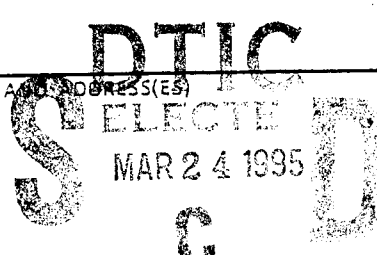


# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE March 8, 1995	3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE A Convenient Synthesis of Diaminoglyoxime and Diaminofurazan: Useful Precursors for the Synthesis of High Density Energetic Materials			5. FUNDING NUMBERS Contract N00014-90-J-1661 Richard S. Miller R&T Code 33E1800---01	
6. AUTHOR(S) Ananthakrishnan Gunasekaran, Thiruvallam Jayachandran, Joseph H. Boyer and Mark L. Trudell*				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of New Orleans Department of Chemistry New Orleans, Louisiana 70148			8. PERFORMING ORGANIZATION REPORT NUMBER  Technical Report No. 1 Contract N00014-90-J-1661	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  Office of Naval Research 800 North Quincy Street Arlington, Virginia 22217			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
				
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT  This document has been approved for public release and sale; its distribution is unlimited			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  The reaction of glyoxime (4) and hydroxylamine hydrochloride in aqueous sodium hydroxide was found to be a safe and inexpensive method for the preparation of multigram quantities of diaminoglyoxime (5). Potassium hydroxide mediated dehydration of 5 furnished diaminofurazan (1) in good yield of exceptional purity. The ready availability of 1 and 5 has facilitated the synthesis of new energetic furazan derivative MNOTO (8).				
19950322 096				
14. SUBJECT TERMS			15. NUMBER OF PAGES 7	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited	

OFFICE OF NAVAL RESEARCH

GRANT OR CONTRACT N00014-90-J-1661

R&T Code 33E1800---01

Richard S. Miller

Technical Report No. 1

A Convenient Synthesis of Diaminoglyoxime and Diaminofurazan: Useful Precursors for the Synthesis of High Density Energetic Materials

by

Ananthkrishnan Gunasekaran, Thiruvallam Jayachandran, Joseph H. Boyer and Mark L. Trudell

Prepared for Publication

in the

Journal of Heterocyclic Chemistry

University of New Orleans  
Department of Chemistry  
New Orleans, LA

March 8, 1995

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale;  
its distribution is unlimited.

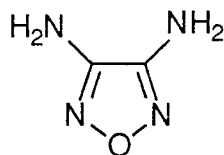
Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Control
A-1	

A Convenient Synthesis of Diaminoglyoxime and Diaminofurazan: Useful Precursors for the Synthesis of High Density Energetic Materials.

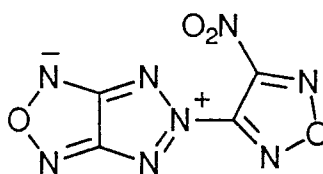
Ananthakrishnan Gunasekaran, Thiruvallam Jayachandran, Joseph H. Boyer and Mark L. Trudell\*

*Department of Chemistry, University of New Orleans, New Orleans, LA 70148*

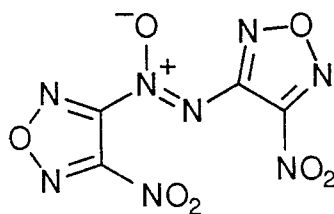
During the course of recent studies directed toward the synthesis of new energetic materials, the furazan ring has been found to be a useful substructure for the design of new high density, high energy materials composed exclusively of carbon, hydrogen, nitrogen and oxygen atoms. [1] The diaminofurazan (**1 DAF**) has been shown to be a useful precursor for the construction of high energy furazan derivatives *NOTO* (**2**) and *DNAF* (**3**). [2,3] However, the preparation of *DAF* (**1**) has been limited by the availability of the precursor diaminoglyoxime (**5 DAG**). There are several reports in the literature which describe methods for the synthesis of *DAG* (**5**). [4–8] However, these procedures require the use of obscure starting materials and hazardous or expensive reagents. Herein we wish to report a facile inexpensive method for the multigram synthesis of *DAG* (**5**) and *DAF* (**1**). In addition, the availability of useful quantities of these intermediates has facilitated the synthesis of a new energetic furazan derivative.



**1**



**2 (NOTO)**

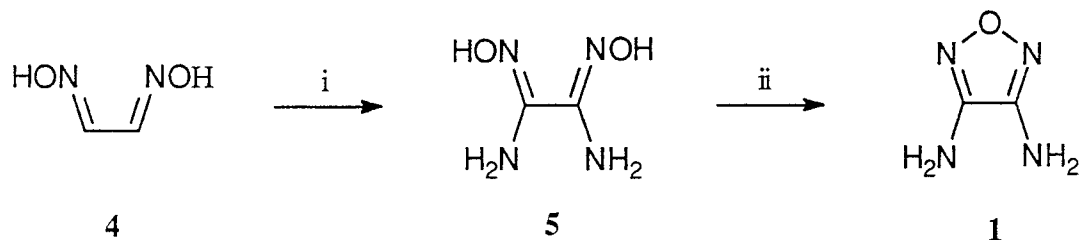


**3 (DNAF)**

## RESULTS AND DISCUSSION

As illustrated in Scheme 1, the synthesis of *DAF* (**1**) was achieved in two steps from readily available glyoxime **4**. [8] The key intermediate *DAG* (**5**) was prepared from the reaction of **4** and hydroxylamine hydrochloride in an alkaline aqueous sodium hydroxide solution at 90 °C. This conversion, originally described without experimental details in a Russian patent, afforded *DAG* (**5**) in 60% yield. [9] This procedure represents an improvement over the methods previously reported in that it avoids the use of cyanogen gas and *DAG* (**5**) can be obtained from commercially available reagents in good yield at low cost.

Scheme 1



Reagents: i)  $\text{NH}_2\text{OH}\cdot\text{HCl}$ ,  $\text{NaOH}$  (aq), 60 °C. ii)  $\text{KOH}$  (aq), 170 °C, stainless steel reactor.

The generation of furazan from the dehydration of glyoxime (**4**) at elevated temperatures in aqueous sodium hydroxide has been known for nearly a century. [10] However, the efficient dehydration of *DAG* (**5**) in aqueous sodium hydroxide has been shown to require higher temperatures in a sealed reaction vessel. [11,12] In this study it was found that a simple stainless steel reactor could be employed to safely and easily perform the dehydration reaction of *DAG* (**5**) on a multigram scale to furnish *DAF* (**1**). Both sodium hydroxide and potassium hydroxide were found to effect the dehydration reaction; however, potassium hydroxide routinely furnished *DAF* (**1**) in high yield (> 70%) in a state of exceptionally high purity (Scheme 1).

With the *DAF* (**1**) in hand, attention turned toward the synthesis of new high density energetic compounds. Based on the detonation performance of the

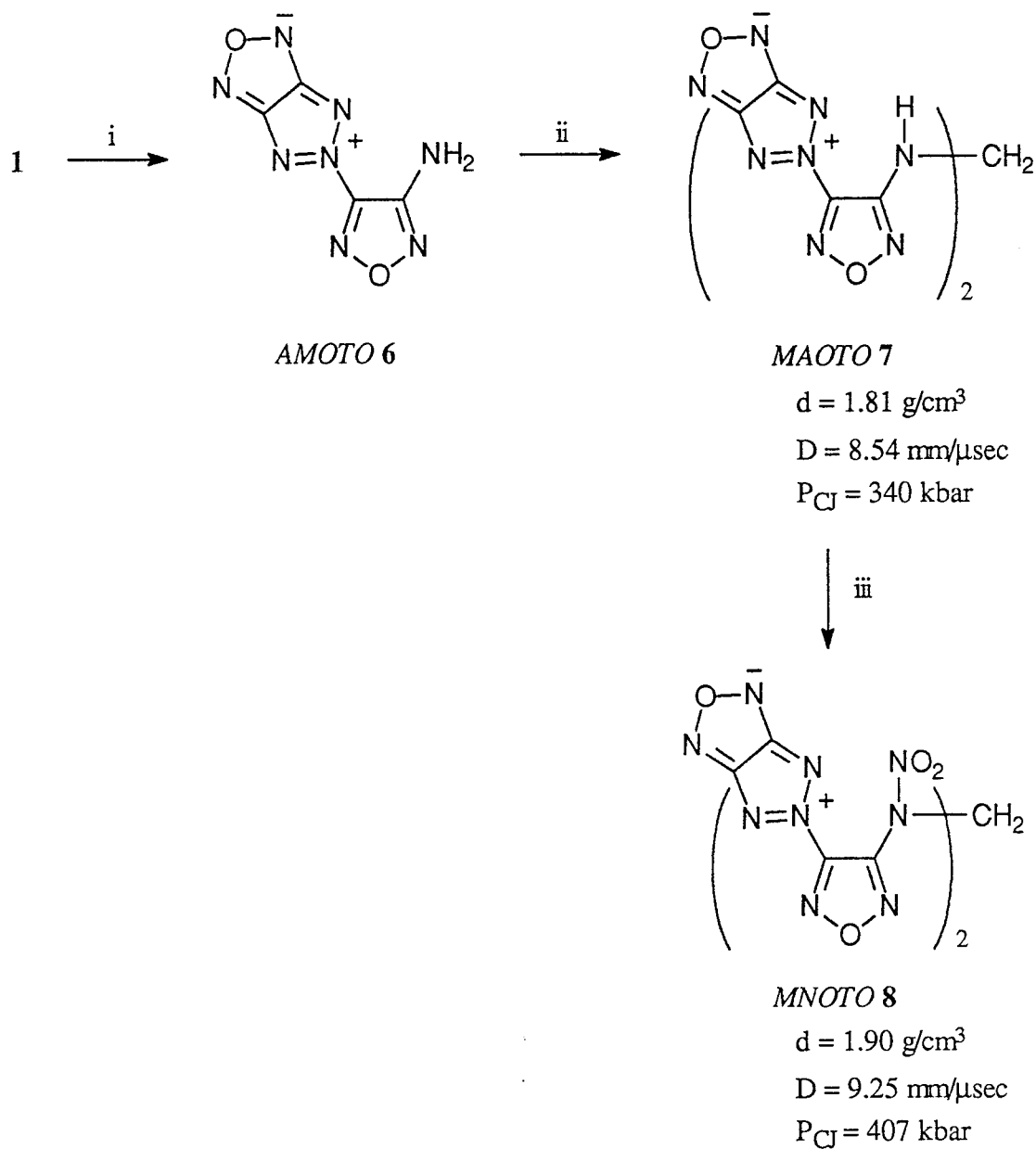
furazan derivatives *NOTO* (2) and *DNAF* (3) [2,3], previously synthesized in these laboratories, the 5,5'-[methanedinitramino-bis(1,2,5-oxadiazol-4,3-diyl)]bis[1*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazolium]bis-(inner salt) (8 *MNOTO*) was viewed as an attractive synthetic target. Excellent calculated density ( $d$ ) and detonation properties [detonation velocity ( $D$ ) and detonation pressure ( $P_{CJ}$ )] suggested that *MNOTO* (8) could be useful as a new solid state explosive or propellant (Scheme 2). [13]

As illustrated in Scheme 2, the synthesis of *MNOTO* (8) proceeded from *DAF* (1) through the intermediate 5-(4-amino-1,2,5-oxadiazol-3-yl)-1*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazolium inner salt (6 *AMOTO*). *AMOTO* (6) was prepared from *DAF* (1) using a two step procedure previously reported. [3] Condensation of *AMOTO* (6) with formaldehyde furnished the 5,5'-[methanediamino-bis(1,2,5-oxadiazol-4,3-diyl)]bis[1*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazolium]-bis(inner salt) (7 *MAOTO*) in 90% yield. *MAOTO* (7) was calculated to possess fair detonation properties and a density of 1.81 g/cm<sup>3</sup>. The compound was found to be thermally stable above 200 °C and shock insensitive (no detonation with a hammer blow).

The *N*-nitration of the amine nitrogen atoms to give *MNOTO* (8) was achieved in a mixture of 100% HNO<sub>3</sub> and acetic anhydride. This provided *MNOTO* (8) in 97% yield as a colorless amorphous solid. As expected the detonation properties of *MNOTO* (8) were greatly enhanced over those of *MAOTO* (7). *MNOTO* (8) was found to be an impact sensitive material which exploded violently with flame when struck by a hammer. In addition, the thermal stability of *MNOTO* (8) was found to be less than that observed for *MAOTO* (7) and furazan derivatives *NOTO* (2) and *DNAF* (3). [2,3]

In summary, *DAF* (1) has again been shown to be a useful precursor for the synthesis of energetic compounds. With a convenient and inexpensive preparation of *DAG* (5) and *DAF* (1) now available, large-scale synthesis of furazan derivatives are now economically feasible. In addition, the ready availability of *DAF* (1) should lead to the development of new furazan based compounds.

Scheme 2



Reagents: i) See conditions cited in Reference 3. ii) 37%  $\text{H}_2\text{CO}$ ,  $\text{HCl}$ ,  $100^\circ\text{C}$ .  
 iii) 100%  $\text{HNO}_3$ ,  $\text{Ac}_2\text{O}$ ,  $-5^\circ$  to  $15^\circ\text{C}$ .

### EXPERIMENTAL

All chemicals were purchased from Aldrich Chemical Company, Milwaukee, WI.  $^1\text{H}$  and  $^{13}\text{C}$  nmr spectra were obtained on a Varian-Gemini Multiprobe 300 MHz nmr spectrometer and

ir spectra were recorded on a Perkin–Elmer 1600 series infrared spectrometer. Melting points were determined on a Mel – Temp II and are reported uncorrected. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN and Midwest Micro Lab, Indianapolis, IN. An inexpensive stainless steel reactor was made in the Machine Shop at the University of New Orleans. [14] *Caution:* *MNOTO* (**8**) should be treated as dangerously explosive.

#### *Diaminoglyoxime (5).*

Aqueous sodium hydroxide (100 mL, 5 M) was added to glyoxime (**4**) (17.6 g, 0.2 mol) and stirred in a 250 mL round bottom flask. Hydroxylamine hydrochloride (27.8 g, 0.4 mol) was then added in one portion. The flask was fitted with a condenser and heated in an oil bath (keeping the bath temperature at 90 °C for 6 h). The reaction mixture was allowed to cool to room temperature and a colorless crystalline solid (needles) precipitated. The isolated solid was washed with cold water (10–15 mL) and dried to give diaminoglyoxime (**5**), 14.0 g (60%), mp 203–205 °C (dec) (water), lit mp 203 °C [6]. <sup>1</sup>H nmr (dimethylsulfoxide–d<sub>6</sub>): δ 5.18 (bs, 4H, NH<sub>2</sub>), 9.76 (s, 2H, OH). <sup>13</sup>C nmr (dimethylsulfoxide–d<sub>6</sub>): δ 145.2.

#### *Diaminofurazan (1).*

A suspension of diaminoglyoxime (**5**) (23.6 g, 0.2 mol) in aqueous potassium hydroxide (80 mL, 2 M) was placed in a stainless steel reactor. The reactor was closed and placed in an oil bath preheated to 170–180 °C and maintained at that temperature for 2 h. The reactor was cooled by immersion in an ice bath for 2 h and opened in a hood to avoid contact with trace amounts of ammonia as it escaped. The mixture was removed by washing the chamber with water (2 × 20 mL) and filtered to give **1** as colorless needles, 14.1 g (70%), mp 179–180 °C, lit mp 180 °C [11]; ir (potassium bromide): 3423, 3318, 1647, 1591, 1353 cm<sup>-1</sup>. <sup>1</sup>H nmr (dimethylsulfoxide–d<sub>6</sub>): δ 5.81 (bs, 4H, NH<sub>2</sub>). <sup>13</sup>C nmr (dimethylsulfoxide–d<sub>6</sub>): δ 149.7.

5,5'-[Methanediamino-bis(1,2,5-oxadiazol-4,3-diyl)]bis[1H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazolium]-bis(innersalt) (7).

To a suspension of AMOTO (6) (1.0 g, 5.2 mmol) in water (20 mL), an aqueous solution of formaldehyde (37%, 0.2 g, 2.6 mmol) and 3 drops of hydrochloric acid (12 M) were added and the mixture refluxed for 2 h. The mixture was then cooled and filtered to furnish a yellow solid which was washed with cold water and dried under vacuum to give 7, 0.94 g (90%), mp 244–245 °C (dec) (DMF/water); ir (potassium bromide): 3410, 1618, 1572, 1046, 1202  $\text{cm}^{-1}$ .  $^1\text{H}$  nmr (dimethylsulfoxide –  $d_6$ ):  $\delta$  5.09 (bs, 2H,  $\text{CH}_2$ ), 7.89 (bs, 2H, NH);  $^{13}\text{C}$  nmr (dimethylsulfoxide –  $d_6$ ):  $\delta$  165.4, 150.6, 145.3, 53.8.

*Anal.* Calcd for  $\text{C}_9\text{H}_4\text{N}_{16}\text{O}_4$ : C, 27.01; H, 1.01; N, 55.99. Found: C, 26.91; H, 1.08; N, 55.73.

5,5'-[Methanedinitramino-bis(1,2,5-oxadiazol-4,3-diyl)]bis[1H-[1,2,3]triazolo[4,5-c][1,2,5]-oxadiazolium]-bis(innersalt) (8).

To a solution of 100%  $\text{HNO}_3$  (1.5 g) and acetic anhydride (1.0 g) at 0 °C was added 7 (1.0 g, 2.5 mmol) in one portion. The reaction mixture was stirred for 30 min then allowed to warm to 10–15 °C with continued stirring for 30 min. The mixture was then poured onto crushed ice (100 g). A colorless precipitate was collected and washed with cold water to give 8, 1.2 g (97%), mp 160 °C (dec) (dichloromethane); ir (potassium bromide): 1608, 1282, 1103, 1038.  $^1\text{H}$  nmr (dimethylsulfoxide –  $d_6$ ):  $\delta$  7.10 (s, 2H,  $\text{CH}_2$ );  $^{13}\text{C}$  nmr (dimethylsulfoxide –  $d_6$ ):  $\delta$  166.9, 151.4, 147.0, 67.2.

*Anal.* Calcd for  $\text{C}_9\text{H}_2\text{N}_{18}\text{O}_8$ : C, 22.05; H, 0.41; N, 51.43. Found: C, 21.97; H, 0.42; N, 51.28.

#### ACKNOWLEDGMENT

Financial support was received from the Office of Naval Research (ONR) and from Army Research Office (ARO). A grant, LEQSF (1990–1991; ENH–53) from the Louisiana Board of Regents provided for the purchase of the Varian Gemini–300 NMR spectrometer.



## REFERENCES AND NOTES

- [1] For a review on the chemistry of energetic materials see A.T. Nielsen, Chemistry of Energetic Materials, G.A. Olah and D.R. Squire, eds, Academic Press, Inc., San Diego, CA, 1991, p 95 and references cited therein.
- [2] A. Gunasekaran and J.H. Boyer, *Heteroatom Chem.*, **4**, 521 (1993).
- [3] A. Gunasekaran, M.L. Trudell and J.H. Boyer, *Heteroatom Chem.* (1994) in press.
- [4] H. Wieland, *Chem. Ber.*, **42**, 4192 (1909).
- [5] J. Houben and H. Kauffmann, *Chem. Ber.*, **46**, 2821 (1913).
- [6] G.A. Pearse, Jr. and R.T. Pflaum, *J. Am. Chem. Soc.*, **81**, 6505 (1959).
- [7] H.E. Ungnade, L.N. Kissinger, A. Narath and D.C. Barham, *J. Org. Chem.*, **28**, 134 (1963).
- [8] D.J. Park, A.G. Stern and R.L. Willer, *Synth. Commun.*, **20**, 2901 (1990).
- [9] T.E. Ivanova, S.N. Vergizov, S.F. Mel'nikova and Tselinski, U.S.S.R. Patent 713,864 (1980); *Chem. Abstr.*, **92**, 197914e (1980).
- [10] L. Wolff, *Chem. Ber.*, **28**, 69 (1895).
- [11] M.D. Coburn, *J. Heterocyclic Chem.*, **5**, 83 (1968).
- [12] A.P. Komin, R.W. Street and M. Carmack, *J. Org. Chem.*, **40**, 2749 (1975).
- [13] We are grateful to Dr. Richard Hollins, Naval Weapons Center, China Lake, CA for providing a computational method to calculate  $d$ ,  $D$  and  $P_{CJ}$  for structural formula restricted to C, H, N, O and F atoms. Target values of  $d \approx 2.0 \text{ g/cm}^3$ ,  $D \approx 10 \text{ mm}/\mu\text{sec}$ ,  $P_{CJ} \approx 400 \text{ kbar}$ .
- [14] Detailed specifications for the stainless steel reactor are available upon request.

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research Chemistry Division, Code 313 800 North Quincy Street Arlington, Virginia 22217-5000	(1)*	Dr. Richard W. Drisko (1) Naval Civil Engineering Laboratory Code L52 Port Hueneme, CA 93043
Defense Technical Information Center Building 5, Cameron Station Alexandria, VA 22314	(2)	Dr. Harold H. Singerman (1) Naval Surface Warfare Center Carderock Division Detachment Annapolis, MD 21402-1198
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	(1)	Dr. Eugene C. Fischer (1) Code 2840 Naval Surface Warfare Center Carderock Division Detachment Annapolis, MD 21402-1198
Dr. Robert Green, Director Chemistry Division, Code 385 Naval Air Weapons Center Weapons Division China Lake, CA 93555-6001	(1)	Dr. Bernard E. Douda (1) Crane Division Naval Surface Warfare Center Crane, Indiana 47522-5000
Dr. Elek Lindner Naval Command, Control and Ocean Surveillance Center RDT&E Division San Diego, CA 92152-5000	(1)	

\* Number of copies to forward