The nitration pattern of energetic 3,6-diamino-1,2,4,5-tetrazine derivatives containing azole functional groups†

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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 \( \text{N}^3,\text{N}^6\text{-bis(1H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (BTATz; 5)} \) and its alkylated derivative \( \text{N}^3,\text{N}^6\text{-bis(2-methyl-2H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 12)} \), using a \( \text{N}^1 \)-labeled nitration agent and monitoring and analyzing products of these reactions by \( \text{N}^1 \) NMR. It was seen that the nitration of both compounds takes place only on the exocyclic ("bridging") secondary amine groups. Possible tetranitro derivative isomers \( \text{N}^3,\text{N}^6\text{-bis(1H,1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine} \) and \( \text{N}^3,\text{N}^6\text{-bis(2-nitro-2H-tetrazol-5-yl)nitramide} \), 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} \( \text{N}^1 \) NMR monitoring of nitration of 5, using \( \text{N}^1 \)-labeled nitrating agents. Following a similar strategy, a new analog of BTATz = \( \text{N}^3,\text{N}^6\text{-bis(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 15)} \) was obtained and its nitration was studied. The reaction of 15 with a \( \text{HNO}_3-\text{Ac}_2\text{O} \) nitration mixture resulted in the formation of a new \( \text{N}^3,\text{N}^6\text{-bis(3-nitro-1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine} \) 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 \( \text{H}_2\text{O}, \text{N}_2, \text{CO}, \text{CO}_2, \text{SO}_2 \) 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 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 tetrazine functionality. However, the majority of nitrogen-rich energetic materials are tetrazole and tetrazine functional groups. However, the majority of nitrogen-rich energetic materials are tetrazole and tetrazine functional groups. However, the majority of nitrogen-rich energetic materials are tetrazole and tetrazine functional groups.

Due to their high density, highly positive enthalpy of formation, good detonation performances and excellent thermal stability in comparison with the conventional energetic materials, nitrogen-rich energetic compounds attract considerable scientific attention. The latter compounds were extensively explored during recent years for their great potential for both civilian and military applications such as in gas generators, low-signature propellants, as well as additives to pyrotechnics and explosives.

Among popular building blocks used in the construction of nitrogen-rich energetic materials are tetrazole and tetrazine 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 nitrazole derivatives as compounds with a balanced oxygen content has become highly-popular.

### 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 N₈,N₈-bis(1H-tetrazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (BTATz 5; OB = −64.5%) – isomers N₈,N₈′-[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-y1)-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

| D–H⋯A | D–H/Å | H⋯A/Å | D⋯A/Å | D–H⋯A/° |
|-------|-------|-------|-------|---------|
| N1–H1⋯O4 | 0.83 | 2.20 | 2.9669 | 153.7 |
| N1–H1⋯O3 | 0.83 | 2.799 | 2.973 | 93.8 |
| N2–H2⋯O2 | 0.87 | 2.10 | 2.9401 | 162.1 |
| N6–H3⋯O1 | 0.80 | 2.06 | 2.8303 | 163 |
| N1–H1⋯N4 | 0.83 | 2.265 | 2.732 | 116 |
groups in the starting materials into N–NO2 groups in the corresponding, more energetic, derivatives.23 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.23 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 HNO3 and 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 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 15N NMR using Na15NO3 in concentrated H2SO4. A reference mixture of Na15NO3 in concentrated H2SO4 exhibited two 15N NMR signals at 383 ppm and 248 ppm, indicating the presence of 15NO3− and 15NO2−, respectively, and was consistent with previous reports.24 Subsequent addition of BTATz to this nitration mixture at 0 °C resulted in the appearance of a new 15N NMR signal at 336 ppm, which was assigned to the formation of a N–NO2 adduct. Although it was obvious that, under the 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 15N NMR measurements did not help us to determine whether edocyclic 9/10 (routes A and B, Fig. 4) or exocyclic 11 (route C, Fig. 4) nitramines were formed, and since the resulting 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 NaHCO3 at room temperature. A comparison of 1H and 13C NMR data obtained for 12 with 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 HNO3 and acetic anhydride (1:2 v/v) resulted in the formation of the new compound N,N′-(1,2,4,5-tetrazine-3,6-diyil)-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 1H NMR analysis in a solution of DMSO-d6 or CD3CN, 13 underwent relatively quick hydrolysis back to the parent compound 12. 1H and 15N NMR studies in DMSO-d6 of the precipitate obtained in the nitration of 12 with a mixture of Na15NO3/HNO3 (prepared separately) and acetic anhydride also showed only the presence of the starting material 12. Yet, in situ 15N NMR studies of the nitration of 12 with Na15NO3 in concentrated H2SO4 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

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**Fig. 4** Possible nitrated derivatives of compound 5. Reaction conditions: Na15NO3, conc. H2SO4.

**Fig. 5** Synthesis of bis-N-methylated compound 12, with its subsequent nitration. Reaction conditions: (i) dimethyl sulfate, NaHCO3, H2O, r.t. (ii) conc. HNO3, Ac2O.

**Fig. 6** Preparation of compound 15 and its perchlorate salt 16 and nitrate salt 17. Reaction conditions: (i) 1H-1,2,4-triazole-5-amine, sulfolane, 135 °C; (ii) HClO4 or HNO3.
perchlorate salt \(16\) and nitrate salt \(17\) were prepared by treating \(15\) 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 C\(_6\)F\(_5\)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 \(^{15}\)N NMR studies of the nitration of \(15\) with Na\(^{15}\)NO\(_3\) in concentrated H\(_2\)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 for isolation of compound \(18\) result in a quick hydrolysis of the 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'-(1,2,4,5\text{-tetrazine}-3,6-diyl)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 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.

\[
\begin{align*}
\text{Nitration} & \rightarrow \\
\text{Nitrate Derivative} & \\
\end{align*}
\]

Fig. 7 Formation of the proposed compound \(18\). Reaction conditions: (i) Na\(^{15}\)NO\(_3\), H\(_2\)SO\(_4\).

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\begin{align*}
\text{Nitration} & \rightarrow \\
\text{Hydrolysis} & \\
\end{align*}
\]

Fig. 8 Synthesis of compounds \(19, 20\) and \(19A\). Reaction conditions: (i) conc. HNO\(_3\), Ac\(_2\)O; (ii) CH\(_3\)CN, 65 °C; (iii) Na\(^{15}\)NO\(_3\)/HNO\(_3\), Ac\(_2\)O.

\(^{15}\)N NMR studies of the precipitate \(19\) (dissolved in DMSO-
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\text{D}_6, \text{obtained from nitration of } 15 \text{ 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 nitrated triazole rings \(N^3,N^6\text{-bis}(3\text{-nitro-1H-1,2,4-triazol-5-yl})\text{-1,2,4,5-tetrazine-3,6-diamine} \(20\). No exocyclic nitramine derivatives (N-\(^{15}\)NO\(_2\)) 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^3,N^6\text{-bis}(3\text{-nitro-1H-1,2,4-triazol-5-yl})\text{-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 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 K\(\alpha\) radiation (\(\lambda = 0.71073 \) 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.\(^{25}\) 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 \(P2_1(1)c\) and a cell volume of 757.49 Å\(^3\). 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 N\(_6\) 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 N\(_6\) and participates in an intramolecular hydro-
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 EXPLO\textsubscript{5} v6.0\textsuperscript{13} 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\textsuperscript{-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).
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 (BTATz; 5) and were used as supplied, without further purification. \(^1\)H, \(^13\)C NMR spectra were recorded on a 400 MHz NMR spectrometer at 25 °C. The chemical shifts are given relative to residual DMSO-d6 peaks or formamide (\(^{15}\)N) 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-QToF 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 4489 using a BAM drop-hammer. The friction sensitivities were tested according to STANAG 4487 using a BAM friction tester. Experimental details were obtained by pycnometry measurements at ambient temperature.

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. \(^1\)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-d6 peaks or formamide (\(^{15}\)N) 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-QToF 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 4489 using a BAM drop-hammer. The friction sensitivities were tested according to STANAG 4487 using a BAM friction tester. Experimental details 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. DEPT135 (100 MHz, DMSO-d₆): δ 40.2 (CH₃). HRMS (ESI⁺): m/z = 277.1127 [M + H⁺].

The reaction mixture was cooled down to RT, DMF (150 mL) 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, 23.90 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 was collected by filtration, washed with MeOH (3 × 80 mL) and dried under vacuum to yield pure 15 (4.77 g; 81%) as an orange solid. DSC (5 °C min⁻¹) 350 °C (decomp.). HRMS (ESI⁺): m/z = 245.0697 [M − H⁻]. Elemental Analysis: calcd (%) for C₂H₄N₁₄O₄: δ 149.7, 158.2, 160.5. FTIR (ATR): ν 3235 (w), 3018 (w), 2865 (w), 1588 (s), 1538 (s), 1428 (s), 1262 (m), 1197 (m), 1049 (s), 950 (s), 898 (w), 815 (w), 744 (m), 672 (m), 547 (s) cm⁻¹.

N⁵,N⁶-Di(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (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, 23.90 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 was collected by filtration, washed with MeOH (3 × 80 mL) and dried under vacuum to yield pure 15 (4.77 g; 81%) as an orange solid. DSC (5 °C min⁻¹) 350 °C (decomp.). HRMS (ESI⁺): m/z = 245.0697 [M − H⁻]. Elemental Analysis: calcd (%) for C₂H₄N₁₄O₄: δ 149.7, 158.2, 160.5. FTIR (ATR): ν 3235 (w), 3018 (w), 2865 (w), 1588 (s), 1538 (s), 1428 (s), 1262 (m), 1197 (m), 1049 (s), 950 (s), 898 (w), 815 (w), 744 (m), 672 (m), 547 (s) cm⁻¹.

N⁵,N⁶-Di(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine perchlorate salt (16). A solid N⁵,N⁶-di(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine (20) (HNO₃ (99%; 2.5 mL, 60.02 mmol) was added to acetic anhydride (7.5 mL, 79.49 mmol) at 0 °C and the mixture was stirred for 30 min. To this mixture, a solid N⁵,N⁶-di(1H-1,2,4-triazol-5-yl)-1,2,4,5-tetrazine-3,6-diamine 15 (494 mg, 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 CF₂CO₂H (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.). ¹³C NMR (100 MHz, DMSO-d₆): δ 149.7, 158.2, 160.5. FTIR (ATR): ν 3247 (w), 2996 (w), 1601 (s), 1541 (s), 1494 (s), 1435 (s), 1417 (s), 1312 (s), 1296 (s), 1151 (m), 1072 (s), 1050 (s), 1018 (m), 950 (s), 891 (m), 835 (m), 748 (m), 692 (s), 570 (s).

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Notes and references

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

2 http://kaleidoscope.cultural-china.com/en/136Kaleidoscope1.html.

3 (a) L. E. Fried, M. R. Manaan, P. F. Pagoria and R. L. Simpson, Ann. Rev. Mater. Res., 2001, 31, 291–321; (b) Q. Wu, W. Zhu and H. Xiao, J. Mater. Chem. A, 2014, 2, 13006–13015; (c) H. Martinez, Z. Zheng and W. R. Dolbier, J. Fluorine Chem., 2012, 143, 112; (d) A. Dippold and T. Klapötke, J. Am. Chem. Soc., 2013, 135, 9931; (e) V. Thottempudi, H. Gao and J. M. Shreeve, J. Am. Chem. Soc., 2011, 1144.

4 (a) P. F. Pagoria, G. S. Lee, A. R. Mitchell and R. D. Schmidt, Thermochim. Acta, 2002, 384, 187; (b) A. K. Sikder and N. Sikder, J. Hazard. Mater., 2004, 112, 1; (c) Z. Zeng, H. Gao, B. Twamley and J. M. Shreeve,
5 (a) D. E. Chavez and M. A. Hiskey, J. Energy Mater., 1999, 17, 357–377; (b) Q. Zhang, J. Zhang, D. A. Parrish and J. M. Shreeve, Chem. – Eur. J., 2013, 19, 11000.

6 (a) D. M. Badgajar, M. B. Talawar, S. N. Asthana and P. P. Mahulikar, J. Hazard. Mater., 2008, 151, 289; (b) M. J. Rossi, J. C. Bottaro and D. F. McMillen, Int. J. Chem. Kinet., 1993, 25, 549; (c) C. Darwich, T. M. Klápótké and C. M. Sabaté, Chem. – Eur. J., 2008, 14, 5756.

7 (a) Q. L. Yan and S. Zeman, Int. J. Quantum Chem., 2013, 113, 1049; (b) M. Cartwright and J. Wilkinson, Propellants, Explos., Pyrotech., 2010, 35, 326; (c) Q. Wu, W. Zhu and H. Xiao, J. Chem. Eng. Data, 2013, 58, 2748.

8 (a) M. Genetier, A. Osmont and G. Baudin, J. Phys.: Conf. Ser., 2014, 500, 192001; (b) M. J. Kamlet and H. G. Adolph, Propellants Explos., 1979, 4, 30; (c) E. S. Shanley and G. A. Melhem, Process Saf. Prog., 1995, 14, 29.

9 (a) C. Zhang, Y. Shu, Y. Huang, X. Zhao and H. Dong, J. Phys. Chem. B, 2005, 109, 8978; (b) B. Tan, X. Long and J. Li, Comput. Theor. Chem., 2012, 993, 66; (c) M. X. Zhang, P. E. Eaton and R. Gilardi, Angew. Chem., Int. Ed., 2000, 39, 401.

10 M. Rahm, G. Bélanger-Chabot, R. Haiges and K. O. Christe, Angew. Chem., Int. Ed., 2014, 53, 6893.

11 T. Wei, W. Zhu, X. Zhang, Y. F. Li and H. Xiao, J. Phys. Chem. A, 2009, 113, 9404.

12 A. A. Korkin and R. J. Bartlett, J. Am. Chem. Soc., 1996, 118, 12244.

13 C. Steffen, K. Thomas, U. Huniar, A. Hellweg, O. Rubner and A. Schroer, J. Comput. Chem., 2010, 31, 2967.

14 Y. Li, W. Liu and S. Pang, Molecules, 2012, 17, 5040–5049.

15 (a) T. M. Klápótké, J. Stierstorfer and A. U. Wallek, Chem. Mater., 2008, 20, 4519; (b) E. G. Gillan, Chem. Mater., 2000, 12, 3906; (c) Y. H. Joo, B. Twamley, S. Garg and J. M. Shreeve, Angew. Chem., Int. Ed., 2008, 47, 6236; (d) Y. Guo, H. Gao, B. Twamley and J. M. Shreeve, Adv. Mater., 2007, 19, 2884; (e) G. Steinhauser and T. M. Klápótké, Angew. Chem., Int. Ed., 2008, 47, 3330; (f) D. Chand, D. Parrish and J. M. Shreeve, J. Mater. Chem. A, 2013, 1, 15383; (g) R. P. Singh, R. D. Verma, D. T. Meshri and J. M. Shreeve, Angew. Chem., Int. Ed., 2006, 45, 3584.

16 (a) D. Srinivas, V. D. Ghule and K. Muralidharan, RSC Adv., 2014, 4, 7041; (b) G. H. Tao, B. Twamley and J. M. Shreeve, J. Mater. Chem., 2009, 19, 5850.

17 (a) T. M. Klápótké and D. G. Piercey, Inorg. Chem., 2011, 50, 2732; (b) Y. H. Joo and J. M. Shreeve, Angew. Chem., Int. Ed., 2010, 49, 7320; (c) Y. H. Joo and J. M. Shreeve, Angew. Chem., Int. Ed., 2009, 48, 564.

18 (a) H. Torii, M. Nakadai, K. Ishihara, S. Saito and H. Yamamoto, Angew. Chem., Int. Ed., 2004, 43, 1983; (b) G. Fischer, G. Hov, T. M. Klápótké and J. Weigand, J. Thermochim. Acta, 2005, 437, 168; (c) T. M. Klápótké and J. Stierstorfer, Helv. Chim. Acta, 2007, 90, 2132; (d) T. M. Klápótké, A. Preimesser and J. Stierstorfer, Z. Naturforsch., B: Chem. Sci., 2013, 68, 1310–1320.

19 (a) P. M. Cormick, M. Rovera and E. N. Durantini, J. Photochem. Photobiol. Chem., 2008, 194, 220; (b) M. Esseffar, E. Quintanilla, J. Z. Dvalos, J. L. M. Abboud and M. Yez, New J. Chem., 2002, 26, 1567; (c) V. D. Ghule, R. Sarangapani, P. M. Jadhav and S. P. Tewari, J. Mol. Model., 2011, 17, 1507; (d) D. Srinivas, V. D. Ghule, S. P. Tewari and K. Muralidharan, Chem. – Eur. J., 2012, 18, 15031; (e) H. Hao Wei, H. Gao and J. M. Shreeve, Chem. – Eur. J., 2014, 20(51), 16943–16952; (f) R. Haiges, G. Bélanger-Chabot, S. M. Kaplan and K. O. Christe, Dalton Trans., 2015, 44, 7586; (g) R. Haiges and K. O. Christe, Inorg. Chem., 2013, 52, 7249.

20 A. Saikia, R. Sivabal, B. G. Polke, G. M. Gore, A. Singh, A. Subhananda Rao and A. K. Sikder, J. Hazard. Mater., 2009, 170, 306.

21 (a) D. E. Chavez, M. A. Hiskey and D. L. Naud, Propellants, Explos., Pyrotech., 2004, 29, 209; (b) T. Wei, J. Wu, W. Zhu, C. Zhang and H. Xiao, J. Mol. Model., 2012, 18(8), 3467–3479.

22 M. Masuda, H. F. Mower, B. Pignatelli, I. Celan, M. D. Friesen, H. Nishino and H. Ohshima, Chem. Res. Toxicol., 2000, 13, 301.

23 (a) G. Olah, A. Orlinkov, A. B. Ozyogolu and G. K. S. Prakash, J. Org. Chem., 1995, 60, 7348; (b) J. G. Hoggett, R. B. Moodie, J. R. Penton and K. Schofield, Nitration and aromatic reactivity, 1971.

24 G. K. S. Prakash, L. Heiliger and G. A. Olah, Inorg. Chem., 1990, 29, 4965–4968.

25 (a) A. A. Dippold and T. M. Klápótké, Chem. – Eur. J., 2012, 18, 16742–16753; (b) A. B. Sheremetev, N. V. Palyseva, M. I. Struchkova and K. Y. Suponitsky, Mendeleev Commun., 2012, 22, 302–304.

26 A. L. Speck, Acta Crystallogr., Sect. D: Biol. Crystallogr., 2009, 65, 148–155.

27 M. H. Keshavarz, J. Hazard. Mater., 2007, 145, 263–269.

28 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. A. Petersson, et al., GAUSSIAN 09 (Revision D.01), Gaussian, Inc., Wallingford, CT, 2009.

29 A. D. Becke, J. Chem. Phys., 1993, 98, 5648.

30 M. Suceska, Mater. Sci. Forum, 2004, 325, 465–466.