Synthesis of Nitro, Dinitro, and Polynitroalkylamino Derivatives of Trifurazanoxide

Raja Duddu,[a*] John Hoare,[a] Peggy Sanchez,[b] Reddy Damavarapu,[b*] and Damon Parrish[c]

[a]Leidos, US Army ARDEC, Bldg-3028, Picatinny Arsenal, Morris County, NJ 07806, USA
[b]US Army ARDEC, Bldg-3028, Picatinny Arsenal, Morris County, NJ 07806, USA
[c]Naval Research Laboratory, 4555 Overlook Avenue, Washington, DC 20375, USA
*E-mail: raja.g.duddu.ctr@mail.mil; reddy.s.damavarapu.civ@mail.mil

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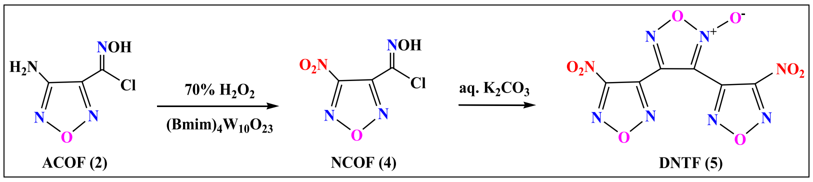

The synthesis and characterization of 3-chlorocarbohydroxymoyl-4-nitro-1,2,5-oxadiazole and its transformation to dinitro trifurazanoxide were described for the first time. Synthesis of new amino nitro and trinitroethylamino trifurazanoxide has been presented.

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INTRODUCTION

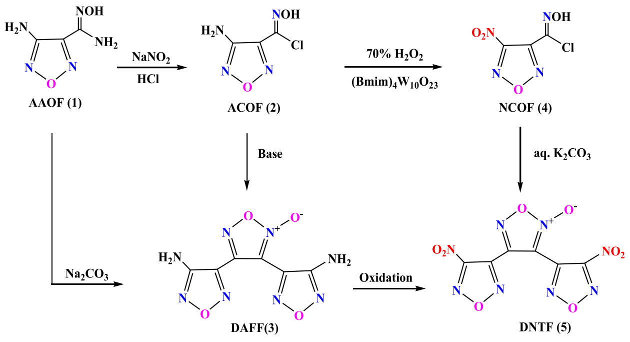
In continuation of efforts on the development of new munitions systems for advanced applications, the Department of Defense Agencies all over the world are in search of materials that yield high energy output. In order to meet increasing regulations, environmentally benign high nitrogen-containing nitro and nitramino heterocycles [1] with high densities having high positive heat of formation are of great interest to the US Department of Defense. Some nitro compounds of furazan and its oxides (furoxans) are quite dense and highly energetic [2]; thus, intense research is being carried out at various laboratories with the aim of developing materials that are thermally stable, insensitive to stimuli, and providing energetic performance significantly greater than in-service materials. A recently developed high-energy, high-density melt-castable energetic material 3,4-bis(4-nitro-1,2,5-oxadizaol-3-yl)-1,2,5-oxadiazole-*N*-oxide [3] (DNTF, **5**, also known as BNFF) has attracted the attention of energetic material community. The reason for this is that DNTF has a crystal density of 1.93 g/cc with a heat of formation of 657 kJ/mol and a melting point of 108–110°C [3a]. Its decomposition temperature is 292°C, while its energetic performance is 168% better than trinitrotoluene [3k]. All characteristics mentioned in the preceding texts make DNTF a highly desirable energetic ingredient for melt–pour formulations, and hence, it is currently being investigated for its application in the development of multipurpose energetic formulations. Our group has actively been involved in the synthesis and development of novel nitro heterocyclic energetic materials [4] for quite some time. It is with this background that the development of methods for preparation of DNTF was carried out.

RESULTS AND DISCUSSION

A careful analysis of literature reports revealed that, thus far, all the synthetic approaches mainly involved oxidation of amino groups of diamino furazanofuroxan (**3**, DAFF) to prepare DNTF (**5**; Scheme 1). Herein is reported a novel method for synthesis of DNTF in which no DAFF preparation is required. Furthermore, the synthesis of two new nitroenergetic materials, monoamino mononitro and bistrinitroethylamino trifurazanoxides derived from DAFF, is described.

Recently, Chinese scientists reported a procedure for DAFF preparation using carboxamide oxime (**1**), using sodium carbonate in solvent ether [5]. In-house attempts to prepare DAFF by using this procedure resulted in recovery of starting material. There was no formation of DAFF. All other literature procedures utilized 3-amino-4-chlorocarbohydroxymoyl-1,2,5-oxadiazole (ACOF, **2**) as starting material for DAFF preparation [3]. The methods that utilized commonly used bases such as sodium carbonate and potassium carbonate reported formation of a mixture of DAFF and a six-member isomer of DAFF (called iso-DAFF) in various ratios, thereby requiring separations via crystallizations [3g]. In 2015, Tsyshevsky and co-workers reported a procedure for exclusive preparation [3k] of DAFF using a relatively expensive base silver carbonate. Thus, an approach in which preparation of DAFF is completely removed was envisioned. Accordingly, it was planned to synthesize 3-chlorocarbohydroxymoyl-4-nitro-1,2,5-oxadiazole (NCOF, **4**) from ACOF (**2**) and then transform **4** to DNTF (**5**). However, Russian scientists reported that their attempts to transform the amino group of ACOF (**2**) to the corresponding nitro group in **4** were not successful [6]. This

Scheme 1 [Color figure can be viewed at wileyonlinelibrary.com]



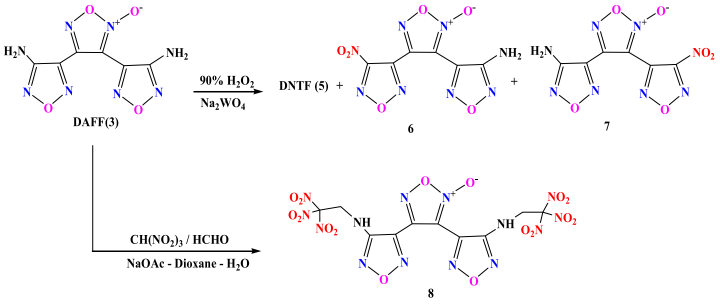
report challenged us to investigate and develop a method for synthesis of NCOF (**4**). The initial attempts to oxidize free amino group of **1** with H_2O_2 in presence of sulfuric acid with or without catalyst yielded either a complex mixture of products or decomposed materials. Many attempts to obtain NCOF by using varying oxidation agent concentrations were not successful. Finally, compound **2** was subjected to oxidation by using aq. 70% H_2O_2 in presence of tungsten-based catalyst $(Bmim)_4W_{10}O_{23}$ [7], initially by stirring the reaction mixture at room temperature, and then heating it at 52°C for 4 h followed by an extractive work-up afforded NCOF (**4**) as a pale yellow liquid. Carbon NMR analysis of this liquid showed a resonance at 158.71 ppm as a triplet due to coupling of the nitro group nitrogen with aromatic ring carbon, suggesting the formation of the desired nitro compound **4**. In an effort to further confirm the identity of this liquid, an ethereal solution of **4** was reacted with an aq. potassium carbonate solution. Stirring the reaction mixture at room temperature for 2 h followed by an extractive workup and removal of solvent yielded the crude DNTF (**5**). Pure DNTF was obtained by triturating the crude with diethyl ether and then separation of the formed solid via filtration. The spectral and thermal data of the white solid thus obtained matched with that of the literature reported values, for DNTF (**5**). Further confirmation was obtained by obtaining a mixed melting point and directly comparing the data with an authentic DNTF sample prepared via oxidation of DAFF [8]. This is a new synthesis method for DNTF preparation.

The focus was changed to the partial oxidation of DAFF (**3**) to obtain monoamino mononitro trifurazanoxide, an energetic material of interest for our applications (Scheme 2). Attempts to produce mononitro product exclusively from DAFF with varying oxidation reagents (30–90% H_2O_2 and H_2SO_4) always resulted in DNTF or in a complex mixtures of products with DNTF being a major identifiable product. Finally, the desired monoamino mononitro product(s) was obtained when DAFF was reacted with 90% aqueous hydrogen peroxide with disodium tungstate as catalyst in the reaction medium under sonication conditions. Sonicating the reaction mixture for 3.5 h, followed by an extractive work-up, yielded a crude gooey material. The NMR analysis of this crude product suggested that it is a mixture of monoamino mononitro compounds **6** and **7** along with DNTF (**5**) and starting material. The crude product was then subjected to Si-gel column chromatography. The desired pure mononitro monoamine products **6** and **7** were isolated in poor, 8.4% and 6.9%, yields, respectively, as white solids along with DNTF in 14% yield.

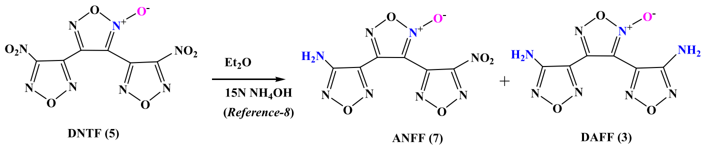
Chung and co-workers [8] (Scheme 3) prepared an amino nitro compound via nucleophilic displacement reaction of ammonia on DNTF and assigned its structure as ANFF (**7**), in which amino and *N*-oxide groups are on the opposite sides.

The spectral and thermal data of one of our pure (**6**) isolated compounds are in good agreement with that of the values reported by Chung's group, thereby allowing us to initially believe that we also isolated the ANFF (**7**). Because Chung's group made the structural assignment based on the assumption of steric hindrance factors, it was decided to determine the structure of this product with no uncertainty. Hence, in an effort to establish the structure of this product unambiguously and in order to

Scheme 2 [Color figure can be viewed at wileyonlinelibrary.com]



Scheme 3 [Color figure can be viewed at wileyonlinelibrary.com]



obtain accurate experimental molecular density, a critically required parameter in estimating the energetic performance of new energetic materials, our material was subjected to single crystal X-ray crystallographic analysis. Surprisingly, X-ray investigations (Fig. 1 and Table 1) [9] revealed that this compound in fact possesses the structure **6**, in which amino and *N*-oxide groups are on the same side, not the ANFF (**7**) structure (where amino and *N*-oxide groups are on the opposite side), as proposed by Chung's group. Thus, based on our data comparison and X-ray investigations, we conclude that Chung and co-workers have indeed obtained **6** but erroneously assigned their isolated compound's structure as ANFF (**7**).

We next paid attention on the characterization of the other isolated new compound. While proton NMR showed a singlet at 6.07 ppm for the amino group, the carbon NMR spectrum of this compound consisted of six carbon signals with carbon attached to the nitro group resonating at 160.97 ppm as a typical triplet due to the coupling of nitrogen of nitro group with aromatic ring carbon. The experimentally determined elemental composition of this compound is in good agreement with that of the calculated values for the monoamino mononitro trifurazanoxide, thereby allowing us to conclude that it is the other monoamino mononitro isomer, **7**, where amino and *N*-oxide groups are on the opposite sides. Our attempts to obtain suitable crystals for single crystal X-ray crystallography investigations were not successful.

Because polynitroalkylamino furazan compounds are also highly dense and energetic compounds of interest [2q,2r], DAFF was subjected to Mannich condensation reaction with trinitroethanol (Scheme 2). The reaction was carried out in the presence of sodium acetate in dioxane-water medium at 58°C for 2 h. The crude product was purified via column chromatography to obtain bis (trinitroethylamino)trifurazanoxide in 15% yield. The structure of product **8** was further unambiguously confirmed by single crystal X-ray crystallography (Fig. 1). Selected [9] single crystal analysis details of compounds **6** and **8** are shown in Table 1.

In summary, for the first time, the synthesis of 3-chlorocarbohydroxymoyl-4-nitro-1,2,5-oxadiazole (**4**) has been achieved and demonstrated its transformation to DNTF (**5**), thus establishing a new method for the synthesis of DNTF. Two energetic materials of interest **7** and **8** have been synthesized and characterized. Structures of **6** and **8** have been established unambiguously via single crystal X-ray crystallography. In this process, literature-reported incorrect structural assignment for ANFF (**7**) has been corrected.

EXPERIMENTAL

Melting points were obtained by using a Thomas Hoover Uni-melt capillary melting point apparatus (Arthur H. Thomas Company, Philadelphia, PA) and is uncorrected. Differential scanning calorimetry (DSC)

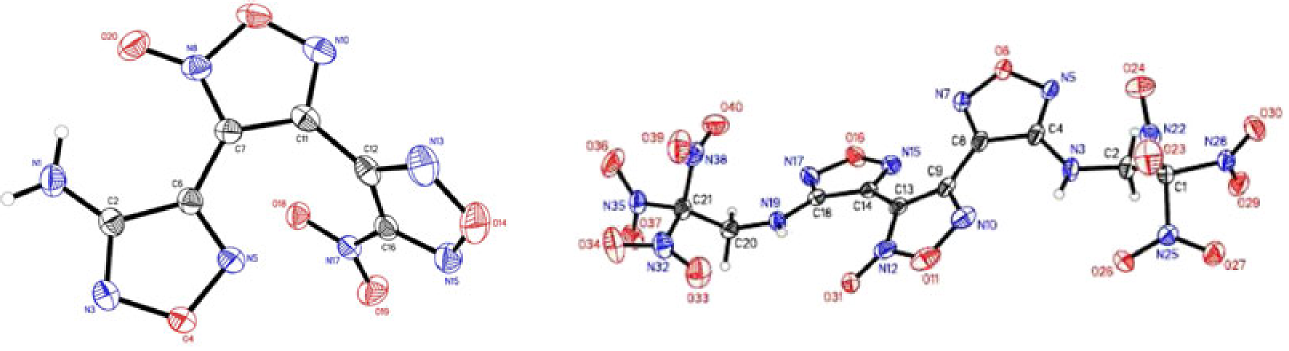


Figure 1. ORTEP diagrams of compounds **6** and **8**. [Color figure can be viewed at wileyonlinelibrary.com]

Table 1

Single crystal X-ray analysis data of compounds **6** and **8**.

	6	**8**
Empirical formula	$C_6H_2N_8O_6$	$C_{10}H_6N_{14}O_{16}$
Formula weight	282.16	578.29
Temperature	296(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
Unit cell dimensions	$a = 7.6896(6)$ Å, $\alpha = 90°$	$a = 12.172(3)$ Å, $\alpha = 90°$
	$b = 13.1271(11)$ Å, $\beta = 103.608(2)°$	$b = 18.806(5)$ Å, $\beta = 111.780(3)°$
	$c = 10.3101(8)$ Å, $\gamma = 90°$	$c = 9.889(2)$ Å, $\gamma = 90°$
Volume	1011.51(14) $Å^3$	2102.2(9) $Å^3$
Z	4	4
Density (−123°C)	1.853 Mg/m^3	—
Density (20°C)	1.807 Mg/m^3	1.827 Mg/m^3
Absorption coefficient	0.167 mm^{-1}	0.174 mm^{-1}
$F(000)$	568	1168
Crystal size	$0.75 \times 0.31 \times 0.28$ mm^3	$0.35 \times 0.07 \times 0.05$ mm^3
Theta range for data collection	2.56 to 26.43°	1.80 to 26.83°
Index ranges	$-9 \le h \le 9, -15 \le k \le 16, -12 \le l \le 12$	$-15 \le h \le 15, -23 \le k \le 23, -12 \le l \le 12$
Reflections collected	9492	18,294
Independent reflections	2076 [$R_{int} = 0.0207$]	4392 [$R_{int} = 0.0637$]
Completeness to theta = 26.43°	99.9%	97.1%
Absorption correction	Semiempirical from equivalents	Semiempirical from equivalents
Max. and min. transmissions	0.9548 and 0.8850	0.9914 and 0.9417
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data/restraints/parameters	2076/0/187	4392/3/365
Goodness-of-fit on F^2	1.047	1.039
Final R indices [$I > 2\text{sigma}(I)$]	$R_1 = 0.0325$, $wR_2 = 0.0811$	$R_1 = 0.0529$, $wR_2 = 0.1238$
R indices (all data)	$R_1 = 0.0352$, $wR_2 = 0.0832$	$R_1 = 0.0882$, $wR_2 = 0.1410$
Largest diff. peak and hole	0.782 and −0.496 $Å^{-3}$	0.782 and −0.496 $Å^{-3}$

measurement was recorded by using a Perkin Elmer DSC-4000 (Perkin Elmer, Waltham, MA). ^1H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 400-MHz NMR spectrometer (Billerica, MA) with acetone-d_6 as solvent. Chemical shift (δ) values are reported in ppm relative to TMS as an internal standard. Column chromatography was performed on Sigma-Aldrich (St. Louis, MO) 70-230 mesh silica gel (St. Louis, MO). ACOF and DAFF were prepared by using literature procedures [3g,3k].

Caution: Although no incidents were encountered with these materials, energetic materials presented in this article are sensitive toward shock and friction. Thus, proper safety precautions (such as wearing safety glasses, face shield, and conductive shoes) must be taken while synthesizing and handling these compounds.

3,4-Bis(4-nitro-1,2,5-oxadizaol-3-yl)-1,2,5-oxadiazole-*N*-oxide (5,DNTF). A heterogeneous mixture of 3-amino-4-chlorohydroximoyl 1-2,4-oxadiazole [3g] (0.4 g, 2.47 mmol) in 70% H_2O_2 (10 mL) and $(Bmim)_4W_{10}O_{23}$ catalyst (200 mg, 0.072 mmol) was stirred at room temperature for 16 h and then kept at 52°C for 4 h. The reaction mixture was diluted with water (100 mL) and extracted with ethylacetate (3 × 30 mL). The combined organic layer was washed with water (2 × 50 mL) and brine (1 × 50 mL), dried (Na_2SO_4), and filtered. The filtrate was evaporated on a rotary evaporator under vacuum at room temperature to dryness, to obtain product **4** (0.32 g, 67% yield) as a colorless liquid. ^1H-NMR (acetone-d_6): 13.03 (br S); ^{13}C-NMR (acetone-d_6): 123.74, 145.38, and 158.719 (t). *Anal.* Calcd. for $C_3HClN_4O_4$: C, 18.72; H, 0.52; N 29.10; Cl, 18.42. Found C, 18.91; H, 0.58; N, 29. 06; Cl, 18.29.

The nitro compound **4** thus obtained in the preceding texts (0.32 g, 1.66 mmol) was dissolved in diethyl ether (5 mL). A solution of potassium carbonate (166 mg, 1.2 mmol) was added in water (3 mL) at room temperature dropwise. The reaction mixture was then stirred at room temperature for 2 h. Ether layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 5 mL). The combined organic layer was then washed with water (1 × 5 mL) and brine (1 × 5 mL), dried (Na_2SO_4), and filtered. The organic solution was evaporated under vacuum at room temperature on a rotary evaporator. The pale yellow crude solid residue thus obtained was triturated with ether (1 mL). The white solid was separated via filtration and air dried. Yield: 68 mg (27% from nitro derivative) mp 107–108°C (lit mp 108–110°C) [3g]. ^{13}C-NMR (acetone-d_6): 104.45, 138.20, 140.55, 143.83, 160.82 (2 C).

4-Amino-1,2,5-oxadiazole-3yl-4-nitro-1,2,5-oxadiazole-4yl-1,2,5-oxadiazole-*N*-oxide and its isomer (6 and **7**). $Na_2WO_4.2H_2O$ (0.69 g, 2.1 mmol) was added to a suspension of DAFF (0.48 g, 1.9 mmol) in 10 mL of 90% H_2O_2 equipped with a thermocouple and magnetic stirring bead over a period of several minutes while maintaining the temperature at 15–20°C. The reaction mixture was sonicated for 3.5 h, and the aqueous solution was extracted with 30 mL of ethyl acetate. The ethyl acetate solution was washed with water (1 × 25 mL) and brine (1 × 25 mL), dried over $MgSO_4$, and evaporated to dryness. The crude product thus obtained was passed through a short silica gel column by using methylene chloride–heptane (3:7) solvent system. The relevant fractions (TLC with an R_f value of 0.64 in 40% ethyl acetate–heptanes) were combined and evaporated to yield product **7** as a white solid. Yield: 37 mg (6.9%); mp 115.8°C. DSC decomposition (5°C/min, decomposition peak): 233.5°C ^{1}H-NMR (acetone-d_6): 6.07 (s, 2H). ^{13}C-NMR (acetone-d_6): 108.73, 134.50, 140.74, 143.94, 156.48, 160.97(t). *Anal.* Calcd. for $C_6H_2N_8O_6$: C, 25.54; H, 0.71; N, 39.72. Found: C, 25.96; H, 0.68; N 38.76.

Further elution of the column and evaporation of the relevant fractions (TLC with an R_f value of 0.59 in 40% ethyl acetate–heptanes) to dryness provided product **6** as a white solid. Yield: 45 mg (8.4%). mp (by DSC). 107°C (lit.[8] 106°C). DSC (5°C/min, decomposition peak): 247°C; ^{1}H-NMR (acetone-d_6): 6.27 (s, 2H); ^{13}C-NMR (acetone-d_6): 102.48, 137.11, 138.40, 147.19, 156.06, 161.08 (t). *Anal.* Calcd. for $C_6H_2N_8O_6$: C, 25.54; H, 0.71; N, 39.72. Found: C, 25.96; H, 0.68; N, 38.76.

3,4-bis[3-(2,2,2-trinitroethyl)aminofurazan-4-yl]furoxan (8). Formaldehyde (500 mg, 37% aq. solution) was added to a cooled (10°C) solution of nitroform (3.0 gm, 30% aq. solution) dropwise. The reaction mixture was stirred at room temperature for 1 h. Then, a solution of the substrate DAFF (**3**, 224 mg, 0.88 mmol) in dioxane (3 mL) combined with sodium acetate (500 mg, 6.09 mmol) in water (1 mL) was added in one portion. The resulting reaction mixture was heated in an oil bath at 58°C for 2 h. The reaction mixture was diluted with water (25 mL) and extracted with ethyl acetate (4 × 25 mL). The combined yellow organic layer was sequentially washed with water (2 × 50 mL) and brine (1 × 50 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated under vacuum to yield a yellow syrupy liquid. This liquid was subjected to column chromatography (Si-gel, 10–20% ethyl acetate–hexanes). The relevant fractions were concentrated to yield pure product **7** (78 mg, 15%) as a white solid. A crystalline sample of **7** for single crystal X-ray analysis was obtained from chloroform–ethyl acetate (1:1) solvent recrystallization. mp 159–160°C; DSC (5°C/min, decomposition onset): 168°C. ^{1}H-NMR (acetone-d_6): 5.48 (d, J = 8.0 Hz, 2H), 5.58 (d, J = 8.0 Hz, 2H), 6.74 (br t, J = 8.0 Hz, 1H), 6.94 (br t, J = 8.0 Hz, 1H). ^{13}C-NMR (acetone-d$_6$): 48.99, 49.21, 105.33, 126.86, 132.73, 134.00, 136.91, 147.26, 156.22, and 157.06. *Anal.* Calcd. for $C_{10}H_6N_{14}O_{16}$: C, 20.77; H, 1.05; N, 33.91. Found: C, 20.82; H, 1.03; N 33.98.

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[9] Complete crystallographic information files for compounds 6 and 8 have been deposited with the Cambridge Crystallographic Data Center as supplementary publications CCDC 1522487 and 1522486, respectively. Copies of this data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ (UK); Tel.: (+44) 1223-336-408, Fax: (+44) 1223-336-033, or E-mail: deposit@ccdc.cam.ac.uk.