The 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, has become very popular. In the framework of this effort, we studied nitration of \(N^3,N^6\)-bis[1H-tetrazol-5-yl]-1,2,4,5-tetrazine-3,6-diamine (BTATz; 5) and its alkylated derivative \(N^3,N^6\)-bis[2-methyl-1H-tetrazol-5-yl]-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 seen that the nitration of both compounds takes place only on the exocyclic ("bridging") secondary amine groups. Possible tetranitro derivative isomers \(NN'-\text{(1,2,4,5-tetrazine-3,6-diyl)bis(N-\text{(1-nitro-1H-tetrazol-5-yl)-nitramide)}}\) 6 and \(NN'-\text{(1,2,4,5-tetrazine-3,6-diyl)bis(N-(2-nitro-1H-tetrazol-5-yl)nitramide)}\) 7, both of which have OB = 0% and calculated VODs of 9790 and 9903 m s\(^{-1}\), respectively, could not be observed in the reaction mixtures, during the \textit{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 – \(N^3,N^6\)-bis[1H-1,2,4-triazol-5-yl]-1,2,4,5-tetrazine-3,6-diamine 15 was 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 \(N^3,N^6\)-bis[3-nitro-1H-1,2,4-triazol-5-yl]-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 the 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 has been 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 are 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 H\(_2\)O, N\(_2\), CO, CO\(_2\), 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 CO\(_2\), all hydrogen atoms to H\(_2\)O, all sulphur atoms to 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.

---

\(^{†}\)Electronic supplementary information (ESI) available: Contains copies of \(^1\)H and \(^{13}\text{C}\) NMR spectra for isolated compounds and \(^{15}\text{N}\) NMR spectra for \(^{15}\text{N}\)-labeled compounds formed \textit{in situ} in the nitration experiments, and crystallographic data for compounds 16 and 20. CCDC 1041768 and 1041769. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5dt01641j

---

School of Chemistry, Faculty of Exact Sciences, Tel-Aviv University, Tel-Aviv 69978, Israel. E-mail: cogozin@gmail.com; Tel: +972-3-640-5878
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 the performance of energetic compounds and their formulations, which have a tendency to reach their best values as their OB values get closer to “zero”. 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 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 absorbs a significant amount of energy, substantially reducing its explosive performance.

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). Other examples include the recently prepared compound nitryl cyanide and the still synthetically-elusive nitrogen-rich compounds – 3,6-dinitro-1,2,4,5-tetrazine, 2,4,6-trinitro-1,3,5-triazine, 2,4,6-trinitro-1,3,5-tetrazine-3,6-diamine (BTATz; OB = −64.5%), 11 isomers N,N′-[1,2,4,5-tetrazine-3,6-diy]-bis(N-(1-nitro-1H-tetrazol-5-yl)-nitramide) 6 and N,N′-[1,2,4,5-tetrazine-3,6-diy]-bis(N-(2-nitro-2H-tetrazol-5-yl)nitramide) 7, both of which have OB values of 0% and calculated VODs of 9790 and 9903 m s⁻¹, 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. Unfortunately, compound 8 displayed decomposition at 134 °C (versus decomposition of BTATz at 318 °C), indicating that other derivatisation strategies should be investigated.

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′-[1H-tetrazol-5-yl]-1,2,4,5-tetrazine-3,6-diamine (BTATz 5; OB = −64.5%) and isomers N,N′-[1,2,4,5-tetrazine-3,6-diy]-bis(N-(1-nitro-1H-tetrazol-5-yl)-nitramide) 6 and N,N′-[1,2,4,5-tetrazine-3,6-diy]-bis(N-(2-nitro-2H-tetrazol-5-yl)nitramide) 7, both of which have OB values of 0% and calculated VODs of 9790 and 9903 m s⁻¹, 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. Unfortunately, compound 8 displayed decomposition at 134 °C (versus decomposition of BTATz at 318 °C), indicating that other derivatisation strategies should be investigated.

Approaches to prepare energetic molecules with improved OB values are frequently based on the conversion of NH

![Fig. 1](image1.png)

**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.

![Fig. 2](image2.png)

**Fig. 2** Structures of compounds 1 (OB = −7.0%), 2 (OB = +6.1%), 3 (OB = −12.3%) and 4 (OB = −3.1%).

![Fig. 3](image3.png)

**Fig. 3** Structures of compounds 5, 6, 7 and 8.

**Table 1** Hydrogen bonds present in the crystal structure of 16

<table>
<thead>
<tr>
<th>D-H...A</th>
<th>D-HÅ</th>
<th>H...AÅ</th>
<th>D-AÅ</th>
<th>D-H...Aº</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>
groups in the starting materials into N–NO$_2$ groups in the corresponding, more energetic, derivatives.

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 HNO$_3$, mixtures of HNO$_3$ and H$_2$SO$_4$, acetic anhydride and HNO$_3$, nitrated silica gel and many others.

Thus, our initial efforts were focused on the 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 HNO$_3$ and mixtures of either HNO$_3$ and H$_2$SO$_4$ (1:1 v/v), HNO$_3$ and acetic anhydride (1:1 v/v) or HNO$_3$ and trifluoroacetic anhydride (1:1 v/v). However, all examined reaction conditions (and all examined temperature regimes) led to one of the two results: recovery of only the starting 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 $^{15}$N NMR using Na$^{15}$NO$_3$ in concentrated H$_2$SO$_4$. A reference mixture of Na$^{15}$NO$_3$ in concentrated H$_2$SO$_4$ exhibited two $^{15}$N NMR signals at 383 ppm and 248 ppm, indicating the presence of $^{15}$NO$_2^-$ and $^{15}$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 $^{15}$N NMR signal at 336 ppm (at the expense of the parent compound and its bis-N-methylated compound 12, with its subsequent nitration. Reaction conditions: (i) dimethylsulfate, NaHCO$_3$, H$_2$O, r.t. (ii) conc. HNO$_3$, Ac$_2$O.

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 $N,N'$-(1,2,4,5-tetrazine-3,6-diyldiyl)-bis(N(2-methyl-2H-tetrazol-5-yl)-nitramide 13 (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 $^1$H NMR analysis in a solution of DMSO-$d_6$ or CD$_3$CN, 13 underwent relatively quick hydrolysis back to the parent compound 12. $^{13}$C and $^{15}$N NMR studies in DMSO-$d_6$ of the precipitate obtained in the nitration of 12 with a mixture of Na$^{15}$NO$_3$/HNO$_3$ (prepared separately) and acetic anhydride also showed only the presence of the starting material 12. Yet, in situ $^{15}$N NMR studies of the nitration of 12 with Na$^{15}$NO$_3$ in concentrated H$_2$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 of compound 5 – $N,N'$-bis(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 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 15 with HClO₄ and HNO₃, 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 HNO₃, a mixture of H₂SO₄ and HNO₃ (1 : 1; v/v), a mixture of CF₃CO₂H and HNO₃ (1 : 1; v/v) or a mixture of NaNO₃ and H₂SO₄. Under all tested temperature regimes, all aforementioned nitratating reagents led invariably to the formation of stable nitrate salt 17.

In order to check whether the structure of 19 was correct, in situ ¹⁵N NMR studies of the “back nitration” of 20 into exocyclic ¹⁵N nitramine 19A were conducted. In these experiments, a solid 20 was slowly added to a mixture of Na¹⁵NO₃ in concentrated H₂SO₄ at 0 °C and, after 30 min, the reaction mixture was analysed by ¹⁵N NMR. A new peak at 336.3 ppm (corresponding to C-¹⁵NO₂ nitrogen) appeared in the spectrum, indicating the formation of nitramine 19A (Fig. 8), which perfectly matches our previous observations 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. The data for the crystals of 16 and 20 were collected using Mo Kα radiation (L = 0.71073 nm). An Oxford low-temperature device was used to keep the crystals at a constant temperature of 110 K during the entire data collecting period. Details of the X-ray data collection and structure refinements are summarized in the ESI. A 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 P2₁/c and a cell volume of 757.49 Å³. A crystal unit cell of 16 contains eight molecules of nitrogen-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 hydro-
Calculations were performed using the Gaussian 09 software.\textsuperscript{28} Theoretical calculations, performance characteristics and hydrogen bond with the solvent (Table 2).

Compound 20 was crystalized as a monoclinic space group \(P2(1)/c\) and a cell volume of 1546.76 Å\(^3\) was calculated. The 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 technique, using the PLATON software.\textsuperscript{26} As a result, the density measured was 1.35 g cm\(^{-3}\), which is significantly lower than 1.87 g cm\(^{-3}\) – the calculated density for this compound.\textsuperscript{27} Fig. 10 shows interactions between nitrogen and hydrogen atoms of compound 20 and molecules of DMF (each molecule of 20 interacts with 10 molecules of DMF). The bond length of the bridge corresponds to a C–N single bond (C10–N9 1.359 Å, N9–C7 1.370 Å). The triazole moiety points towards atom N6 and participates in an intramolecular hydrogen bond – N6–H6⋯N12 – which has a D⋯A length of 2.7781 Å and a D–H⋯A angle of 117° and an intermolecular hydrogen bond with the solvent (Table 2).

**Theoretical calculations, performance characteristics and thermal stabilities**

Calculations were performed using the Gaussian 09 software.\textsuperscript{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.\textsuperscript{29} The optimized structures of all materials correspond to, at least, a local energy minimum on the potential energy surface. In order to predict the energetic properties of new materials, the EXPLO5\_v6.0\textsuperscript{130} 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 a 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 (\(T_{\text{decomp.}}\) of 302 °C), high detonation velocity (VOD of 8903 m s\(^{-1}\)) 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).
Table 3  Physico-chemical properties of compounds 5, 6, 7, 9/10, 11, 12, 13, 15, 16, 17, 18, 19 and 20

<table>
<thead>
<tr>
<th>Compound</th>
<th>Mw [g mol⁻¹]</th>
<th>%N² [wt%]</th>
<th>Tₐ [°C]</th>
<th>P [g cm⁻³]</th>
<th>$\Omega$ [t]</th>
<th>$\Delta H_f$ [kJ mol⁻¹]</th>
<th>$\Delta U_f$ [kJ kg⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>248</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>6</td>
<td>428</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>7</td>
<td>428</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>9/10</td>
<td>338</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>11</td>
<td>338</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>12</td>
<td>276</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>13</td>
<td>366</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>15</td>
<td>246</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>16</td>
<td>447</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>17</td>
<td>372</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>18</td>
<td>336</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>19</td>
<td>426</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
<tr>
<td>20</td>
<td>336</td>
<td>60</td>
<td>16.8</td>
<td>60</td>
<td>1.87</td>
<td>1032.9</td>
<td>1548.1</td>
</tr>
</tbody>
</table>

# 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 the 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 $N^3,N^6$-bis(1H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (BTATz; 5), with improved oxygen balance characteristics, could be prepared. By using $^{15}$N-labeling methodology, we found that although nitramine derivatives of 5, as well as its dimethyl analogue $N^3,N^6$-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 $N^3,N^6$-bis(1H-tetrazol-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 the presence of 1,2,4-triazole functional groups in the structure of 15, a new N-NO₂ derivative $N^3,N^6$-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 6-311G+d,p level of theory, showing highly-positive values of 831.5 kJ mol⁻¹ and 1032.9 kJ mol⁻¹ 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 8903 m s⁻¹ were calculated for 20, making it a highly promising new energetic compound.

# Experimental section

**Caution!** As certain triazole, tetrazole and tetrazine derivatives are unstable and can ignite or explode under the influence of impact, friction or heating, proper safety precautions should be taken when working 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. $^1H$, $^{13}$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-d₆ peaks or formamide ($^{15}$N) as external standards and coupling constants are given in hertz (Hz). Infra-red (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⁻¹ in closed aluminium sample pans with a small hole in the lid under a nitrogen flow of 20 mL min⁻¹ 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 4487 using a BAM friction tester. The friction sensitivities were tested according to STANAG 4487 using a BAM friction tester. Experimental densities were obtained by pycnometry measurements at ambient temperature.

**General procedures**

$N^3,N^6$-Bis(2-methyl-2H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (12). A solid $N^3,N^6$-di(1H-tetrazol-5-yl)-1,2,4,5-tetra-
zine-3,6-diamine (816 mg, 3.29 mmol) was added to a solution of NaHCO₃ (690 mg, 8.21 mmol) in H₂O (30 mL) and stirred at RT for 30 min, until dissolution. To the resulting solution, dimethylsulfate (1.04 g, 8.22 mmol) was added and the reaction mixture was stirred at RT for 3 days. Then, 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⁻¹) 306 °C (decomp.). ¹H NMR (400 MHz, DMSO-d₆): δ 4.32 (s, 6H). ¹³C NMR (100 MHz, DMSO-d₆): δ 159.0, 160.1. ¹⁹F DFT135 (100 MHz, DMSO-d₆): δ 40.2 (CH₃). HRMS (ESI⁻): m/z = 277.1127 [M + H⁻]. Elemental analysis: calcd (%) for C₂H₆N₁₄: C 29.27, N 68.27, H 2.46; found: C 29.92, N 68.73, H 2.40.

N³,N⁶-Di(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine perchlorate salt (15). A solid 1H-1,2,4-triazol-5-amine (4.23 g, 50.31 mmol) was added to a solution of 3,6-bis(3,5-dimethyl-1H-pyrazol-1-yl)-1,2,4,5-tetrazine-14 (6.46 g, 29.30 mmol) in sulfolane (150 mL) and the reaction mixture was heated at 135 °C for 24 h. Then, the reaction mixture was cooled down to RT, DMF (150 mL) was added and the mixture was stirred for 1 h. The precipitate formed was collected by filtration, washed with MeOH (3 × 80 mL) and dried under vacuum to yield 15 (4.77 g; 81%) as an orange solid. DSC (5 °C min⁻¹) 350 °C (decomp.). HRMS (ESI⁻): m/z = 254.0697 [M − H⁻]. Elemental analysis: calcd (%) for C₁₄H₁₁N₁₅: C 24.67, N 68.27, H 2.46; found: C 24.92, N 68.73.

N³,N⁶-Di(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine perchlorate salt (16). A solid N³,N⁶-di(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 15 (500 mg, 2.03 mmol) was added to aqueous HClO₄ (5 mL, 70%) and the mixture was stirred at RT for 15 min. To the resulting mixture, CH₂CN (5 mL) was added and the reaction mixture was stirred at RT for an additional 10 min. Then, the precipitate formed was collected by filtration, washed with CH₂CN (3 × 3 mL) and dried under vacuum to yield pure 16 (653 mg; 72%) as an orange solid. DSC (5 °C min⁻¹) 246 °C (decomp.). ¹H NMR (400 MHz, DMSO-d₆): δ 8.56 (s, 2.0 mmol) was slowly added at 0 °C and the reaction mixture was stirred at this temperature for 2 h under anhydrous conditions. Then, the reaction mixture was allowed to warm up to RT and the orange precipitate formed (very sensitive explosive!) was collected by filtration, quickly washed with CF₃CO₂H (2 × 2 mL) and immediately re-dissolved in hot CH₂CN (30 mL). The resulting CH₂CN solution was heated at 65 °C for 30 min and then cooled to RT. The precipitate formed was collected by filtration, washed with CH₂CN (3 × 5 mL) and dried under vacuum to yield pure 20 (211 mg; 31%) as an orange solid. DSC (5 °C min⁻¹) 302 °C (decomp.). ¹⁹F NMR (100 MHz, DMSO-d₆): δ 14.97, 158.2, 160.5. HRMS (ESI⁻): m/z = 335.0492 [M − H⁻]. Elemental analysis: calcd (%) for C₁₄H₁₁N₁₅O₄: C 21.44, N 58.33, H 1.20; found: C 21.75, N 57.56, H 1.30. FTIR (ATR): ν 3274 (w), 2996 (w), 1601 (s), 1541 (s), 1494 (s), 1435 (s), 1317 (s), 1296 (s), 1215 (m), 1072 (s), 1018 (s), 950 (s), 891 (m), 835 (s), 748 (m), 692 (s), 570 (s).

Acknowledgements

The authors would like to acknowledge the financial support provided by the Tel Aviv University and Dr S. Lipstman, Dr C. Evangelisti, Dr D. Krepel, Dr H. Titi and S. Fishman for their valuable contribution.

Notes and references

1 http://chemistry.about.com/od/historyofchemistry/a/gunpowder.htm.