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# Energetic 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine: a novel nitrogen-rich fused heterocyclic cation with high density

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**ABSTRACT:** Fused heterocyclic energetic cation was rarely reported despite the development of energetic cation has attracted increasing attention in recent years. In this work, a new 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine was synthesized in a one-step reaction, which was used as a cation to prepare 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine perchlorate. Interestingly, when the synthesis was accomplished in different conditions, two crystal forms of perchlorate  $\alpha$ -**4** and  $\beta$ -**4** were obtained, which were further confirmed by X-ray single crystal diffraction, X-ray powder diffractograms, infrared and multinuclear NMR spectra. These salts showed high density (1.88-1.93 g cm<sup>-3</sup> at 293(2) K), moderate detonation performance (D: 8128-8437 m s<sup>-1</sup>, P: 29.4-32.86 GPa) and good thermal stability (T<sub>d</sub>: 272-274 °C). Compared with those known energetic perchlorates, the density and sensitivity (IS: 14-20 J, FS: 144-168 J) of **4** were also significantly improved. Through theoretical calculations and experiment results, the explanations for the differences in physicochemical properties of these two crystal forms were illustrated. Density overlap indicator (DORI) analysis was also employed to perform the necessary visualization and quantification of covalent and non-covalent interactions. It is evident that ionic bonds, hydrogen bonds, and  $\pi$ - $\pi$  interactions are responsible for the high density and excellent performance of 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine perchlorate, indicating that as-synthesized new material is a very promising cation in the construction of low-sensitivity high-energy compounds.

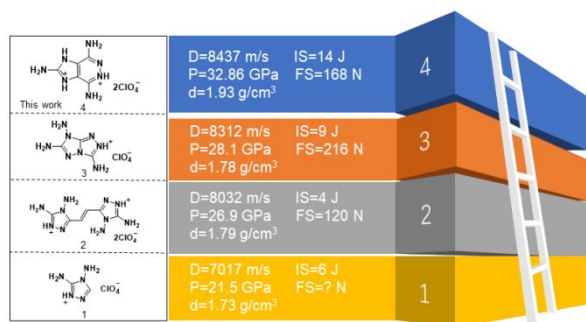
## INTRODUCTION

The main challenge in developing the next generation of high energy density materials (HEDMs) is to find a ingenious balance between energy and sensitivity since the higher detonation performance is usually at the cost of molecular stability.<sup>1-4</sup> Due to the good properties, such as high density, low vapour pressure, and good physical & chemical stability,<sup>5</sup> high energetic ionic salts is considered as one of the powerful routes to achieve high detonation performance and acceptable stability simultaneously. However, the research on energetic salts mainly focused on the design and synthesis of new energetic anions, while fewer studies on energetic cations was reported comparatively.<sup>6</sup> The most commonly used cations in the development of energetic salts can be mainly divided into the following sections: 1) acyclic nitrogen-containing cations, e.g., guanidine and hydroxylamine;<sup>7</sup> 2) nitrogen-containing mono-heterocyclic cations, e.g., 3,4,5-triamino-1,2,4-Triazole, 5-amino-1,2,3,4-tetrazole;<sup>8-10</sup> 3) bridged nitrogen-containing cations, e.g., 3,3'-diamino-4,4'-azobis-1,2,4-triazole, 4H, 4'H- [3,3'-bi (1,2,4-triazole)]-4,4', 5,5'-tetraamine;<sup>11</sup> 4) fused heterocyclic cation: 3,6,7-triamino-

[1,2,4] triazole [4,3-b] [1,2,4] triazole (TATOT), 3,7-diamino-7H- [1,2,4] triazole [4,3-b] [1,2,4] triazole.<sup>12</sup>

In contrast to acyclic and mono-heterocyclic nitrogen-containing cations, fused heterocyclic cations consist of larger  $\pi$ -conjugated system which is of benefit to the structural stability through electron delocalization and the  $\pi$ - $\pi$  stacking because of their improved planarity, as already well known during the strategies in increasing crystal density and lowering sensitivity.<sup>13</sup> In addition, nitrogen-rich fused heterocyclic cations exhibit high nitrogen content and generate nitrogen molecules during the explosion, which not only provides thrust but also meets environmental protection requirements.<sup>14</sup> The performance of some nitrogen-rich heterocyclic cations were compared in the form of perchlorate based on the same anion as listed in Figure 1. As a typical instance, TATOT is composed of 3-amino-1,2,4-triazole and 3,4-diamino-1,2,4-triazole, and its perchlorate (**3**) shows good detonation performance (8312 m s<sup>-1</sup>, 28.1 GPa), acceptable sensitivity (IS: 9 J, FS: 216 N) and decomposition temperature at 264 °C,<sup>15</sup> Compared with 3-amino-1,2,4-triazole perchlorate (**1**) (7017 m s<sup>-1</sup>, 21.5 GPa, IS: 6 J)<sup>16</sup> and 1,1'-(Ethane-5-yl)bis(3,4-diamino-1,2,4-triazolium)

diperchlorate(2) ( $8032 \text{ m s}^{-1}$ ,  $26.9 \text{ GPa}$ ,  $IS: 4 \text{ J}$ ),<sup>17</sup> the detonation performance and impact sensitivity of **3** have been improved significantly. Based on the previous discussion, the development of nitrogen-rich fused heterocyclic cations is significant for finding high-energy ionic salts with low-sensitivity.



**Figure 1.** Different strategies for building energetic cations

Given this background, a novel nitrogen-rich fused heterocyclic cation 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine was synthesized by one-step reaction from 4,5-dicyano-2-aminoimidazole and hydrazine hydrate.<sup>18</sup> Then, by reacting with perchloric acid at room temperature, 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine perchlorate ( $\alpha$ -4) was obtained and confirmed by X-ray single crystal diffraction. 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine perchlorate shows high density ( $1.93 \text{ g cm}^{-3}$ ), good exothermic behaviour ( $274 \text{ }^\circ\text{C}$ ) and acceptable mechanical sensitivity ( $IS: 14 \text{ J}$ ,  $FS: 168 \text{ N}$ ). This may be related to its coplanar structure and the  $\pi$ - $\pi$  interaction that are prevalent in the molecule.<sup>19-23</sup> Interestingly, with the exception of new polymorph  $\alpha$ -4 of its perchlorate, a different polymorph  $\beta$ -4 was also achieved under different solvent effect. Although the density and energy level of  $\beta$ -4 slightly decreased, the mechanical sensitivity was clearly improved. The relationship between the crystal stacking mode and energetic performance was also explored through experimental approaches and theoretical calculations.

## EXPERIMENTAL SECTION

**Safety precautions.** The prepared compounds are explosive with sensitivity towards various stimuli. Although we had no problems during synthesis, proper protective equipment (gloves, eye-protecting glasses, face shield, etc) should be worn. Extra precautions should be taken when working on larger scale.

**Materials, measurements and computations.** All chemicals used in this study were analytical grade materials purchased by Sigma Aldrich. <sup>1</sup>H, <sup>13</sup>C NMR spectra

were recorded on a nuclear magnetic resonance spectrometer running at 400 MHz (Bruker AVANCE 400). Relative to  $\text{Me}_4\text{Si}$  as an external standard, chemical shifts in <sup>1</sup>H and <sup>13</sup>C spectra. Differential scanning calorimetry (DSC) was performed using a differential scanning calorimeter-thermogravimeter (TGA/DSC2, METTLER TOLEDO STARE system) at a heating rate of  $5 \text{ }^\circ\text{C min}^{-1}$ . Infrared (IR) spectra were measured on a SHIMADZU IRTracer-100 FT-IR spectrometer in the form of KBr particles in the range of  $4000\text{-}400 \text{ cm}^{-1}$  at  $25^\circ\text{C}$ . Elemental analysis (C, H, N) was performed on an elemental analyzer (Vario EL Cube, Germany). The BAM friction tester and BAM Fallhammer were used to determine the sensitivity to friction and impact. Powder X-ray diffraction data were recorded on a Bruker D8 Advance X-ray diffractometer equipped with Cu-  $K\alpha$  radiation source ( $\lambda = 1.54180 \text{ \AA}$ ,  $40\text{kV}$ ,  $40 \text{ mA}$ ). The samples were scanned in a range of  $2\theta$  from  $5^\circ$  to  $50^\circ$ , with a scan rate of  $0.02^\circ$  and a heating rate of  $0.5 \text{ }^\circ\text{C s}^{-1}$ .

Data of  $\alpha$ -4,  $\beta$ -4 and  $6 \cdot \text{H}_2\text{O}$  were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. During the data collection process, Kryoflex cryogenic equipment was used to maintain the crystals at a constant temperature of  $293(2) \text{ K}$ . Firstly, APEX2 (v2010.3-0) was used for data collection and initial unit cell optimization. Data reduction using SAINT (v7.68 A) and XPREP (v2008/2). Corrections for Lorentz, polarization and absorption effects were made using SADABS (v2008/1). The structure is inferred and improved with the help of programs in the program SHELXTL-plus (v2008 / 4) system. All non-hydrogen atoms are refined. All hydrogen atoms have been located and refined.

The finalized CIF files were checked with checkCIF, and deposited at the Cambridge Crystallographic Data Centre as supplementary publications. Intra- or intermolecular hydrogen-bonding interactions were analyzed with Diamond software (version 3.2K) as well as the illustrations of molecular structures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Density overlap regions indicator (DORI) was outputted based on a wfn file which was computed via crystal structure of those compounds by employing Multiwfn 3.6 program.<sup>24</sup>

**Synthesis of 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine (5).** 50% acetic acid solution ( $4.0 \text{ mL}$ ,  $0.035 \text{ mol}$ ) was added to 1,4-dioxane solution ( $27 \text{ mL}$ ) while stirring at  $25 \text{ }^\circ\text{C}$ , followed by the addition of 4,5-dicyano-2-aminoimidazole ( $2.67 \text{ g}$ ,  $0.02 \text{ mol}$ ), and hydrazine hydrate ( $5.9 \text{ mL}$ ,  $0.12 \text{ mol}$ ) slowly. The reaction was heated to reflux

for 4 h. Suction filtration, washing the filter cake with a large amount of distilled water, and vacuum drying to obtain compound **5** (White solid, 3.31 g, 100%). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  162.46, 145.70, 131.00. IR (KBr pellet): 3408 (s), 3324 (s), 3201 (s), 3102 (s), 2759 (w), 1906 (w), 1651 (s), 1612 (s), 1560 (s), 1475 (s), 1443 (s), 1278 (m), 1223 (w), 1069 (w), 1048 (w), 864 (w), 800 (m), 694 (m), 635 (m), 602 (m), 569 (m), 468 (w)  $\text{cm}^{-1}$ . Elemental analysis: (%) calculated for  $\text{C}_5\text{H}_7\text{N}_7$ : C, 36.36; H, 4.27; N, 59.37 %; found C, 35.27; H, 3.89; N, 60.11 %.

**Synthesis of 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine perchlorate ( $\alpha$ -4).** A suspension of **5** (413 mg, 2.5 mmol) in 10 mL distilled water was stirred at room temperature while 70% perchloric acid (0.6 mL, 7.5 mmol) in 10 mL water was added. The reaction was stirred for 2 h, then left to stand and naturally volatilized to obtain  $\alpha$ -4 (colorless crystal, 590 mg, 99%). <sup>13</sup>C NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  153.38, 143.33, 123.44. IR (KBr pellet): 3306 (s), 3111 (s), 1682 (s), 1625 (s), 1579 (s), 1508 (m), 1445 (m), 1372 (w), 1283 (w), 1089 (s), 1018 (m), 921 (w), 801 (w), 682 (w), 627 (s)  $\text{cm}^{-1}$ . Elemental analysis: (%) calculated for  $\text{C}_5\text{H}_7\text{Cl}_2\text{N}_7\text{O}_8$ : C, 16.32; H, 3.01; N, 26.64 %; found C, 16.07; H, 2.37; N, 26.32 %.

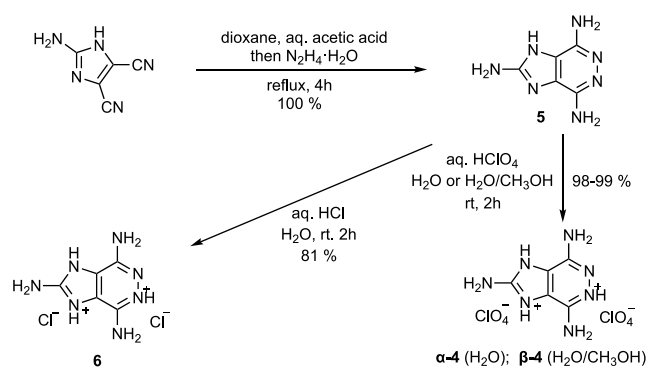
**Synthesis of 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine perchlorate ( $\beta$ -4).** A suspension of **5** (414 mg, 2.5 mmol) in 10 mL Methanol was stirred at room temperature while 70% perchloric acid (0.6 mL, 7.5 mmol) in 10 mL water was added. The reaction was stirred for 2 h, then left to stand and naturally volatilized to obtain  $\beta$ -4 (colorless crystal, 583 mg, 98 %). <sup>13</sup>C NMR (101 MHz,  $\text{D}_2\text{O}$ )  $\delta$  153.60, 143.40, 123.67. IR (KBr pellet): 3447 (s), 3306 (s), 3111 (s), 1682 (s), 1625 (s), 1578 (s), 1508 (m), 1446 (m), 1372 (w), 1283 (w), 1089 (s), 1015 (m), 922 (w), 801 (w), 683 (w), 627 (s)  $\text{cm}^{-1}$ . Elemental analysis: (%) calculated for  $\text{C}_5\text{H}_7\text{Cl}_2\text{N}_7\text{O}_8$ : C, 16.32; H, 3.01; N, 26.64 %; found C, 15.98; H, 2.46; N, 26.17 %.

**Synthesis of 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine Hydrochloride (6).** A suspension of **5** (416 mg, 2.5 mmol) in 10 mL distilled water was stirred at room temperature while 36% hydrochloric acid (0.6 mL, 7.5 mmol) in 10 mL water was added. The reaction was stirred at this temperature for 2 h and then the solvent was removed by rotary evaporation. The remaining residue was dried under vacuum to yield **6** (white solid, 482 mg, 81 %). <sup>13</sup>C NMR (101 MHz, DMSO)  $\delta$  152.29, 143.51, 123.15. Elemental analysis: (%) calculated for  $\text{C}_5\text{H}_7\text{Cl}_2\text{N}_7\text{O}_8$ : C, 25.23; H, 3.81; N, 41.18 %; found C, 23.51; H, 3.862; N, 39.33 %.

## RESULTS AND DISCUSSION

**Synthesis.** The industry application of high-energy materials is affected with many factors, such as a facile and effective synthetic route, economic and commercial starting materials, etc. 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine (**5**) was synthesized through the cyclization reaction of commercially available 4,5-dicyano-2-aminoimidazole and hydrazine hydrate under refluxing condition. The crystal of 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine hydrochloride (**6**) was prepared and confirmed by XRD to define the structure of **5**. Subsequently, compound **5** was reacted with perchloric acid in different solution to afford perchlorate  $\alpha$ -4 and  $\beta$ -4.  $\alpha$ -4 was synthesized when water was used as a solvent, while  $\beta$ -4 was achieved using a mixed solution of water and methanol.

**Scheme 1.** Synthesis route of 4-6



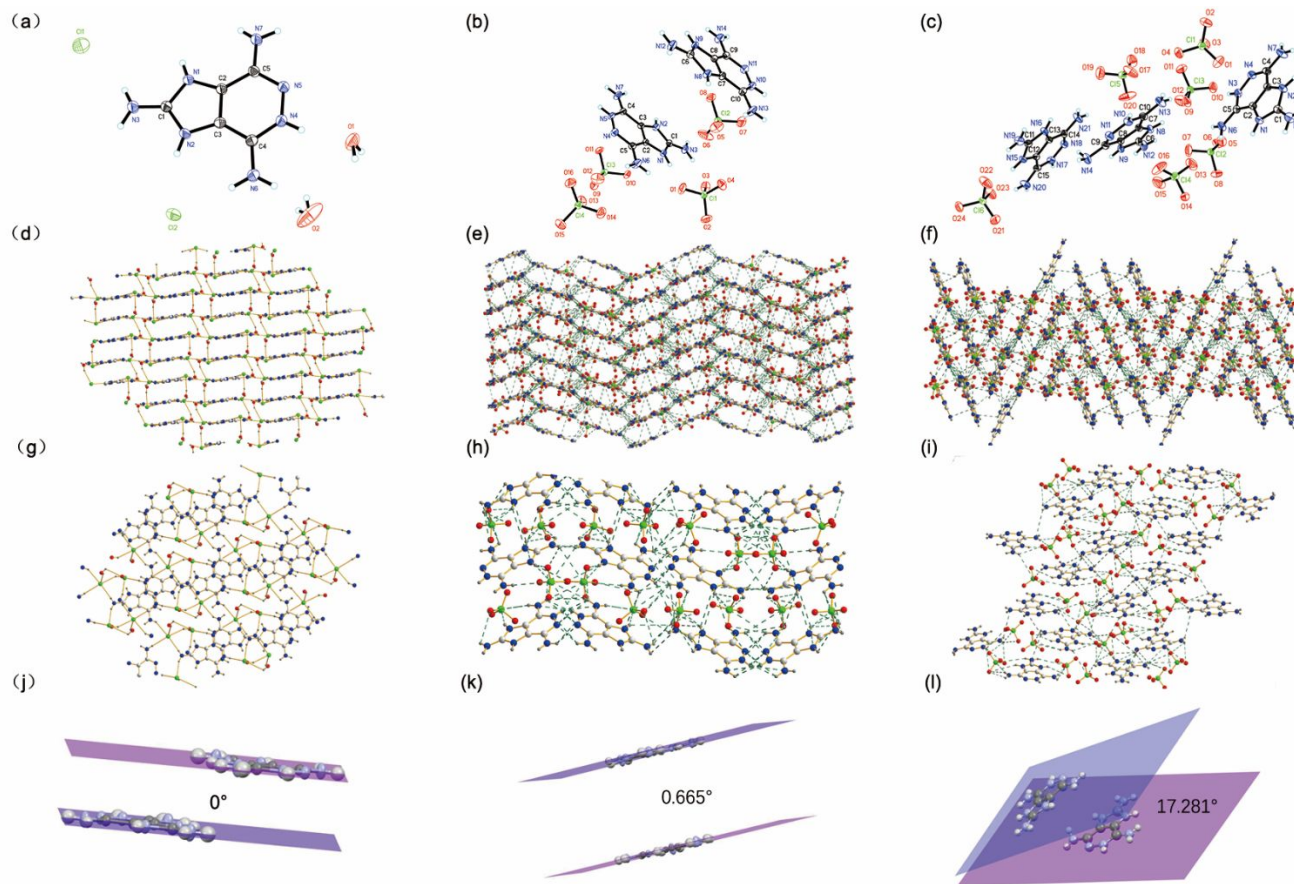
**X-ray diffraction and intermolecular interactions.** Crystal structure of compound **6** •  $\text{H}_2\text{O}$  belongs to the orthorhombic space group P-1 with a crystal density of 1.584  $\text{g cm}^{-3}$  at 293(2) K. The crystal asymmetric unit consists of two independent molecules ( $Z = 2$ ). In the structure of **6** •  $\text{H}_2\text{O}$ , its crystal packing is dominated by a parallel face to face  $\pi$ - $\pi$  arrangement (shown in Figure 2d).

$\alpha$ -4 belongs to the monoclinic space group  $P2_1/c$ , each unit cell includes 8 molecules ( $Z = 8$ ), and its crystal density is 1.930  $\text{g cm}^{-3}$  under the condition of 293 (2) K. The molecular structure is shown in Figure 2b. In the cation, the imidazole ring and pyridazine ring are located in the coplanar plane [C (5) -C (2) -C (3) -N (2) = -179.5 (2)°], and each substituents are coplanar with this fused framework [N (4) -N (5) -C (4) -N (7) = -178.9 (2)°, N (5) -N (4) -C (5) -N (6) = -179.1 (2)°, C (3) -N (2) -C (1) -N (3) = -179.6 (2)°]. From the c-axis,  $\alpha$ -4 can form a intensely wave-like crystal stack (Figure 2e), and in the same layer, the inclination angle between cations is 0.665° (Figure 2k). As shown in Figure 2e and 2h, an extensive hydrogen bond network is formed between the molecules, mainly composed of oxygen atoms in perchlorate. With the widely existing amino groups in cations (N (3) -H (3A) ... O (4), N (7) -H (7A) ... O (13), N (6) -H (6B) ... O (1), etc.) The main

hydrogen bonds are N ... H ... O and N ... H ... N, with a range of 2.791–3.283 Å.

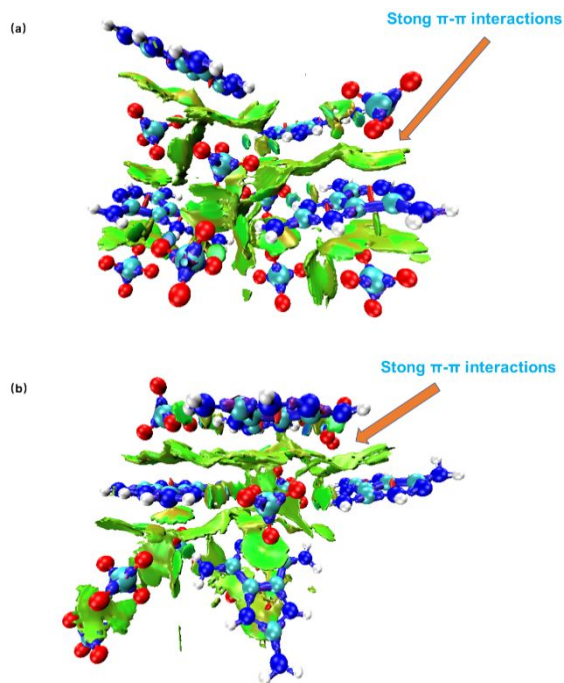
$\beta$ -4 belongs to the monoclinic space group  $P2_1/n$ , and each unit cell contains 12 molecules ( $Z = 12$ ). The crystal density calculated at the same temperature is 1.88 g cm<sup>-3</sup>. The molecular structure is shown in Figure 2c. Compared to  $\alpha$ -4, it is stacked in a V-shape (Figure 2f). There is a large

tilt angle (17.281°) between the cations in the same layer. This irregular arrangement has caused the molecular arrangement in the unit volume to be relatively loose, which could decrease its packing density in contrast to  $\alpha$ -4 in turn.



**Figure 2.** (a–c) Thermal ellipsoid plot (50%) and labelling scheme for  $6 \cdot \text{H}_2\text{O}$ ,  $\alpha$ -4 and  $\beta$ -4. Hydrogen atoms are included but are omitted for clarity. (d–f) Packing diagram of  $6 \cdot \text{H}_2\text{O}$  (viewed along from b axis),  $\alpha$ -4 (viewed along from c axis) and  $\beta$ -4 (viewed along from b axis). Dashed lines represent hydrogen bonding. (g–i) The 2D layer in the crystal structure of  $6 \cdot \text{H}_2\text{O}$  (viewed along from a axis),  $\alpha$ -4 (viewed along from c axis) and  $\beta$ -4 (viewed along from b axis). Dashed lines represent hydrogen bonds. (j–l) The planes of cations in the same layer and the dihedral angle between two planes in  $6 \cdot \text{H}_2\text{O}$ ,  $\alpha$ -4 and  $\beta$ -4.



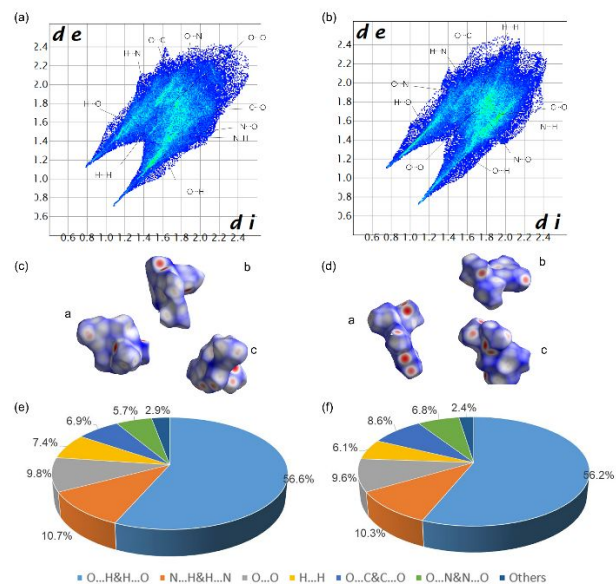


**Figure 3.** The Density Overlap Regions Indicator (DORI) analysis for dimers of  $\alpha$ -4 (a),  $\beta$ -4 (b) (the strong chemical bonding regions are nicely portrayed as blue isosurfaces, and those large regions in blue-green-brown-red color represent hydrogen bonding interaction, van der Waals (VdW) interaction, weak steric effect and strong steric effect, respectively).

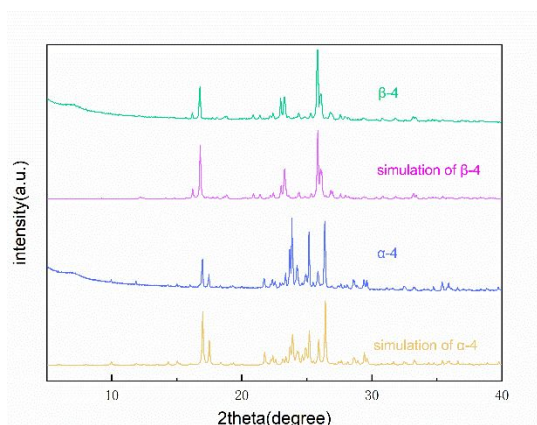
From the perspective of theoretical research,  $\alpha$ -4 and  $\beta$ -4 were analyzed by DORI. Four organic ligands and eight perchlorates were taken from the crystals for comparison, as illustrated in Figure 3. The imidazole and pyridazine rings show conjugated units (all chemical bonds are covered by blue cylinders of different lengths as shown in the DORI maps). Both  $\alpha$ -4 and  $\beta$ -4 exhibit strong  $\pi$ - $\pi$  interactions and hydrogen bonding, as shown by the isosurfaces in Figure 3. This strong  $\pi$ - $\pi$  interaction can be revealed by measuring the interlayer distance. For example, the interlayer distance of  $\alpha$ -4 is: 3.369 Å (typical set parameter of aromatic  $\pi$ - $\pi$  interaction: 3.65-4.00 Å)<sup>24</sup>. In addition, it can be seen from Figures 3a and 3b that the stacking method of  $\alpha$ -4 is more compact, while  $\beta$ -4 is dispersedly arranged with a larger tilt angle, so the interaction of  $\alpha$ -4 is stronger, suggesting it is rational that  $\alpha$ -4 behaves more dense than  $\beta$ -4.

In order to get further studies of the relationship between the crystal stacking mode and the mechanical sensitivity of 4, the intermolecular interactions were analysed by the Hirshfeld surface map and 2D fingerprint by using Crystalexplorer 3.0 software. Figure 4(c) and Figure 4(d) show the Hirshfeld surfaces of  $\alpha$ -4 and  $\beta$ -4

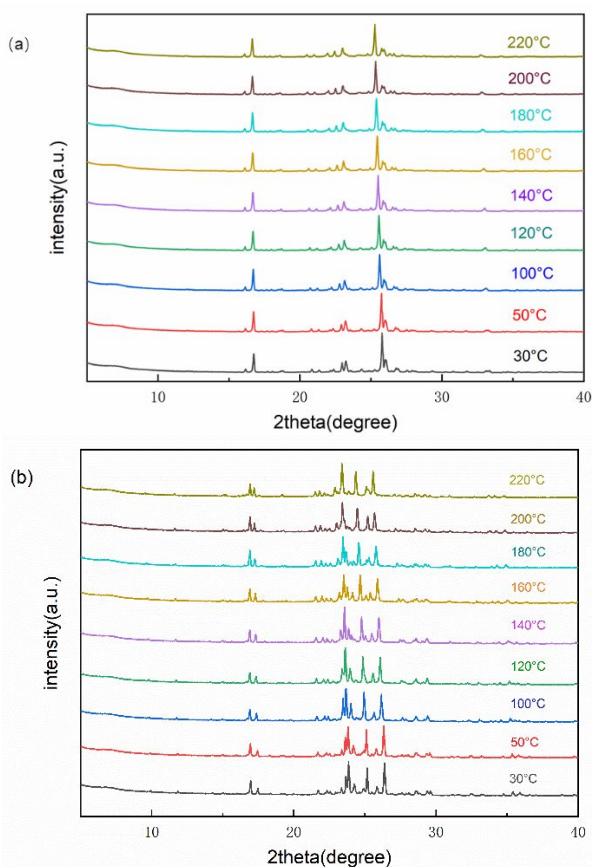
(white,  $d$  = van der Waals (vdW) distance; blue,  $d > \text{vdW}$  distance; red,  $d < \text{vdW}$  distance). The red and blue areas on the Hirshfeld surface represent high and low close contact portions, respectively. Compared with  $\alpha$ -4,  $\beta$ -4 tends to have a flat plate-like structure, and most of the red dots which shows the intermolecular close contacts are located on the side faces of the molecule, indicating that a large number of hydrogen bonds existed to maintain stability of crystal structure. As shown in Figure 4(a) and 4(b), O...H, H...O, N...H and H...N are in close contact, and the pair of spikes at bottom left denote that the hydrogen bonds are similar to each other for  $\alpha$ -4 and  $\beta$ -4. Figure 4(e) and 4(f) show the percentage contribution of single-atom contact to the Hirshfeld surface, respectively. O-H and N-H accounted for 67.3 % of  $\beta$ -4 and 66.5 % of  $\alpha$ -4, which shows that the intermolecular stability is mainly maintained by ionic bonds (between the oxygen atom of the high chloride radical and N-H on the cation ring),  $\pi$ - $\pi$  interaction forces, and hydrogen bonds. As these strong interactions are beneficial to the mechanical sensitivity of energetic materials, it is reasonable to understand that  $\alpha$ -4 and  $\beta$ -4 present better sensitivities than other energetic perchlorates.



**Figure 4.** a) Fingerprint plots in crystal stacking found in  $\alpha$ -4. b) Fingerprint plots in crystal stacking found in  $\beta$ -4. c) Hirshfeld surface of  $\alpha$ -4. d) Hirshfeld surface of  $\beta$ -4. e) Percentage contributions of the individual atomic contacts to the Hirshfeld surface for  $\alpha$ -4. f) Percentage contributions of the individual atomic contacts to the Hirshfeld surface for  $\beta$ -4.



**Figure 5.** Powder diffraction patterns of  $\alpha$ -4,  $\beta$ -4 and the results by experiment.

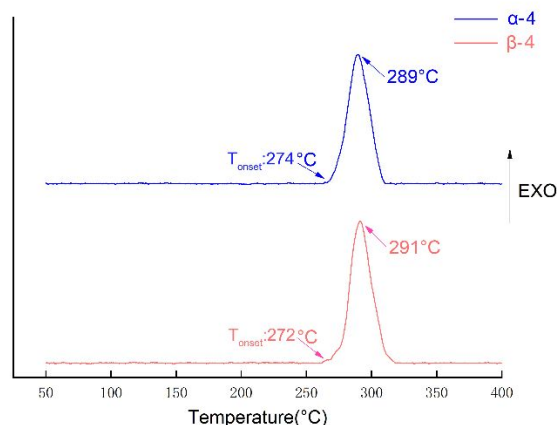


**Figure 6.** (a) Powder diffraction patterns of  $\alpha$ -4 at different temperatures. (b) Powder diffraction patterns of  $\beta$ -4 at different temperatures.

X-ray powder diffractograms show distinct differences in the position of the peaks of  $\alpha$ -4 and  $\beta$ -4, which clearly indicating different crystal lattices. As can be seen from the XRPD pattern of Figure 5, the characteristic peaks of  $\alpha$ -4 at  $2\theta = 16.19, 16.79, 23.04, 23.28, 25.78, 26.08^\circ$ . The characteristic peaks of  $\beta$ -4 at  $17.04, 17.52, 23.72, 23.93, 24.92, 25.23, 25.9, 26.42^\circ$ . These obvious peak differences (such as  $23.93, 26.42^\circ$ ) prove that  $\alpha$ -4 and  $\beta$ -4 belong to different

crystal forms, which are also in accord with those simulated patterns from their individual single crystals.

In terms of thermal stability, it is of considerable benefit to determine whether the forms are monotropic or enantiotropic,<sup>25</sup> since metastable polymorphs tend to convert to stable polymorphs. Therefore, the in-situ XRD technique was used to study the thermal stability of  $\alpha$ -4 and  $\beta$ -4 at different temperatures. It can be seen from the Figure 6 that during the temperature range from 30 to  $220^\circ\text{C}$ ,  $\alpha$ -4 and  $\beta$ -4 possess no tendency of polymorph transformation, suggesting that under the circumstances of elevating temperature, these two crystal forms are not monotropic or enantiotropic.



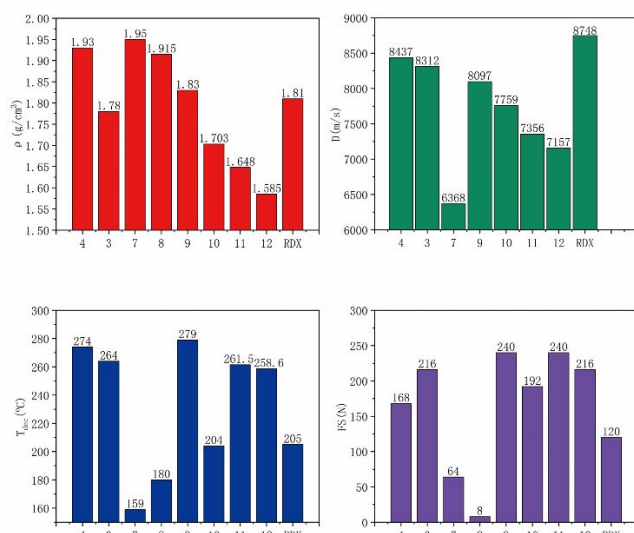
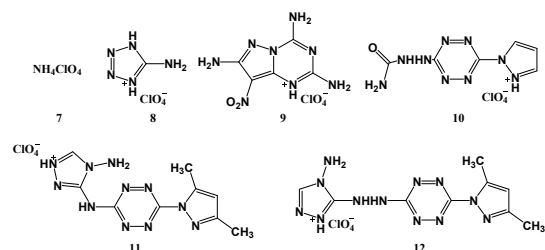
**Figure 7.** The DSC curves of  $\alpha$ -4 and  $\beta$ -4 measured with a heating rate of  $5^\circ\text{C min}^{-1}$ .

According to the density of the crystal and the measured enthalpy of formation, their explosion characteristics were computed using EXPLO5 (version 6.01). As shown in Table 1,  $\alpha$ -4 shows good detonation performance ( $D: 8437\text{ m s}^{-1}$ ,  $P: 32.86\text{ GPa}$ ) due to the high density ( $1.93\text{ g cm}^{-3}$ ) and positive formation enthalpy ( $0.33\text{ kJ g}^{-1}$ ). The detonation performance of  $\beta$ -4 ( $D: 8128\text{ m s}^{-1}$ ,  $P: 29.4\text{ GPa}$ ) is slightly reduced, but with better impact sensitivity ( $> 20\text{J}$ ). Compared with a previously reported salt with the same anion (TATOT perchlorate (3),  $1.78\text{ g cm}^{-3}$ ), the density of 4 ( $1.88\text{--}1.93\text{ g cm}^{-3}$ ) is considerably increased. Meanwhile, 4 exhibits superior thermal stability ( $T_d: 272\text{--}274^\circ\text{C}$ , as shown in Figure 7) and sensitivity (IS:  $14\text{--}20\text{J}$ , FS:  $144\text{--}168\text{ J}$ ) to those of RDX ( $205^\circ\text{C}$ , IS:  $7.4\text{ J}$ , FS:  $120\text{ N}$ ).

**Table 1.** Physicochemical and energetic properties of compounds **4** compared with some known perchlorate-based energetic materials as well as RDX.

	$P$ (g cm <sup>-3</sup> ) <sup>[a]</sup>	$D$ (m s <sup>-1</sup> ) <sup>[b]</sup>	$P$ (GPa) <sup>[c]</sup>	$\Delta H_f$ (kJ g <sup>-1</sup> ) <sup>[d]</sup>	$T_{dec}$ (°C) <sup>[e]</sup>	$IS$ (J) <sup>[f]</sup>	$FS$ (N) <sup>[g]</sup>
<b><math>\alpha</math>-4</b>	1.93	8437	32.86	0.33	274	14	168
<b><math>\beta</math>-4</b>	1.88	8128	29.4	-0.13	272	20	144
<b>3<sup>15</sup></b>	1.78	8312	28.1	1.33	264	9	216
<b>7<sup>26</sup></b>	1.95	6368	15.8	-1.13	159	3	64
<b>8<sup>9</sup></b>	1.915	-	-	-	180	1.5	8
<b>9<sup>23</sup></b>	1.83	8097	28	0.34	279	40	240
<b>10<sup>27</sup></b>	1.703	7759	24.6	1.97	204	-	192
<b>11<sup>27</sup></b>	1.648	7356	20.5	2.4	261.5	-	240
<b>12<sup>27</sup></b>	1.585	7157	18.8	2.09	258.6	-	216
<b>RDX<sup>28</sup></b>	1.81	8748	34.9	0.36	205	7.4	120

[a] Density measured by single-crystal X-ray diffraction at 293(2) K; [b] Calculated detonation velocity; [c] Calculated detonation pressure; [d] Measured by using an oxygen bomb calorimeter; [e] Onset decomposition temperature from DSC (heating rate of 5°C min<sup>-1</sup>); [f] Impact sensitivity measured by BAM drop-hammer test; [g] Friction sensitivity measured by a BAM friction tester.

**Scheme 2.** Structural of the compounds **7-12**.**Figure 8.** Physical performances of **4** compared with some known perchlorate-based energetic materials as well as RDX.

## CONCLUSION

In conclusion, 1H-imidazo[4,5-d]pyridazine-2,4,7-triamine was synthesized efficiently based on a one-step reaction of 4,5-dicyano-2-aminoimidazole. Two crystal phases of its perchlorates  $\alpha$ -4 and  $\beta$ -4 were achieved in different solvent.  $\alpha$ -4 shows a high density of 1.93 g cm<sup>-3</sup> and good explosive performance (8437 m s<sup>-1</sup>, 32.86 GPa).  $\beta$ -4 shows slightly lower density (1.88 g cm<sup>-3</sup>) and explosive performance (8128 m s<sup>-1</sup>, 29.4 GPa), but with better impact sensitivity (> 20 J). Both of them show good decomposition temperatures ( $T_d$ : 272-274 °C). Based on the theoretical calculation, it is proved that  $\pi$ - $\pi$  interaction and hydrogen bonding interaction are the mainly intermolecular force of  $\alpha$ -4 and  $\beta$ -4 beside electrostatic attraction. Reasons for the low sensitivity and the difference of density between these two crystal forms are also explained. This work provided a promising nitrogen-rich fused heterocyclic cation, and its perchlorates show good detonation performance, acceptable sensitivity and excellent thermal stability compared with those of other energetic perchlorates. This novel fused heterocyclic cation has showed its perspective in the development of some promising energetic ionic salts.

## ASSOCIATED CONTENT

**Supporting Information.** The Supporting Information is available free of charge on the ACS Publications website: Crystallographic data for these crystals (CCDC No.: 1973870, 1973871 and 1973872), NMR data, FT-IR data, Theoretical simulation of the energetic properties, Hirschfeld surfaces, X-ray powder diffraction pattern.

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### Notes

The authors declare no competing financial interest.

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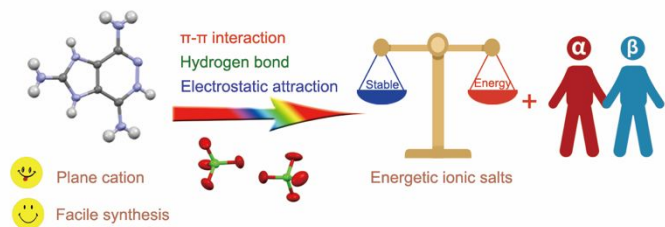
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26 Synopsis

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