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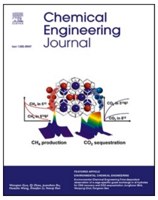

Energetic compounds based on a new fused triazolo[4,5-d]pyridazine ring: Nitroimino lights up energetic performance

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ABSTRACT

A series of highly energetic materials with good detonation performance, high density and low impact sensitivity based on a new triazolo[4,5–d]pyridazine fused ring was synthesized and characterized. 4-Nitroamino-7-nitroimino-triazolo[4,5–d]pyridazine (**5**) was characterized by single crystal X-ray structure analysis, which shows that the proton of one nitroamino group was transferred to the pyridazine ring forming a nitroimino moiety. The electrostatic potential (ESP) of **5** shows the nitroimino group has the lowest negative value, while the nitroamino area has a high positive value. The analysis of NCI plots indicates strong intramolecular hydrogen bonds (HB) and π-π interactions which arise from the newly formed nitroimino group. This supports that the rearrangement of the nitroamino group to form the nitroimino moiety lowers the impact sensitivity. Compound **5**·H_2O exhibits face-to-face packing, which gives rise to a relatively high density of 1.87 g cm^{-3} and a low impact sensitivity of 18 J. Its hydrazinium and hydroxylammonium salts have high detonation velocities of 9351 m s^{-1} and 9307 m s^{-1}, respectively. Their impact and friction sensitivities (7 J, 120 N and 8 J, 160 N) are similar to HMX. This proclivity for rearrangement by a nitroamino group provides new insight into the design of next generation high energy density materials.

1. Introduction

Fused heterocycles have become a topic of considerable interest in the design of new generation high energy density materials (HEDMs)[1] because the coplanar molecular structure and the large conjugate system, which can enhance the density and heat of formation (HOF), lead to high detonation performance.[2] Several kinds of fused cyclic energetic materials have been synthesized and characterized; their high detonation performances, good thermal stabilities and low sensitivities suggest that these fused ring compounds could be identified as the next generation of energetic materials.[3]

Fused ring compounds are synthesized from a single ring followed by a subsequent ring closing reaction. There are a large number of ring formation reactions, such as a hydrazine group reacting with cyanogen bromide[4] or diethoxymethylacetate[5] to form a triazole ring; an amino group reacting with sodium nitrite to form a diazonium moiety, which is then reacted with nitroacetonitrile to form a triazine ring,[6] The introduction of an azide group can ring close to form a tetrazole ring,[7] etc. In the design of energetic materials, high nitrogen rings such as tetrazole,[8] tetrazine,[9] furazan,[10] furoxan[11] and triazole [12] rings have been well studied. Rings with lower nitrogen content such as the pyridazine ring have attracted less attention because the low nitrogen content does not give rise to desirable detonation performance. However, a low nitrogen fused ring provides additional positions at which energetic groups can be introduced – another way to improve energy. A method often used to synthesize the pyridazine fused ring is the reaction of hydrazine with a neighboring dicyano group. Based on this methodology, 6,7-diamino-oxadiazolo[3,4–c]pyridazine,[13] 4,7-diamino-imidazolo[4,5–d] pyridazine[14] and 2,4,7-diamino-imidazolo [4,5–d]pyridazine[15] fused rings have been reported (Fig. 1). However, energetic materials

based on these fused rings show low detonation performance, giving rise to this kind of reaction getting less attention in the design of of new energetic materials. But does this suggest that fused rings with low nitrogen content have no future in energetics?

Energetic groups such as nitro ($-NO_2$),[16] nitrato ($-ONO_2$),[17] nitroamino ($-NNO_2$),[18] and azido ($-N_3$)[19] are most often used in the design of energetics, because they can enhance density and heat of formation. Among them, nitroamino can increase the oxygen balance and density of compounds, which results in superior detonation

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properties. Furthermore, nitroamino can form energetic salts by reacting with an energetic base, thus providing a useful path to energetic materials with higher detonation performance and lower sensitivity.[4] Energetic materials with two nitroamino groups are very attractive because they exhibit high detonation performance. However, many neutral compounds containing two nitroamino moieties possess low thermal stability and high sensitivity. Because the design of fused rings mainly uses a high nitrogen and oxygen content backbone which has few positions that are available for energetic substituents, nitroamino groups are often found in different heterocycles of the fused ring. A single ring with two nitroamino groups is sensitive with low thermal stability, which makes them difficult to obtain (Fig. 2a).[20] When nitroamino is replaced with nitroimino, the stability is improved to some extent (Fig. 2b).[21] However, when the single ring is replaced by a fused ring, the sensitivity and stability of the compound is improved considerably (Fig. 2c).[22] It is known that a nitroimino-substituted ring is more stable than the nitroamino analogy, and that a fused ring exhibits better sensitivity and stability than a single ring.

4,5-Dicyanotriazole (**1**)[23] is reacted with hydrazine (without acetic acid as catalyst) to ring close to 4,7-diamino-triazolo[4,5–d]pyridazine fused ring (**4**) (Scheme 1). The two amino groups in pyridazine react with fuming nitric acid to form 4-nitroamino-7-nitroimino-triazolo[4,5–d]pyridazine (**5**), in which one nitroamino group undergoes rearrangement to leave a nitroimino substituent. A similar rearrangement was also observed in di(nitroamino)triazole,[21c] di(nitroamino)tetrazole,[21b] and 4,7-di(nitroamino)-imidazole[4,5–d]pyridazine[22], which is a convenient way to stabilize molecules (Fig. 2). Especially in the case of the latter, a strong HB (hydrogen bond) system is formed by the rearrangement of nitroamino to nitroimino, which leads to face-to-face stacking giving rise to low impact sensitivity. A similar situation was found for the new fused ring compound (**5**). This rearrangement of the nitroamino moiety results in strong intramolecular and intermolecular HBs. The nitroimino group is conjugated with the fused ring, in which strong π-π interactions are found. These interactions in neutral compounds also lead to face-to-face stacking which permits **5**$\cdot H_2O$ to exhibit low impact sensitivity (18 J) and a thermal stability >150°C. Disalts of compound **5** were obtained by reacting with energetic bases, resulting in higher detonation velocities than that of **5**$\cdot H_2O$. However, unlike most salts of di(nitroamino) compounds, they are more impact sensitive than the neutral precursor.

2. Preparation and structure

2.1. Synthesis

The synthetic route is given in Scheme 1. The starting material, 4,5-dicyanotriazole (**1**) was obtained based on the literature.[23] Based on the literature, the reaction of the 4,5-dicyano-substituted heterocycle with hydrazine requires acetic acid as a catalyst.[13–15] However, the intermediate compound 4,5-carbohydrazonamidetriazole (**2**), which is obtained by reacting compound **1** with hydrazine, reacts with acetic acid to form a mixture of 4-carbohydrazonamide-5-(5-methyl-1,2,4-triazole-3-yl)-triazole (**3**) and 4,7-dinitramino-triazolo[4,5–d]pyridazine (**4**), showing that the reported reaction method is not applicable for the synthesis of **4**. When acetic acid is replaced by hydrazine in DMF at 80°C, compound **4** precipitates. Compound **4** can be also obtained directly by heating **1** in a mixture of hydrazine and DMF. Compound **4** reacts with $KMnO_4$ to give 4′-diamino-7,7′-azo-triazolo[4,5–d]pyridazine (**9**). The amino groups in **4** and **9** react with 100% nitric acid to form compounds **5**$\cdot H_2O$ and **10**$\cdot\cdot 4H_2O$. Reacting **5** with energetic bases gives three energetic salts. However, compound **10** forms **9** when reacted with a base (hydrazine monohydride or aqueous ammonia) in a mixture of water and methanol.

2.2. Crystal structure

The new compounds were fully characterized by multinuclear NMR and infrared spectroscopy and elemental analysis. The crystal of neutral compound **5** (Fig. 3) was grown from methanol at room temperature and characterized by single crystal X-ray structure analysis. Compound **5**$\cdot H_2O$ crystallizes in the monoclinic crystal system with space group $P2_1/c$ ($Z = 4$) symmetry and has a crystal density of 1.947 g cm^{-3} (100 K). The X-ray structure and data are given in Fig. 3c and Table S1, respectively. The asymmetric unit of **5** contains one water molecule which could not be removed. The water serves as a significant link to connect those molecules by forming intermolecular hydrogen bonds (HBs). First, the water forms two HBs (N5-H5…O1W and O1W-H1WA…N8) with two different molecules in the same layer (Fig. 3b). Second, the

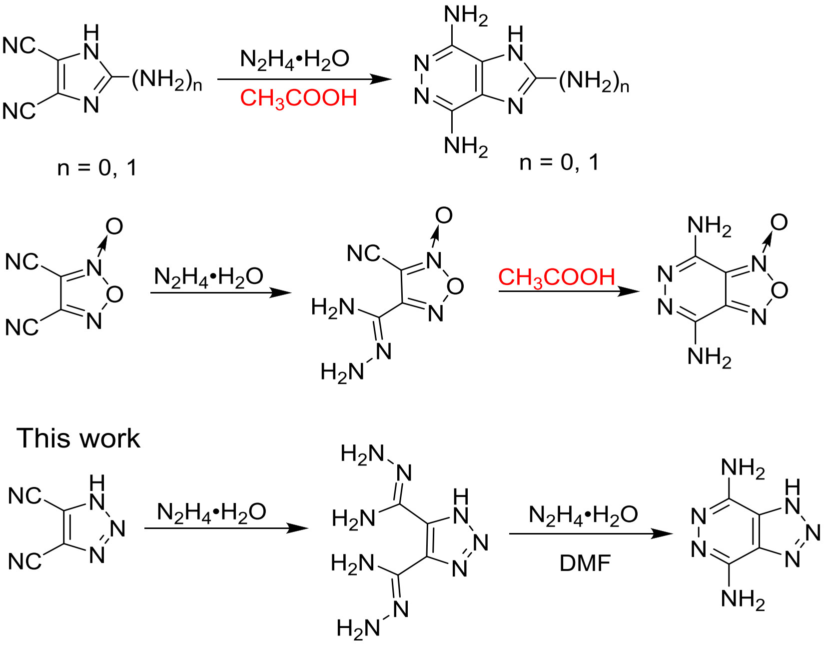


Fig. 1. Syntheses of fused rings based on a pyridazine ring.

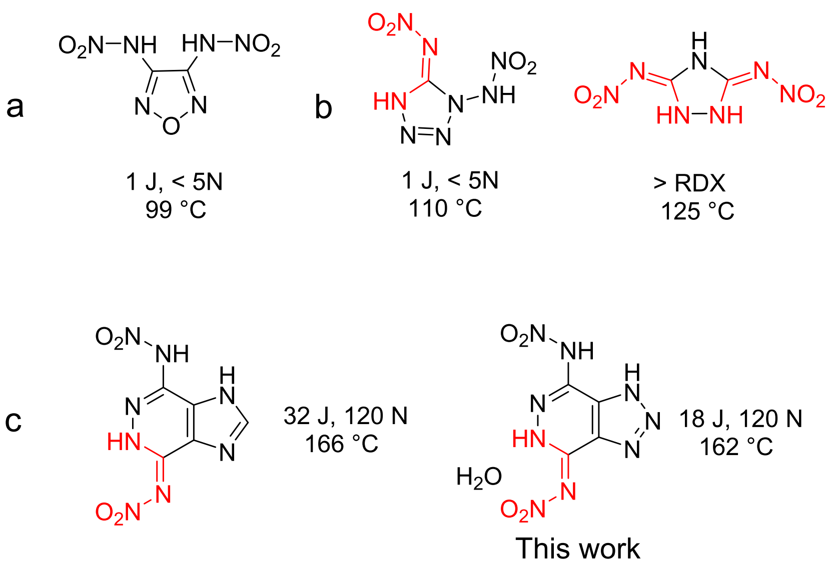
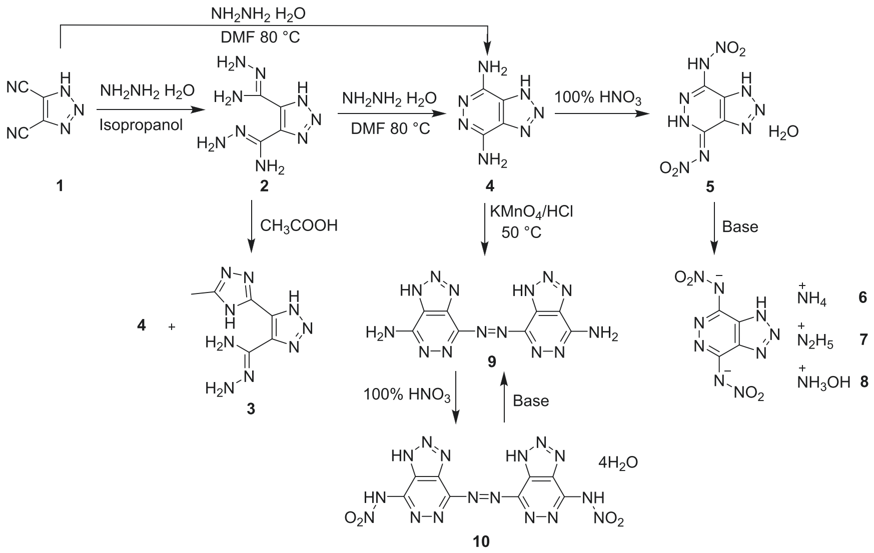


Fig. 2. a) Two nitroamino groups substituted on a single ring; b) One nitroamino and one nitroimino group or two nitroimino groups substituted on a single ring; c) One nitroamino and one nitroimino group substituted on a ring which is fused with another.



Scheme 1. Syntheses of 4-nitroamino-7-nitroimino-triazolo[4,5–d]pyridazine (5) and its derivatives.

O1W-H1WA…O2 HB connects the water with another molecule in a different direction which forms a wave-like layer structure. Third, the O1W-H1WA…O1 HB connects the molecules in different layers (Fig. 3c). Finally, the water aids in wave-like packing (Fig. 3d). In addition to the HBs formed by water, the intramolecular HBs formed by the transformation of nitroamino to nitroimino provides another route to form wave-like stacking, which gives rise to a high packing coefficient of 0.78. The structure-directing role of the water can be also seen in some pharmaceutical multicomponent crystals.[24] The newly formed nitroimino group is nearly planar with the fused ring, with torsion angles of C1-N8-N9-O3 = 177.78(13) °, C1-N8-N9-O4 = -2.5(2) °, N9-N8-C1-N5 = −0.4(2) ° and N9-N8-C1-C2 = 179.69 (12) °. However, the remaining nitroamino group is twisted totally out of the plane with N7-N6-C4-N4 = 150.39° (14) and N6-N5-C4-C3 = –33° (2).

3. Energetic properties

3.1. Density and heat of formation

The density and heat of formation (HOF) values of a compound are significant factors in calculation of detonation performance. High density and high HOF give higher energy. The densities of all the new compounds were measured at 25°C by using a gas pycnometer. The HOFs of the new energetic materials were calculated using the Gaussian 03 (Revision D.01) suite of programs[27] and determined based on isodesmic reactions. As shown in Table 1, the neutral compound (**5**·H_2O) has the highest density at 1.87 g cm^{-3}, but it has the lowest HOF at 303.0 kJ mol^{-1}. The hydroxylammonium salt (**8**) also has a rather high density of 1.83 g cm^{-3} as well as a high HOF of 615.8 kJ mol^{-1}. The hydrazinium (**7**) and ammonium (**6**) salts have similar densities at 1.78 g cm^{-3} and 1.77 g cm^{-3}, respectively. However, the HOF of the hydrazinium salt (827.5 kJ mol^{-1}) is much higher than that of ammonium salt (490.3 kJ mol^{-1}).

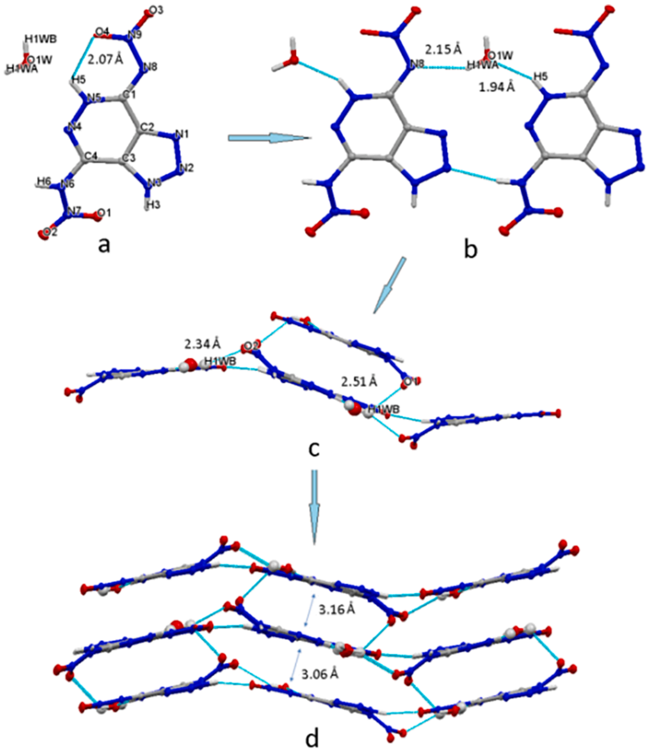


Fig. 3. a) Crystal structure of compound **5**·H_2O with an intramolecular HB. b) HBs resulting with H_2O to connect molecules to form layers; c) HBs with H_2O connecting molecules in the same layers and interlayer; d) wave like face-to-face stacking resulting from HBs.

3.2. Detonation performance

Based on the measured densities and the calculated HOFs, the detonation pressures (P) and detonation velocities (*v*D) of those new energetic materials were obtained by using the EXPLO5 (v6.01) program.[28] Because **5**·H_2O has the lowest HOF, it has the lowest detonation velocity of 8875 m s^{-1} and a detonation pressure of 34.5 GPa. The ammonium (**6**) salt has a slightly higher detonation velocity of 8900 m s^{-1} but a lower detonation pressure of 31.0 GPa. As a result of a high density and a high HOF, the hydrazinium (**7**) and hydroxylammonium (**8**) salts exhibit good detonation performances, with detonation velocities at 9351 m s^{-1} and 9307 m s^{-1}, and detonation pressures of 34.5 GPa and 37.4 GPa, respectively, which are comparable to those of HMX.[26]

3.3. Thermal stability

The decomposition temperatures were determined by differential scanning calorimetry (DSC) at a heating rate of 5°C min^{-1}. As shown in Fig. S5 and Table 1, all compounds exhibit a sharp exothermic peak, with decomposition temperatures (onset temperature) higher than 150°C. These values, especially for compound **6**–**8**, meet most military and civilian requirements. The bond dissociation enthalpies (BDEs) for the N – NO_2 bonds in **5**·H_2O were calculated. The BDEs for the nitroiamino is 197.3 kJ mol^{-1}, which is much higher than the nitroamino (122.5 kJ mol^{-1}), indicating that rearrangement of the nitroimino group shows better thermal stability than the traditional nitroamino group. The neutral compound **5**·H_2O has a low decomposition temperature at 163°C, which is higher than most di(nitroamino) compounds (<150°C). The ammonium (**6**) and hydrazinium salts (**7**) have the highest decomposition temperatures at 210°C and 212°C, which are similar to RDX and TKX-50, while the hydroxylammonium (**8**) salt has a lower decomposition temperature at 178 °C. Compound **10**·4H_2O has the lowest decomposition temperature at 151°C, the strong endothermic peaks can be observed loss of water.

3.4. Mechanical sensitivity

Sensitivity is an important factor for energetic materials. The sensitivities of all the new compounds towards impact (IS) and friction (FS) were evaluated by standard BAM procedures.[29] As shown in Table 1, unlike the high impact sensitivities of most neutral di(nitroamino) compounds, **5**·H_2O has a low impact sensitivity at 18 J relative to its derivatives, which results from the face-to-face stacking and π-π interactions between layers. However, the friction sensitivity is similar to that of the salts at 120 N, which arises from one nitroamino moiety being twisted out of the plane of the structure. Compared with the neutral compound, all salts show higher impact sensitivities, because the HB system and strong π-π interactions in **5**·H_2O decrease the impact sensitivity. The ammonium salt (**6**) possesses an impact sensitivity of 12 J, and friction sensitivity of 160 N. The hydrazinium (7 J, 120 N) and hydroxylammonium (8 J, 160 N) salts possess sensitivities similar to HMX. As a result of four water molecules, compound **10** possesses low sensitivities (>40 J, >360 N).

The electrostatic potentials (ESP) of the neutral compound, which are closely related to the impact sensitivity, were analyzed. As shown in Fig. 4a. the positive and negative potentials are given in red and blue respectively; larger and stronger positive potentials usually indicate higher impact sensitivities.[19] The maxima and minima of ESP are represented as orange and cyan spheres, respectively. As is seen in Fig. 4a, the nitroimino moiety possesses minimum potential parts, which are −37.53 and –33.41 kcal mol^{-1} for the nitro group, and −41.07 and −40.67 kcal mol^{-1} for the N-NO_2 moiety. While the only nitroamino group in **5** possesses maximum potentials, where the electrostatic potentials increase to −11.16 and −14.62 kcal mol^{-1} for the nitro group, and 40.29 and 58.79 kcal mol^{-1} for the NH-NO_2 group, indicating that the transfer of the proton to the fused ring reduces the impact sensitivity, which is consistent with the experimental results. This also explains why the neutral compound has lower sensitivity than most di(nitroamino) compounds. In Fig. 4b is seen the quantitative distributions of the surface electrostatic potentials. The ranges of positive and negative electrostatic potentials are almost the same which indicates that this compound is only slightly sensitive. Similar results can be found by

Table 1
Physical properties of 4-nitroamino-7-nitroimino-triazolo [4,5–d]pyridazine (5) and its derivatives.

Compound	N^a (%)	T^b_{dec} (°C)	d^c (g cm^{-3})	ΔH^d_f (kJ mol^{-1}/kJ g^{-1})	*v*D^e (m s^{-1})	P^f (GPa)	IS^g (J)	FS^h (N)
5·H_2O	52.3	162	1.87	303.0/1.48	8875	34.5	18	120
6	56	210	1.77	490.3/1.61	8900	31	12	160
7	59.7	211	1.78	827.5/2.06	9351	34.5	7	120
8	50.2	178	1.83	615.8/1.69	9307	37.4	8	160
10 4H_2O	57.7	151	1.73	−27.5/-0.08	–	–	>32	>240
TKX-50^i	65.9	221	1.88	446.6/2.62	9698	40.1	20	120
HMX^j	32.56	280	1.9	105.0/0.36	9320	39.5	7	120

a) Nitrogen content; b) Thermal decomposition temperature; c) Measured density; d) Calculated heat of formation; e) Calculated detonation velocity; f) Calculated detonation pressure; g) Impact sensitivity; h) friction sensitivity; i) [25]; j) [26].

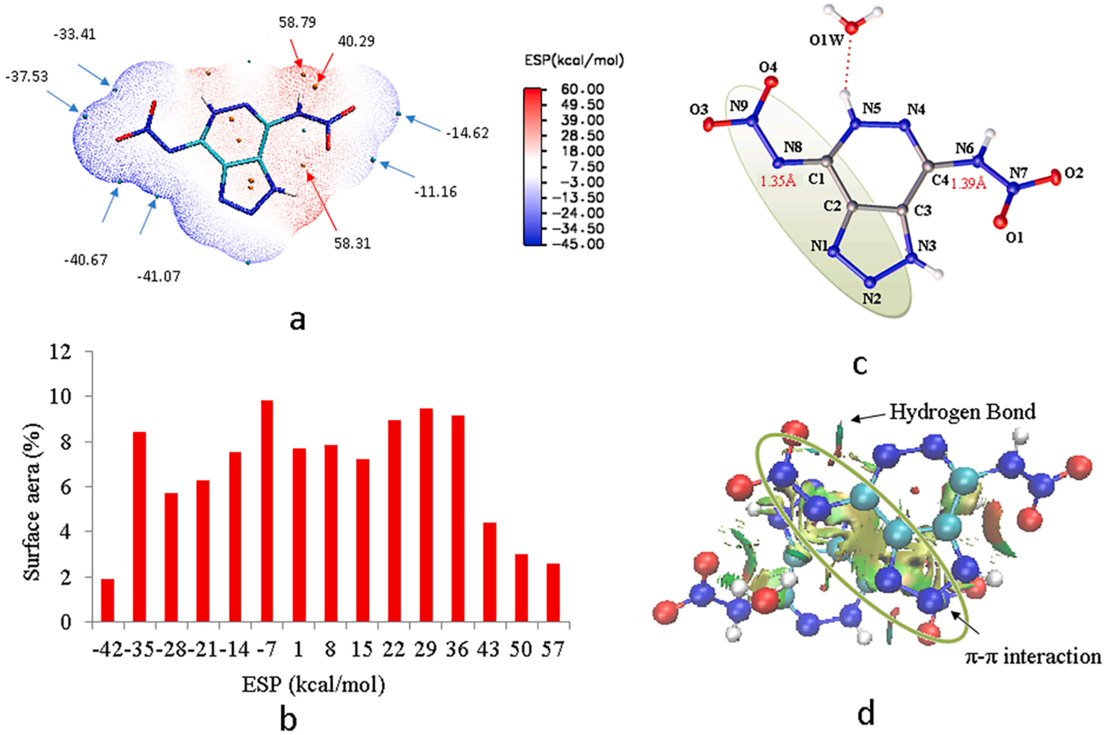


Fig. 4. a) ESP-mapped molecular vdW surface of **5**·H_2O; b) Contributions of the ESP in bar graphs; c) Bond distances in molecule **5**·H_2O; d) π-π stacking in NIC plots of gradient isosurfaces (s = 0.5 au) of the unit cells of **5**·H_2O.

analysis of the relationship between the reduced density gradient $(s = 1/2(3\pi2)1/3)|\nabla\rho|/\rho4/3)$ and the quantum–mechanical electron density (ρ). The noncovalent interaction (NCI) plots are used to study the differences between HBs, van der Waals interactions, and repulsive steric clashes.[30] In Fig. 4d, strong intramolecular and intermolecular HBs are found. For the face-to-face π-π interactions, the NCI domains between the nitroimino-rearranged system are abundant and larger than the nitroamino part, which indicates that the nitroimino present with the fused ring to form a stronger conjugated system. There are only a few NCI domains under the nitroamino part of the pyradazine ring. As can be seen in Fig. 4c, the bond distance C1 – N8 distance in the nitroimino group is 1.35 Å, which arises from conjugation. The bond distance C – N in nitroamino is 1.39 Å which is longer than that in the nitroimino and no π-π interactions are found.

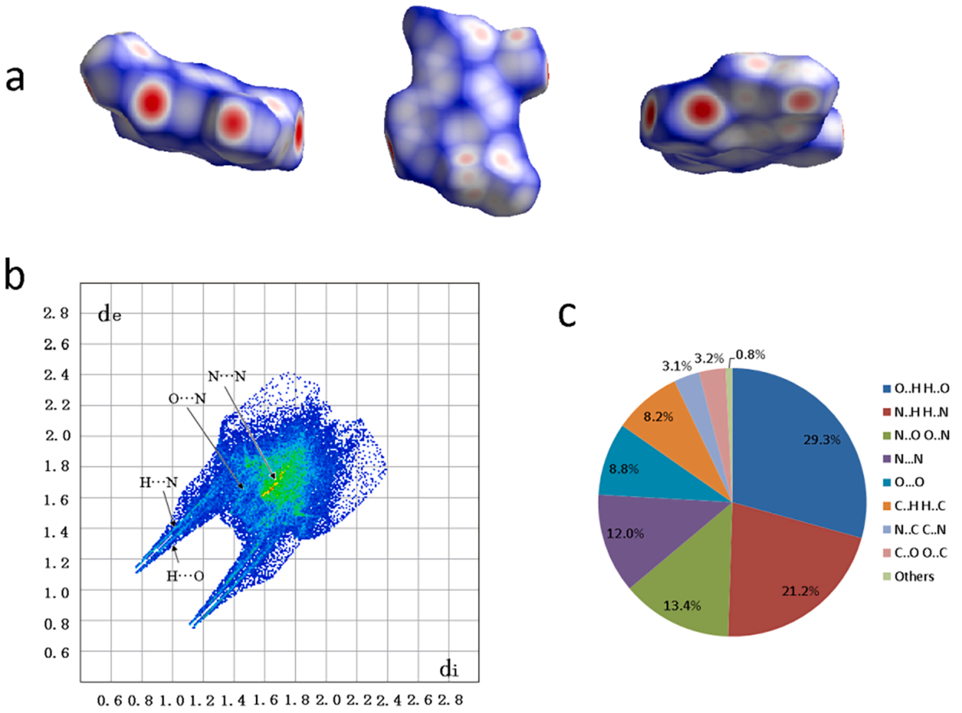


Fig. 5. (a) and (b) 2D fingerprint plots in crystal stacking for 5; (c) Contributions of the individual atomic contacts in the pie graphs for **5**.

For further insight into the weak inter/intra molecular interactions, the single crystal of **5**·H_2O has been investigated by using Crystal Explorer 17.[31] The Hirshfeld surface and the 2D fingerprint spectra of **5**·H_2O were analyzed. As shown in Fig. 5a, because of the fused ring structure backbone, **5** is planar.

The red and blue areas in the plane in the Hirshfeld surface represent high and low close contact, respectively. As shown in Fig. 5a, the red spots are found mainly on the side faces of the plate, which denote the close interactions due to the HBs. The blue portion covers the front faces of the plate denoting van der Waals interactions derived from N…N and N…C interactions. The analysis of the 2D-fingerprint plot is given in Fig. 5b. The remarkable spikes on the bottom are identified as strong O…H and N…H HB interactions. Because one water molecule is present, the total HB interactions contribute 50.5% of the total weak interactions. The interactions arising from N…N are 13.41% and from N…O are 12.0% of the total interactions, which indicate the conjugated fused ring structure. This is a characteristic found in slightly sensitive energetic compounds[32] which corresponds to the low impact sensitivity of 18 J for **5**·H_2O.

4. Conclusion

In conclusion, a series of highly energetic materials based on the new triazolo[4,5–d]pyridazine fused ring and its salts was synthesized and characterized by IR and NMR spectroscopy and elemental analysis. The neutral compound **5**·H_2O was characterized by single crystal X-ray structure analysis. The asymmetric unit of **5**·H_2O contains one water molecule which serves as a significant link to connect those molecules by forming intermolecular hydrogen bonds. The hydrogen bond interactions are ~50% of the complete weak interactions. In addition, a proton of one nitroamino group was transferred to the pyridazine ring forming a nitroimino moiety. The electrostatic potential (ESP) of the neutral compounds indicates that the nitroimino group possesses the lowest negative ESP value in the entire molecule, while the nitroamino moiety has the highest positive value. This supports the experimental observation that the rearrangement of the nitroamino to nitroimino decreases the sensitivity of the molecule. Additionally, by the analysis of noncovalent interaction (NCI) plots, strong intramolecular HBs are found in the molecules and strong π-π interactions are found between the layers of the nitroimino group and fused ring. This indicates that the formation of the nitroimino group assists in forming a better stacking style which lowers the impact sensitivity. With these interactions, **5**·H_2O has face-to-face packing, resulting in a high density of 1.87 g cm^{-3} and low impact sensitivity of 18 J. The hydrazinium and hydroxylammonium salts have high detonation velocities of 9351 m s^{-1} and 9307 m s^{-1}, respectively, and similar impact and friction sensitivities (7 J, 120 N and 8 J, 160 N) comparable to HMX. Furthermore, the synthesis of the neutral compound **5** is cost effective and can be obtained in gram-scale (2 g), which suggests that it may be suitable for industrial production. This rearrangement of nitroamino to nitroimino provides new insight in designing HEDMs which may be valuable for industrial production and practical application.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2021.129839.

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