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Hydrogen bond system generated by nitroamino rearrangement: new character for designing next generation energetic materials†

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A new hydrogen bond system is formed by the transfer of a proton from nitroamino to form nitroimino. The proton and the oxygen in nitroimino form an intramolecular hydrogen bond and two intermolecular hydrogen bonds that shorten the distance between molecules both vertically and horizontally leading to higher density.

Designing new energetic materials for practical use is a long-term goal in the energetics field. New energetic compounds are required to possess similar or better properties than commonly used energetics, such as the benchmarks, RDX (1,3,5-trinitro-1,3,5-triazinane) and HMX (2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane).[1] These compounds must have a high density which will result in a significant increase of the detonation performance and good thermal stabilities and low sensitivities enhancing safe syntheses, transfer, and storage.[2,3] However, while there are a fair number of high energetic density materials (HEDMs) that possess such properties,[4–7] not many of them can be reduced to practical use due to the high cost of a large-scale synthesis and the low overall yield. For safety reasons, most compounds are synthesized initially in small quantities and scale-up to multiple gram quantities often becomes costly.[8] Therefore, in order to synthesize the new candidate as an energetic material easily and cheaply in large-scale, it is helpful if the starting material is commercially available at a very low price. Additionally, the product should be obtained in a few steps in excellent yield.[2,9]

The nitroamino group (–$NHNO_2$) is one of the most often used energetic groups in the design of HEDMs.[10–13] The introduction of a nitroamino moiety can significantly increase density and heat of formation which can lead to compounds possessing superior detonation properties. In addition, the nitroamino group can behave as an anion to combine with an energetic cation to form energetic salts which is a reasonable way to realize higher detonation performance and lower sensitivities.[14,15] However, compounds with the dinitroamino group almost always exhibit higher sensitivities to impact and friction stimuli and traditionally have lower thermal stabilities.[16–18] Additionally, most of them show good solubility in water and must be extracted with low polarity solvents, which results in low yield and precludes large scale syntheses making them unlikely candidates for practical use.[19]

Hydrogen bonds (HBs) play an important role in the design of energetic compounds because of their positive influence on both physical and chemical properties.[20,21] Intramolecular hydrogen bonds often observed in energetic materials are generated from interaction of a nitro moiety with a neighboring amino group and are exemplified in such stable compounds as 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 2,2-dinitroethylene-1,1-diamine (FOX-7) (Fig. 1). The presence of HBs can increase the density of a compound resulting from closer packing and decreasing sensitivity through the formation of a better stacking style.[22] Both TATB and

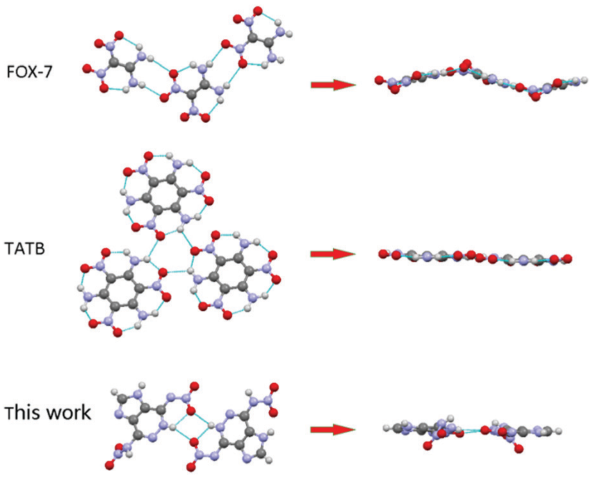

Fig. 1 The HBs and layer structures of FOX-7, TATB and compound **3**.

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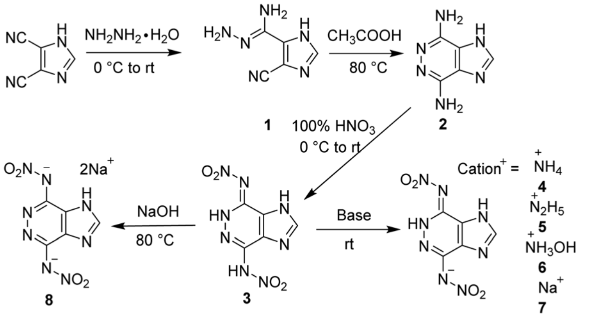
FOX-7 contain many intermolecular HB systems with neighboring molecules, which result in higher density and lower sensitivity.[23]

However, relative to the nitro group, the nitroamino group has a smaller proclivity to form intramolecular HBs, which makes it less likely to contribute to the practical use of the material. Now we report a new kind of hydrogen bond system which was generated by the rearrangement of a nitroamino group bonded to a pyridazine ring to form a nitroimino functionality by the transfer of the proton to the *ortho* nitrogen of the pyridazine ring. That proton forms an intramolecular hydrogen bond with the nitroimino oxygen moiety. Additionally, the proton and the oxygen form head-to-head intermolecular hydrogen bonds with a neighboring molecule to give a parallelogram of hydrogen bonds. This HB system connects these molecules in one layer to form face-to-face stacking which is characteristic of high-energy materials with low sensitivity. This hydrogen bond system reduces the amount of free space between molecules which helps to increase the thermal stability, to lower the solubility and to enhance the density. These improve the ease and yield of syntheses which may have a positive impact on industrial production.

Therefore, a series of new compounds which contain this HB system based on the imidazolo[4,5-*d*]pyridazine fused ring and its salts were synthesized. The 4,7-diamino-imidazolo[4,5-*d*]pyridazine fused ring (**2**) was obtained in high yield and purity by using low cost commercial 4,5-dicyanoimidazole (Scheme 1). By reacting **2** with fuming nitric acid, the two amino groups on the fused ring are oxidized to nitroamino groups to give 4-nitroamino-7-nitroimino-6-dihydro-imidazolo[4,5-*d*]pyridazine imidazolo[4,5-*d*]pyridazine where a hydrogen atom is transferred from one of the nitroamino moieties to the pyridazine ring to form a nitroimine group. The intramolecular HBs reduce the amount of free space in **3** which decreases water solubility making it easily obtainable by filtration after adding ice. Because of the presence of intramolecular HBs, the proton on the pyridazine ring is not as active as the proton on a nitroamino group, which can leave easily to form an anion. Therefore, only energetic monosalts were obtained by reacting **3** with bases.

4,7-Diamino-imidazo[4,5-*d*]pyridazine (**2**) was obtained by reacting 4,5-dicyanoimidazole with aqueous hydrazine monohydride as reactant and solvent with acetic acid as catalyst.[24] Since the method found in the literature uses a large amount of aqueous hydrazine which is a potential carcinogen, and to reach the pure product requires multiple recrystallizations resulting in a yield of only 21%, a new method to obtain **2** was adopted.



Scheme 1 Synthesis of **1–4**.

Commercial 4,5-dicyanoimidazole was reacted with hydrazine monohydride (3*N*) in isopropanol leading to 4-cyano-5-carbamidrazone imidazole (**1**) followed by ring closure with acetic acid to give pure **2** in a good yield of 92%. When reacted with fuming nitric acid, the two amino groups in **2** are converted to nitroamino moieties followed by a structural rearrangement where a hydrogen from one nitroamino group transfers to the pyridazine ring. Because of poor solubility in water, **3** can be obtained easily in moderate yield (62%) by filtration. Since there is only one nitroamino group with an acidic hydrogen, it was not possible to form a disalt when **3** is reacted with ammonia, hydroxylamine or hydrazine. However, when **3** is reacted with sodium hydroxide, the disodium salt (**8**) is obtained (Scheme 1).

The new compounds were fully characterized using ^{1}H and ^{13}C NMR spectral data, and infrared spectroscopy as well as elemental analysis. The ^{1}H NMR signal shift for the C–H in the imidazole group of **3** is found at δ 8.73 ppm (Fig. S1, ESI†). When a monocation is formed, the ^{1}H NMR signal shifts to δ 8.42 ppm for **4**; δ 8.45 ppm for **5** and **7**; and δ 8.49 ppm for **6**. In the disodium salt, the signal is at δ 7.99 ppm (Fig. S13, ESI†). When attempts were made to synthesize diammonium, dihydrazinium and dihydroxylammonium disalts, ^{1}H and ^{13}C NMR signal shifts occurred compared with the monosalts, but none of the compounds passed elemental analysis as disalts. For example, the hydrazinium derivative which was obtained at high temperature has a single ^{1}H NMR signal at δ 8.32 ppm and a group of ^{13}C NMR signals at δ 134.1, 148.3, 149.1 ppm (^{1}H NMR for di and mono sodium salts are δ 7.99 and δ 8. 45; ^{13}C NMR for di and mono sodium salts are δ 137.3, 150.5, 152.8 ppm and δ 132.8, 145.3, 148.7 ppm), but the elemental analysis supports the presence of only 1.5 hydrazinium groups. The NMR signals indicate only one compound suggesting that the mono and dihydrazinium salts are evenly distributed in DMSO-D6, which results in the same NMR shift. A similar situation was observed for the mixture of mono and disodium salts, and the neutral compound with the monosodium salt. The disodium salt can be obtained largely because the sodium hydroxide is a strong base with a pK_b of −0.56, while hydrazine and ammonia are weak bases with pK_b of 5.9 and 4.75, respectively, and hydroxylamine is much weaker with a pK_b of 7.97. None of these is strong enough to give the disalts.

Crystals of **3** were obtained from a mixture of water and DMSO, which resulted in the unit cell containing one water and two DMSO molecules. It crystallized in the triclinic space group with $P\bar{1}$ ($Z = 4$) symmetry, with a crystal density of 1.63 g cm^{-3} at 173 K. The single-crystal X-ray structures and data are given in Fig. 2 and Table S1 (ESI†), respectively. The value of Z' is two, indicating that there are two independent molecules (molecules A and B) in the asymmetric unit. As shown in Fig. 2a, the N–H on imidazole is on the same side with the nitroamino in molecule A, but on the side of nitroimino in molecule B (red circles).

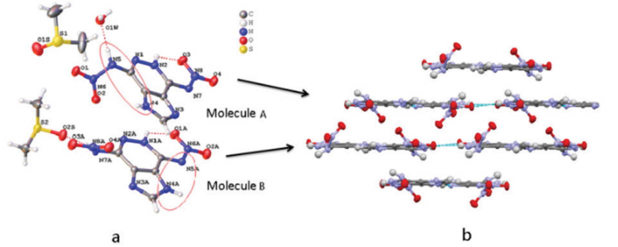


Fig. 2 (a) Single-crystal X-ray structures of **3** (molecules A and B). (b) Face-to-face stacking.

For one nitroamino group, one proton transfers to the pyridazine ring and forms an intramolecular HB with the oxygen in the nitroimino group, which causes this nitroimino group to be almost planar with the fused ring which have the torsion angles of C2–N7–N8–O4 = 176.06(14)°, C2–N7–N8–O3 = −4.1(2)°, N8–N7–C2–C3 = 179.75(14)°, N8–N7–C2–N2 = −3.2(3)° in molecule A, and N6A–N5A–C1A–C5A = 178.06(14)°, C1A–N5A–N6A–O1A = −0.1(2)°, C1A–N5A–N6A–O2A = −179.2(14)° in molecule B. However, the other nitroamino moiety is totally twisted out of the plane with N6–N5–C1–N1 = 117.5° and N6–N5–C1–C5 = 66.9° for molecule A, and N8A–N7A–C2A–N2A = −127.7°, N8A–N7A–C2A–C3A = 59.0° for molecule B. Because of the proton transfer to the pyridazine ring, a head to head HB system is formed, in which there is one intramolecular HB and HBs between oxygen in nitroimino and proton in the pyridazine ring. This HB system is in the same plane, making those molecules planar which results in face to face stacking (Fig. 2b). As shown in Fig. 3a, the proton of the nitroamino group in molecule A forms an HB with the oxygen in water, while in molecule B, the HB was formed with an in oxygen in DMSO. An intermolecular HB formed between the proton the imidazole of molecule B and the nitrogen in the imidazole of molecule A. The HBs and face-to-face π–π interactions can be easily observed by analysis of the relationship between the quantum-mechanical electron density (ρ) and the reduced density gradient ($s = 1/2(3\pi2)1/3)|\nabla\rho|/\rho4/3$). As shown in Fig. 3b and d, the noncovalent interaction (NCI) plots of **3** unit cells can be obtained in real space where the differences between HBs, van der Waals interactions, and repulsive steric clashes can be observed. As shown in Fig. 3b, the Z type interaction between two molecules (head-to-head) indicates strong intramolecular and intermolecular HBs. In Fig. 3d, the NCI domains are abundant between the parallel layers, resulting in a short interlayer distance of 2.87 Å, which indicate a strong conjugated system between layers. In this structure, the NCI domains not only exist on the parallel part of the fused rings, but also between the C–NNO_2 group because of the C–N and N–N distance both are 1.35 Å, which indicate double bonds suggesting an obvious conjugation effect (Fig. 3d).

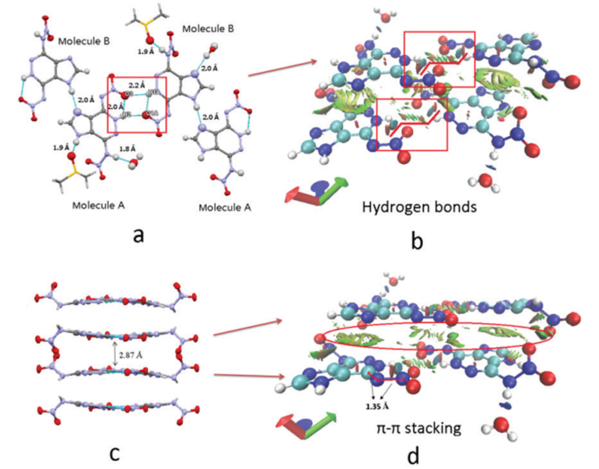


Fig. 3 (a) Head-to-head intermolecular HBs in **3**; (b) hydrogen bond system in NIC plots of gradient isosurfaces (s = 0.5 au) of the unit cells of **3**; (c) two different layers in **3**; (d) π–π stacking in NIC plots of gradient isosurfaces (s = 0.5 au) of the unit cells of **3**.

The density and heats of formation (HOF) values of a compound are closely related to the detonation performance. The HOFs of the new energetic materials were calculated by the Gaussian03 (Revision D.01) suite of programs.[25] As shown in Table 1, the neutral compound (**3**) has the highest density at 1.82 g cm^{-3}, and has the lowest HOF at 355.2 kJ mol^{-1}. The ammonium salt (**4**) has the lowest density of 1.75 g cm^{-3} and a HOF of 412.8 kJ mol^{-1}. The hydrazinium (**5**) and hydroxylammonium (**6**) salts have the same density at 1.78 g cm^{-3}, but the HOF of the hydrazinium salt (561.4 kJ mol^{-1}) is a little higher than that of hydroxylammonium salt (461.3 kJ mol^{-1}). Based on the density and HOF of those new energetic compounds, the detonation performance was obtained by using the EXPLO5 (v6.01) program.[26] Because of having the highest HOF, the hydrazinium salt (**5**) has the highest detonation velocity at 8782 m s^{-1} and a detonation pressure of 30.6 GPa, which approach those of RDX. These are followed by the hydroxylammonium (**6**) and ammonium (**4**) salts, with detonation velocities of 8673 m s^{-1} and 8425 m s^{-1}, respectively. Because of the lowest HOF, **3** also has the lowest detonation velocity of 8360 m s^{-1}.

Both thermal stability and sensitivity are key properties in the decision about practical application. As seen in Fig. S19 (ESI†), all compounds exhibit a sharp exothermic peak, with good decomposition temperatures (onset temperature) >150 °C. For the nitroamino compound, the trigger bonds are the N–NO_2 bonds. The bond dissociation enthalpy (BDE) for

Table 1 Physical properties of 4-nitroamino-7-nitroimino-6-dihydro-imidazole [4,5-*d*]pyridazine and its derivatives (**3**)

Compound	N^a (%)	$T_{dec}{}^b$ (°C)	d^c (g cm^{-3})	$\Delta_f H^d$ (kJ mol^{-1}/ kJ g^{-1})	v^e (m s^{-1})	p^f (GPa)	IS^g (J)	FS^h (N)
3	46.7	166	1.82	355.2/1.48	8360	29.0	32	120
4	49.0	212	1.75	412.8/1.61	8425	27.8	24	240
5	51.5	228	1.78	561.4/2.06	8782	30.6	16	120
6	46.2	199	1.78	461.3/1.69	8673	31.1	18	160
RDX[i]	37.8	204	1.80	70.3/0.32	8795	34.9	7.5	120
TATB[j]	32. 6	350	1.93	−154.2/−0.6	8504	31.7	50	353

[a] Nitrogen content. [b] Thermal decomposition temperature (DSC, 5 °C min^{-1}. [c] Measured density, gas pycnometer (25 °C). [d] Calculated heat of formation. [e] Calculated detonation velocity. [f] Calculated detonation pressure. [g] Impact sensitivity. [h] Friction sensitivity. [i] Ref. 22. [j] Ref. 22.

the nitroimino is 205.8 kJ mol^{-1}, which is much larger than that for the nitroamino (127.1 kJ mol^{-1}). Therefore, compared with the traditional nitroamino group, the rearranged nitroimino group has better thermal stability. Although the neutral compound has the lowest decomposition temperature at 166 °C, it is still higher than most dinitroamino compounds. The hydrazinium salt (**5**) has the highest decomposition temperature at 228 °C. The ammonium (**4**) and hydroxylammonium (**6**) salts decompose at 212 and 199 °C, respectively.

The impact (IS) and friction (FS) sensitivities of all the new compounds were determined by standard BAM drop hammer and friction tester techniques.[27] All compounds are less impact sensitive than RDX. Compared with the salts, molecule **3** has the lowest sensitivity to impact which may arise from the special face to face stacking. However, because one nitroamino moiety is twisted out from the planar structure, the friction sensitivity is similar to that of RDX. Among the salts, the ammonium salt (**4**) possesses the lowest sensitivities, with an impact sensitivity of 24 J, and friction sensitivity of 240 N. Next is the hydrazinium (**5**) (16 J, 120 N) and hydroxylammonium salts (**6**) (18 J, 160 N), which are less impact sensitive than RDX.

In conclusion, a series of new energetic materials based on the imidazolo[4,5-*d*]pyridazine fused ring and its salts were synthesized and characterized by IR, and NMR spectroscopy, and elemental analysis. Compound **3** was also characterized by single crystal X-ray structure analysis showing a proton of the nitroamino was transferred to the pyridazine ring to form a head-to-head HB system with a neighboring molecule. By analysis, the noncovalent interaction (NCI) plots, strong π–π interactions can be found between both the fused rings but also the HB system. With this special HB system, compound **3** possesses face-to-face packing style, resulting in a moderately high density of 1.82 g cm^{-3} and low impact sensitivity of 32 J. The hydrazinium salt has a detonation velocity of 8782 m s^{-1} and impact and friction sensitivity (16 J, 120 N) somewhat like RDX. This special HB system reduces the free space in molecules, and unlike most water soluble dinitroamino compounds, all new compounds have poor solubility in water, which makes them easy to recover after reaction. The synthesis of the neutral compound is extremely cost effective and can be obtained on large scale (5 g), which means it may be suitable for industrial production. This new kind of HB system provides a promising pathway to design HEDMs which is available for industrial production and practical application.

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Conflicts of interest

There are no conflicts to declare.

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