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

Alexander A. Dippold and Thomas M. Kläpötke*[a]

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 calculated 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.[11,12] 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[13] 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),[14] 2-azido-5-nitrimino-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] Shreve 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, nitrimino, 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(1H-1,2,4-triazole) (DABT, 1), was first synthesized with a moderate yield of 56% by Shreve and Charlesworth.\textsuperscript{[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).

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 sodium nitrite.\textsuperscript{[15]} The formation of 3,3'-dinitro-5,5'-bis(1H-1,2,4-triazole) (DABT, 2) was first mentioned by Russian scientists with a low yield of 31%.\textsuperscript{[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,\textsuperscript{[16]} by using 1-amino-2-nitroguanidine with oxalic acid,\textsuperscript{[10b]} or by using 1-methyl-2-nitro-1-nitrosoguanidine and oxalic acid dihydrazide.\textsuperscript{[10c]} We followed the most efficient method first mentioned by Astachov et al.,\textsuperscript{[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 recrystallization from water, compound 4 can be isolated as the insensitive dihydrate.

The synthesis of the dinitromethyl-bis1,2,4-triazole (DNMBT) was achieved through a completely different synthetic pathway (Scheme 3). The chlorination of sodium cyanide in ethanol and subsequent reaction with hydrazine leads to the formation of the oxalimidohydrazide.\textsuperscript{[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. The nitration was optimized by using concentrated sulfuric and nitric acid in a ratio of 3:1 resulting in a yield of 77%.

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.\textsuperscript{[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.\textsuperscript{[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).\textsuperscript{[18]}
Due to the very low solubility in any solvent, crystals of 5,5'-diamino-3,3'-bis-(1H-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) \( \text{Å}^3 \) and two molecular moieties in the unit cell, the crystal structure together with the labeling scheme is displayed in Figure 1.

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\(^\circ\). The angles surrounding the N4 atom are larger than expected for a sp\(^3\) atom in the range of 116(1) (C2-N4-H5b) to 118(1) (C2-N4-H5a) to 118(1)\(^\circ\). The formula unit of compound 1 consists of 4 molecules in the unit cell, the calculated density at 173 K is 1.902 g cm\(^{-3}\) and the D···A distance of 2.890(2) and 3.055(2)\(^\circ\) (Figure 2).

The layers are connected by two strong network of hydrogen bonds in the bc plane. Thermal ellipsoids are set to 50\% probability. Symmetry operators: \( i \) \(-x, y, 2\)\(z\); \( ii \) \(3/2-x, 1/2+y, 1/2-z\); \( iii \) \(2-x, 1/2+y, 1/2-z\).

Table 1. Hydrogen bonds present in compound 1.

<table>
<thead>
<tr>
<th>D···H···A</th>
<th>(d(D···H))</th>
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<tr>
<td>N1···H1···N3((i))</td>
<td>0.881(18)</td>
<td>2.017(19)</td>
<td>2.890(2)</td>
<td>170.8(17)</td>
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<td>N4···H5a···N2((ii))</td>
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All hydrogen-bond lengths lie well within the sum of the van der Waals radii \(r_D(N)=3.20\text{ Å}\),\(^{18a}\) 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-(1H-1,2,4-triazole) (2) crystallizes in the monoclinic space group \( P2_1/n \) with a cell volume of 394.73(8) \( \text{Å}^3 \) 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\(^{-3}\)). Again, the molecule shows a completely planar assembly with a torsion angle of the nitro group towards the triazole ring of 2.9(2)\(^\circ\).

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In contrast to compound 1, the structure is build up by only one individual hydrogen bond N1···H1···O1. The D···H···A angle is close to 180\(^\circ\) with 171.9(2)\(^\circ\) and the D···A length is shorter than the sum of the van der Waals radii \(r_D(O)+r_D(N)=3.07\text{ Å}\)\(^{18a}\) with 2.902(2)\(^\text{Å}\) (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\(^\circ\). The layers are stacked above each other with a layer distance of \(d=2.96\text{ Å}\). The layers are connected by two short contacts, N2···N4(\(ii\)) and C1···O1(\(iii\)) (symmetry operators: \( i \) \(-x, -1/2+y, 1/2-z\); \( iii \) \(3/2-x, -1/2+y, 1/2-z\)). Both contacts are shorter than the sum of the van der Waals radii\(^{18d}\) with N2···N4 being the shortest (2.922(2)\(^\text{Å}\) and C1···O1 being the longest (3.051(2)\(^\text{Å}\) 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 \( P1 \) with a cell volume of 256.34(9) \( \text{Å}^3 \) 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 to the oxygen atom.
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)°. 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···O1(i). As shown in Table 2, the D–H···A angle is close to 180° with 174(2)° and the D···A length is considerably shorter than the sum of the van der Waals radii \( r_s(O) + r_s(N) = 3.07 \text{ Å} \).\(^{[19a]}\)

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–N6(i) with a distance of 3.067(2) Å (symmetry code: \( \text{i}) 1-x, -y, 1-z \). \( 3,3’\)-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 comparison 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-1H-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=\( \equiv \)C double bond (1.440(2) Å).\(^{[18a]}\)

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

\[ \text{Table 2. Hydrogen bonds present in compound 4.} \]

<table>
<thead>
<tr>
<th>D–H···A</th>
<th>( d(D–H) ) [Å]</th>
<th>( d(H···A) ) [Å]</th>
<th>( d(D–H···A) ) [Å]</th>
<th>( \angle(D–H···A) ) [°]</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1–H1···O1(i)</td>
<td>0.98(2)</td>
<td>1.70(2)</td>
<td>2.676(2)</td>
<td>174(2)</td>
</tr>
<tr>
<td>O1–H1b···N2(ii)</td>
<td>0.92(2)</td>
<td>1.98(2)</td>
<td>2.892(2)</td>
<td>174(2)</td>
</tr>
</tbody>
</table>

\[ \text{[a] Symmetry operators: i) } x, 1+y, z; \text{ ii) } 2−x, 1−y, −z. \]

\[ \text{Figure 5. Crystal structure of compound 4. Thermal ellipsoids are set to } 50\% \text{ probability. Symmetry operators: i) } 1−x, 1−y, 2−z; \text{ ii) } −x, −y, 2−z; \text{ iii) } x, −1+y, 1+z. \]

\[ \text{Figure 6. Hydrogen-bonding scheme in the crystal structure of compound 4. Thermal ellipsoids are set to } 50\% \text{ probability. Symmetry operators: i) } 1−x, 1−y, 1−z; \text{ ii) } −x, −y, 2−z; \text{ iii) } x, −1+y, 1+z. \]
Thermal ellipsoids are set to 50% probability. Symmetry operators: i) 1/2 + x, 1/2 – y, –z.

The planar assembly is encouraged by the formation of two intramolecular hydrogen bonds, that is, N1–H1⋯O1 and N3–H3⋯O3. Both interactions show rather small D–H⋯A angles of 117.9(16) and 113(2)°, respectively, but considerably short D–H⋯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.

<table>
<thead>
<tr>
<th>D–H⋯A</th>
<th>d(D–H)</th>
<th>d(H⋯A)</th>
<th>d(D–H⋯A)</th>
<th>χ(D–H⋯A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1–H1⋯O1</td>
<td>0.79(2)</td>
<td>2.090(18)</td>
<td>2.558(2)</td>
<td>117.9(16)</td>
</tr>
<tr>
<td>N1–H1⋯O2(ii)</td>
<td>0.79(2)</td>
<td>2.11(2)</td>
<td>2.839(2)</td>
<td>152.6(18)</td>
</tr>
<tr>
<td>N3–H3⋯O3</td>
<td>0.92(3)</td>
<td>2.10(3)</td>
<td>2.603(2)</td>
<td>113(2)</td>
</tr>
<tr>
<td>N3–H3⋯O5(iii)</td>
<td>0.92(3)</td>
<td>1.83(3)</td>
<td>2.711(2)</td>
<td>160(2)</td>
</tr>
<tr>
<td>O5–H5b⋯O3(iii)</td>
<td>0.80(3)</td>
<td>2.09(3)</td>
<td>2.883(2)</td>
<td>173(3)</td>
</tr>
</tbody>
</table>

[a] Symmetry operators: i) 1/2 + x, 1/2 – y, –z; ii) 1–x, 1–y, –z; iii) –x, –1/2 + y, 1/2 – z; iv) –x, 1/2 + y, 1/2 – 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 involved as donor atoms in further hydrogen bonds, that is, N1–H1⋯O2 and N3–H3⋯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 \( \tilde{\nu} = 1579 \text{ cm}^{-1} \). 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 nitrimino moiety of compound 3 can be observed at \( \tilde{\nu} = 1565 (\nu_{\text{sym}}) \) and 1298 cm\(^{-1}\) (\( \nu_{\text{asym}} \)). 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 azido 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 \(^1\)H, \(^13\)C and \(^14\)N NMR spectroscopy. Additional \(^13\)C\{\(^1\)H\} and \(^1\)H 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 \(^14\)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
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 $^{14}$N{1H} 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 [D$_6$]DMSO.

<table>
<thead>
<tr>
<th></th>
<th>$^{13}$C{1H}</th>
<th>$^{14}$N{1H}</th>
<th>$^1$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>157.3, 149.3</td>
<td>–</td>
<td>6.46</td>
</tr>
<tr>
<td>2</td>
<td>162.7, 145.6</td>
<td>–</td>
<td>9.68</td>
</tr>
<tr>
<td>3</td>
<td>153.1, 142.1</td>
<td>–</td>
<td>5.19</td>
</tr>
<tr>
<td>4</td>
<td>157.7, 145.9</td>
<td>–</td>
<td>14.86</td>
</tr>
<tr>
<td>5</td>
<td>151.1, 149.3$^a$</td>
<td>–</td>
<td>3.90</td>
</tr>
</tbody>
</table>

$^a$Recorded at 60°C. C(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 $^{13}$C{1H} and $^1$H 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 atom (C3) is the thermodynamically most stable configuration. However, the signals of both isomers could be observed in both the $^{13}$C{1H} and $^1$H 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 $^1$H NMR spectra at different temperatures.

![1H NMR](image)

Figure 10. Comparison of $^1$H NMR spectra of DNMBT (5) at room temperature and at elevated temperatures in [D$_6$]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 $\delta = 8.70$ (N$_\text{triazole}$-H) and...
3.87 ppm (C sp3/C0H). Owing to the fact that compound 5 is very acidic and was used as dihydrate (as obtained after recrystallisation), the constant signal at δ = 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 δ = 8.60–8.70 ppm.

As shown in Figure 11, the signals of the carbon atoms of the 1,2,4-triazole in the 13C{1H} NMR spectrum at room temperature interfere with each other resulting in a broad multiplet at δ = 150.0 ppm. The sp2 carbon atom of isomer 5a (C3) appears at δ = 124.3 ppm, the sp3 carbon atom of isomer 5b (C3’) could be found at δ = 106.5 ppm. For comparison, similar sp2 carbon atoms appear at δ = 124.9 (3,3’-bis(dinitromethylene)-5,5’-azo-1H-1,2,4-triazole) and at 121.5 ppm (5-dinitromethylene-4,5-dihydro-1H-tetrazole).

At 60°C, only the signals of isomer 5b could be observed. The triazole carbon atoms now show two well-resolved resonances at δ = 151.1 and 149.3 ppm, the sp2 carbon atom C3 can be found at the identical chemical shift of δ = 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 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 assembly 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 sp3 carbon atoms in the similar bis(dinitromethylene)-5,5’-azo-1H-1,2,4-triazole.

Due to insufficient solubility, 15N NMR spectra could only be obtained for compounds 2 and 4. Four well-resolved resonances are observed in the 15N NMR spectrum for the four nitrogen atoms of the dinitro compound 2 (Figure 13). The signals were assigned by comparison to literature values. 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 Δδ = 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. Because very detailed descriptions of the calculation process have been published earlier and can be found in specialized books, 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 parameterized version of the original CBS-4 computational method and also includes additional empirical calculations. The enthalpies of formation for the gas-phase species were computed according to the atomization energy method, by using NIST values as standardized values for the atoms standard heats of formation (\( \Delta H^0_{\text{f}} \)) according to Equation (1).

\[
\Delta H^0_{\text{f}}(\text{g, Molecule 288}) = H_{\text{(Molecule)}}, \text{gas} - \sum H_{\text{(Atoms)}} + \sum \Delta H^0_{\text{(Atoms, NIST)}}, \text{gas}
\]

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

\[
\Delta H_m = \Delta H^0_{\text{f}}(\text{g, Molecule 288}) - \Delta H_{\text{sub}}
\]

The solid-state enthalpies of formation for the ionic compounds are derived from the calculation of the corresponding lattice energies \( (U_i) \) and the lattice enthalpies \( (H_i) \), calculated from the corresponding molecular volumes, by using the equations provided by Jenkins et al. The derived molar standard enthalpies of formation for the solid state \( (\Delta H_m) \) were used to calculate the solid-state energies of formation \( (\Delta U_m) \) according to Equation (3), with \( \Delta n \) being the change of moles of the gaseous components.

\[
\Delta U_m = \Delta H_m - \Delta n RT
\]

The calculated standard energies of formation were used to perform predictions of the detonation parameters with the program package EXPLO5, Version 5.05. 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. 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 \( (\alpha, \beta, \kappa, \theta) \) given below in Equation (4), in which \( X_i \) is the mol fraction of the ith gaseous detonation product, whereas \( k_i \) is the molar co-volume of the ith gaseous detonation product.

\[
pV/RT = 1 + x \alpha e^\beta \]

\[
x = (\kappa \Sigma X_i k_i)/[V(\theta + 1)]
\]

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 3,5-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 with an insensitivity towards friction and a moderate sensitivity towards impact (10 J). The beneficial detonation parameters of DNBTT with \( v_{\text{det}} = 8413 \text{ m s}^{-1} \) are based on the X-ray densities of the dihydrate species and additional pycnometer measurements of the anhydrous compounds.

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>DNBTT (2)</th>
<th>DNABT (3)</th>
<th>DAABT (4)</th>
<th>DMBBT (5)</th>
<th>RDX*</th>
</tr>
</thead>
<tbody>
<tr>
<td>formula</td>
<td>C(_4)H(_8)N(_8)O(_4)</td>
<td>C(_4)H(_8)N(_9)O(_5)</td>
<td>C(_4)H(_8)N(_7)</td>
<td>C(_4)H(_8)N(_8)O(_4)</td>
<td>C(_4)H(_8)N(_9)O(_5)</td>
</tr>
<tr>
<td>molecular mass [g mol(^{-1})]</td>
<td>226.1</td>
<td>256.1</td>
<td>218.2</td>
<td>344.2</td>
<td>222.1</td>
</tr>
<tr>
<td>impact sensitivity [J](^{[a]})</td>
<td>10</td>
<td>3</td>
<td>3</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>friction sensitivity [N](^{[b]})</td>
<td>360</td>
<td>108</td>
<td>48</td>
<td>360</td>
<td>120</td>
</tr>
<tr>
<td>ESD test [J]</td>
<td>0.1</td>
<td>0.5</td>
<td>0.04</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td>N [%](^{[c]})</td>
<td>49.45</td>
<td>54.68</td>
<td>77.05</td>
<td>40.70</td>
<td>37.8</td>
</tr>
<tr>
<td>Ω [%](^{[d]})</td>
<td>–35.4</td>
<td>–37.5</td>
<td>–66.0</td>
<td>–27.9</td>
<td>–21.6</td>
</tr>
<tr>
<td>T(_{\text{decomp}}) [°C](^{[e]})</td>
<td>251</td>
<td>194</td>
<td>201</td>
<td>121</td>
<td>210</td>
</tr>
<tr>
<td>p [g cm(^{-3})]</td>
<td>1.90</td>
<td>1.80</td>
<td>1.70</td>
<td>1.95</td>
<td>1.80</td>
</tr>
<tr>
<td>ΔH(_m) [kJ mol(^{-1})]</td>
<td>265</td>
<td>405</td>
<td>971</td>
<td>298</td>
<td>70</td>
</tr>
<tr>
<td>ΔV(_{\text{exp}}) [kJ kg(^{-1})]</td>
<td>1338</td>
<td>1667</td>
<td>4532</td>
<td>946</td>
<td>417</td>
</tr>
</tbody>
</table>

\( \text{[a]}\) Bundesanstalt für Materialforschung (BAM) drop hammer. \( \text{[b]}\) BAM friction tester. \( \text{[c]}\) Nitrogen content. \( \text{[d]}\) Oxygen balance. \( \text{[e]}\) Temperature of decomposition by DSC (\( \beta = 5°C, \text{ onset values} \)). \( \text{[f]}\) Derived from the X-ray structure. \( \text{[g]}\) Molar enthalpy of formation. \( \text{[h]}\) Energy of formation. \( \text{[i]}\) Energy of explosion. \( \text{[j]}\) Explosion temperature. \( \text{[k]}\) Detonation pressure. \( \text{[l]}\) Detonation velocity. \( \text{[m]}\) Assuming only gaseous products. \( \text{[n]}\) Values based on reference [11] 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-1H-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(1H-1,2,4-triazole)\(^{[33]}\) (DNBT, 2) and 5,5’-dinitrimino-3,3’-bis(1H-1,2,4-triazole)\(^{[32]}\) (DNABT, 3) resulted in excellent yields and high purities. The previously unknown syntheses of 3,3’-diazido-5,5’-bis(1H-1,2,4-triazole) (DAzBT, 4) as well as 3,3’-dinitromethyl-5,5’-bis(1H-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 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(1H-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-
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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 (98.9 g, 1.4 mol, 10 equiv) in water (140 mL) at 0°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% v/v) 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-(H2O) (15.5 g, 59 mmol, 82%) as a crystalline solid.

1H NMR (400 MHz, CD3SOCD2): δ = 6.98 ppm (s, 2H; H-2m); 13C NMR (100 MHz, CD3SOCD2): δ = 162.7, 145.6 ppm; 12N NMR (28.9 MHz, CD3SOCD2): δ = −26 ppm (NO2-); 15N NMR (40.5 MHz, CD3SOCD2): δ = −27.94 (N1), −88.8 (N2), −141.7 (N3), −156.1 ppm (N1); IR: v = 2359 (mm9), 3499 (mm6), 3052 (wm8), 2948 (mm7), 2670 (nm1), 2621 (nm2), 2574 (nm3), 2530 (mm4), 2488 (nm5), 2419 (mm4), 1844 (mm6), 1552 (vs6), 1466 (ww6), 1416 (vs6), 1314 (vs7), 1245 (mm7), 1183 (mm6), 1024 (mm5), 953 (sm7), 849 (wm5), 690 (mm5), 690 cm−1 (s); MS (FAB−): m/z = 225.1 [C4H7N8O4]; elemental analysis (%) calcd for C4H6N10: C 28.92, H 3.64, N 66.47; found: C 28.72, H 3.58, N 66.11.

3.3-Dinitrimino-5,5′-bis(1H-1,2,4-triazole) (DNABT, 3): Compound 3 was synthesized according to a modified literature-known procedure.10 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-(H2O) (3.5 g, 4.6 mmol, 77%) as yellow crystalline solid.

1H NMR (400 MHz, CD3SOCD2): δ = 5.52 ppm (s, 2H; H-2m); 13C NMR (100 MHz, CD3SOCD2): δ = 153.1, 142.1 ppm; 14N NMR (28.9 MHz, CD3SOCD2): δ = −21 ppm (NO2-); IR: v = 2315 (mm9), 3154 (mm9), 1565 (vs6), 1508 (vs8), 1463 (mm6), 1446 (mm6), 1360 (mm8), 1292 (mm8), 1140 (mm6), 1085 (mm8), 1054 (mm6), 989 (mm6), 947 (mm8), 849 (mm7), 778 (mm6), 766 (sm6), 751 (sm6), 708 cm−1 (s); MS (FAB−): m/z = 225.1 [C4H7N8O4]; elemental analysis (%) calcd for CHN3O6: C 26.42, H 3.99, N 49.19; sensitivities (grain size < 100 μm): friction = 360 N, impact = 10 J, ESD = 0.1 J; DSC (onset, 5°C min−1): Tdecomp = 194°C.

3.3-Triazido-5,5′-bis(1H-1,2,4-triazole) (DiazBT, 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 50°C for one hour. After cooling down to room temperature, a solution of sodium azide (5.9 g, 90.0 mmol, 5 equiv) in water (2.0 mL) was added dropwise. (DANGER: EVOLUTION OF NH3.) The suspension was stirred overnight at room temperature to remove the excess of sodium azide and extracted with ethyl acetate (3x20 mL). The solvent was evaporated and the resulting solid was recrystallized from water. Collection of the colorless precipitate affords 4-(H2O) (0.25 g, 1.0 mmol, 56%) as crystalline needles.

1H NMR (400 MHz, CD3SOCD2): δ = 14.86 ppm (s, 2H; H-2m); 13C NMR (100 MHz, CD3SOCD2): δ = 157.7, 145.9 ppm (C=N); 12N NMR (28.9 MHz, CD3SOCD2): δ = −145 ppm (NO2-); 15N NMR (40.5 MHz, CD3SOCD2): δ = −115.33 (N2), −141.9 (N3), −154.6 (N4), −153.0 (N5), −173.2 (N6), −295.2 ppm (N7); IR: v = 3141 (sm3), 3042 (sm3), 2870 (sm3), 2710 (sm5), 2635 (sm8), 2571 (sm5), 2435 (sm5), 2262 (sm5), 2226 (sm2), 2163 (sm6), 2136 (sm6), 2137 (sm8), 1541 (vs17), 1483 (vs17), 1457 (sm6), 1420 (sm6), 1418 (vs17), 1391 (sm5), 1333 (sm5), 1299 (sm9), 1275 (sm3), 1241 (sm5), 1218 (sm6), 1189 (sm5), 1142 (sm5), 1033 (sm6), 1014 (sm6), 980 (sm8), 958 (sm6), 846 (mm7), 789 (sm8), 728 (sm3), 714 (sm6), 651 (sm2) cm−1; MS (FAB−): m/z = 2171 (14), 2142 (17), 1620 (50), 1650 (100), 1551 (17), 1551 (16), 1549 (17), 1548 (17), 1547 (17), 1515 (44), 1503 (24), 1501 (26), 1500 (27), 1423...


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[16751]
(16), 1422 (16), 1421 (15), 1399 (15), 1335 (20), 1298 (5), 1288 (10), 1168 (6), 1148 (17), 1147 (17), 1147 (16), 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 (11), 326 (24), 262 (9), 247 (3) cm⁻¹ (16); MS: (DEI⁺); m/z: 218.13 \left(\text{[C}_4\text{H}_2\text{N}_4\text{O}_2]^+\right); \text{elemental analysis } (\%): \text{calcd for } \text{C}_4\text{H}_6\text{N}_12\text{O}_2: \text{C } 18.90, \text{H } 2.38, \text{N } 66.13; \text{found: C } 19.41, \text{H } 2.14, \text{N } 65.75; \text{sensitivities (grain size < 100 \mu m): friction = 48 N, impact = 3J, ESD = 0.04 J; DSC (onset, 5°C min⁻¹): } T_{\text{dsc}} = 102°C.

3,3'-Dinitromethyl-5,5'-bis(1,2,4-triazole) (DNMBT, 5). The precursors were synthesized according to references [16a] and [16b]. 3,3'-Diethyl-acetate-5,5'-dinitromethyl derivatives (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); 15N 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: ν = 3544 (m), 3467 (m), 3340 (m), 3283 (m), 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 ppm (14); MS: (FAB-); M+c= m/z: 343 [M-H⁻]; sensitivities (grain size < 100 \mu m): friction = 360 N, impact > 20 J, ESD = 0.2 J; DSC (onset, 5°C min⁻¹): T_{\text{dsc}} = 130°C.

Acknowledgements

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[29] EXPLO5.05 program, M. Suceska, Zagreb, Croatia, 2010.


[34] WIWEB-Standardarbeitsanweisung 4.5.1.02, Ermittlung der Explosionsfähigkeit, hier: der Schlagempfindlichkeit mit dem Fallhammer, 2002.


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