

Taming of 3,4-Di(nitramino)furazan

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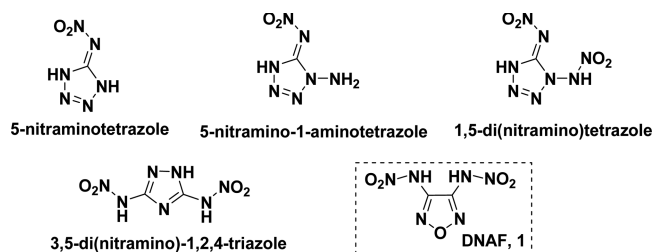
S Supporting Information

ABSTRACT: Highly energetic 3,4-di(nitramino)furazan (**1**, DNAF) was synthesized and confirmed structurally by using single-crystal X-ray diffraction. Its highly sensitive nature can be attributed to the shortage of hydrogen-bonding interactions and an interactive nitro chain in the crystal structure. In order to stabilize this structure, a series of corresponding nitrogen-rich salts (**3–10**) has been prepared and fully characterized. Among these energetic materials, dihydrazinium 3,4-dinitraminofurazanate (**5**) exhibits a very promising detonation performance ($\nu D = 9849 \text{ m s}^{-1}$; $P = 40.9 \text{ GPa}$) and is one of the most powerful explosives to date. To ensure the practical applications of **5**, rather than preparing the salts of **1** through acid-base reactions, an alternative route through the nitration of *N*-ethoxycarbonyl-protected 3,4-diaminofurazan and aqueous alkaline workup was developed.

Energetic materials, including explosives, propellants, and pyrotechnics, have been used extensively for nearly two centuries for military purposes and civilian engineering applications.¹ Some traditional energetic materials, such as 2,4,6-trinitrotoluene (TNT), 2,4,6-triamino-1,3,5-trinitrobenzene (TATB), cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), and 1,3,5,7-tetranitrotetraazacyclooctane (HMX), are still effective and widely used.^{1a} However, driven by mounting demands for superior performance and growing environmental and safety concerns, considerable research continues to promote the generation of environmentally benign high energy density materials (HEDMs) with improved properties.²

All-carbon-nitrated/nitramino-functionalized azoles are of particular interest in the development of HEDMs since they typically possess high densities, high positive heats of formation, and good oxygen balance.³ Moreover, the high-nitrogen content of these materials ensures gaseous nitrogen as a major decomposition product which is desired in order to avoid environmental pollution as well as traceable signatures.⁴ In comparison with all-carbon-nitrated azoles, the known all-carbon-nitramino-functionalized azoles are limited to 1,2,4-triazole and tetrazole backbones, and only four examples have been reported (Scheme 1).^{3a} In the field of energetic materials, 3,4-di(nitramino)furazan (**1**; DNAF) has been identified by theorists as a suitable goal because of its structure and outstanding predicted detonation performance.⁵ However, even though the synthesis of **1** may have been attempted numerous times, it has not been reported thus far with only several structurally similar nitramino-furazans being established.⁶

Scheme 1. Structures of the Reported All-Carbon-Nitramino-Functionalized Azoles and Target Molecule **1**



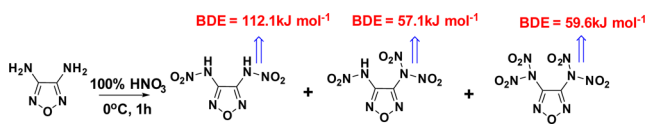
We describe the synthesis and complete characterization of **1**, which exhibits remarkable properties but prohibitive drawbacks in terms of thermal instability and high impact sensitivity. 3,4-Diaminofurazan (**2**) was foreseen as an important precursor of **1**. The synthesis of **2** was first reported in 1968 obtained from glyoxal and hydroxylamine hydrochloride at 180 °C and under high pressure.⁷ The optimized preparation of **2** was also reported recently by our group.^{6a} An efficient route was realized by a facile one-pot reaction at 125 °C and constant pressure. The final ring closing to form the furazan was performed by using urea as a dehydrating agent to give **2** in 45% yield.

Usually, C-nitraminoazoles are synthesized using common acidic nitration conditions.^{3a} With **2** in hand, we first tried direct nitration using 100% HNO₃ at 0 °C. Based on our experience with the preparation of 4,4'-bis(nitramino)azofurazan and 4,4'-bis(nitramino)azoxyfurazan, the ratio of **2** to 100% HNO₃ (mmol vs volume) was selected as 10:1 for the first trial. However, after 1 h of continuous stirring at 0 °C, the workup was very problematic. The reaction mixture was added to ice which resulted in an impure yellow oil after extraction with ethyl acetate. Note: A severe explosion occurred during regular handling of this yellow oil. Therefore, the purification on silica gel was abandoned due to the high sensitivity of the crude products. In addition, based on the observation of several spots on a TLC plate, we hypothesized that instead of preparing a pure nitramino compound, some dinitramide products were also formed after the nitration (Scheme 2). Several researchers have illustrated that the sensitivity of energetic materials is commonly associated with the bond dissociation enthalpy (BDE) for the weakest bond of the molecule.⁸ In this work, the BDEs of the N-NO₂ bonds in **1** as well as in the predicted dinitramide products were calculated using the UB3LYP/6-31G* method to help us understand their stabilities.⁹ It is shown in Scheme 2, that the BDEs of N-NO₂ in

Received: September 18, 2015

Published: December 15, 2015

Scheme 2. Proposed Nitration Products of 3,4-Diaminofurazan Using 100% HNO₃ at 0 °C and the Calculated BDE Values of the Weakest N-NO₂ Bonds



ditramide-furazans are $\sim 55 \text{ kJ mol}^{-1}$ lower than that of **1**. Moreover, all of these values are much lower than those of RDX (161 kJ mol^{-1}), HMX (166 kJ mol^{-1}), and TATB (355 kJ mol^{-1}), which theoretically confirm the observed highly sensitive nature of these target molecules.^{8b}

To reduce undesired byproducts, the reaction conditions were reoptimized in the following study. First, the ratio of **2** to the nitrating agent was decreased to 5:1. Second, the reaction temperature was lowered to $-10 \text{ }^\circ\text{C}$, and reaction time was reduced to 30 min. Under these conditions, a white precipitate was formed at the end of the nitration which was isolated by suction filtration. To remove the impurity and acid residues, the isolated solid was washed with trifluoroacetic acid and dried in air to yield pure **1** in moderate yield (66%), (see Supporting Information (SI) for details).

DNAF was fully characterized with multinuclear NMR and differential scanning calorimetry (DSC). The impact and friction sensitivities (*IS* and *FS*, respectively) were determined by using standard Bundesanstalt für Materialforschung (BAM) techniques.¹⁰ This material is both physically and thermally unstable with *IS* < 1 J, *FS* < 5 N and an onset decomposition temperature of $99 \text{ }^\circ\text{C}$. In addition, **1** slowly decomposes at ambient temperature especially on exposure to air, but it is stable at $-20 \text{ }^\circ\text{C}$. Although the highly sensitive nature of **1** is partly related to its intrinsic properties such as high heat of detonation and positive region dominated surface potentials (see SI for details),¹¹ its crystal packing pattern provides further understanding of the relationship between structural factors and sensitivity for energetic nitramine materials. Therefore, low-temperature X-ray diffraction (XRD) was used to confirm its structure. Suitable crystals of **1** were obtained by evaporation of an acetonitrile solution at $5 \text{ }^\circ\text{C}$. It crystallizes in the monoclinic *P21/c* space group with four molecules in the unit cell having a calculated density of 1.912 g cm^{-3} at 150 K. The crystal structure is shown in Figure 1a, in which the *N*-nitramines are twisted out of the furazan ring plane (torsion angle of N7–N8–C6–N1 and N4–N8–C9–N5 is 127.2° and 126.0° , respectively). Only two sets of hydrogen bonds which are N5 and N1 between the neighboring H8–N8 and H3–N3, respectively, can be found in the crystal structure (Figure 1c). No hydrogen-bond interaction

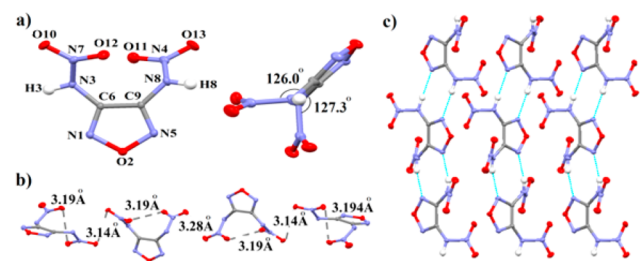
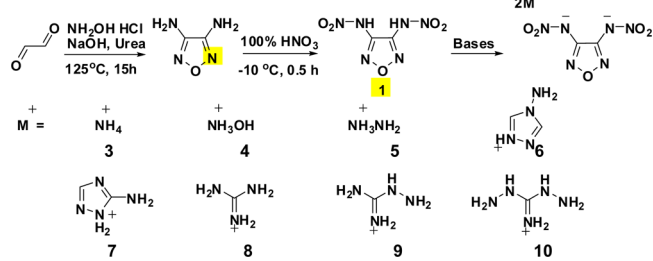


Figure 1. (a) View of the molecular unit of **1** and its atom labeling. (b) Fragment of a nitro chain in solid-phase **1**. (c) Unit cell view along the *b* axis.

between the nitro groups and H3/H8 is observed, which may help to rationalize in part the high sensitivity of this material. Based on the unit cell viewed along the *b* axis (Figure 1b), the nitro groups of the neighboring molecules are very close to each other, which provide extensive O···O closed-shell interactions. Such interactions are also found in many sensitive energetic materials such as pentaerythritol tetranitrate and hexanitrohexaazaisowurtzitane.¹² The remarkably high sensitivity of **1** can also be rationalized in terms of interactive nitro chains. As shown in Figure 1b, the **1** molecules are organized as a series where the nitro groups are separated by $\sim 3.2 \text{ \AA}$, which is in accord with a previous study.^{12d} Therefore, the swing of a single nitro group toward mechanical stimulus will probably induce whole chain response and result in lattice deformation.

Although **1** has been prepared successfully and fully characterized, the unstable nature of the nitramino group seriously hinders its potential application. On the other hand, the deprotonation of the $-\text{NHNO}_2$ group opens possibilities for structural modification in order to produce more stable ionic derivatives. Therefore, a series of nitrogen-rich DNAF-based energetic salts was synthesized in a straightforward manner by acid-base reactions, and all products were isolated in high yields (Scheme 3) (see SI for details).

Scheme 3. Synthesis of **1 and Its Energetic Salts (**3**–**10**)**



Characterization of these compounds was accomplished using standard procedures, and their physicochemical properties are given in Table 1. To our delight, all the newly prepared salts are

Table 1. Physical and Detonation Properties of the Newly Prepared Energetic Materials (1** and **3**–**10**) Compared With RDX and HMX**

mat. ^a	<i>T</i> _d ^b (°C)	ρ^c (g cm ³)	$\Delta_f H^d$ (kJ g ⁻¹)	vD^e (m s ⁻¹)	<i>P</i> ^f (Gpa)	<i>IS</i> ^g (J)	<i>FS</i> ^h (N)
1	99	1.899	1.51	9376	40.5	<1	<5
3	191	1.716	0.16	8702	30.3	8	240
4	181	1.857	0.60	9579	40.4	5	120
5	206	1.873	1.36	9849	40.9	12	160
6	172	1.787	2.48	8942	32.1	22	240
7	122	1.700	1.79	8332	26.5	28	360
8	282	1.654	0.39	8196	24.6	30	360
9	217	1.645	1.04	8434	26.2	28	360
10	213	1.736	1.54	9100	31.3	25	360
RDX	204	1.800	0.32	8795	34.9	7.4	120
HMX	280	1.905	0.25	9144	39.2	7.4	120

^aAll the newly prepared materials are anhydrous for testing. ^bThermal decomposition temperature (onset) under nitrogen gas (DSC, $5 \text{ }^\circ\text{C}/\text{min}$). ^cDensity was measured by gas pycnometer at room temperature. ^dCalculated heat of formation. ^eDetonation velocity. ^fDetonation pressure. ^gImpact sensitivity. ^hFriction sensitivity.

water insensitive and can be stored for long periods in air. While **1** decomposes thermally at 99 °C, its salts are more stable thermally with decomposition temperatures ranging from 122 (7) to 282 (8) °C. The experimentally determined densities of **1** and the anhydrous salts (1.645–1.899 g cm⁻³) were obtained using a gas pycnometer at 25 °C. Among them, **1** (1.899 g cm⁻³), **4** (1.857 g cm⁻³), and **5** (1.873 g cm⁻³) have relatively high densities that are comparable to that of RDX (1.800 g cm⁻³).

To evaluate the energetic properties of **1** and its ionic derivatives, the heats of formation for **1** and its corresponding anion were obtained by employing the isodesmic reaction approach. For **3–10**, the solid-state heats of formation are obtained based on the Born–Haber energy cycle (see SI for calculation details).¹³ As shown in Table 1, the calculated values vary between 0.16 and 2.48 kJ g⁻¹, and most of them are higher than that of RDX (0.32 kJ g⁻¹). With measured densities and calculated heats of formation in hand, the detonation properties of **1** and **3–10** were determined by EXPLO5 (v6.01) program.¹⁴ As shown in Table 1, the calculated detonation velocities and pressures are in the range from 8196 to 9849 m s⁻¹ and 24.6 to 40.9 GPa, respectively. Of these materials, **5** exhibits superior detonation properties, especially in terms of detonation velocity (9849 m s⁻¹), which significantly outperforms RDX (8795 m s⁻¹) and HMX (9144 m s⁻¹). Impact and friction sensitivity measurements for **3–10** were obtained using BAM techniques. By pairing with nitrogen-rich cations, the DNAF-based salts are well stabilized and thus exhibit lower impact and friction sensitivities (5–30 J for IS and 120–360 N for FS).

To further understand the sensitivity differences between **1** and its salts, suitable crystals of **3** and **5** were characterized by using single-crystal XRD. Rather than obtaining water-free structures, the dihydrate of **3** and monohydrate of **5** were confirmed. In contrast to the parent compound, the structures of 3,4-dinitraminofurazanate in 3·2H₂O and 5·H₂O crystals are nearly planar, and as a result face-to-face π - π interactions were also observed in both crystals.

More importantly, the introduction of amino-containing cations supplies sufficient hydrogen-bonding donor character to form extensive hydrogen-bonding networks (Figures 2 and 3).

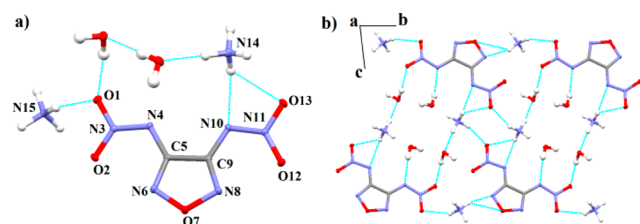


Figure 2. (a) View of molecular unit of 3·2H₂O and its atom labeling. (b) Unit cell view along the *a* axis.

Therefore, the “solid” O···O closed-shell interactions in **1** can be replaced by “soft” N···H and O···H hydrogen-bonding interactions which will absorb mechanical stimuli more readily.^{8c,15} Hirshfeld surfaces can be used to analyze the weak interactions of crystal structures. Based on this method, O···O interaction possesses 29.0% of total weak interactions for **1**, while the same interaction in 3·2H₂O and 5·H₂O is as low as 4.7% and 2.4%, respectively (Table 2).¹⁶ Fortunately, all of the new salts exhibit improved stability compared to **1**, which can be attributed to the combined effects of π - π , hydrogen-bonding, and cation–anion interactions.

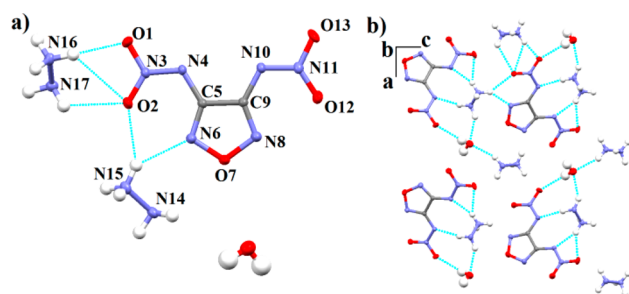


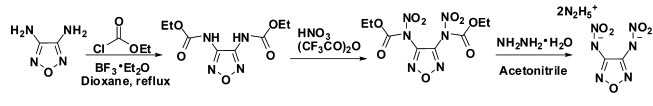
Figure 3. (a) View of molecular unit of 5·H₂O and its atom labeling. (b) Unit cell view along the *b* axis.

Table 2. Individual Atomic Contacts Percentage Contribution to the Hirshfeld Surface of **1, 3·2H₂O, and 5·H₂O**

crystal	interactions (%)		
	O···O	N···H and H···N	O···H and H···O
1	29.0	15.6	19.3
3·2H ₂ O	4.7	16.6	46.2
5·H ₂ O	2.4	25.1	46.9

In general, a useful HEDM needs to exhibit the following properties: (a) high detonation performance; (b) acceptable sensitivity toward external stimuli; (c) thermal stability to ≥ 150 °C; (d) stability upon storage for long periods of time; and (e) ease and safety of synthesis.¹⁷ In the case of **5**, the excellent detonation properties coupled with relatively high thermal stability and acceptable sensitivities suggest that this material may be an attractive candidate as a high explosive. However, according to the above synthetic route (Scheme 3), the isolation of highly sensitive **1** will be a major safety concern and will restrict the practical manufacture and the application of **5**. Therefore, an alternative route was also investigated in this work. To increase the stability of the nitration product of 3,4-diaminofurazan, *N*-ethoxycarbonyl protected 3,4-diaminofurazan was selected as an appropriate precursor. The synthesis of 3,4-*N,N'*-bis(ethoxycarboxamido)-furazan (Scheme 4) is ini-

Scheme 4. An Alternative Synthetic Route to **5 from *N*-Ethoxycarbonyl-Protected 3,4-Diaminofurazan**



tiated using commercially available ethyl chloroformate and 3,4-diaminofurazan, which is catalyzed by BF₃·Et₂O in refluxing dioxane to give the desired product **11** in good yield. Nitration of **11** can be accomplished by using a mixture of 100% nitric acid and trifluoroacetic anhydride as nitration agent to yield **12**. Finally, an aqueous alkaline workup using hydrazine hydrate precipitates dihydrazinium 3,4-dinitraminofurazanate (**5**) in a yield of 80%. The purity of **5** was confirmed by ¹H and ¹³C NMR analysis, which agrees with the data obtained for **5** via Scheme 3. In addition, the structure of the key intermediate, **12**, has been fully characterized as well and further confirmed based on single-crystal XRD (Figure 4). More importantly, due to the protecting group, the measured IS and FS values for the nitrated product **12** are 36 J and 240 N, respectively, which moderate safety concerns and ensure the potential application of **5** as a practical energetic material on a large scale.

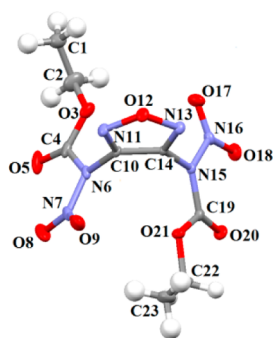


Figure 4. View of molecular unit of 12 and its atom labeling.

In summary, **1** has been synthesized and characterized structurally for the first time. This long awaited material possesses excellent explosive performance as well as extreme sensitivity. Insight into the crystal structure of **1** suggests that the interactive nitro chain and shortage of hydrogen-bonding interactions might be the reason for its instability. To our delight, **1** was stabilized by the formation of corresponding nitrogen-rich salts (**3–10**). All salts were also characterized by NMR and IR as well as elemental analysis. For compounds **3**·2H₂O and **5**·H₂O, structures were further confirmed with single-crystal XRD analyses. Among all these materials, **5** exhibits very promising detonation performance ($\nu D = 9849 \text{ m s}^{-1}$; $P = 40.9 \text{ GPa}$), which is one of the most powerful explosives synthesized to date. Furthermore, the combination of exceedingly high performance, good thermal stability, and acceptable sensitivities highlights this novel material as a suitable replacement for commonly used high explosives. To ensure the potential application of **5** on a large scale, an alternative route through the nitration of *N*-ethoxycarbonyl-protected 3,4-diaminofurazan and aqueous alkaline workup was developed. This optimized method can be utilized to prepare the desired salt **5** directly rather than requiring isolation of the highly sensitive **1** and in so doing reduces safety concerns markedly.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b09831.

Synthesis, characterization data, calculation detail, crystal refinements (PDF)

Crystallographic data for **1** (TXT)

Crystallographic data for **3**·2H₂O (TXT)

Crystallographic data for **5**·H₂O (TXT)

Crystallographic data for **12** (TXT)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support of the Office of Naval Research (N00014-12-1-0536), the Defense Threat Reduction Agency (HDTRA 1-11-1-0034), and CFD Research Corporation are gratefully acknowledged.

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