Novel family of nitrogen-rich energetic (1,2,4-triazolyl) furoxan salts with balanced performance

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Nitrogen-rich energetic materials comprised of a combination of several heterocyclic subunits retain their leading position in the field of materials science. In this regard, a preparation of novel high-energy materials with balanced set of physicochemical properties is highly desired. Herein, we report the synthesis of a new series of energetic salts incorporating a (1,2,4-triazolyl) furoxan core and complete evaluation of their energetic properties. All target energetic materials were well characterized with IR and multinuclear NMR spectroscopy and elemental analysis, while compound 6 was further characterized by single-crystal X-ray diffraction study. Prepared nitrogen-rich salts have high thermal stability (up to 232°C), good experimental densities (up to 1.80 g cm$^{-3}$) and high positive enthalpies of formation (344–1,095 kJ mol$^{-1}$). As a result, synthesized energetic salts have good detonation performance ($D = 7.0–8.4$ km s$^{-1}$; $p = 22–32$ GPa), while their sensitivities to impact and friction are quite low.

KEYWORDS nitrogen heterocycle, energetic material, energetic salts, 1,2,4-triazole, furoxan

1 Introduction

Functional organic materials are one of the most important and emerging area of research in state-of-the-art materials science (Li and Yu, 2021; Liu et al., 2021). Construction of potential high-performance materials as well as their essential components is needed to be achieved according to modern requirements of sustainable and environmentally-focused society. This issue is still relevant in the field of energetic materials science (Fershtat and Makhova, 2020; O’Sullivan and Zdilla, 2020; Zhou et al., 2022). Performance and sensitivity of currently used high-energy compounds (TNT: 2,4,6-trinitrotoluene, RDX: 1,3,5-trinitro-1,3,5-triazinane, PETN: pentaerythritol tetranitrate) are usually unbalanced, while their ecological and toxicological profiles are unfavorable. In this regard, preparation of novel eco-friendly energetic materials with
high nitrogen content and acceptable safety requirements remains urgent (Kuchurov et al., 2017; Zlotin et al., 2021).

In recent decade, synthesis of organic energetic materials is often performed through a combination of various polynitrogen and nitrogen-oxygen heterocyclic scaffolds: tetrazole-furazan (Liang et al., 2012; Huang et al., 2012; Liang et al., 2013), tetrazole-furoxan (Fershtat et al., 2015a; Larin et al., 2019), 1,2,4-triazole-furazan (Xu et al., 2018; Ma et al., 2019a; Ma et al., 2019b; Sheremetev et al., 2019; Aleksandrova et al., 2020; Ma et al., 2020; Chinnam et al., 2021), tetrazole-furoxan-1,2,4-oxadiazole (Liu et al., 2018) (Figure 1). A combination of structurally diversified nitrogen-rich heterocycles linked via N, N'-ethylene bridges was also reported as one of the promising approaches to balance energetic properties of the resulted energy-rich materials (Kumar et al., 2016a; Kumar et al., 2016b). Recently, our team reported a preparation of energetic (1,2,4-triazoly) furoxans with good detonation performance and decreased sensitivity (Larin et al., 2022). However, it is known that NH-fragment of the 1,2,4-triazole ring is weakly acidic (Garratt, 1996) and may stimulate corrosivity which is undesired for any potential application. Although examples on the preparation of energetic salts bearing a 1,2,4-triazolate anion are rather scarce (except NTO-based those) (Parisi et al., 2021; Cregan et al., 2022), such strategy may serve as a convenient solution to overcome this issue. High-energy salts usually have acceptable thermal stability (>150°C) and moderate sensitivity to mechanical stimuli, while owing to the high nitrogen content these metal-free salts have a high level of environmental compatibility (Larin et al., 2019; Larin and Fershtat, 2021). Herein, we present the synthesis of a new series of energetic salts comprising a (1,2,4-triazolyl) furoxan core (Figure 1) and complete evaluation of their energetic properties.

2 Materials and methods

CAUTION! Although we have encountered no difficulties during preparation and handling of the compounds described in this paper, they are potentially explosive energetic materials that are sensitive to impact and friction. Mechanical actions of these energetic materials, involving scratching or scraping, must be avoided. Any manipulations must be carried out by using appropriate standard safety precautions.

All reactions were carried out in well-cleaned oven-dried glassware with magnetic stirring. 1H and 13C NMR spectra were recorded with a Bruker AM-300 (300.13 and 75.47 MHz, respectively) spectrometer and referenced to the residual solvent peak. 14N NMR spectra were measured with a Bruker AM-300 (21.69 MHz) spectrometer by using MeNO2 [δ(14N) = 0.0 ppm] as an external standard. 15N NMR spectra were recorded with a Bruker DRX500 instrument (the frequency for 15N was 50.7 MHz) at room temperature. The chemical shifts are reported in ppm (δ). Coupling constants, J, are reported in Hertz. The IR spectra were recorded with a Bruker “Alpha” spectrometer in the range 400–4,000 cm⁻¹ (resolution 2 cm⁻¹). Elemental analyses were performed by the CHN Analyzer PerkinElmer 2,400. The melting points were determined with a Stuart SMP20 apparatus and are uncorrected. All standard reagents were purchased from Aldrich or Acros Organics and used without further purification. Amidrazones 2a (Fershtat et al., 2015b) and 2b (Larin et al., 2021), 3-cyano-4-(1H-1,2,4-triazol-3-yl)furoxan 3a and 4-azido-3-(1H-1,2,4-triazol-3-yl)furoxan 3b (Larin et al., 2022) were synthesized according to the literature.

2.1 X-ray diffraction study

The colorless single crystals of 6 were grown from DMF. At 100 K crystals of 6 (C₅H₆N₁₀O₂) are triclinic, space group P-1: a = 4.8372(2), b = 9.6045(4), c = 10.1054(4) Å, α = 94.895(3), β = 92.103(2), γ = 98.814(2), V = 461.66(3) Å³, Z = 2, dcalc = 1.714 g cm⁻³, F(000) = 244. Intensities of 4,822 reflections were measured with a Bruker APEX II CCD diffractometer (λ(MoKa) = 0.71073 Å, ω-scans, 2θ < 58°) and 2,198 independent reflections [Rint = 0.0336]
were used in further refinement. The structure was solved by direct method and refined by the full-matrix least-squares technique against F² in the isotropic-anisotropic approximation. The hydrogen atoms were found in difference Fourier synthesis and refined in the isotropic approximation. For 6, the refinement converged to wR² = 0.1207, GOOF = 0.992 and R1 = 0.0429 for 1.602 independent reflections with 1 > 2σ(I). All calculations were performed using SHELXL-2014/6 (Sheldrick, 2015). As for the CCDC, 2193015 contains the supplementary crystallographic data for 6-H₂O. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge, CB21EZ, UK; or deposit@ccdc.cam.ac.uk).

### 2.2 Computational methods

All DFT calculations for 6, TILMEI and DUQGUT were performed with the Gaussian09 program (Frisch et al., 2016). The optimization procedures of all model structures (together with the optimization of hydrogen atoms positions for the isolated ions in crystal geometries) are done invoking the standard cutoff criteria and using the def2-TZVP basis set (Weigend and Ahlrichs, 2005; Weigend, 2006) and the PBE0 functional (Perdew et al., 1996; Adamo and Barone, 1999) with the Grimme et al. (2010) empirical dispersion correction and Becke-Johnson damping (Grimme et al., 2011). The non-specific solution effects are modelled for 6 by means of the set of displaced point charge sites by program FitMEP (Dzyabchenko, 2008a).

The ΔOED analysis for 6, TILMEI and DUQGUT were done based on the HF/3-21G electron densities calculated for the crystal fragments and the PBE0/def2-TZVP electron densities calculated for the isolated ions in crystal geometries. The X-H bond lengths for all these calculations were fixed on the values obtained upon the partial optimization of isolated ions in crystal geometries. The crystal fragments contain 24 anions and 24 cations for the DUQGUT structure, 23 anions and 23 cations for the TILMEI structure and 22 anions and 22 cations for 6. The partitioning of real space into atoms was done within the “Atoms in Molecules” theory. The volume integration (both, over the atomic basins for the central molecule in a cluster and over the volume enclosed by 0.0004 a.u. isosurface of electron density for isolated ions) was performed using the Multiwfn program (Lu and Chen, 2012). The SHELX (Sheldrick, 2015) atomic mass table was used to calculate density values.

The heat of formation calculations were carried out combining the atomization energy method (Eq. 1) (Ochterski et al., 1996; Montgomery et al., 2000) with CBS-4M electronic enthalpies (Klapötke, 2012; Khakimov et al., 2015). CBS-4M energies of the atoms were calculated with the Gaussian 09 software package (Frisch et al., 2016). Values for ΔH (atoms) were taken from the NIST database.

\[ \Delta H_f(g, 298) = H(Molecule, 298) - \sum H^+(Atoms, 298) + \sum \Delta H^+(Atoms, 298) \] (1)

Geometric optimization of all structures for crystal packing calculation was carried out using the DFT/B3LYP functional and the aug-cc-PVDZ basis set with a Grimme (2011) D2 dispersion correction. The optimized structures were conformed to be true local energy minima on the potential-energy surface by frequency analyses at the same level.

In the calculation of lattice energy, the molecules were treated as rigid bodies with fixed point groups. We apply pairwise atom-atom potentials to describe the van der Waals and electrostatic point charges for Coulomb components of intermolecular energy. At the initial stage '6-12' Lenard-Jones (LJ) type potential parameters were used (Momany et al., 1974). The electrostatic energy was calculated with a set of displaced point charge sites by program FitMEP (Dzyabchenko, 2008a). The lattice energy simulations were performed with the program PMC (Dzyabchenko, 2008b).

It is well known that the majority of organic crystal structures studied experimentally belong to a rather limited number of space groups (Belsky et al., 1995). For brief assessment of crystal packing, we get the following ordered list of the most likely structural classes: P2₁/c, P2₁₂₁₂₁, P-1, Pca2₁ and P1 with two independent molecules in cell, which cover more than 80% of the whole number of crystal structures in total (Belsky et al., 1995). Taking into account low deviation in crystal lattice energies of polymorphs, such calculation is considered reasonable.

Enthalpies of sublimation for 1a and 1b were calculated by formula:

\[ \Delta H_{sub} = -E_{latt} - 2RT, \]

where R is the universal gas constant, E_{latt} is the lattice energy, T is temperature (298 K). The new approach for salts proposes a technique based on modeling the crystal packing for a salt and a similar neutral compound (quasi-salt, cocystal). The enthalpy of formation in this case is calculated as the average value between these two structures (Khakimov and Pivina, 2022).

Detonation performance parameters (detonation velocity at maximal density and Chapman-Jouguet pressure) were calculated by recently suggested set of empirical methods from...
2.3 Thermal analysis and sensitivity measurements

Thermal analysis of the substances was carried out with a Netzsch DSC 204 HP apparatus. Samples (0.2–3.0 mg, depending on their heat release rate) were placed in aluminum pans covered with pierced lids. The samples were heated up to 400°C at a constant rate of 5 K min⁻¹. Impact sensitivity tests were performed by using a BAM-type fallhammer according to STANAG 4489 standard. The reported values (IS) are the drop energies corresponding to 50% probability of explosion obtained by Brucceron analysis. Friction sensitivity was evaluated in agreement with STANAG 4487 standard. The reported quantity (FS) is the friction force corresponding to 50% probability of explosion. The details of safety test procedures can be found elsewhere (Muravyev et al., 2021).

2.4 Syntheses

General procedure for the preparation of (1,2,4-triazolyl) furazans silver salts 3a,b. A solution of AgNO₃ (2.04 g, 12 mmol) in H₂O (50 ml) was added dropwise to a magnetically stirred solution of the corresponding 1H-1,2,4-triazol-3-yl-furoxan 1a,b (12 mmol) in MeOH (45 ml). The resulting mixture was stirred at ambient temperature for 5 h, the solid formed was filtered off, washed with water (3 × 100 ml) and dried in air.

Silver 3-(4-azido-2-oxido-1,2,5-oxadiazol-3-yl)-1,2,4-triazol-1-ide (3a): Yield 3.38 g (94%); white solid; elemental analysis calcd (%) for C₇H₇N₃O₂ (243.14): C 26.47, H 1.65, N 51.71; found: C 26.1, H 1.6, N 51.5;

Silver 3-(3-cyano-2-oxido-1,2,5-oxadiazol-4-yl)-1,2,4-triazol-1-ide (3b): Yield 3.01 g (88%); white solid; elemental analysis calcd (%) for C₇H₇N₃O₂ (229.99): C 31.17, H 1.48, N 59.15; found: C 31.1, H 1.4, N 58.9.

General procedure for the preparation of energetic salts 4a-c, 5a-c: Corresponding chloride (2 mmol) was added to a magnetically stirred suspension of the silver salt 3a,b (2 mmol) in H₂O (30 ml) at 20 C. The resulting mixture was stirred at 60°C for 24 h. Then AgCl was removed by filtration and the solvent was evaporated in vacuo. The residue was recrystallized from water and dried in a vacuum desiccator over P₂O₅ for 24 h.

3,6,7-Triamino-7-[1,2,4]triazolo[4,3-b][1,2,4]triazol-2-ium 3-(4-azido-2-oxido-1,2,5-oxadiazol-3-yl)-1,2,4-triazol-1-ide (4a): Yield 0.54 g (78%); red solid; ¹H NMR (300 MHz, DMSO-d₆): δ = 8.87 (s, 1H), 6.79 (s, 2H), 6.72 (s, 2H), 5.69 (s, 2H); ¹³C[¹H] NMR (75.5 MHz, DMSO-d₆): δ = 159.7, 153.1, 148.7, 147.1, 146.0, 142.9, 105.5; ¹⁴N NMR (21.7 MHz, DMSO-d₆): δ = –146.7 (s, N₃); IR (KBr): 3418, 3306, 3330, 3254, 1630, 1618, 1548, 1438, 1336, 1277, 1154, 1044 cm⁻¹; elemental analysis calcd (%) for C₇H₇N₇O₃ (348.10): C 28.42, H 1.78, N 61.67; found: C 28.3, H 1.8, N 61.7; IR (KBr): 3306, 3254, 1630, 1618, 1548, 1438, 1336, 1277, 1154, 1044 cm⁻¹; elemental analysis calcd (%) for C₇H₇N₇O₃ (348.10): C 28.42, H 1.78, N 61.67; found: C 28.3, H 1.8, N 61.7; IR (KBr):
3,313, 3,280, 3,103, 1,700, 1,645, 1,622, 1,590, 1,536, 1,427, 1,384, 1,215, 1,114, 1,002, 960, 751 cm\(^{-1}\); elemental analysis calcd (%) for C\(_8\)H\(_7\)N\(_{13}\)O\(_2\) (317.08): C 30.29, H 2.22, N 57.40; found: C 30.52, H 2.06, N 57.21; IS: 22 J, FS: 350 N.

**Synthesis of ammonium 3-(3-cyano-2-oxido-1,2,5-oxadiazol-4-yl)-1,2,4-triazol-1-ide (5d)**

Ammonia was bubbled through a solution of 1b (0.88 g, 4.9 mmol) in CH\(_3\)CN (10 ml). The saturated solution was stirred for 0.5 h. The precipitate was filtered off and washed with Et\(_2\)O (2 × 10 mL) to give energetic salt 5d. Yield 0.83 g (86%); light orange solid; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta = 8.37\) (s, 1H), 6.35 (br. s, 4H); \(^{13}\)C\{\(^1\)H\} NMR (75.5 MHz, DMSO-\(d_6\)): \(\delta = 151.0, 150.8, 148.6, 107.8, 98.0\); \(^{14}\)N NMR (21.7 MHz, DMSO-\(d_6\)): \(\delta = -361.0\) (br. s, NH\(_4\)); IR (KBr): 3,324, 3,146, 2,857, 2,252, 1,621, 1,583, 1,536, 1,453, 1,346, 1,276, 1,178, 1,057, 970, 874, 832 cm\(^{-1}\); elemental analysis calcd (%) for C\(_5\)H\(_5\)N\(_7\)O\(_2\) (195.05): C 30.78, H 2.58, N 50.24; found: C 30.74, H 2.76, N 49.98; IS: 11 J, FS: >360 N.

**Synthesis of ammonium 5-(2-oxido-4-(1H-1,2,4-triazol-3-yl)-1,2,5-oxadiazol-3-yl)tetrazol-1-ide 6**

TMSN\(_3\) (2.5 mmol, 0.33 ml) and NH\(_4\)F (1 mmol, 0.037 g) were added to a magnetically stirred mixture of cyanofuroxan 3a (1 mmol) in MeCN (5 ml). The reaction mixture was stirred at 35°C for 10 h until full consumption of substrate 3a (TLC monitoring). Then, the precipitate formed was filtered off, washed with CH\(_3\)CN (5 ml) and dried in a vacuum desiccator over P\(_2\)O\(_5\). Yield 0.20 g (84%); beige solid; \(^1\)H NMR (300 MHz, DMSO-\(d_6\)): \(\delta = 8.65\) (s, 5H); \(^{13}\)C\{\(^1\)H\} NMR (75.5 MHz, DMSO-\(d_6\)): \(\delta = 150.4, 149.8, 147.7, 147.4, 110.4\); \(^{14}\)N NMR (21.7 MHz, DMSO-\(d_6\)): \(\delta = -358.8\) (s, NH\(_4\)); \(^{15}\)N NMR (60.8 MHz, DMSO-\(d_6\)): \(\delta = 12.3, -8.0, -9.9, -12.3, -24.7, -58.3, -130.9, -358.1\); IR (KBr): 3,342, 3,120, 2,989, 1,598, 1,523, 1,448, 1,416, 1,270, 1,220, 1,145, 1,076, 976, 989, 835 cm\(^{-1}\); elemental analysis calcd (%) for C\(_5\)H\(_6\)N\(_{10}\)O\(_2\) (238.17): C 25.22, H 2.54, N 58.81; found: C 25.03, H 2.68, N 58.49; IS: 12 J, FS: >360 N.

3 Results and discussion

Parent biheterocyclic cores, namely 4-azido-3-(1H-1,2,4-triazol-3-yl)furoxan 1a and 3-cyano-4-(1H-1,2,4-triazol-3-yl)furoxan 1b were synthesized according to our recently reported procedure (Larin et al., 2022) via PTSA-catalyzed cyclocondensation of the available amidrazones 2a,b with trimethyl orthoformate. Thus formed biheterocyclic compounds 1a,b were treated with AgNO\(_3\) to obtain corresponding silver salts 3a,b which were further subjected to a metathesis reaction with various nitrogen-rich bases (in a form of hydrochlorides) affording two arrays of high-nitrogen energetic salts 4a-c and 5a-d. Cyano group in compound 1a was also converted to the tetrazolate anion through cycloaddition with in situ generated TMSN\(_3\) (Scheme 1). This approach enabled a selective formation of the (tetrazolyl)furoxan ammonium salt 6 bearing neutral 1,2,4-triazole scaffold.

All newly synthesized compounds were fully characterized by IR and multinuclear (\(^1\)H, \(^{13}\)C, \(^{14}\)N) NMR spectroscopy as well as elemental analysis. Because the synthesized energetic salts have a high nitrogen content, several representatives, namely salts 5c and 6, were additionally characterized by \(^{15}\)N NMR spectroscopy (Figure 2). The signals were assigned by comparison with similar structures (Thottempudi and Shreeve, 2011; Tang et al., 2021). There are thirteen signals in the \(^{15}\)N NMR spectrum of 5c. The
nitrogen atom signals of the two amino groups are observed in the upfield region ($\delta = -317.5$ ppm (N7) and $\delta = -328.7$ ppm (N8). The resonance peaks for N12 and N13 in the cation counter-part are nearly overlapping for structure 5c. The 1,2,4-triazolium anion has characteristic signals at $\delta = -9.6$ (N4), $\delta = -11.2$ (N5), $\delta = -94.6$ (N6), while corresponding peaks of the furoxan ring are located at $\delta = 3.6$ (N2) $\delta = -18.4$ ppm (N3). Only eight signals are presented in the $^{15}$N NMR spectrum of 6. The chemical shift of the nitrogen atom of the ammonium cation (N1) is found at $\delta = -358.1$ ppm which correlates with the corresponding $^{15}$N NMR spectrum of 6. Due to the symmetric structure of the tetrazolate anion in 6, two signals were found at $\delta = -24.7$ ppm (N7, N10) and $-58.3$ ppm (N8, N9). Two signals of nitrogen atoms of the furoxan ring were observed in a downfield region at $\delta = 12.3$ ppm (N2) and $-8.0$ ppm (N3).

The structure of compound 6 was further confirmed by X-ray diffraction study (Figure 3). In crystal, the anionic moiety is nearly planar: the C1C2C4N7 and C2C1C3N3 torsion angles are 1.95° and 6.36°, respectively, while the mean deviation from plane composed by non-hydrogen atoms is only 0.0436 Å. The main packing motif for 6 is the aggregation of anions into
centrosymmetric dimers (Figure 4) by means of two bifurcate H-bonds between the N8(H) groups of triazolyl cycle and the N3 and N7 nitrogen atoms of tetrazole and triazolyl, respectively (N8...N3 and N8...N7 distances are 2.811 and 2.923 Å, correspondingly). The further binding of these dimers is determined by the ammonia cations (Supplementary Figure S1) which form 1) one weak bifurcate NH...O H-bond with exocyclic furoxan oxygen atoms (N...O 3.018 and 3.051 Å), 2) two moderate NH...N hydrogen bonds with the tetrazole fragments (N...N 2.876, 2.954 Å, γ(NHN) 160.6–161.2°) and 3) one moderate NH...N H-bond with the triazole ring (N...N 2.936 Å, γ(NHN) 167.2°). The two former types of H-bonds aggregate the nearly planar dianionic dimers into infinite columns which are additionally stabilized by furoxan...tetrazole and triazole...triazole stacking interactions (the interplane distance is 3.140 Å, Figure 5). Despite the whole crystal packing pattern resembles the layer-like supramolecular aggregation, the mentioned columns are shifted against each other due to the mentioned NH...N H-bonds between the cation and triazole ring (Figure 6).

The compound 6 was found to be an excellent example of the influence of supramolecular forces on the molecular structure. Although the planar conformation of the anion is expected for this class of compounds according to the processing of Cambridge Structural Database (Groom et al., 2016), the DFT calculations of several isolated models demonstrate quite the opposite picture (Supplementary Figures S2–S8). For instance, the triazolyl cycle is perpendicular to the tetrazolyl-furoxan plane in the isolated anion even if the non-specific solvation effects are accounted for. The significant violation of π-conjugation is also found for the isolated...
clusters which were optimized using different fragments of crystal structure of 6 as starting geometries. Here, two factors should be noted: the interplay between triazole and tetrazole moieties to form π-conjugation with the central furoxan ring and the crystal media influence (see Supplementary Table S1 for the information on torsion angles). As an example, the SCRF calculations of isolated anion resulted in the increase of triazole-furoxan conjugation and the decrease of the tetrazole-furoxan one. In its turn, only the formation of rather close to those in the equilibrium isolated structures: the azidotetrazolylfuroxan and nitrotetrazolylfuroxan anions are rationalized by the combination of factors. First of all, the crystal packing of TILMEI and DUQGUT structures are both more isotropic than the column-type packing of TILMEI (Liang et al., 2013 ) and nitrotetrazolylfuroxan (CSD refcode TILMEI) (Liang et al., 2013 ). The TILMEI and DUQGUT structures have been already analyzed by us when the role of cation in physico-chemical properties of tetrazolyl-furoxan salts was under consideration (Larin et al., 2019 ). The comparison of these two structures with 6 is vital to determine the role of a furoxan’s substituent in these salts.

Despite similar composition of 6, TILMEI and DUQGUT, the IS value for 6 (12 J, see Table 1 below) is pronouncedly larger than that for the nitro and azido salts (2.0 and 2.2 J, respectively) (Liang et al., 2013; Larin et al., 2019). As mentioned above, this can be rationalized by the combination of factors. First of all, the crystal packings of TILMEI and DUQGUT structures are both more isotropic than the column-type packing of 6 (see Supplementary Figure S5). Furthermore, the crystal geometries of azidotetrazolylfuroxan and nitrotetrazolylfuroxan anions are rather close to those in the equilibrium isolated structures: the rmsd value for non-hydrogen atoms are 0.0703 and 0.2628 Å for DUQGUT and TILMEI (Supplementary Figure S10), whereas the energy difference between the isolated and crystal (optimized hydrogen atoms) geometries is 3.2 and 4.3 kcal mol⁻¹.

TABLE 1 Physical properties and detonation parameters.

| Compound | T₉ [°C] | ρ [g cm⁻³] | N [g %] | O [g %] | ²ΔHⁿ solid [kJ mol⁻¹] | ²ΔHfs solid [kJ g⁻¹] | D [km s⁻¹] | ²P⁺ [GPa] | ²IS [J] | ²FS [N] |
|----------|---------|------------|---------|---------|-----------------|-----------------|----------|--------|--------|--------|--------|
| 1a       | 154     | 1.70       | 57.7    | 74.2    | 623             | 3.2             | 8.0      | 29     | 4      | 270    |
| 4a       | 155     | 1.68       | 64.4    | 73.6    | 1,044           | 3.0             | 7.9      | 27     | 8      | >360   |
| 4b       | 150     | 1.80       | 65.2    | 76.7    | 896             | 3.2             | 8.4      | 32     | 9      | >360   |
| 4c       | 152     | 1.68       | 63.1    | 72.7    | 1,095           | 3.3             | 7.9      | 28     | 5      | 260    |
| 1b       | 229     | 1.55       | 47.2    | 65.2    | 453             | 2.5             | 7.0      | 22     | 19     | 220    |
| 5a       | 153     | 1.68       | 59.0    | 68.7    | 834             | 2.5             | 7.5      | 25     | 14     | 290    |
| 5b       | 172     | 1.76       | 58.6    | 70.7    | 703             | 2.7             | 7.9      | 29     | 21     | 250    |
| 5c       | 154     | 1.66       | 57.4    | 67.5    | 887             | 2.8             | 7.5      | 26     | 22     | 350    |
| 5d       | 232     | 1.61       | 50.3    | 66.7    | 344             | 1.8             | 7.2      | 23     | 11     | 260    |
| 6        | 217     | 1.64       | 58.8    | 72.2    | 467             | 2.0             | 7.5      | 24     | 12     | >360   |
| TNT      | 275     | 1.64       | 18.5    | 60.8    | -62             | -0.3            | 6.9      | 23     | 30     | >360   |
| PETN     | 165     | 1.78       | 17.7    | 78.5    | -561            | -1.8            | 8.4      | 32     | 3      | 70     |

² Decomposition temperature (DSC, 5 K min⁻¹).
² Density (gas pycnometer, 298 K).
² Nitrogen content.
² Nitrogen and oxygen content.
² Calculated enthalpy of formation.
² Calculated detonation velocity.
² Calculated detonation pressure.
² Impact sensitivity.
² Friction sensitivity.
The Δ allows to estimate density tetrazolylfuroxan salts on density of their crystals. This approach (2018b) was utilized to explore the in
density. Finally, the low IS values for DUQGUT and TILMEI agree well
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for isolated states, the triazole ring in
positively affects the density of azidotetrazolylfuroxan are slightly less dense (1.71 g cm
of azide moiety in DUQGUT while it becomes considerably
denser than that of DUQGUT. In the same manner, the dense
NO2 group usually decreases its volume to a large extent due to
the participation in a number of shortened intermolecular
contacts; the presence of this group in TILMEI leads to a
pronounced densification of this salt and its large crystal
density. Finally, it is interesting to note, that the statistical
consideration of ΔOED values for fragments of 6, DUQGUT
and TILMEI also indicates the influence of crystal packing
effects on the impact sensitivity. The sample variance is the
same in TILMEI and DUQGUT (0.007 g2 cm
3) while it is larger
for 6 (0.010 g2 cm
3). Indeed, a larger variance corresponds to a
more dispersive densification of fragments that is obtained by less
isotropic distribution of non-covalent interactions.

Physicochemical and sensitivity properties as well as detonation
performance of all synthesized compounds were evaluated and the
results are summarized in Table 1. As for thermal stability, most of
the investigated salts have acceptable thermal decomposition onsets in the
range of 150–172 °C. The exceptions are neutral compound 1b and
two ammonium salts 5d and 6, which all have thermal stability in
conventional linear heating DSC tests above 200°C (Figure 7).

Synthesized compounds have good densities (1.61–1.80 g
3) and considerable amount of nitrogen and oxygen
within the molecule (65%–74%). Calculated enthalpies of
formation of the synthesized energetic salts are in a range of
344–1,095 kJ mol
1. Based on the experimental densities and
calculated enthalpies of formation, detonation performance of all
synthesized energetic salts was estimated and compared to
benchmark explosives TNT and PETN (all calculations were
performed using PILEM software). Detonation velocity values
were found to be within 7.0–8.4 km s
−1, while the calculated
detonation pressures fall in a range of 22–32 GPa. Therefore, the
energetic performance of these new compounds outperform
benchmark explosive trinitrotoluene (TNT), but are inferior to
booster explosive pentaerythritol tetrannitrate (PETN). These two
temporary energetic materials also serve as limits for
synthesized compounds from the mechanical sensitivity
aspect. Impact sensitivity for (1,2,4-triazolyl)furoxan energetic
salts varies from sensitive 5 J for 4c to less sensitive 5b,c with
21–22 J. Analyzed species are not very sensitive to friction
stimulus, e.g., compounds 4a,b, 6 are even not sensitive at all.

4 Conclusion

In conclusion, an array of novel nitrogen-rich energetic salts
comprising of the (1,2,4-triazolyl) furoxan core was designed and
synthesized. All target high-energy materials were prepared in
high yields starting from readily available furoxan precursors
bearing amidrazone functionality and well characterized with IR

respectively. The crystal structure of anion in 6 is significantly
more stressed: the corresponding values are larger due to the
mentioned rotation of triazole cycle (0.7295 Å and 8.1 kcal mol
1).
Finally, the low IS values for DUQGUT and TILMEI agree well
with the presence of explosphoric N3 group in the former and the
dense packing of the latter (1.85 vs. 1.71 g cm
3) for 6).

It is interesting to note that the crystal density value does not
 correlate with the impact sensitivity for 6 and DUQGUT; crystals
of azidotetrazolylfuroxan are slightly less dense (1.71 g cm
3).
The ΔOED formalism (Dalinger et al., 2018a; Dalinger et al.,
2018b) was utilized to explore the influence of a substituent in
tetrazolylfuroxan salts on density of their crystals. This approach
allows to estimate densification (ΔOED) of a system upon the
gas-to-crystal transition as it is based on the comparison of volumes
which are filled by a system in the isolated state (0.0004 a. u.
isosurface of electron density function) and in crystal. More
information can be gathered by means of the exhaustive
partitioning of real 3D space (for example, by means of the
"Atoms in Molecules" theory) that allows to decompose the
crystal density into the density of chemically meaningful
fragments. This technique was found to be particularly helpful
for the analysis of salts and co-crystals (Larin et al., 2019). The
details of such calculations for 6, DUQGUT and TILMEI are
listed in Supplementary Table S2 of Supporting Information.

It was found that the presence of substituent with the
increasing ability to be densified upon crystal formation
positively affects the densification of the whole salt. In the
isolated states, the triazole ring in 6 is less dense that the
azide moiety in DUQGUT while it becomes considerably
denser than N3 in corresponding crystals. The large
densification of triazole evidently produced by a greater
number of short non-covalent interactions (rather strong
H-bonds in the case of 6) increases the densification of all
other fragments. As a result, the structure of 6 is slightly
denser than that of DUQGUT. In the same manner, the dense
NO2 group usually decreases its volume to a large extent due to
the participation in a number of shortened intermolecular
contacts; the presence of this group in TILMEI leads to a
pronounced densification of this salt and its large crystal
density. Finally, it is interesting to note, that the statistical
consideration of ΔOED values for fragments of 6, DUQGUT
and TILMEI also indicates the influence of crystal packing
effects on the impact sensitivity. The sample variance is the
same in TILMEI and DUQGUT (0.007 g2 cm
3) while it is larger
for 6 (0.010 g2 cm
3). Indeed, a larger variance corresponds to a
more dispersive densification of fragments that is obtained by less
isotropic distribution of non-covalent interactions.

Physicochemical and sensitivity properties as well as detonation
performance of all synthesized compounds were evaluated and the
results are summarized in Table 1. As for thermal stability, most of
the investigated salts have acceptable thermal decomposition onsets in the
range of 150–172 °C. The exceptions are neutral compound 1b and
two ammonium salts 5d and 6, which all have thermal stability in
conventional linear heating DSC tests above 200°C (Figure 7).

Synthesized compounds have good densities (1.61–1.80 g
3) and considerable amount of nitrogen and oxygen
within the molecule (65%–74%). Calculated enthalpies of
formation of the synthesized energetic salts are in a range of
344–1,095 kJ mol
1. Based on the experimental densities and
calculated enthalpies of formation, detonation performance of all
synthesized energetic salts was estimated and compared to
benchmark explosives TNT and PETN (all calculations were
performed using PILEM software). Detonation velocity values
were found to be within 7.0–8.4 km s
−1, while the calculated
detonation pressures fall in a range of 22–32 GPa. Therefore, the
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4 Conclusion

In conclusion, an array of novel nitrogen-rich energetic salts
comprising of the (1,2,4-triazolyl) furoxan core was designed and
synthesized. All target high-energy materials were prepared in
high yields starting from readily available furoxan precursors
bearing amidrazone functionality and well characterized with IR
and multinuclear NMR spectroscopy, elemental analysis and X-ray diffraction study. According to the X-ray diffraction study, the large densification of the 1,2,4-triazole heterocycle evidently produced by a greater number of short non-covalent interactions (rather strong H-bonds in the case of 6) increases the densification of all other fragments. Thermal stabilities of the synthesized energetic materials were determined using differential scanning calorimetry. It was found that most of the investigated salts have acceptable thermal decomposition onsets in the range of 150°C–172°C, while two ammonium salts 5d and 6 possess excellent thermal stabilities far above 200°C. A combination of good experimental densities (1.61–1.80 g cm⁻³) and high positive calculated enthalpies of formation (344–1,095 kJ mol⁻¹) provides good detonation performance of the synthesized energetic salts (D = 7.0–8.4 km s⁻¹; p = 22–32 GPa) exceeding that of benchmark explosive TNT (D = 6.9 km s⁻¹; p = 23 GPa) and reaching the limits of booster PETN (D = 8.4 km s⁻¹; p = 32 GPa). At the same time, sensitivities of the prepared (1,2,4-triazolyl) furoxan salts to impact are quite moderate, while their sensitivities to friction are even lower, mainly on the level of insensitive TNT. To the best of our knowledge, the present study is one of the rarely reported high-energy materials incorporating a 1,2,4-triazole heterocycle as an anion counter-part and a first example of (1,2,4-triazolyl) furoxan energetic salts.

Data availability statement

The datasets presented in this study can be found in online repositories. The names of the repository/repositories and accession numbers can be found in the article/Supplementary Material.

Author contributions

AL contributed to the synthesis, purification and characterization of all compounds, AP performed physicochemical studies, thermal stability and sensitivity measurements, IA conducted single-crystal X-ray diffraction study and performed quantum chemical modelling, DK performed calculations of the enthalpies of formation, LF designed and supervised the research and revised the manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2022.1012605/full#supplementary-material

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