs), 832 (s), 779 (w), 779 (w), 745 (s), 722 (s), 666 cm⁻¹ (m); Raman (200 mW): $\tilde{\nu}$ (rel. intensity) = 1646 (78), 1575 (75), 1559 (100), 1517 (20), 1490 (4), 1473 (3), 1419 (3), 1403 (10), 1341 (55), 1320 (30), 1302 (24), 1226 (59), 1213 (43), 1163 (15), 1101 (4), 1025 (4), 967 (46), 834 (16), 783 (10), 753 (2), 699 (3), 475 (7), 435 (4), 435 (4), 379 (2), 326 (3), 209 cm⁻¹ (4); MS: (FAB-): *m/z*: 343 [M-H]⁻; sensitivities: (grain size < 100 μm): friction = 360 N, impact > 20 J, ESD = 0.2 J; DSC (onset, 5 °C min⁻¹): *T*_{decomp} = 130 °C.

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