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Fused rings with N-oxide and -NH₂: good combination for high density and low sensitivity energetic materials

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Oxidation reactions of 3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine give four N-oxide compounds. Because of the presence of an amino group and the N-oxide moiety, these compounds are extensively hydrogen bonded. Resulting from π - π stacking interactions between the fused rings, compounds 1-3 are impact and friction insensitive, are thermally stable and have good density.

Desirable characteristics for modern explosives and propellants include high density, high detonation velocity and pressure, good thermal stability and low impact and friction sensitivity. However, it is a huge challenge to find a good balance between high detonation performance and low sensitivity since higher energy most often occurs concomitantly with low stability.¹ Therefore, research on the design and synthesis of novel low-sensitivity and high-density-energy molecules continues at a rapid pace worldwide. There are a number of ways to improve the density and the detonation performance of an explosive, such as choosing a backbone with high N content² or introducing a more energetic group into the backbone, like -NO₂,³ -NNO₂,⁴ C(NO₂)₃,⁵ -N=N-,⁶ and so on. However, these methods may lead to an increase in sensitivity to mechanical stimulation. There are some specific classes of molecules which may have a good balance between high performance and low sensitivity, including some energetic salts,¹ molecules which possess strong hydrogen-bonds (HBs) and species which exhibit π - π stacking.⁷

The presence of strong hydrogen bonds (HBs) has a positive influence on the physical and chemical properties of a molecule. Intermolecular HBs which decrease sensitivity by forming closer packing and reducing the amount of free space in the crystal lattice

are one of the most efficient ways to stabilize energetic materials.⁸ Hydrogen bonding is found frequently in molecules containing amino and nitro groups (i.e., N-H₂ and N-O₂).⁹ Empirical evidence shows this combination is a promising approach to reduce sensitivity,¹⁰ which is exemplified by 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), 2,6-diamino-3,5-dinitropyrazine-1-oxide (LLM-105),¹¹ and 2,2-dinitroethylene-1,1-diamine (FOX-7)⁴ (Figure 1a). HBs encourage more efficient crystal packing which can result in high density and low sensitivity.¹² Hydrogen bonding also arises from interaction between the amino group and N-oxide. Introduction of the N-oxide moiety into a molecule helps by improving oxygen balance, density and detonation properties.³ However, the N-oxide moiety most often lowers molecular stability because it causes elongation of chemical bonds by narrowing the gap between the highest occupied and lowest unoccupied molecular orbitals.¹¹ When N-oxide interacts with amino, the strong HBs which form aid in the reduction of sensitivity, as exemplified by 3,4-bis(3-aminofurazan-4-yl)furoxan (insensitive),¹³ 3,4-bis(4'-aminofuroxano-3')furoxan (13 J, 240 N),³ and 4,4-diamino-3,3-bisfuroxan (10 J, >360 N),¹⁴ which possess lower impact and friction sensitivities than 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX: 7 J, 120 N) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX: 7 J, 120 N) (Figure 1b).

Because of the high nitrogen content and a large conjugated system, fused rings provide an ideal way to obtain high energy density materials (HEDMs).¹⁵ However, the syntheses of fused ring systems that contain both the N-oxide moiety and the amino group

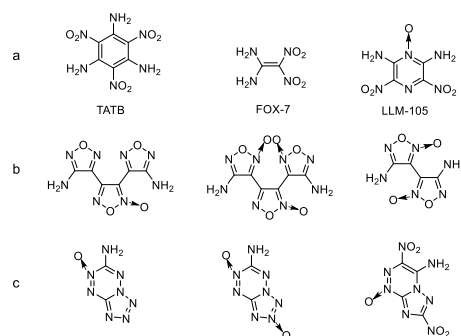


Figure 1. a, HBs between NH₂ and NO₂; b, HBs between NH₂ and N-oxide; c.

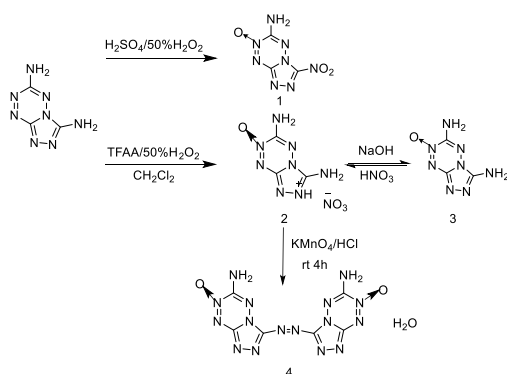
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Fused ring with NH₂ and N-oxide.



Scheme 1. Synthesis of 1-4.

are less well studied. A few examples include the tetrazolo 1,2,4,5-tetrazine fused ring, 6-aminotetrazolo[1,5-b]-1,2,4,5-tetrazine-7-N-oxides (10 J, 60 N),¹⁶ 6-aminotetrazolo[1,5-b]-1,2,4,5-tetrazine-4,7-N-oxides (6 J, 109 N),¹⁷ and 4-amino-3,7-dinitrotriazolo-[5,1-c][1,2,4] triazine-4-oxide (10.3 J, 258 N)¹⁸ (Figure 1c). All of them possess good detonation performance and also acceptable sensitivity. Previously, our group reported a series HEDMs of another fused ring system, triazolo-[1,2,4,5]tetrazine, which has one more functional position and lower sensitivity than the tetrazolo-1,2,4,5-tetrazine and also, better detonation performance than triazolo-1,2,4-triazine, and proved to be a good backbone that could balance high detonation performance and low sensitivity.¹⁹

Now we have selected 3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine as the starting material, which was oxidized by using 50% H₂O₂ to the N-oxide compound, 3-nitro-6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (**1**), 3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine-7-N-oxide (**3**) and its NO₃⁻ salt (**2**) and azo compound (**4**). Compounds **1-3** are less sensitive with a better detonation performance than RDX. Compound **1** has a decomposition temperature of 220 °C, good detonation performance ($v_D = 9384 \text{ m s}^{-1}$; $P = 39 \text{ GPa}$) and low sensitivity (25 J, 240 N).

The starting material, 3,6-diamino-1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine, was prepared according to the literature.²⁰ There are several reagents that are useful in introducing the N-oxide moiety into tetrazines, including hypofluorous acid [HOF],²¹ H₂O₂/TFAA,²² H₂O₂/H₂SO₄, and so on. During this work, HOF, 50% H₂O₂/TFAA, and 50% H₂O₂/H₂SO₄ were tried. The H₂O₂/TFAA mixture

which is less reactive than HOF is the best way to introduce N-oxide here.²³ Usually the reaction is started at 0 °C and warmed to room temperature; however, in this case, under these conditions, an impure product was obtained in lower yield, so the reaction was carried out at room temperature. A mixture of **2** and **3** was found in 55% yield (Scheme 1) where **2** precipitated and single crystal X-ray diffraction showed it to be the nitrate salt. In this reaction, when reacted at low temperature and for a short time, less **2** (solid) was obtained. To insure all starting material turned to the N-oxide format, longer reaction time at room temperature was used, which suggests that this condition encourages the conversion of **3** to **2**. The NO₃⁻ comes from the oxidation of the decomposition product from **2**. Compound **2** and **3** can be converted from one to the other using either nitric acid or sodium hydroxide. Newly synthesized HOF is the most effective oxidizing agent. The ¹H NMR and ¹³C NMR resonance bands of **1** are seen, but due to low yield and a large number of products it was impossible to separate them and obtain a pure product. When a 50% H₂O₂/H₂SO₄ mixture is utilized as oxidizer, the yield of **1** is still very low, but the pure product was obtained by using column separation. Attempts to oxidize either **2** or **3** with 50% H₂O₂/H₂SO₄ did not result in the formation of **1**. Compound **4** was obtained as the monohydrate by reacting **2** with KMnO₄/HCl. The water could not be removed.

All the compounds were fully characterized by ¹H and ¹³C NMR, elemental analysis and IR spectroscopy. In the ¹H NMR spectra, the intense, sharp resonance bands assignable to the amino groups can be seen clearly for **1** and **3**, but for **2**, possibly due to the influence of the anion, the resonance of the amino group at position 3 is a very weak, broad peak. Differential scanning calorimetric (DSC) measurements were used to determine the thermal stability. The decomposition temperatures (onset) of **1**, **2**, **3** and **4** are 220, 191, 196 and 210 °C, respectively. Each of these compounds has a sharp exothermic peak which indicates rapid decomposition. The densities, measured by using a gas pycnometer, are > 1.80 g cm⁻³. Compound **1** has the highest density at 1.86 g cm⁻³, with **2**, **3** and **4** having densities of 1.81, 1.82, and 1.82 g cm⁻³, respectively.

The heats of formation for the newly prepared energetic materials were obtained by using the Gaussian03 (Revision D.01) suite of programs.²⁴ As given in Table 1, all compounds have positive heats of formation which fall in the range between 2.13 kJ g⁻¹ to 3.76 kJ g⁻¹, and which are higher than the currently used explosives RDX (0.36 kJ g⁻¹) and HMX (0.36 kJ g⁻¹). Compounds **1** and **4** have the higher values at 1062 kJ mol⁻¹ (2.99 kJ g⁻¹), and 744 kJ mol⁻¹ (3.76 kJ g⁻¹), while **2** and **3** are slightly lower. The oxygen balance

Table 1. Physical properties of N-oxide of 1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine fused rings.

Compound	T _d ^[a] (°C)	d ^[b] (g cm ⁻³)	Δ _f H ^[c] (kJ mol ⁻¹ /kJ g ⁻¹)	v _D ^[d] (m s ⁻¹)	P ^[e] (GPa)	IS ^[f] (J)	FS ^[g] (N)	N+O ^[h] (%)	Ω ^[i]
1	220	1.86	744/3.76	9384	39.1	25	240	80.8	-8.1
2	191	1.81	502.3/2.76	8808	30.1	>40	>360	81.9	-13.2
3	196	1.82	492/2.13	9008	34.7	>40	>360	76.2	-27.7
4·H ₂ O	210	1.82	1062/2.99	8542	28.8	22	40	84.6	-27.0
RDX	230	1.80	85.0/0.42	8795	34.9	7	120	81.1	0
HMX	280	1.90	104.8/0.36	9320	39.5	7	120	81.1	0

[a] Decomposition temperature (onset temperature at a heating rate of 5 °C min⁻¹). [b] Density, gas pycnometer (25 °C). [c] Calculated heat of formation. [d] Calculated detonation velocity - EXPLOS V6.01. [e] Calculated detonation pressure - EXPLOS V6.01. [f] Impact sensitivity. [g] Friction sensitivity. [h] Combined

nitrogen and oxygen content. [i] Oxygen balance (based on CO) for $C_aH_bO_cN_d$, $1600(c - a - b/2)/MW$, MW = molecular weight.

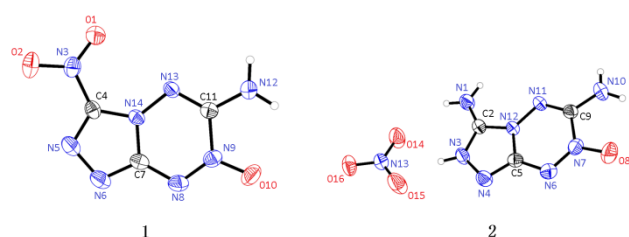


Figure 2. Single-crystal X-ray structures of **1** and **2**.

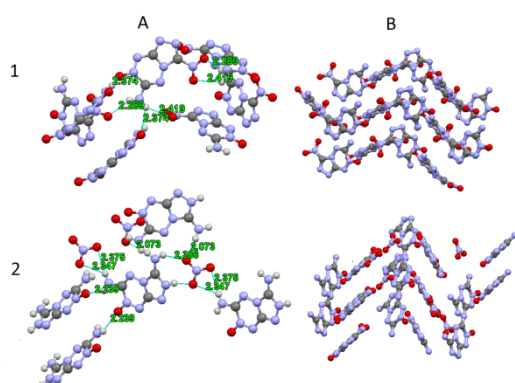


Figure 3. HBs (A) and mixed stacking of crystals (B) in **1** and **2**.

(OB) value indicates the degree to which all of the carbon could be converted into carbon monoxide and all hydrogen into water. In this study, the OBs of the four compounds fall in the range of -27.7% to -8.1%, where **1** and **2** have smaller negative OBs because of the presence of NO_2 and NO_3 . Based on the densities and heats of formation, the detonation properties were calculated by employing the EXPLO5 (v6.01) program.²⁵ As can be seen in Table 1, each compound exhibits good calculated detonation velocities in the range of 8542 to 9384 $m\ s^{-1}$ and detonation pressures between 28.8–39.1 GPa. Compound **1** exhibits a superior detonation performance, with a detonation velocity of 9384 $m\ s^{-1}$, which is comparable to RDX

and HMX.

The impact (IS) and friction (FS) sensitivities were measured by using standard BAM drop hammer and friction tester techniques.²⁶ As shown in Table 1, all three compounds have low impact and friction sensitivities, which can be explained from analysis of crystal intermolecular interactions. Compounds **2** and **3** are insensitive to both impact and friction, with IS greater than 40 J and FS greater than 360 N. The sensitivity of **4** has increased (22 J, 40 N) slightly because of the presence of the azo group. For **1**, the impact and friction sensitivities are measured to be 25 J and 240 N, which are considerably less sensitive than RDX and HMX.

Suitable crystals of the energetic compounds **1** and **2** were obtained from methanol and ethanol at room temperature, respectively, and both crystallize in the monoclinic space group with $P2_12_12_1$ ($Z = 4$) symmetry. Their calculated crystal densities at 293 K are 1.859 $g\ cm^{-3}$ and 1.809 $g\ cm^{-3}$, respectively. The single-crystal X-ray structures and data are shown in Figure 2 and Table S1, respectively. The cation of **2** is planar which is supported by the dihedral angles: $O(8)-N(7)-C(9)-N(11) = 179.6(2)^\circ$; $O(8)-N(7)-C(9)-N(10) = -0.6(3)^\circ$. However, for **1**, the dihedral angle of $-NO_2$ with the fused ring is observed to be $O(1)-N(3)-C(4)-N(5) = -163.0(2)^\circ$; $O(2)-N(3)-C(4)-N(5) = 17.9(3)^\circ$; $O(1)-N(3)-C(4)-N(14) = 20.0(3)^\circ$; $O(2)-N(3)-C(4)-N(14) = -159.13(18)^\circ$, which shows that it is twisted slightly out of the plane. As a result, **1** is a little more sensitive to impact and friction than the other two compounds, which is supported by its larger impact and friction sensitivities (Table 1). In **1**, three kinds of intermolecular H-bonds are formed. All H and O atoms in structure form $N-H\cdots O$ or $N-O\cdots H$ bonds with neighboring molecules in different directions which results in mixed stacking. In **2**, six kinds of H-bonds are present. Two intramolecular H-bonds between H on the fused ring with O on NO_3 , and four intermolecular H-bonds form with three neighbor molecular in different directions which also result in mixed stacking (Figure 3). Furthermore, the intermolecular interactions in the crystal are effectively reflected by the Hirshfeld surface. As shown in Figures 3c and 3d, because of the fused ring backbone structures, the surfaces of these two molecules appear almost as plate shapes, and most of the red dots

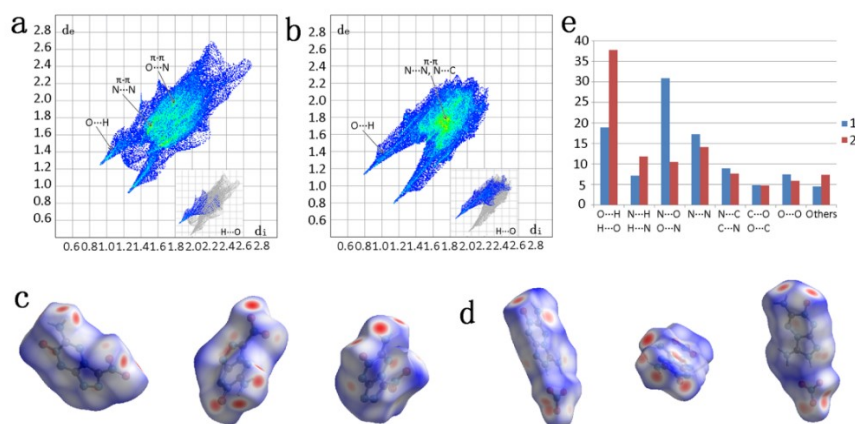


Figure 4. The 2D fingerprint plots in crystal stacking for (a) **1** and (b) **2**. Images (c) and (d) show the Hirshfeld surfaces for **1** and **2** (white, distance d equals the van der Waals distance; blue, d exceeds the van der Waals distance; red, d is less than the van der Waals distance). In image e, the individual atomic contacts percentage are in the bar graphs for **1** and **2**, respectively.

which shows the intermolecular close contacts are located on the side faces of the plate. The red dots belong mainly to the intermolecular HB interactions, and the blue parts to O–C, C–C, and C–N interactions, suggesting π - π stacking. These features are characteristic of insensitive and high-energy materials. As shown by the two-dimensional fingerprint plots in Figure 4a and 4b, the spikes for **2** (Figure 4b) on the bottom left which denotes the hydrogen bonds are broader than those for compound **1** (Figure 4a) which indicate that more hydrogen bonds are observed. Based on the crystal structures of **1** and **2**, **2** has two intramolecular and eight intermolecular HBs in each molecule, providing 67% more compared to **1** (six intermolecular HBs in each molecule). This can also be ascertained by the data shown in Figure 4e, in which O...H and N...H possess 49.6% of total weak interactions for **2**, almost twice that of **1** (26%). Both **1** and **2** have high percentages (26.2% and 21.8 %) of N...N, N...C and C...N interactions which denote π - π stacking. Higher percentages of O...O indicate more oxygen atoms are exposed on the molecular surfaces and lead to an increase in sensitivity. Compound **1** has 7.5% of O...O interactions, a little higher than **2** (5.9%). These data are in agreement with the experimental IS and FS values, i.e., that both **1** and **2** have low sensitivity, but **2** is less sensitive than **1** because of a higher concentration of hydrogen bonds and fewer O...O interactions.

In conclusion, four new N-oxide compounds based on fused 1,2,4-triazolo[4,3-b][1,2,4,5]tetrazine rings were prepared. Each new energetic compound was fully characterized by IR, and NMR spectroscopy and elemental analysis. Because of the conjugated structure of the fused ring, and the intermolecular hydrogen bonds between the N-oxide moiety and the amino group, compounds 1-3 possess good thermal stability, and impact and friction sensitivities. Compounds **1** and **2** were characterized by single-crystal X-ray diffraction. Analysis of the Hirshfeld surfaces shows the intermolecular interactions of **1** and **2** with large amounts of HBs and π - π stacking leads to insensitivity, and also the number of HBs and O...O interactions supports the experimental observation that **2** is less sensitive than **1**. Compound **1** has a density of 1.86 g cm⁻³, and a calculated detonation velocity of 9387 m s⁻¹ which is comparable to HMX. Detailed properties of these energetic materials with an N-oxide moiety and an amino group suggest a promising alternative to the design of low-sensitivity high-energy materials.

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Conflicts of interest

There are no conflicts to declare.

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