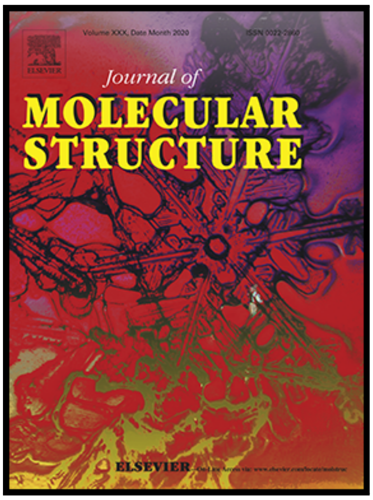

# Synthesis and Properties of Novel Nitrogen- and Oxygen-Enriched Dicationic 3,4-diaminotriazolium Salts as Attractive Energetic Materials

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## Highlights

- Novel dicationic 3,4-diaminotriazolium salts were designed and synthesized.
- These salts displayed superb physicochemical properties and acceptable sensitivities.
- These salts exhibited excellent detonation properties comparable to those of HMX.

# Synthesis and Properties of Novel Nitrogen- and Oxygen-Enriched Dicationic 3,4-diaminotriazolium Salts as Attractive Energetic Materials

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**Abstract:** The incorporation of both fuel and oxidizer properties into a single molecule to effectively improve the oxygen balance of energetic compounds has become one of the most acceptable strategies for the design of modern high-energy-density materials (HEDMs). To identify more powerful and less sensitive HEDMs with favorable oxygen balance, novel nitrogen- and oxygen-enriched dicationic 3,4-diaminotriazolium salts were prepared *via* the quaternization of 3,4-diamino-triazole with 4,4′-bis(nitramino)azofurazan and 4,4′-bis(nitramino)azoxyfurazan, and then fully characterized. These compounds exhibited favorable thermal stabilities with decomposition temperatures up to 216°C, high densities over 1.82 g·cm$^{-3}$ as well as acceptable sensitivities. In addition, the two-dimensional fingerprint spectra based on Hirshfeld surface analysis were adopted to illustrate structure–property relationships. Based on the combination of experimentally determined densities and heats of formation calculated with Gaussian 03, the energetic properties were determined using the EXPLO5 v6.02 program. The newly synthesized ionic salts displayed excellent detonation properties ($V_d$, 9115-9220 m·s$^{-1}$; $P$, 33.9-35.9 GPa), comparable to those of 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), thus highlighting their potential in energetic material applications.

**Keywords:** Ionic salt; oxygen balance; energetic material; detonation properties.

## 1. Introduction

In recent years, research on energetic materials (explosives, propellants, and pyrotechnics) has attracted considerable interest owing to their continuously growing applications in civilian as well as military areas [1-5]. Desirable characteristics for modern energetic materials include high energetic performance, mechanical insensitivity, thermal stability, along with environmental and toxicological acceptability [6-10]. Unfortunately, it is well known that excellent detonation properties in energetic materials are rarely accompanied by low sensitivities. Hence, designing and synthesizing novel high-energy-density materials (HEDMs) with an appropriate balance between sensitivity and energetic properties still represents an important and challenging research subject [11-14].

A favorable oxygen balance (OB) is one of the desirable characteristics of modern HEDMs, and exercises great influence upon the sensitivity, strength, and brisance of an explosive [15, 16]. To achieve a favorable oxygen balance, incorporating both fuel and oxidizer properties into a single molecule is one of the most effective strategies, which should enhance the combustion and therefore support release of large amounts of energy [17-22]. The replacement of a nitrogen atom in triazole ring with an oxygen atom gives rise to the well-known family of energetic oxadiazoles, which are increasingly being used as key moieties for improving oxygen balance in HEDMs [23, 24]. Comparing the density, thermal stability and heat of formation of the possible oxadiazoles, 1,2,5-oxadiazole (furazan) is the best choice as an effective building block for the generation of HEDMs [17]. In addition, the azo linkage is another important energetic moiety, whose presence not only increases the heat of formation of the energetic compounds, but also decreases the sensitivity. In particular, high nitrogen content compounds containing furazan rings linked with an azo group show particularly desirable energetic properties, insensitivity and thermal stability arising from the aromaticity [25]. Furthermore, the incorporation of the nitramino (–$NHNO_2$) moiety in the furazan ring can provide an acidic proton and enable the molecule to serve as an anion, which has been used as an effective strategy to construct advanced energetic salts [26]. Therefore, the combination of furazan rings, an azo bridge, and a nitramino group in a molecule should lead to interesting results with respect to various energetic properties. Recently, 4,4′-bis(nitramino)-azofurazan, 4,4′-bis(nitramino)-azoxyfurazan, as well as their ionic derivatives were synthesized and showed superior detonation performances [17, 27-32].

As a general principle, the presence of amino groups in triazolium cations is advantageous for the development of intramolecular and intermolecular hydrogen bond interactions with an anion containing nitro or nitramine groups, which is in favour of improving density, sensitivity and stability of energetic salts [32, 33]. Therefore, the readily available and relatively inexpensive 3,4-diamino-triazole (DATr) is a good candidate as an energetic cation [34]. Herein, with our continuing efforts to seek more powerful, less sensitive HEDMs, two kinds of energetic salts were designed and synthesized, using DATr as the cation, combined with energetic anions of 4,4′-bis(nitramino)-azofurazan and 4,4′-bis(nitramino)-azoxyfurazan. These compounds were fully characterized by single-crystal X-ray diffraction analysis, elemental analysis, differential scanning calorimetry (DSC), multinuclear NMR and IR spectroscopy. In addition, experimental and theoretical analyses were conducted to evaluate the potential applications of these compounds as energetic materials. Compared to previous work, the newly prepared energetic salts exhibit excellent integrated properties, including superb detonation performance, high thermal stability, and simultaneously low sensitivity.

## 2. Experimental section

### 2.1. General methods

Analytical-grade reagents were purchased from Aladdin and Aldrich and used as received. $^1$H and $^{13}$C spectra were recorded with a Bruker AVANCE 400 nuclear magnetic resonance spectrometer. Dimethyl sulfoxide $d_6$ ($d_6$-DMSO) was used as a locking solvent unless otherwise stated, and $^1$H and $^{13}$C chemical shifts were reported relative to $Me_4Si$. Elemental analysis was conducted on a CE-440 Elemental Analyzer. Melting and decomposition points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q20) at a heating rate of $5°C·min^{-1}$. Impact and friction sensitivity were measured on a standard BAM Fallhammer and a BAM friction tester, respectively. Density measurements were performed at 25°C using a Micromeritics AccuPyc 1330 gas pycnometer.

### 2.2. X-ray crystallography

A yellow plate crystal of dimensions $0.124 \times 0.115 \times 0.026$ mm$^3$ for $1a·2H_2O$ and a pale yellow plate crystal of dimensions $0.400 \times 0.360 \times 0.210$ mm$^3$ for $2a·2H_2O$ were used for single-crystal X-ray diffraction analysis. The X-ray intensity data were collected on a Bruker three-circle platform diffractometer equipped with a Smart Apex II charge-coupled detector (CCD). The crystals were irradiated using graphite monochromated Mo $K_\alpha$ radiation ($\lambda$ = 0.71073 Å). The frames were integrated using the Bruker SAINT software package with a narrow-frame algorithm, and data were corrected for absorption effects by the multiscan method (SADABS) [35, 36]. The obtained structures were solved and refined with the aid of the Bruker SHELXTL software package [37]. The full-matrix least-squares refinement on $F^2$ included atomic coordinates and anisotropic thermal parameters for all non-H atoms, while the H atoms were included based on a riding model.

### *2.3. Syntheses*

### *2.3.1. 4,4′-Bis(nitramino)-azofurazan (1)*

Compound 1 was prepared according to a method reported in literature [30] and obtained as a yellow solid (0.72g, 76%). $^1$H NMR: $\delta$ 10.3 (s, 2H, N-NO$_2$) ppm; $^{13}$C NMR: $\delta$ 159.5, 148.0 ppm; Elemental analysis calcd (%) for $C_4H_2N_{10}O_6$ (286.12): C, 16.79; H, 0.70; N, 48.95; Found: C, 16.61; H, 0.75; N, 49.12.

### *2.3.2. 4,4′-Bis(nitramino)-azoxyfurazan (2)*

Compound 2 was prepared according to a previously reported method [17] and obtained as an ivory solid (0.81g, 82%). $^1$H NMR: $\delta$ 13.6 (s, 2H, N−NO$_2$) ppm; $^{13}$C NMR: $\delta$ 155.2, 153.1, 150.8, 148.3 ppm; Elemental analysis calcd (%) for $C_4H_2N_{10}O_7$: C, 15.90; H, 0.67; N, 46.36; Found: C, 15.63; H, 0.69; N, 45.47.

### *2.3.3. Di(3,4-diamino-1,2,4-triazolium) 4,4′-bis(nitramino)-azofurazanate (1a)*

3,4-Diamino-1,2,4-triazole (0.40 g, 4 mmol) was added to a solution of 1 (0.57 g, 2 mmol) in a minimum amount of ethanol. The mixture was heated at 50°C for 1 h. After cooling to room temperature, the precipitate was collected by filtration to give 1a (0.76g, 78%) as a yellow solid. $^1$H NMR: $\delta$ 8.4 (s, 2H, CH), 8.2 (s, 4H, NH$_2$), 6.1 (s, 4H, NH$_2$) ppm; $^{13}$C NMR: $\delta$ 161.3, 154.0, 152.0, 143.2 ppm; IR (KBr): 3415, 3332, 3219, 1701, 1661, 1559, 1490, 1425, 1388, 1276, 1055, 997, 810, 778 cm$^{-1}$; Elemental analysis calcd (%) for $C_8H_{12}N_{20}O_6$: C, 19.84; H, 2.50; N, 57.84; Found: C, 19.82, H, 2.54, N, 57.55.

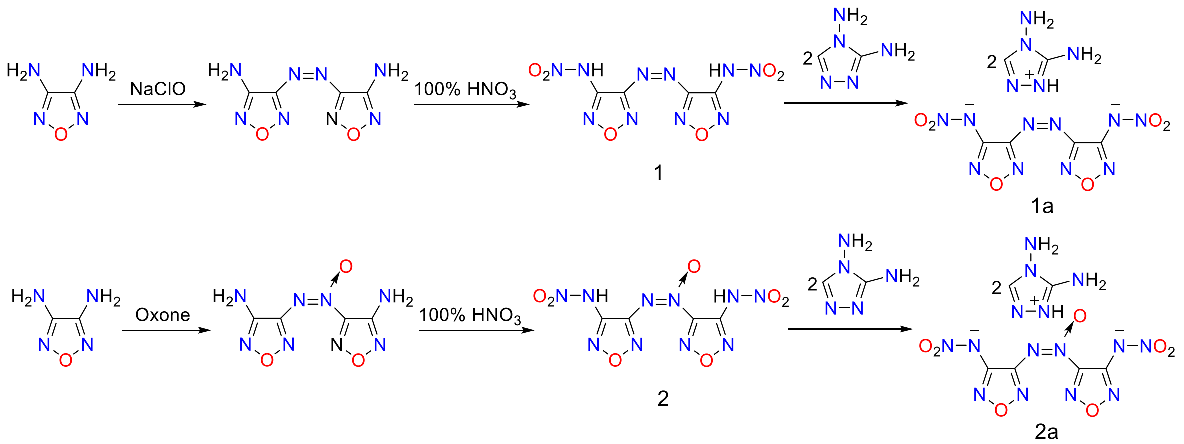
### *2.3.4. Di(3,4-diamino-1,2,4-triazolium) 4,4′-bis(nitramino)-azoxyfurazanate (2a)*

3,4-Diamino-1,2,4-triazole (0.40 g, 4 mmol) was added to a solution of 2 (0.60 g, 2 mmol) in minimum ethanol. The mixture was heated at 50°C for 1 h. After cooling to room temperature, the precipitate was collected by filtration to give 2a (0.79g, 79%) as a light yellow solid. $^1$H NMR: $\delta$ 8.4 (s, 2H, CH), 8.1 (s, 4H, $NH_2$), 6.1 (s, 4H, $NH_2$) ppm; $^{13}$C NMR: $\delta$ 156.4, 156.3, 155.2, 152.5, 152.0, 143.1 ppm; IR (KBr): 3358, 3282, 3124, 2752, 1707, 1626, 1566, 1502, 1302, 1010, 955, 849, 771, 708 cm$^{-1}$; Elemental analysis calcd (%) for $C_8H_{12}N_{20}O_7$: C, 19.21, H, 2.42, N, 55.99; Found: C, 18.61, H, 2.41, N, 55.39.

## 3. Results and discussion

### *3.1. Synthesis*

Some readily available starting materials were used for the synthesis of the energetic salts *via* a straightforward three-step procedure as illustrated in Scheme 1. In the first step, 3,4-diaminofurazan was reacted with either hypochlorite or oxone in aqueous solution to form azo and azoxy aminofurazans, respectively. Subsequently, the azo and azoxy nitraminofurazans (1 and 2) were obtained by nitration of the corresponding aminofurazans in 100% $HNO_3$ at 0–5°C for 2 h, followed by quenching with ice water. Finally, energetic salts of di(3,4-diamino-1,2,4-triazolium) 4,4′-bis(nitramino)-azofurazanate (1a) and di(3,4-diamino-1,2,4-triazolium) 4,4′-bis(nitramino)-azoxyfurazanate (2a) were generated via deprotonation of the azo and azoxy nitraminofurazans (1 and 2) with 3,4-diamino-1,2,4-triazole. Both salts were isolated as crystalline solids in good yields. The structure of resulting salts was confirmed by $^1$H and $^{13}$C NMR spectroscopy, X-ray crystallography, infrared spectroscopy, and elemental analysis, showing a high purity level of all synthesized ionic structures.



**Scheme 1.** Synthesis of the energetic salts investigated in this study.

### 3.2. *Single crystal X-ray structure analysis*

Single crystals of di(3,4-diamino-1,2,4-triazolium) 4,4′-bis(nitramino)-azofurazanate with two water molecules ($1a{\cdot}2H_2O$) and di(3,4-diamino-1,2,4-triazolium) 4,4′-bis(nitramino)-azoxyfurazanate with two water molecules ($2a{\cdot}2H_2O$) were obtained through slow recrystallization from aqueous solutions at room temperature and ambient pressure, and the suitable crystals were selected for crystal-structure analysis. The structures of compounds $1a{\cdot}2H_2O$ and $2a{\cdot}2H_2O$ are shown in Fig. 1 and 2, respectively. As can be seen in Table 1, both of $1a{\cdot}2H_2O$ and $2a{\cdot}2H_2O$ crystallized in the triclinic system with *P*-1 space group. Due to the presence of water molecules in the unit cell, low calculated densities of 1.670 and 1.729 $g{\cdot}cm^{-3}$ were obtained for crystals $1a{\cdot}2H_2O$ and $2a{\cdot}2H_2O$, respectively. As reported in a previous work, the two furazan rings, azo or azoxy linkage, and the N-nitro moieties are coplanar for the neutral compounds 1 and 2 [17]. However, it is interesting to note that one of the furazan rings is bent away from the azo or azoxy linkage and the other ring in $1a{\cdot}2H_2O$ (torsion angle N8−C9−N10−N10A, -167.0°) and $2a{\cdot}2H_2O$ (torsion angle N6−C4−N10−N10A, 147.5°). This may be due to the intramolecular hydrogen bond between cations and anions present in the ionic salts. As shown in Fig.1 and 2, the crystal structures of compounds 1a·$2H_2O$ and 2a·$2H_2O$ were built up by several hydrogen bonds, which use hydrogen atoms of the DATr cation and water molecule as donor atoms. For compound 1a·$2H_2O$, H···A lengths of hydrogen bonds were in the range of 1.77-2.59 Å, with the strongest contact supported by O1S with the N11···H11. With respect to compound 2a·$2H_2O$, H···A lengths of hydrogen bonds lay within the range of 1.71-2.56 Å, with the strongest contact supported by O5 with the N1···H1. For both compounds 1a·$2H_2O$ and 2a·$2H_2O$, the DATr cations, azo- or azoxy anions and water molecules were linked through hydrogen bonds and constituted a dense 3D interspace network. The details can be found in the ESI.

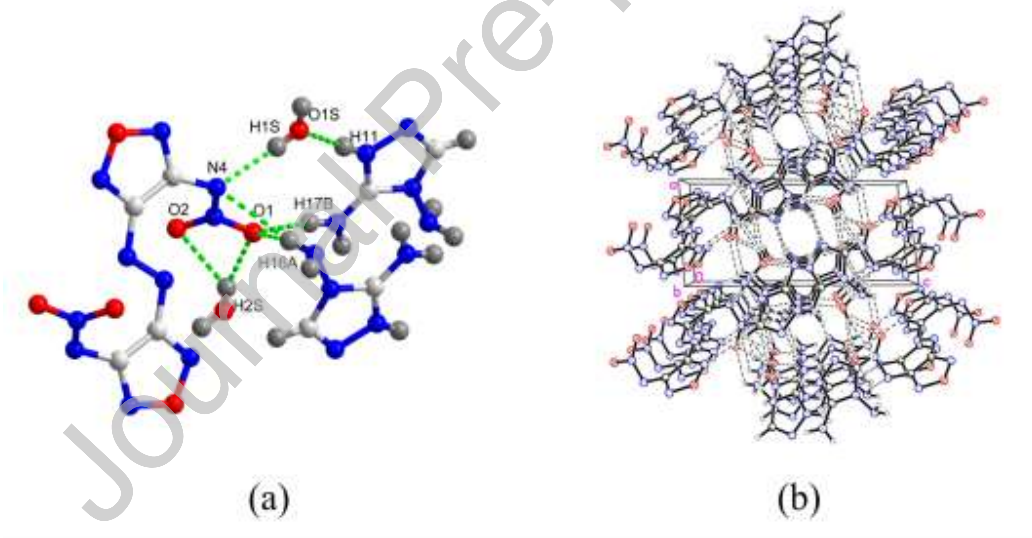


**Fig. 1.** (a) Single-crystal X-ray structure and (b) Packing diagram of 1a·$2H_2O$.

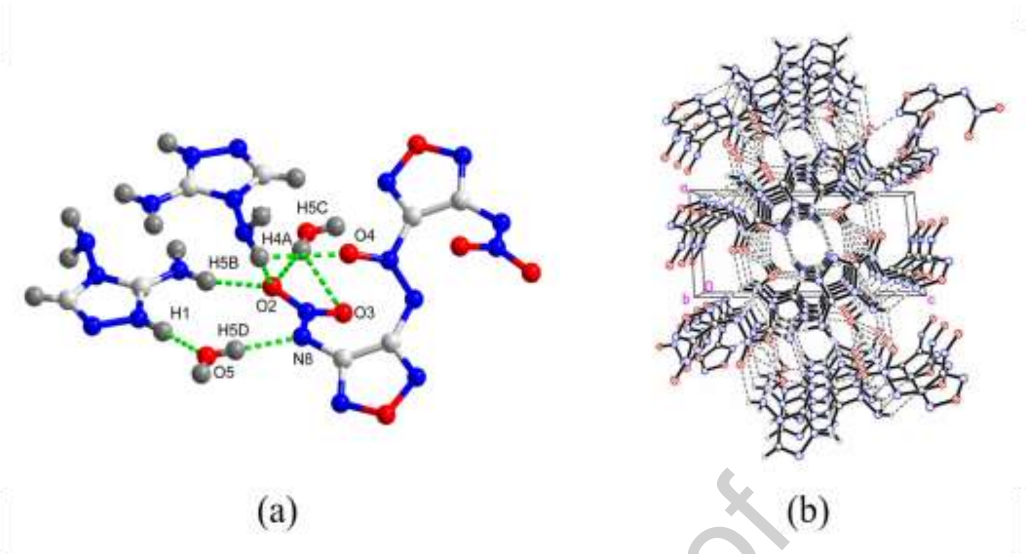


**Fig. 2.** (a) Single-crystal X-ray structure and (b) Packing diagram of 2a·$2H_2O$.

**Table 1** Crystallographic data for 1a·$2H_2O$ and 2a·$2H_2O$.

| Compound | 1a·$2H_2O$ | 2a·$2H_2O$ |
|---|---|---|
| Formula | $C_8H_{16}N_{20}O_8$ | $C_8H_{16}N_{20}O_9$ |
| Formula weight | 520.41 | 536.41 |
| CCDC number | 1999077 | 1999078 |
| Crystal size ($mm^3$) | 0.124×0.115×0.026 | 0.400×0.360×0.210 |
| Crystal system | Triclinic | Triclinic |
| Space group | *P*-1 | *P*-1 |
| $a$ (Å) | 6.183(14) | 6.168(2) |
| $b$ (Å) | 7.082(18) | 7.010(2) |
| $c$ (Å) | 12.947(3) | 13.087(4) |
| $\alpha$ (°) | 98.831(9) | 99.061(10) |
| $\beta$ (°) | 91.346(9) | 91.215(10) |
| $\gamma$ (°) | 111.936(9) | 112.201(10) |
| $V$ ($Å^3$) | 517.6(2) | 515.3(3) |
| $Z$ | 1 | 1 |
| $\rho_{calc}$($g \cdot cm^{-3}$) | 1.670 | 1.729 |
| $\mu$ ($mm^{-1}$) | 0.146 | 0.153 |
| F (000) | 268 | 276 |
| $\theta$ (°) | 1.598 to 26.456 | 3.165 to 28.636 |

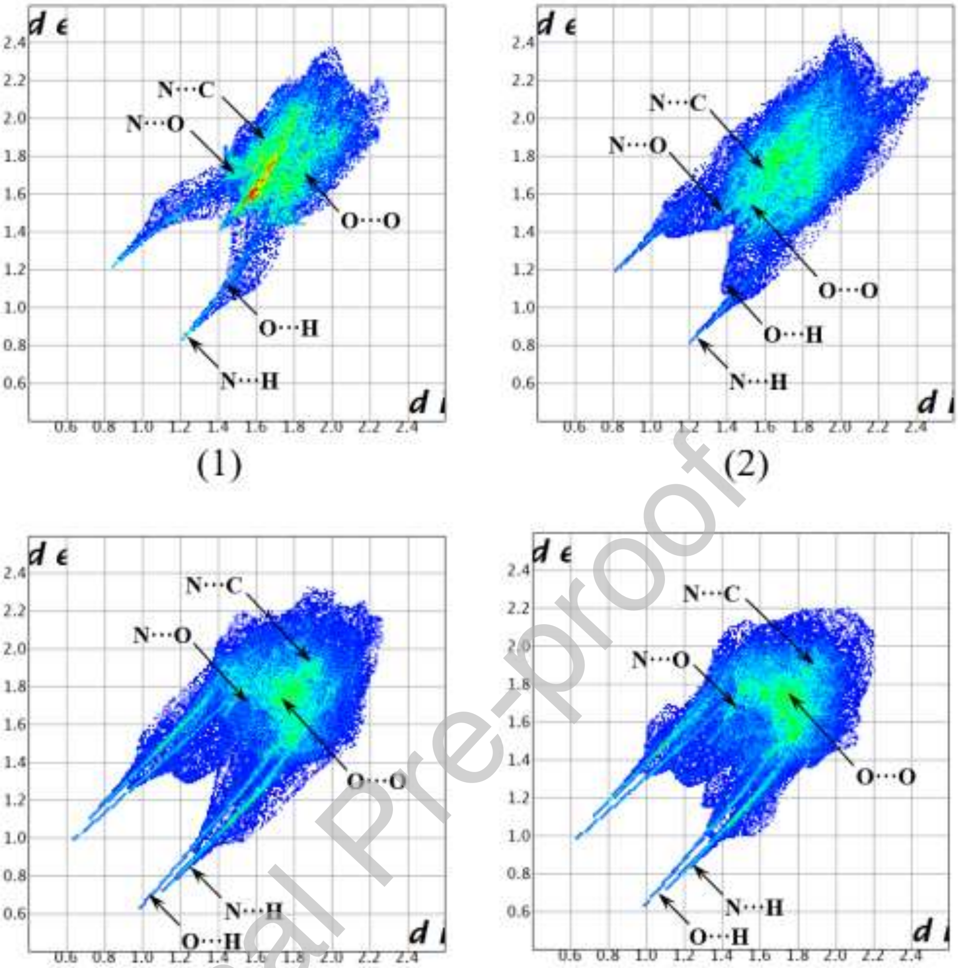
| | | |
|---|---|---|
| Index ranges | -7<=h<=7;<br>-8<=k<=8;<br>-16<=l<=16 | -8<=h<=8;<br>-9<=k<=9;<br>-17<=l<=17 |
| Reflections collected | 5000 | 14296 |
| Independent reflections ($R_{\mathrm{int}}$) | 2114 (0.0307) | 2626 (0.0419) |
| Data/restraints/parameters | 2114/0/184 | 2626/0/204 |
| GOF on $F^2$ | 1.043 | 1.035 |
| $R_1$ ($I$>=2$\sigma$(I)) | 0.0358 | 0.0330 |
| $wR_2$ ($I$>=2$\sigma$(I)) | 0.082 | 0.0916 |
| $R_1$ (all data) | 0.0592 | 0.0380 |
| $wR_2$ (all data) | 0.1025 | 0.0938 |
| Largest diff. peak/hole (e Å$^{-3}$) | 0.193/-0.187 | 0.345/-0.306 |

### *3.3. Thermal stability and sensitivity*

The thermal properties are among the most important properties of energetic materials. The phase transition temperature ($T_g$/$T_m$) and thermal decomposition temperature ($T_d$) were determined by means of differential scanning calorimetric (DSC) measurements (Table 2). It should be noted that neither of the synthesized compounds melts prior to decomposition. As expected, the $T_d$ values of 1a (216°C) and 2a (191°C) were more than 100°C higher than those of the corresponding neutral compounds 1 (100°C) and 2 (90°C), indicating much higher thermal stabilities. In addition, the anions were found to have a significant effect on $T_d$. In the case of the same cation, the azofurazan-based ionic salt 1a showed a higher decomposition temperature than the azoxyfurazan-based ionic salt 2a, with the same trend exhibited by their neutral anion precursors.

Moreover, the impact and friction sensitivities were determined by using standard BAM procedures. As shown in Table 2, both synthesized ionic salts displayed superior sensitivities to their neutral anion precursors whose impact and friction sensitivities were 2 J and 10 N, respectively, as those of salt 1a were 22 J and 160 N, respectively, while those of salt 2a were 26 J and 160 N, respectively. Meanwhile, it is clear that both the azo and azoxy salts are less sensitive than cyclo-1,3,5-trimethylene-2,4,6-trinitamine (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), which highlights their promising potential as safe energetic materials.

With the aim of gaining a deep insight into the weak interactions of the obtained compounds, Hirshfeld surfaces analyses were conducted for crystals 1a·$2H_2O$, 2a·$2H_2O$, as well as 1 and 2 obtained from our previous work. The two-dimensional (2D) fingerprint spectra of crystals derived from Hirshfeld surfaces and the percentage of contribution for each type of interaction to the total weak interactions are shown in Fig. 3 and 4, respectively. The hydrogen bonds indicators of O···H and N···H interactions accounted for 60.3% and 58.6% of the total weak interactions for 1a·$2H_2O$ and 2a·$2H_2O$, respectively, which were nearly three times as high as those of their neutral anion precursors. At the same time, the percentages of O···O interactions in 1a·$2H_2O$ and 2a·$2H_2O$ showed a sharp decrease from 25.6% and 22.8% to 1.8% and 5.2%, respectively, compared to those of 1 and 2. This indicates that 1a·$2H_2O$ and 2a·$2H_2O$ may be less sensitive than 1 and 2, as the O···O interactions reflecting the possibility of unexpected explosion. Furthermore, the N···O interactions in 1 and 2 were higher than those in 1a·$2H_2O$ and 2a·$2H_2O$, showing a higher percentage of interlayer contact. Based on the above analysis, the results of the Hirshfeld surfaces appear to support the higher stability and lower sensitivity of the ionic salts compared to their neutral anion precursors.



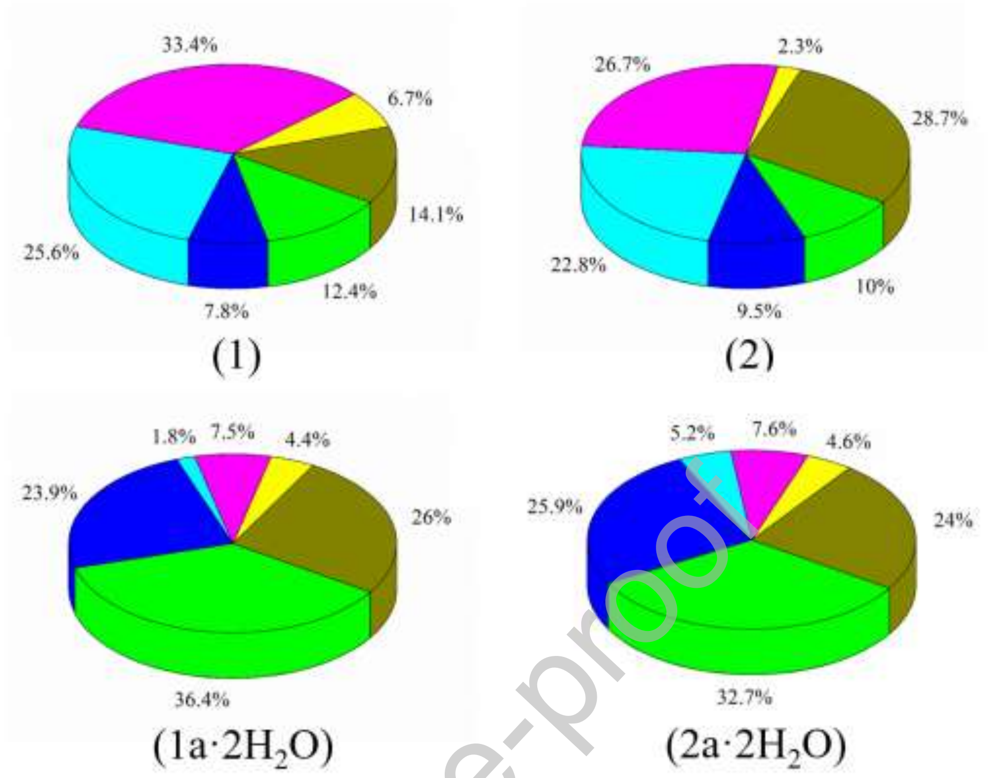
(1)

(2)

(1a·2H$_2$O)

(2a·2H$_2$O)

**Fig. 3.** Two-dimensional fingerprint plots for 1, 2, 1a·2H$_2$O and 2a·2H$_2$O.



(1) (2) ($1a\cdot2H_2O$) ($2a\cdot2H_2O$)

**Fig. 4.** Individual atomic contact percentage contribution to the Hirshfeld surface for 1, 2, $1a\cdot2H_2O$ and $2a\cdot2H_2O$.

■ N···H, ■ O···H, ■ O···O, ■ N···O, ■ N···C, ■ other

*3.4. Density*

In addition to thermal properties and sensitivities, density is another vital parameter for evaluating energy level of energetic materials. In general, the higher density usually means the higher mole number of energetic materials that can be packed into a limited volume, thereby providing higher energy and combustion contribution to the explosive composition. As shown in Fig. 5 and Table 2, the synthesized ionic salts 1a and 2a showed favorable densities of 1.82 and 1.85 $g\cdot cm^{-3}$, respectively, both of which were higher than those of TNT (1.65 $g\cdot cm^{-3}$) and RDX (1.81 $g\cdot cm^{-3}$). As described in our previous work, the higher density of azoxy salt 2a than azo salt

1a could be attributed to the participation of the N-oxide and the nitrogen-rich cations being involved in multiple intermolecular hydrogen-bonding interactions. In addition, the advantages of introducing the N-oxide moiety into the azo linkage were further confirmed by the observed density increase.

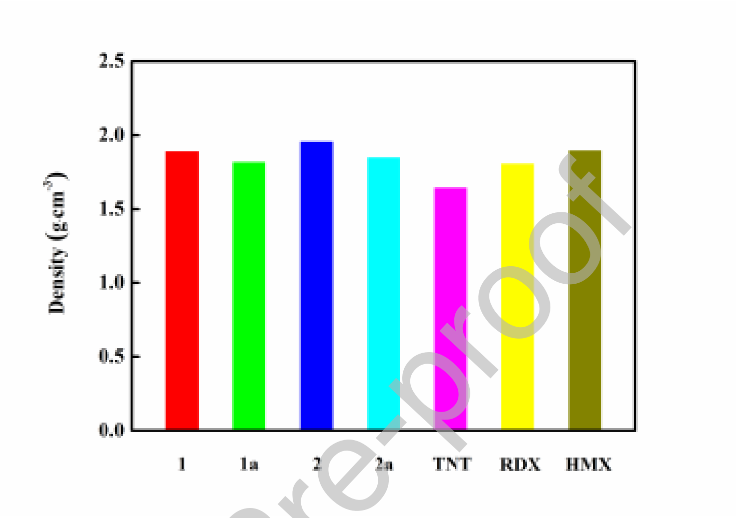
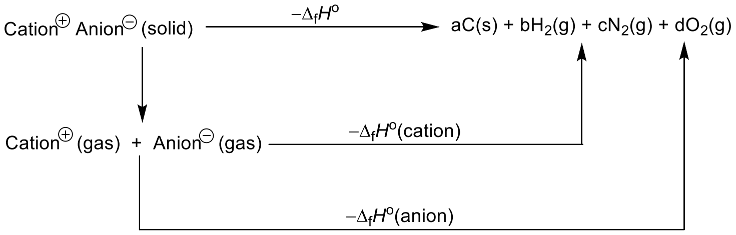


**Fig. 5.** Comparison of density values of synthesized salts, neutral anion precursors, and traditional energetic materials.

### *3.5. Heat of formation*

The heat of formation (HOF, $\Delta_f H^o$) is one of the key properties of energetic compounds, and is closely related to the energy and the prediction of the detonation performance. For both energetic salts investigated in this work, the solid-phase HOFs can be simplified by Eq. (1) on the basis of Born-Haber energy cycle (Scheme 2) [38]. The HOFs of the cation and anions were determined according to the literature [39] or our previous work [30], in which these values were calculated using the Gaussian 03 suite of programs.



**Scheme 2.** Born-Haber cycle for the formation of energetic salts.

$$\Delta_f H^o(\text{salt, 298 K}) = \Sigma\Delta_f H^o(\text{cation, 298 K}) + \Sigma\Delta_f H^o(\text{anion, 298 K}) - \Delta H_L \quad (1)$$

The lattice energy $\Delta H_L$ in Eq. (1) was predicted using Eq. (2) [38], as suggested by Jenkins et al. In this equation, the parameters $n_M$ and $n_X$ depend on the nature of the ions $M_p^+$ and $X_q^-$, respectively.

$$\Delta H_L = U_{POT} + [p(n_M/2\text{-}2) + q(n_x/2\text{-}2)]RT \quad (2)$$

The lattice-potential energy ($U_{POT}$) was calculated according to Eq. (3):

$$U_{POT} = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

in which $\rho_m$ and $M_m$ represent the density and chemical formula mass of the ionic compound, respectively, while the $\gamma$ and $\delta$ coefficients were obtained from the literature [38].

As shown in Table 2, the HOFs estimated for both energetic salts (1a and 2a) were greater than those of currently used explosives such as TNT (-67.0 kJ·mol$^{-1}$, -0.30 kJ·g$^{-1}$), RDX (80 kJ·mol$^{-1}$, 0.36 kJ·g$^{-1}$) and HMX (74.8 kJ·mol$^{-1}$, 0.25 kJ·g$^{-1}$). This is due to the presence of a large number of N−N or N=N bonds within the molecules, and in particular to the introduction of azo or azoxy linkages. Among the present materials, the azo salt 1a exhibited a much higher HOF (1444.7 kJ·mol$^{-1}$, 2.98 kJ·g$^{-1}$) than the azoxy salt 2a (1374.5 kJ·mol$^{-1}$, 2.75 kJ·g$^{-1}$).

**Table 2** Physicochemical properties of the energy salts.

| ILs | $T_d$[a] | $\rho$[b] | $\Delta_f H$[c] | $V_d$[d] | $P$[e] | IS[f] | FS[g] | OB[h] |
|---|---|---|---|---|---|---|---|---|
| | °C | $g \cdot cm^{-3}$ | $kJ \cdot mol^{-1}/kJ \cdot g^{-1}$ | $m \cdot s^{-1}$ | GPa | J | N | % |
| 1 | 100 | 1.89 | 820.2/2.86 | 9517 | 41.1 | 2 | 10 | -16.7 |
| 1a | 216 | 1.82 | 1444.7/2.98 | 9115 | 33.9 | 22 | 160 | -52.9 |
| 2 | 90 | 1.96 | 730.0/2.42 | 9746 | 44.1 | 2 | 10 | -10.6 |
| 2a | 191 | 1.85 | 1374.5/2.75 | 9220 | 35.4 | 26 | 160 | -48.0 |
| TNT | 295 | 1.65 | -67.0/-0.30 | 6881 | 19.5 | 15 | 353 | -24.7 |
| RDX | 205 | 1.81 | 80/0.36 | 8748 | 34.9 | 7.4 | 120 | -21.6 |
| HMX | 280 | 1.90 | 74.8/0.25 | 9144 | 39.2 | 7.4 | 120 | -21.6 |

[a] Decomposition temperature (onset); [b] Density measured by using a gas pycnometer at 25°C; [c] Calculated heat of formation in the solid state; [d] Detonation velocity; [e] Detonation pressure; [f] Impact sensitivity; [g] Friction sensitivity; [h] Oxygen balance for $C_aH_bO_cN_d$, $1600(c-2 \cdot a-b/2)/M_w$; $M_w$ = molecular mass.

### *3.6. Energetic properties*

Using the calculated HOFs and the experimentally measured densities, the values of detonation properties were calculated with Explo5 v6.02 software [40]. Table 2 shows that 1a and 2a exhibit favorable detonation properties, with detonation velocities of 9115 and 9220 $m \cdot s^{-1}$ and detonation pressures of 33.9 and 35.4 GPa, respectively, thus outperforming TNT and RDX, while showing performances comparable with those of HMX. It is not surprising that the azoxy salt (2a) showed better performances than the azo salt (1a), due to its relatively higher density. The oxygen balance (OB) is used to represent the deficiency or excess of oxygen in an energetic compound required to be oxidized. In general, the OB value can be calculated based on the molecular formula needed to convert all carbon into carbon dioxide and all hydrogen into water [41]. Furthermore, the sensitivity and detonation properties of an explosive directly relate to the oxygen balance and tend to reach their maxima as the oxygen balance approaches zero [15, 16]. In this study, the azoxy salt 2a showed a higher oxygen balance than the azo salt 1a, as the addition of the single oxygen atom to the azo linkage improved the oxygen balance.

## 4. Conclusion

In summary, two types of novel nitrogen- and oxygen-enriched dicationic 3,4-diaminotriazolium salts were designed and synthesized, in combination with 4,4′-bis(nitramino)azofurazan and 4,4′-bis(nitramino)azoxyfurazan anions. These compounds displayed excellent physiochemical properties including high thermal stability, high density, as well as low sensitivities. Furthermore, theoretical analyses showed that the calculated detonation properties of the newly prepared ionic salts were superior to those of RDX and comparable to those of HMX, which highlights their promising potential as ingredients in energetic materials applications.

## Supplementary data

Crystal structure data, Infrared Spectra, $^{1}$H-NMR and $^{13}$C-NMR Spectra.

## Notes

The authors declare no competing financial interest.

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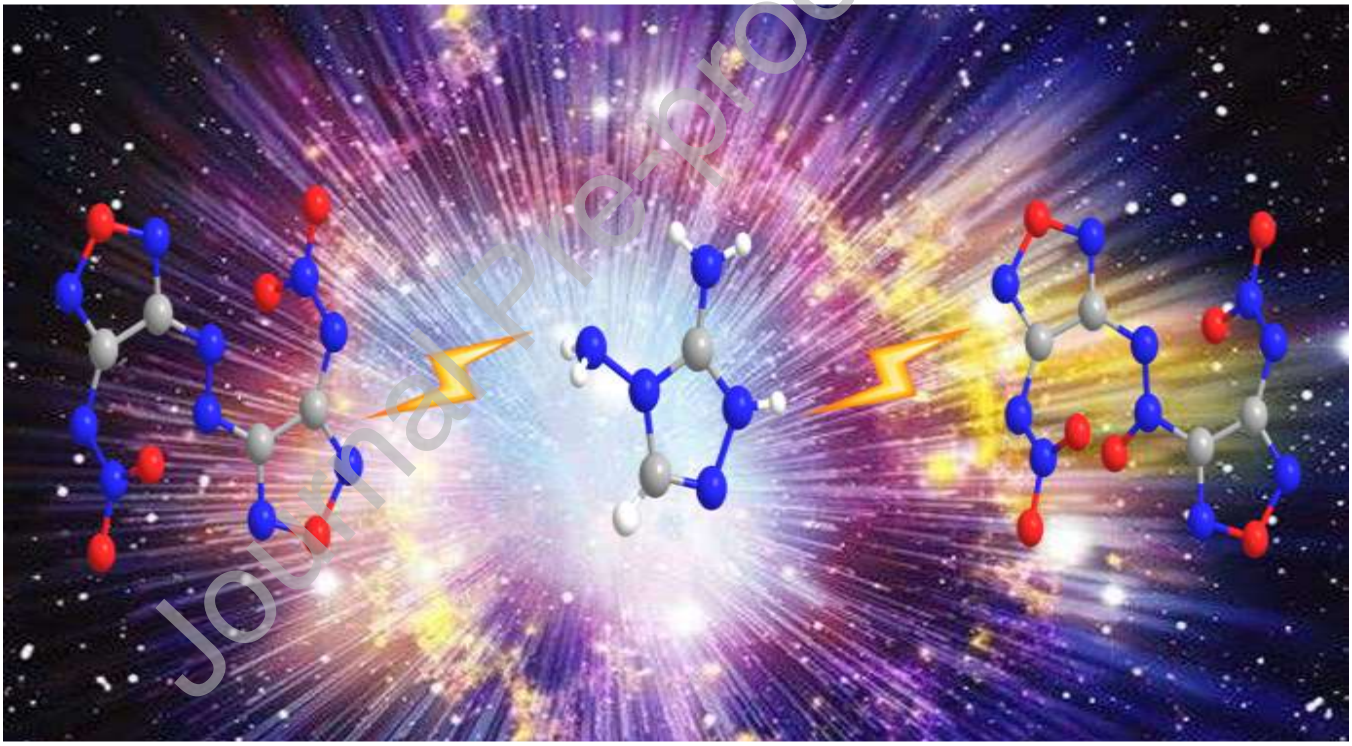
## Credit Author Statement

Mi Wang and Zhenyuan Wang contribute equally to this work, they performed the IR, NMR, physicochemical and energetic properties experiments. Mi Wang, Zhenyuan Wang and Jiaheng Zhang wrote the paper. Jichuan Zhang and Binshen Wang performed the theoretical calculations. Jiaheng Zhang and Jichuan Zhang conceived and designed the project.

## Conflict of Interest

The authors declare that they have no conflict of interest to this work.

**Graphical abstract**



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