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Nitration Pattern of Energetic 3,6-Diamino-1, 2, 4, 5-tetrazine Derivatives Containing Azole Functional Groups

A. Aizikovich, A. Shlomovich, A. Cohen and M. Gozin*

One of the successful strategies for the design of promising new energetic materials is the incorporation of both fuel and oxidizer moieties into the same molecule. Therefore, during recent years, synthesis of various nitro-azole derivatives, as compounds with a more balanced oxygen content, became very popular. In the frame of this effort, we studied nitration of \( N_3N^2\text{-bis(1H-tetrazol-5-yl)\text{-1,2,4,5-tetrazine-3,6-diamine (BTATz; 5) and its alkylated derivative N}_3N^2\text{-bis(2-methyl-2H-tetrazol-5-yl)\text{-1,2,4,5-tetrazine-3,6-diamine 12,}} \) using a \(^{15}\text{N}\)-labeled nitration agent and monitoring and analyzing products of these reactions by \(^{15}\text{N}\) NMR. It was shown that the nitration of both compounds takes place only on the exocyclic ("bridging") secondary amine groups. Possible tetranitro derivative isomers \( N_3N_2\text{(1,2,4,5-tetrazine-3,6-diy)bis(N-(1-nitro-1H-tetrazol-5-yl)nitramide) 6 and N}_3N_2\text{(1,2,4,5-tetrazine-3,6-diy)bis(N-(2-nitro-2H-tetrazol-5-yl)nitramide) 7, both of which have OB = 0% and calculated VODs of 9,790 and 9,903 m/sec, respectively, could not be observed in the reaction mixesures, during the in situ \(^{15}\text{N}\) NMR monitoring of nitration of 5, using \(^{15}\text{N}\)-labeled nitrating agents. Following a similar strategy, a new analog of BTATz – \( N_3N^2\text{-Bis(1H-1,2,4-triazol-5-yl)\text{-1,2,4,5-tetrazine-3,6-diamine 15 obtained and its nitration was studied. The reaction of 15 with a HNO}_3\text{Ac}_2\text{O nitration mixture resulted in the formation of a new N}_3N^2\text{-bis(3-nitro-1H-1,2,4-triazol-5-yl)\text{-1,2,4,5-tetrazine-3,6-diamine derivative 20 in a moderate yield. Structures and properties of 15 (in the form of its perchlorate salt, 16) and 20 were measured by FTIR, multinuclear NMR, MS, DSC and x-ray crystallography. It is important to note that compound 20 exhibits exothermic decomposition at 302 °C (DSC) and >353 N (sensitivity to friction), making it a highly-promising thermally-insensitive energetic material for further development.}\)

Introduction

The history of discovery and development of new energetic materials goes back to gunpowder, which was invented in Imperial China around the 9th century, in an attempt to create an immortality potion.\(^1\) This ground-breaking discovery led to the invention of fireworks and a variety of weapons in China and, later, throughout the world.\(^2\) Since the earliest findings, tremendous progress was made in the rational design and preparation of novel energetic materials and compositions.\(^3\) Important properties of such materials, which are commonly taken into account by the designers span heat of formation (HOF), density, melting and decomposition temperatures, sensitivity to friction and shock, velocity of detonation (VOD), synthetic complexity,\(^4\) as well as carbon content, nitrogen content and oxygen balance (OB).\(^5\)

Energetic materials typically contain both oxidizing and reducing functional groups in their molecular structure (or in the structure of their components). Under high temperature and pressure conditions, these materials would transform into more thermodynamically-stable products, including small molecules with low heats of formation, such as \( \text{H}_2\text{O, N}_2\text{, CO, CO}_2\text{, SO}_2\) and metal oxides.\(^6\) The OB is a mathematical formula used to calculate the degree to which a given explosive or propellant could be oxidized. A “zero” OB value will be calculated when the chemical composition of the calculated energetic material will have the exact amount of oxygen atoms needed to convert all the carbon atoms to \( \text{CO}_2\), all hydrogen atoms to \( \text{H}_2\text{O}\), all sulphur atoms to \( \text{SO}_2\) and all metal atoms (if present in the material) to metal oxides. An energetic material would have a positive OB value if it contains more oxygen atoms than required for complete combustion and a negative OB value when the amount of oxygen atoms is insufficient for complete oxidation. The results of OB calculations were shown to have an excellent correlation with both sensitivity properties and performance of energetic compounds and their formulations, which have a tendency to reach their best values as their OB values are getting closer to “zero”.\(^7\) When an energetic material has a negative OB value (an insufficient amount of oxygen for complete oxidation), it will typically exhibit an incomplete combustion, resulting in the formation of large amounts of toxic CO gas, smoke, soot and solid residues. Commonly, as the OB values for a certain explosive

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\(^{2}\) Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x
get lower, poorer performance for this explosive is observed, and the VOD and generated pressure for this explosive also become smaller.

In cases where an energetic material contains “too much oxygen” (has a positive OB value), the O₂ produced during explosion is absorbing a significant amount of energy, substantially reducing this explosive performance.⁸

There are several fascinating examples of energetic compounds possessing an OB value of 0%, such as the most potent chemical explosive known – octanitrocubane (ONC; R.E. factor = 2.38).⁹ Other examples include the recently prepared compound nitryl cyanide¹⁰ and the still synthetically-elusive nitrogen-rich compounds – 3,6-dinitro-1,2,4,5-tetrazine,¹¹ 2,4,6-trinitro-1,3,5-triazine,¹² [1,2,3,4]-tetrazino[5,6-e][1,2,3,4]-tetrazine-1,3,5,7-tetraoxide (TTTO),¹³ and (5-nitro-2H-tetrazol-2-yl)-methyl nitrate (Fig. 1).¹⁴

Due to their high density, highly positive enthalpy of formation, good detonation performances and excellent thermal stability in comparison to the conventional energetic materials, nitrogen-rich energetic compounds attract considerable scientific attention.¹⁵ The latter compounds were extensively explored during recent years for their great potential for both civilian and military applications such as gas generators, low-signature propellants, as well as additives to pyrotechnics and explosives.¹⁶ Among popular building blocks used in the construction of nitrogen-rich energetic materials are tetrazole¹⁷ and tetrazine¹⁸ functional groups. However, the majority of nitrogen-rich organic compounds are oxygen-deficient. Since one of the most popular strategies for the design of promising new energetic materials is incorporating both fuel and oxidizer properties into a single molecule, one of the important challenges in this field is the preparation of new nitrogen-rich compounds with a low OB value. Therefore, in recent years, the synthesis and evaluation of various nitroazole derivatives as compounds with a balanced oxygen content became highly-popular.¹⁹

Results and discussion

In our perspective, as part of the framework of these efforts, one of the interesting challenges was exploring the synthesis of unreported tetra-nitro derivatives of N,N’-bis(1H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (BTATz ⁵; OB = -64.5%)²⁰ –

![Fig. 1 Structures of ONC, nitryl cyanide, 3,6-dinitro-1,2,4,5-tetrazine, 2,4,6-trinitro-1,3,5-triazine, TTTO and (5-nitro-2H-tetrazol-2-yl)-methyl nitrate.](image)

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Fig. 1 Structures of ONC, nitryl cyanide, 3,6-dinitro-1,2,4,5-tetrazine, 2,4,6-trinitro-1,3,5-triazine, TTTO and (5-nitro-2H-tetrazol-2-yl)-methyl nitrate.

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Fig. 2 Structures of compounds 1 (OB = -7.0%), 2 (OB = +6.1%), 3 (OB = -12.3%) and 4 (OB = -3.1%). isothers N,N’-(1,2,4,5-tetrazine-3,6-diyi)bis(N-(1-nitro-1H-tetrazol-5-yl)-nitramide) ⁶ and N,N’-(1,2,4,5-tetrazine-3,6-diyl)bis(N-(2-nitro-2H-tetrazol-5-yl)nitramide) ⁷, both of which have OB values of 0% and calculated VODs of 9,790 and 9,903 m/sec, respectively (Fig. 3, Table 1). Although it would seem that BTATz analogues exhibiting better OB values should be of significant interest, only a single example of such derivatives – 1,4-di-N-oxide ⁸ (OB = -45.7%) – was prepared by Chaves and coworkers.²¹ Unfortunately, compound ⁸ displayed decomposition at 134 °C (versus decomposition of BTATz at 318 °C), indicating that other derivatisation strategies should be investigated.²²,²³

Approaches to prepare energetic molecules with improved OB values are frequently based on the conversion of NH groups in the starting materials into N-NO₂ groups in the corresponding, more energetic, derivatives.²⁴ Since the BTATz molecule has two pairs of NH groups in its structure, we decided to probe whether the nitration of this molecule would lead to the development of more potent energetic compounds (ultimately, to compounds ⁶ and ⁷). There are many methods for the conversion of amines to nitramines: using nitrating agents such as HNO₃, mixtures of HNO₃ and H₂SO₄, acetic anhydride and HNO₃, nitrated silica gel and many others.²⁵ Thus, our initial efforts were focused on a direct nitration of compound ⁵ under various reaction conditions. More specifically, we evaluated a series of nitrating conditions and temperature regimes which included the use of red fuming HNO₃, mixtures of either HNO₃ and H₂SO₄ (1:1 v/v), HNO₃ and acetic anhydride (1:1 v/v) or HNO₃ and trifluoroacetic anhydride (1:1 v/v). However, all examined reaction conditions (and all examined temperature regimes) led to one of two results: recovery of only staring compound ⁵ at the end of the reaction or decomposition of ⁵.

We further attempted to establish whether any nitration of compound ⁵ actually takes place, with the formed nitramines hydrolysing back to the starting material upon dilution of the...
purpose, we conducted in situ studies of the nitration of 5 by \(^{15}\text{N}\) NMR using Na\(^{15}\text{NO}_3\) in concentrated H\(_2\text{SO}_4\). A reference mixture of Na\(^{15}\text{NO}_3\) in concentrated H\(_2\text{SO}_4\) exhibited two \(^{15}\text{N}\) NMR signals at 383 ppm and 248 ppm, indicating the presence of \(^{15}\text{NO}_2^-\) and \(^{15}\text{NO}_3^-\), respectively, and was consistent with previous reports. Subsequent addition of BTATz to this nitration mixture at 0°C resulted in the appearance of a new \(^{15}\text{N}\) NMR signal at 336 ppm, which was assigned to the formation of a N-NO\(_3\) adduct. Although it was obvious that, under explored conditions, no further nitration of 5 could be obtained, it was not clear which amine group in this compound underwent nitration (Fig. 4). Since the in situ \(^{15}\text{N}\) NMR measurements did not help us determine whether edocyclic 9/10 (routes A and B, Fig. 4) or exocyclic 11 (route C, Fig. 4) nitramines were formed, and since the resulted product could not be isolated for further analysis due to its instability, other approaches were required. Therefore, we synthesized a model compound \(N,N'\)-bis(2-methyl-2H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 12 in which both endocyclic NH groups in the tetrazole rings were methylated (Fig. 5). The successful conversion of 5 to 12 was achieved by using dimethyl-sulfate in aqueous NaHCO\(_3\) at room temperature. Comparison of \(^1\text{H}\) and \(^{13}\text{C}\) NMR data obtained for 12 to published reports for 2-methyl-2H-tetrazole derivatives (versus 1-methyl-1H-tetrazole derivatives) strongly suggested that the methylation of 5 took place on the second nitrogen atom of the tetrazole ring.

Further nitration of 12 with a mixture of concentrated HNO\(_3\) and acetic anhydride (1:2 v/v) resulted in the formation of the new compound \(N,N'\)-bis(2-methyl-2H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 12 in which both endocyclic NH groups in the tetrazole rings were methylated (Fig. 5). The successful conversion of 5 to 12 was achieved by using dimethyl-sulfate in aqueous NaHCO\(_3\) at room temperature. Comparison of \(^1\text{H}\) and \(^{13}\text{C}\) NMR data obtained for 12 to published reports for 2-methyl-2H-tetrazole derivatives (versus 1-methyl-1H-tetrazole derivatives) strongly suggested that the methylation of 5 took place on the second nitrogen atom of the tetrazole ring.

Further nitration of 12 with a mixture of concentrated HNO\(_3\) and acetic anhydride (1:2 v/v) resulted in the formation of the new compound \(N,N'\)-bis(2-methyl-2H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 12 in which both endocyclic NH groups in the tetrazole rings were methylated (Fig. 5). Unfortunately, nitramide 13 could not be fully characterized due to its very high sensitivity to impact and friction (primary explosive). Also, based on \(^1\text{H}\) NMR analysis in solution of DMSO-\(_d_6\) or CD\(_3\)CN, 13 underwent relatively quick hydrolysis back to the parent compound 12. \(^{13}\text{C}\) and \(^{15}\text{N}\) NMR studies in DMSO-\(_d_6\) of the precipitate obtained in the nitration of 12 with a mixture of Na\(^{15}\text{NO}_3\)/HNO\(_3\) (prepared separately) and acetic anhydride also showed only the presence of the starting material 12. Yet, in situ \(^{15}\text{N}\) NMR studies of the nitration of 12 with Na\(^{15}\text{NO}_3\) in concentrated H\(_2\text{SO}_4\) exhibited a new peak at 336 ppm (at the identical position of the nitramine’s nitrate peak in compound 11), strongly supporting our hypothesis that both compounds 5 and 12 undergo nitration on their exocyclic NH groups.

After realizing that the nitration of 5 (and its bis-N-methyl-tetrazole analog 12) could not lead to the formation of stable nitramine products, we explored whether the nitration of the unreported 1,2,4-triazole analog 15 would produce better results. The synthesis of compound 15 was achieved in an 81% yield, in a similar fashion to the synthesis of 5, by reacting 3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine (BPT, 14) with 1H-1,2,4-triazole-5-amine in sulfolane at 135 °C (Fig. 6). The corresponding, more soluble, energetic perchlorate salt 16 and nitrate salt 17 were prepared by treating

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{N} \quad \text{N} \quad \text{N} \\
\text{C} & \quad \text{C} \\
\text{N} & \quad \text{N} \\
\text{N} & \quad \text{N} \\
\end{align*}
\]

with HClO\(_4\) and HNO\(_3\), respectively (Fig. 6). The Structure of 16 was confirmed by X-ray crystallography (Fig. 9). Subsequently, a direct nitration of compound 15 was explored under various reaction conditions, which included either HNO\(_3\), a mixture of H\(_2\)SO\(_4\) and HNO\(_3\) (1:1; v/v), a mixture of CF\(_3\)CO\(_2\)H and HNO\(_3\) (1:1; v/v) or a mixture of NaNO\(_3\) and H\(_2\)SO\(_4\). Under all tested temperature regimes, all aforementioned nitrating reagents led invariably to the formation of stable nitrate salt 17.

In situ \(^{15}\text{N}\) NMR studies of the nitration of 15 with Na\(^{15}\text{NO}_3\) in concentrated H\(_2\text{SO}_4\) (at 0 °C) displayed a peak at 336 ppm (at the identical position of the nitramine’s nitrate peak in compound 13), clearly indicating that the first nitration reaction takes place on the exocyclic NH groups of 15 and not on the CH or NH groups of its triazole rings (Fig. 7). This interesting observation demonstrates a similar nitration pattern for structurally related compounds 5, 12 and 15. We believe that similarly to 11 and 13, attempts of isolation of compound 18 results in a quick hydrolysis of exocyclic nitramine group back to the original amine. In contrast to previous attempts, the nitration of 15 with a mixture of HNO\(_3\) and acetic anhydride (1:1; v/v) at 0 °C resulted in the formation of a new nitramine – \(N,N'\)-bis(2-methyl-2H-tetrazole-3,6-diyli)bis(N(3-nitro-1H-1,2,4-triazol-5-yl)-nitramide) 19, which was isolated by precipitation (Fig. 8). The latter compound could not be fully characterized due to its high sensitivity to impact and friction (primary explosive!). The
Formation of a new derivative with nitrat ed triazole rings after its separation from the nitration reaction mixture, crystallography (Fig. 6).  

Solubility properties, sensitivity and thermal behaviour of 19 suggested its analogous structure to the exocyclic nitramine 13. Controlled gradual heating of approximately 0.2 mg of wet 19 in a glass capillary (suitable for melting point measurements) resulted via its explosion at 110-112 °C, shuttering the capillary.

$^{15}$N NMR studies of the precipitate 19 (dissolved in DMSO-$d_6$), obtained in nitration of 15 with a mixture of Na$^{15}$NO$_3$/HNO$_3$ and acetic anhydride, showed the appearance of a new peak at 356.8 ppm (corresponding to C$^{15}$NO$_2$ nitrogen), indicating the formation of a new derivative with nitrat ed triazole rings $N^\prime,N^\prime\prime$-bis(3-nitro-1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 20. No exocyclic nitramine derivatives ($N^{15}$NO$_3$) of compound 15 were observed upon dissolution of 19 in DMSO-$d_6$ most reasonably due to the hydrolysis of 19 into the hydrolytically stable 20. Also, the dissolution of 19 in hot CH$_3$CN (with further heating at 65 °C for 30 min) immediately after its separation from the nitration reaction mixture, resulted in the formation of a new compound $N^\prime,N^\prime\prime$-bis(3-nitro-1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 20 (Fig. 8). The structure of 20 was confirmed by X-ray crystallography (Fig. 10).

In order to check whether the structure of 19 was correct, in situ $^{15}$N NMR studies of the “back nitration” of 20 into exocyclic $^{15}$N nitramine 19A were conducted. In these experiments, a solid 20 was slowly added to a mixture of Na$^{15}$NO$_3$ in concentrated H$_2$SO$_4$ at 0 °C and, after 30 min, the reaction mixture was analysed by $^{15}$N NMR. A new peak at 336.3 ppm (corresponding to the exocyclic N$^{15}$NO$_2$ nitrogen) appeared in the spectrum, indicating the formation of nitramine 19A (Fig. 8), which perfectly matches our previous observation and conclusions.

Crystal Structures

X-ray measurements for single crystals of compounds 16 (perchlorate salt of compound 15; CCDC 1041768) and 20 (CCDC 1041769) were performed. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The data for the crystals of 16 and 20 were collected using MoKα radiation (L = 0.71073 nm). An Oxford low-temperature device was used to keep the crystals at a constant temperature of 110K during the entire data collecting period. Details of the X-ray data collection and structure refinements are summarized in the Supporting Information. Detailed examination of the crystal structures obtained for 16 and 20 showed no significant differences in bond lengths and torsion angles reported for structures of other compounds containing 1,2,4-triazole and 1,2,4,5-tetrazine functional groups. Both 16 and 20 molecules were found to be completely planar, due to an extensive delocalization of electrons in these molecules.

Compound 16 was crystallized as solvent-free crystals with the monoclinic space group P2(1)/c and a cell volume of 757.49 Å$^3$. A crystal unit cell of 16 contains eight molecules of nitrogren-rich cations and four perchlorate anions. The measured density for 16 was found to be 1.960 g/cm$^3$. The nitrogen-rich cation is protonated at nitrogen atom N6 in both triazole rings. Fig. 9 shows interactions between hydrogen atoms in compound 16 and oxygen atoms in perchlorate anions (each nitrogen-rich cation interacts with eight perchlorate anions).

The hydrogen bonding parameters of these interactions are detailed in Table 1. The triazole moiety of 16 points towards nitrogen atom N6 and participates in an intramolecular hydrogen bond N1-H1···N4 with a D···A length of 2.732Å and a D-H···A angle of 116°.

Compound 20 was crystallized as a monoclinic space group P2(1)/c and a cell volume of 1546.76 Å$^3$ was calculated. Crystal unit cell of this compound contains eight molecules of 20 and ten molecules of DMF. The unit cell contains two additional disordered DMF molecules, which could not be reliably modelled by discrete atoms. Correspondingly, its contribution was subtracted from the diffraction pattern by the Squeeze...
Fig. 9 (top): Molecular structure of compound 16, (bottom): interactions between 16 and surrounding perchlorate anions.

Fig. 10 (top): Molecular structure of compound 20, (bottom): interactions between 20 and surrounding DMF molecules.

Table 1 Hydrogen bonds present in crystal structure of 16.

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>D-H/Å</th>
<th>H···A/Å</th>
<th>D···A/Å</th>
<th>D-H···A/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-H1···O4</td>
<td>0.83</td>
<td>2.20</td>
<td>2.9669</td>
<td>153.7</td>
</tr>
<tr>
<td>N1-H1···O1</td>
<td>0.83</td>
<td>2.799</td>
<td>2.973</td>
<td>93.8</td>
</tr>
<tr>
<td>N2-H2···O2</td>
<td>0.87</td>
<td>2.10</td>
<td>2.9401</td>
<td>162.1</td>
</tr>
<tr>
<td>N6-H3···O1</td>
<td>0.80</td>
<td>2.06</td>
<td>2.8303</td>
<td>163</td>
</tr>
<tr>
<td>N1-H1···N4</td>
<td>0.83</td>
<td>2.265</td>
<td>2.732</td>
<td>116</td>
</tr>
</tbody>
</table>

Table 2 Hydrogen bonds present in crystal structure of 20.

<table>
<thead>
<tr>
<th>D-H···A</th>
<th>D-H/Å</th>
<th>H···A/Å</th>
<th>D···A/Å</th>
<th>D-H···A/°</th>
</tr>
</thead>
<tbody>
<tr>
<td>N6-H6···N12</td>
<td>0.88</td>
<td>2.27</td>
<td>2.7781</td>
<td>117</td>
</tr>
<tr>
<td>N6-H6···O19(ii)</td>
<td>0.88</td>
<td>1.94</td>
<td>2.6939</td>
<td>143</td>
</tr>
<tr>
<td>N9-H9···O13(iii)</td>
<td>0.88</td>
<td>1.86</td>
<td>2.7333</td>
<td>175</td>
</tr>
<tr>
<td>C14-H14···N8(iv)</td>
<td>0.95</td>
<td>2.43</td>
<td>3.2085</td>
<td>139</td>
</tr>
<tr>
<td>C16-H16A···O13</td>
<td>0.98</td>
<td>2.46</td>
<td>2.8005</td>
<td>100</td>
</tr>
<tr>
<td>C20-H20···N12(v)</td>
<td>0.95</td>
<td>2.58</td>
<td>3.2438</td>
<td>127</td>
</tr>
<tr>
<td>C20-H20···N11(vi)</td>
<td>0.95</td>
<td>2.43</td>
<td>3.3178</td>
<td>155=ze</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) 1-x, -1/2+y, z (ii) 1+x, y, z (iii) 1-x, y, z (iv) 1-x, 1/2+y, z (v) 1+y, 1/2-z (vi) 1-x, -1/2+y, -z

Theoretical Calculations, Performance Characteristics and Thermal Stabilities

Calculations were performed using the Gaussian 09 software.\(^{28}\) The geometric optimization of the structures and frequency analyses were carried out by using the B3LYP functional with the 6-311+G(d,p) basis set.\(^{29}\) The optimized structures of all materials correspond to, at least, a local energy minimum on the potential energy surface. In order to predict energetic properties of new materials, the EXPLO5_v6.01 software was used. This software utilizes an algorithm based on the Becker-Kistiakowsky-Wilson equation of state (BKW EOS) for gaseous detonation products. Thermal stability is a very important property of energetic materials. The onset temperatures for thermal decomposition of compounds 5, 12, 15, 16, 17 and 20 were determined using differential scanning calorimeter (DSC). The results of these calculations and the experimental data are summarized in Table 3.

In contrast to compounds 15, 16 and 17, dinitro derivative 20 exhibited high thermal stability (T<sub>decomp.</sub> of 302°C), high detonation velocity (VOD of 8,903 m/s) and high detonation pressure, performing comparably to BTATz 5. In addition, BAM measurements of dropping-hammer (7.67 Nm) and friction (> 353 N) for compound 20 indicate a relatively high stability of this energetic material under mechanical stress (for comparison, the equivalent values for RDX are 7.5 Nm and 120 N, respectively).

Conclusions

A methodical study of nitration patterns was conducted on a series of 3,6-diamino-1,2,4,5-tetrazine derivatives, revealing the specificity of the nitration in this type of nitrogen-rich compounds, as well as stability of the formed nitramines towards hydrolysis. The general motivation of this study was to evaluate whether energetic nitrogen-rich compounds, structurally-related to the N<sup>3</sup>,N<sup>6</sup>-bis(1H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (BTATz; 5), with improved oxygen balance characteristics, could be prepared. By 15N-labeling methodology, we found that although nitramine derivatives of 5, as well as its dimethyl analogue N<sup>3</sup>,N<sup>6</sup>-bis(2-methyl-2H-
tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (12), are formed in the reaction mixture, these nitramines could not be successfully isolated and quickly undergo hydrolysis back to the starting materials. Therefore, subsequent efforts were focused on more stable nitro derivatives of the newly synthesized compound $N^6,N^7$-bis(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (15). The nitration of 15 was studied by $^{15}$N NMR, showing a similar initial reactivity pattern of 5 and 12. Yet, due to a presence of 1,2,4-triazole functional groups in the structure of 15, new C-NO$_2$ derivative $N^5,N^6$-bis(3-nitro-1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (20) was obtained in a moderate yield. The structures of 16 (perchlorate salt of 15) and 20 (with 4 molecules of DMF) were determined by x-ray crystallography. Importantly, it was found that compound 20 exhibited high stability towards friction (> 353 N) and very high thermal stability, decomposing at 302°C (by DSC). The standard heats of formation for all compounds in this study were calculated on the B3LYP 6311G$+$d,p level of theory, showing highly-positive values of 831.5 kJ/mol and 1032.9 kJ/mol for 15 and 20, respectively. Detonation parameters for all compounds were calculated with the EXPLO5_v6.01 program. Theoretical density of 1.87 g/cm$^3$ and velocity of detonation of 8,903 m/s were calculated for 20, making it a highly promising new energetic compound.

### Experimental Section

**Caution!** As certain triazole, tetrazol and tetrazine derivatives are unstable and can ignite or explode under the influence of impact, friction or heating, proper safety precautions should be taken in work with these materials. Lab personnel and equipment should be properly grounded and protective equipment including protective coat, Kevlar gloves, ear protection and face shield should be used.

### General Information

All used chemical reagents and solvents were of analytical grade and were used as supplied, without further purification. $^1$H, $^13$C and $^{15}$N NMR spectra were recorded on a 400 MHz NMR spectrometer at 25°C. The chemical shifts are given relative to the residual DMSO-d$_6$ or formamide (15N) as external standards and coupling constants are given in Hertz (Hz). Infrared (IR) spectra were recorded on a FTIR spectrometer equipped with a diamond ATR unit. Mass spectra were recorded on a high-resolution ESI-Q-ToF machine. Elemental analyses (CHN) were performed at the service facility of the Hebrew University. Decomposition points were determined by differential scanning calorimetry (DSC). Measurements were performed at a heating rate of 5 °C/min in closed aluminium sample pans with a small hole in the lid under a nitrogen flow of 20 mL/min using an empty aluminium sample pan as a reference. Melting points were measured on a melting point apparatus in open glass capillaries. The impact sensitivities were tested according to STANAG 4489 using a BAM drop-hammer. The friction sensitivities were tested

### Table 3: Physico-chemical properties of compounds 5, 6, 7, 9/10, 11, 12, 13, 15, 16, 17, 18, 19, 19 and 20.

<table>
<thead>
<tr>
<th></th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>9/10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
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</thead>
<tbody>
<tr>
<td>Mw [g/mol]</td>
<td>248</td>
<td>428</td>
<td>428</td>
<td>338</td>
<td>338</td>
<td>276</td>
<td>366</td>
<td>246</td>
<td>447</td>
<td>372</td>
<td>336</td>
<td>426</td>
<td>336</td>
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<tr>
<td>%N [wt%]</td>
<td>79</td>
<td>60</td>
<td>60</td>
<td>61.5</td>
<td>61.5</td>
<td>71</td>
<td>61</td>
<td>68</td>
<td>33.3</td>
<td>41.1</td>
<td>50</td>
<td>50</td>
<td>58</td>
</tr>
<tr>
<td>$p$ [g/cm$^3$]</td>
<td>1.88</td>
<td>2.03</td>
<td>2.03</td>
<td>1.98</td>
<td>1.98</td>
<td>1.77</td>
<td>1.88</td>
<td>1.36</td>
<td>1.96</td>
<td>1.74</td>
<td>1.74</td>
<td>1.74</td>
<td>1.74</td>
</tr>
<tr>
<td>$\Omega$ [%]</td>
<td>918</td>
<td>1148</td>
<td>1,334</td>
<td>113</td>
<td>964</td>
<td>1,022</td>
<td>996</td>
<td>831</td>
<td>-504</td>
<td>-655</td>
<td>965</td>
<td>864</td>
<td>1032</td>
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<tr>
<td>$\Delta H_{f}$ [kJ/mol]</td>
<td>3789</td>
<td>2756</td>
<td>3190</td>
<td>3436</td>
<td>2933</td>
<td>3801</td>
<td>2808</td>
<td>3468</td>
<td>-1056</td>
<td>-1667</td>
<td>2952</td>
<td>2103</td>
<td>3151</td>
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<tr>
<td>$\Delta U^*$ [kJ/kg]</td>
<td>4002</td>
<td>6,048</td>
<td>6400</td>
<td>5492</td>
<td>5032</td>
<td>4185</td>
<td>5097</td>
<td>3728</td>
<td>2947</td>
<td>1921</td>
<td>5121</td>
<td>5315</td>
<td>5398</td>
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<tr>
<td>$T_d$ [K]</td>
<td>2905</td>
<td>4632</td>
<td>4856</td>
<td>4101</td>
<td>3872</td>
<td>2763</td>
<td>3597</td>
<td>2805</td>
<td>2630</td>
<td>1873</td>
<td>3782</td>
<td>4091</td>
<td>3891</td>
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<tr>
<td>$P_d$ [GPa]</td>
<td>301</td>
<td>443</td>
<td>456</td>
<td>415</td>
<td>394</td>
<td>265</td>
<td>333</td>
<td>124</td>
<td>251</td>
<td>161</td>
<td>329</td>
<td>390</td>
<td>339</td>
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<tr>
<td>$V_{gas}$ [m/s]</td>
<td>8809</td>
<td>9790</td>
<td>9903</td>
<td>9604</td>
<td>9429</td>
<td>8492</td>
<td>8932</td>
<td>6240</td>
<td>711</td>
<td>6833</td>
<td>8830</td>
<td>9310</td>
<td>8903</td>
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<tr>
<td>Gas vol. [L/kg]</td>
<td>758</td>
<td>759</td>
<td>762</td>
<td>794</td>
<td>789</td>
<td>743</td>
<td>778</td>
<td>734</td>
<td>751</td>
<td>792</td>
<td>753</td>
<td>777</td>
<td>753</td>
</tr>
</tbody>
</table>

(a) Nitrogen content; (b) measured by DSC start of decomposition temperature; (c) calculated density; (d) density value that was obtained by a single-crystal x-ray diffraction; (e) calculated volume of gaseous products. (f) gas pycnometry at 25 °C; (g) density value that was obtained by a single-crystal x-ray diffraction; (h) calculated temperature of detonation; (i) calculated pressure of detonation; (j) calculated velocity of detonation; (k) calculated volume of gaseous products.
according to STANAG 4487 using a BAM friction tester. Experimental densities were obtained by pycnometry measurements at ambient temperature.

**General Procedures**

\( N^1,N^6\)-bis(2-methyl-2H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (12). A solid \( N^1,N^6\)-di(1H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (816 mg, 3.29 mmol) was added to a solution of NaHCO\(_3\) (690 mg, 8.21 mmol) in H\(_2\)O (30 mL) and stirred at RT for 30 min, until dissolution. To the resulted solution, dimethylsulfate (1.04 g, 8.22 mmol) was added and the reaction mixture was stirred at RT for 3 days. After that time, the precipitate formed was collected by filtration, washed with a mixture of triethylamine in MeOH (1:20 v/v; 3×10 mL) and dried under vacuum to yield pure 12 (536 mg; 59%) as a red solid. DSC (5 °C/min) 306 °C (decomp.). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)): δ 4.32 (s, 6H). \(^13\)C NMR (100 MHz, DMSO-d\(_6\)): δ 40.2, 159.0, 160.6. \( ^{15} \)C DEPT135 (100 MHz, DMSO-\( d_6\)): δ 40.2 (CH\(_3\)). HRMS (ESI\(^+\)): m/z = 277.1127 [M+H\(^+\)]. Elemental analysis: calcd. (%) for C\(_{26}\)H\(_{24}\)N\(_{12}\): C 40.25, H 3.16, N 46.59. Found: C 40.18, H 3.19, N 46.63.

**Notes and references**


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