Energetic Materials

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Enhancing Energetic Properties and Sensitivity by Incorporating Amino and Nitramino Groups into a 1,2,4-Oxadiazole Building Block

*Yongxing Tang, Haixiang Gao, Lauren A. Mitchell, Damon A. Parrish, and Jean'ne M. Shreeve**

Abstract: *A single nitrogen-rich heterocyclic ring with many energetic groups is expected to exhibit excellent detonation performance. We report an effective approach for the synthesis of 3-amino-5-nitramino-1,2,4-oxadiazole, which has nitramino and amino groups in the same building block. The single-crystal X-ray structure shows layered hydrogen-bonding pairs as well as the presence of a water molecule which ensure insensitivity. Through incorporation of a cation, the hydrazinium or hydroxylammonium salts exhibit good energetic performance and acceptable sensitivities.*

In recent decades, the design and synthesis of new energetic compounds have received considerable attention.[1] When considering the newly designed compounds for practical applications, the final result is often based on performance and safety. The basic strategy is a combination of various energetic units with different backbones in a molecule.[2]

At first glance, the more cyclic structures present in a molecule, the superior the performance. Fully C-substituted energetic groups in two or more nitrogen-rich heterocyclic rings show higher heats of formation than those in single rings because of the presence of more nitrogen atoms in the molecule. Nevertheless, the single rings show superior detonation properties. For example, dipotassium dinitraminobistetrazolate[3] with two nitramino groups in two rings has a higher heat of formation than potassium 1,5-dinitraminotetrazolate,[4] which has two nitramino groups in a single heterocyclic ring. However, the detonation performance is reversed; the latter has a higher detonation performance than the former dipotassium salt. A similar trend is observed for 3,5-dinitramino-1,2,4-triazole[5] and 3,3′-dinitramino-5,5′-bis(1*H*-1,2,4-triazole)[6] (Figure 1). Therefore, it is easy to see that single-ring energetic compounds are more competitive than polycyclic ones.

The nitramino group is an important energetic functional group in the design of energetic compounds and could greatly enhance the detonation properties of the target molecule.

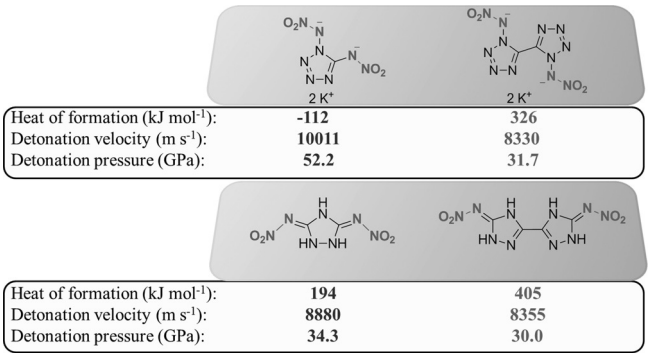


Figure 1. Comparison of properties of compounds with the same energetic groups bonded to different backbones.

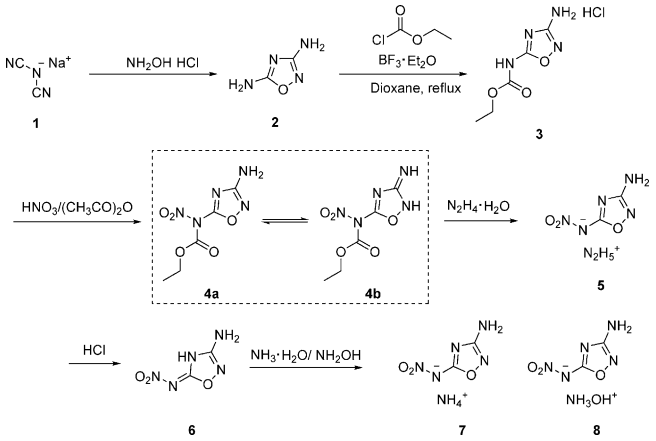
Concomitantly, the acidic proton in the nitramino group facilitates the synthesis of salt derivatives of the compound.[7] However, the field of single-ring energetic compounds is facing another challenge, that is, single rings bearing only one nitramino group often lead to extreme instability and sensitivity.[5,8] In order to avoid this drawback, the combination of an amino group with nitramino group in a nitrogen-rich heterocyclic ring can be utilized to stabilize the molecule while maintaining good detonation performance.[9] Additionally, not only is the density increased because of H-bond formation, but simultaneously, sensitivity is decreased.[10]

On the basis of a comprehensive analysis, a strategy to access promising energetic compounds is achieved by incorporation of amino and nitramino groups in a single nitrogen-rich heterocyclic ring. 1,2,4-Oxadiazole, an isomer of furazan, is rarely reported as a single ring in an energetic compound.[11] Herein the syntheses and energetic properties of new insensitive compounds that combine nitramino and amino groups on a 1,2,4-oxadiazole ring are explored.

3,5-Diamino-1,2,4-oxadiazole (**2**) was prepared according to a previously reported procedure.[12] Compound **2** was treated with ethyl chloroformate in the presence of catalytic amounts of $BF_3{\cdot}Et_2O$ in dioxane at reflux for 2 hours to produce **3** (Scheme 1), which is then nitrated with 100 % nitric acid in acetic anhydride to give only the tautomer **4b** (based on ^{1}H NMR spectroscopy). Compound **4b** was treated with hydrazine hydrate in acetonitrile to give **5** as a white precipitate. After acidification with concentrated hydrochloric acid, **6** was obtained in good yield when extracted with ethyl acetate. The structures of **5** and **6** were verified by single-crystal X-ray diffraction analysis. The ammonium (**7**) and hydroxylammonium (**8**) salts were prepared by dissolving **6** in methanol and reacting it with the respective base in aqueous solution.

[*] Dr. Y. Tang, Prof. Dr. J. M. Shreeve
Department of Chemistry, University of Idaho
Moscow, ID 83844-2343 (USA)
E-mail: jshreeve@uidaho.edu
Dr. H. Gao
Department of Applied Chemistry, China Agricultural University
Beijing 100193 (China)
Dr. L. A. Mitchell, Dr. D. A. Parrish
Naval Research Laboratory
4555 Overlook Avenue, Washington, DC 20375 (USA)

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/anie.201509985.



Scheme 1. Synthesis of 3-amino-5-nitramino-1,2,4-oxadiazole and its selected nitrogen-rich salts.

Attempts to synthesize 3,5-dinitramino-1,2,4-oxadiazole by using 100% nitric acid,[13] a mixture of nitric acid and concentrated sulfuric acid,[14] or nitric acid in acetic anhydride[15] failed. The reason may be that the dinitramino-substituted product is fundamentally unstable. To gain more information on reactive activity and stability, nitro-group charges (Q_{nitro}) were employed.[16] The details and results are presented in the Supporting Information. The Q_{nitro} of **4b** and **6** are −0.262 e and −0.243 e, respectively. However, the four possible tautomers of 3,5-dinitramino-1,2,4-oxadiazole have much lower negative values than **4b** or **6**. These values indicate that the dinitramino-substituted product is theoretically very unstable, which is consistent with the experimental result.

Compounds **5** and **6** were characterized by using single-crystal X-ray structure analysis. Compound **5** crystallizes in the triclinic space group P-1 with a density of 1.701 g cm^{-3} at 296 K and two molecules in the unit cell (Figure 2). The nitramino moiety attached to the oxadiazole ring is nearly planar (∡ C5-N7-N8-O9 = −179.2°). The torsion angle of N1-C2-N6-C5 is 176.9°, which is almost perpendicular to the rings forming hydrogen bonds with the nitrogen atoms (N3, N6, and N7).

As shown in Figure 3a, compound **6** was found as a monohydrate. It is important to note that the water molecules play an important role in forming layers of hydrogen-bonding pairs.[17] As can be seen, the water molecule is not only a hydrogen-bond acceptor but also a hydrogen-bond donor. Each water molecule can participate in three different kinds of hydrogen-bond pairings, that is, (N-H···O), sharing its two hydrogen atoms with two neighboring nitrogen atoms (O(1S-H2S···N3, O(1S-H1S···N7), and accepting one further hydrogen atom associated with a nitrogen atom (N6-H6···O1S). These hydrogen-bonding pairs and additional bond interactions formed by amino groups and nitro groups (N1-H1A···O10, N1-H1B···O9, N1-H1B···O10, N6-H6···O9) lead to a stable planar structure (Figure 3b). A simplified drawing of the layer hydrogen-bonding pairs is shown in Figure 3c. The face-to-face stacking of **6**·H_2O is shown in Figure 3d. All molecular planes in the crystal are parallel to one another.

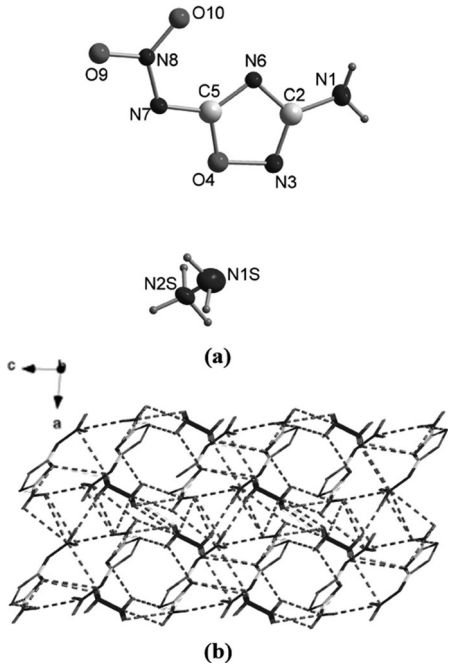


Figure 2. a) X-ray crystal structure of compound **5**. b) Intermolecular interactions in the crystal structure of **5** (view along *b*-axis), hydrogen bonds are marked as dashed lines.

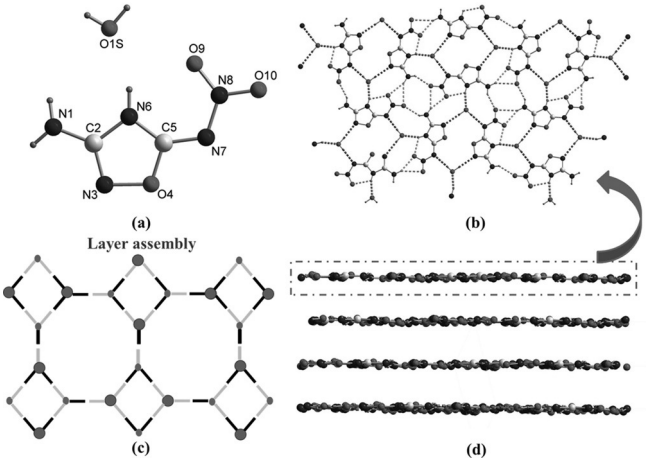


Figure 3. a) X-ray crystal structure of compound **6**·H_2O. b) 2D layered intermolecular interactions in the crystal structure of **6**·H_2O (view along *c*-axis), Hydrogen bonds are marked as dotted lines. c) Simplified drawing of the layered structure. Large ball: **6**; Small ball: H_2O; Black line: donor H bond; Light-gray line: acceptor H bond. d) 3D structural layer network in **6**·H_2O.

To determine if these compounds have potential applications as energetic materials, their thermal stability, density, detonation performance as well as sensitivity properties were investigated. The results are given in Table 1. Compound **6** melts at 114 °C prior to decomposition at 168 °C. The ammonium salt **7** is the most thermally stable with a decomposition temperature of 214 °C, which is comparable to RDX. Compounds **5** and **8** decompose at 152 and 144 °C, respectively.

Table 1: Energetic performance parameters of **5**–**8** compared with RDX.

	ρ[a] [g cm^{-3}]	Dv [b] [m s^{-1}]	P[c] [GPa]	ΔH_f[d] [kJ mol^{-1}]/[kJ g^{-1}]	T_m[e] [°C]	T_{dec}[f] [°C]	IS[g] [J]	FS[h] [N]
5	1.70	8897	30.6	271.2/1.53		152	20	240
6·H$_2$O	1.70	8033	25.6	−196.3/−1.20	114	168	40	360
7	1.68	8493	27.5	116.7/0.72		214	28	360
8	1.73	8854	32.5	179.0/0.95		144	16	240
RDX	1.80	8795	34.9	70.3/0.32	–	204	7.5	120

[a] Density measured by a gas pycnometer at 25 °C. [b] Calculated detonation velocity. [c] Calculated detonation pressure. [d] Calculated molar enthalpy of formation in solid state. [e] Melting point. [f] Temperature of decomposition (onset). [g] Impact sensitivity. [h] Friction sensitivity.

The heats of formation of **5**–**8** were calculated by using the program package Gaussian 03 (Revision D.01).[18] As can be seen in Table 1, the enthalpies of formation range from −1.20 to 1.53 kJ g^{-1}. Among them, the negative heat of formation for **6** arises from the presence of a water molecule. To evaluate the detonation performance of these compounds, detonation velocity and pressure were calculated based on traditional Chapman–Jouget thermodynamic detonation theory using the Explo5 program (version 6.01)[19] from the calculated values of the heats of formation and the experimental values for the densities (gas pycnometer, 25 °C). The data are shown in Table 1. Compound **5** has the highest detonation velocity (8897 m s^{-1}), which is superior to RDX. Compound **8** also exhibits a slightly higher detonation velocity than RDX. However, compared to RDX, the detonation pressures of **5** and **8** are lower (**5**: 30.6 GPa; **8**: 32.5 Gpa). Compound **6** and **7** exhibit a moderate detonation performance with velocity of 8033 and 8493 m s^{-1}, and pressure of 25.6 and 27.5 GPa, respectively.

The sensitivities toward impact and friction were determined using standard BAM techniques.[20] For **6**, the impact sensitivity is 40 J, while the friction sensitivity is 360 N. The insensitive properties arise from the double effect of the stable layer-by-layer stacking and the presence of water molecules. Compounds **5** and **8** also have acceptable impact sensitivities (**5**: 20 J; **8**: 16 J) relative to RDX. Both of them have the same friction sensitivity at 240 N.

In summary, a new molecule with a single energetic ring substituted with amino and nitramino groups, 3-amino-5-nitramino-1,2,4-oxadiazole (**6**), was synthesized, as were its ammonium (**7**), hydrazinium (**5**), and hydroxylammonium (**8**) salts. All of them were fully characterized. In addition, the structures of **5** and **6** were confirmed by single-crystal X-ray diffraction. Examination of the crystal structure of **6** shows a layer-by-layer structure. Each layer forms hydrogen-bond pairs arising from the presence of water molecules. The physical properties, and detonation performance as well as the sensitivities of these new compounds were determined. Compounds **5** and **7** have good detonation performances and acceptable sensitivities comparable to those of RDX. The most promising compound is the hydrazinium salt **5**, which can be synthesized in a straightforward manner from inexpensive materials. The combination of high performance and insensitivity suggests this material may find practical use as an RDX replacement.

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Keywords: amines · detonation · energetic materials · nitramino groups · oxadiazoles

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