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Dense Energetic Compounds of C, H, N, and O Atoms. III. 5-[4-Nitro-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole

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Dense Energetic Compounds of C, H, N, and O Atoms. III. 5-[4-Nitro-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole

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ABSTRACT

Diazoazofurazan **8** was obtained from the bis-diazonium salt of diaminoazofurazan **7** by treatment with sodium azide and underwent thermolysis to 5-[4-azido-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole **5**. The corresponding amine **13** was obtained from the azide **5** by reduction with stannous chloride and was oxidized by ammonium persulfate to 5-[4-nitro-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole **1**. The azide **5** was converted to a phosphinimine **9** in a reaction with triphenylphosphine.

INTRODUCTION

In an ongoing search [1] for high energy molecules restricted in composition to carbon, hydrogen, nitrogen, and oxygen atoms to qualify as superior energetic material [2] the candidacy of 5-[4-nitro-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole (NOTO) **1** was proposed after very good values were calculated for its density and detonation properties [3].

This rarely encountered triazolooxadiazole (triazolofurazan) ring system was discovered in 1974 [4]. In one instance a thermolytic cyclization converted 3-azido-4-phenylazofurazan to 5-phenyl-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole **2** [5] in a reaction related to the thermolysis and the photolysis of *o,o'*-diazidoazobenzene **3** to 2-(*o*-azidophenyl)-2H-benzotriazole **4** [6].

The present investigation was facilitated by an improved preparation for diaminofurazan **6** [7,8] and its oxidation by ammonium persulfate to diaminoazofurazan **7** [9].

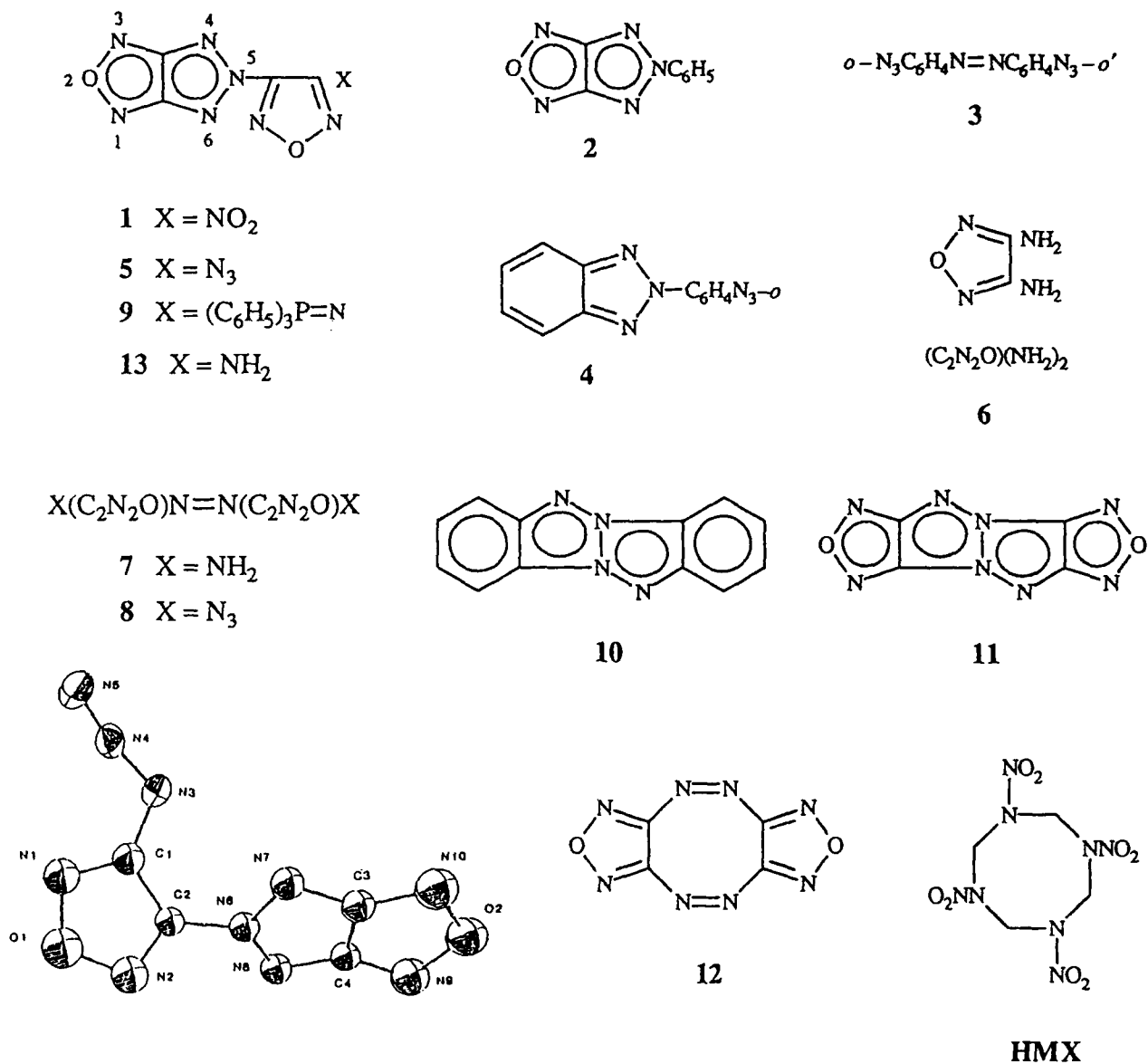


Fig 1. 5 Ortep Plot

### RESULTS AND DISCUSSION

The bis-diazonium salt of the diamine 7 was converted to diazidoazofurazan 8 by treatment with sodium azide. Under mild conditions thermolysis of the diazide 8 gave 5-[4-azido-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole 5. For characterization the azide 5 was treated with triphenylphosphine to give 5-[4-triphenylphosphorimino-(1,2,5)oxadiazolyl]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole 9. On the other hand nitrogen evolution was thwarted by

distillation when attempts were made to bring about thermal decomposition of the neat azide 5, bp 165 °C. Although the azide 4 in inert solvents underwent both thermolysis and photolysis to give dibenzo-1,3a,4,6a-tetraazapentalene 10 [6], similar experiments with the azide 5 gave unidentified and intractable material without the detection of either difurazano-1,3a,4,6a-tetraazapentalene 11 or the isomeric difurazano-1,2,5,6-tetraazacyclooctatetraene 12 [10]. The structure of the azide 5 was confirmed by an X-ray crystallographic analysis and is shown by the Ortep plot in Fig 1 [11].

After 5-[4-amino-(1,2,5)oxadiazolyl]-5H-[1,2,3]-triazolo[4,5-c][1,2,5]oxadiazole 13 was obtained from the azide 5 by reduction with stannous chloride it was oxidized by treatment with ammonium persulfate to NOTO 1. The latter was obtained as a thick orange-yellow oil with solidification at -25 °C. It was indefinitely stable to storage under ordinary conditions. Although an anticipated thermolysis was precluded by distillation a violent explosion occurred when the compound was heated to 160 °C in a closed capillary tube. In a test for shock sensitivity both NOTO 1 and the azides 5 and 8 were violently brisant with an evolution of flame. A density determined by the flotation method in aqueous zinc iodide solutions as  $1.658 \pm 0.007$  established NOTO as one of the densest liquid nitro compounds composed of carbon, nitrogen, and oxygen atoms [12]. In addition to its zero hydrogen content and an optimal composition ( $C_4N_8O_4$ ) for self conversion to carbon monoxide and nitrogen, excellent values were calculated for the density ( $d$ , g/cm<sup>3</sup>), detonation velocity ( $D_v$ , mm/ $\mu$ sec), and detonation pressure ( $D_p$ , Kbar) for NOTO 1 as a solid:  $d$  1.92 [13],  $D_v$  9.1, and  $D_p$  434 and as a liquid:  $d$  1.69,  $D_v$  8.8, and  $D_p$  366 [3]. For comparison the values for 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), a solid, are  $d$  1.90,  $D_v$  9.1, and  $D_p$  390 [14].

### EXPERIMENTAL

Instruments included: Perkin Elmer 1600 series FT-IR, Hewlett-Packard 5985 (70 eV) GC-MS, and Varian-Gemini 300 NMR (internal standards were  $(CH_3)_4Si$  for <sup>1</sup>H NMR and  $CDCl_3$

and DMSO- $d_6$  for  $^{13}\text{C}$  NMR). Photolysis was carried out in a Rayonet Photochemical Reactor. A stainless steel reactor (59 mm inner diameter, 3.7 mm wall thickness, and 66 mm deep) with a threaded cap and a teflon gasket was constructed. It had a metal square top, 25 mm  $\times$  25 mm and 12 mm thick and a bottom metal square 45 mm  $\times$  45 mm and 10 mm thick with a flange attached to facilitate opening. Solvents were removed by rotary evaporation under reduced pressure unless otherwise indicated. Melting and decomposition points were determined on a Mel-Temp II apparatus. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN, and Midwest Microlab, Indianapolis, IN. Dithiooxamide was obtained from the Sigma Chemical Company. The structures assigned to new compounds 1, 5, 8, 9, and 13 were consistent with their *ir spectra*.

*Diaminoglyoxime* ( $\text{H}_2\text{NC}=\text{NOH}$ )<sub>2</sub> [15]

Hydroxylamine hydrochloride (28.0 g, 0.40 mol) in water (60 mL) was treated with anhydrous sodium carbonate (21.2 g, 0.20 mol) added in small portions with stirring. The clear solution was combined with ethanol (95%, 275 mL). Dithiooxamide ( $\text{H}_2\text{NC}=\text{S}$ )<sub>2</sub> (24.0 g, 0.20 mol) was added with stirring. The reaction mixture was heated at 80 °C for 1 h in a hood to insure removal of hydrogen sulfide fumes. After solvent was removed the crude diaminoglyoxime recrystallized from water as colorless needles (19.5 g, 83%) mp 203–205 °C (dec) (lit. [15] mp ranged from 192 °C to 210 °C (dec)).

*Diaminofurazan 6*

In a modification of a procedure [7] a mixture of diaminoglyoxime (23.6 g, 0.20 mol) and aqueous sodium hydroxide (8.0 g in 75 mL of water) in a closed stainless steel reactor was heated in an oil bath for 2 h at 170–180 °C. The reactor was cooled in an ice-bath and opened. A precipitate was isolated, washed with cold water (3  $\times$  20 mL) and dried to give diaminofurazan 6, as colorless needles, 13.0 g (70%), mp 179–180 °C after recrystallization from water (lit. [7] mp 178.5–180.5 °C).

*Diaminoazofurazan 7* [9]

Diaminofurazan 6 (8.0 g, 80 mmol) was added to a stirred solution of ammonium persulfate (120.0 g) in water (160 mL) at 70 °C and stirred for 1.5 h. A precipitate was isolated and washed with hot water to give the diamine 7 as an orange amorphous solid 3.8 g (49%), dec 320 °C (lit. [9] dec 325 °C).

*Diazidoazofurazan 8*

A solution of diaminoazofurazan 7 (4.0 g, 20.4 mmol) in concentrated sulfuric acid (20 mL) was added to a solution of sodium nitrite (4 g) in concentrated sulfuric acid (60 mL) at 0–5 °C and diluted with glacial acetic acid (80 mL) added dropwise at 0–5 °C with stirring. A solution of sodium azide (4 g) in water (50 mL) was added slowly to keep the mixture between 0 and 5 °C. After storage for 30 min with stirring at the same temperature the mixture was poured onto crushed ice (400 g). A yellow solid was isolated and washed with cold water (3 × 25 mL) and dried. Elution of the crude product through a column (silica gel, pentane/dichloromethane 9:1) afforded the diazide 8 as yellow platelets 2.3 g (46%), dec 68 °C (pentane/dichloromethane). EI–MS *m/z* (relative intensity): 248 (5) M<sup>+</sup>, 138 (43), 69 (56), 54 (42), 52 (100), 43 (50), 41 (60), 38 (53). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 156.48, 147.30; a third signal at δ 166.00 was observed after refrigeration for 4 days and was attributed to a partial conversion of the diazide 8 into the azide 5. Conversion of a neat sample of the diazide 8 to the azide 5 was complete after 7 d, 30 °C. This facile thermolysis of the diazide 8 (C<sub>4</sub>N<sub>12</sub>O<sub>2</sub>) precluded its elemental analysis.

*5-[4-Azido-(1,2,5)oxadiazoly]-5H[1,2,3]-triazolo[4,5-c][1,2,5]oxadiazole 5*

The diazide 8 (1.5 g, 6.0 mmol) was heated (80 °C) in acetonitrile (25 mL) for 6 h. Removal of the solvent gave a colorless residue. After recrystallization from pentane/dichloromethane the azide 5 was obtained as colorless needles 1.3 g (98%), mp 103–104 °C. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 165.9, 149.0, 146.2. EI–MS *m/z* (relative intensity): 220, M<sup>+</sup>, (38), 138 (53), 69 (16), 54 (73), 52 (100), 38 (49). Anal. calcd for C<sub>4</sub>N<sub>10</sub>O<sub>2</sub>: C, 21.82; N, 63.64. Found: C, 21.50, 21.87; N,

63.66, 63.67.

When the azide 5 (0.22 g) was heated at 150–160 °C in a short-path distillation assembly it was collected as a condensate of colorless needles shown to be the unchanged azide identified by IR, tlc and mp. Thermolyses in solvents, e.g., benzene, decalin, and *N,N*-dimethylformamide, at temperatures ranging from 70 to 200 °C for 3 to 8 h gave intractable material. A solution of the azide 5 (1.0 g, 4.5 mmol) in benzene (200 mL) was irradiated at 300 nm for 36 h as the disappearance of the azide was monitored by tlc. After removal of the solvent chromatographic separation of a brown solid residue (silica gel column, pentane) gave an unidentified material isolated as colorless needles, 100 mg, mp 50–51 °C. IR (KBr):  $\nu/\text{cm}^{-1}$  2145, 1584, 1549, 1515, 1466, 1389, 1338, 1312, 1297, 1173, 992, 925, 889, 776, 716, 688, 588, 530 and 510.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.48–7.95;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  131.08, 129.08, 127.70, 124.24. EI-MS,  $m/z$  (relative intensity): 188 (2), 187 (20), 103 (13), 77 (53), 51 (19), 30 (100). Anal. calcd for  $\text{C}_9\text{H}_7\text{N}_5\text{O}$  (mw 201): C, 53.73; H, 3.48; N, 34.83. Found: C, 53.31; H, 3.40; N, 34.18. The replacement of benzene with ethanol or acetonitrile led to intractable material.

*5-[4-Amino-(1,2,5)oxadiazoly]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole 13*

To a suspension of stannous chloride (2.20 g, 11.6 mmol) in methanol (50 mL), the azide 6 (1.60 g, 7.3 mmol) was added in small portions at room temperature with stirring. After stirring for 2 h at the same temperature methanol was removed and the residue was eluted through a column (silica gel, pentane/dichloromethane 2:1) to obtain yellow needles of the amine 13 1.05 g (74%), mp 132–133 °C.  $^1\text{H}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  7.17 (s);  $^{13}\text{C}$  NMR ( $\text{DMSO-}d_6$ ):  $\delta$  165.44, 151.44, 145.55. Anal. calcd for  $\text{C}_4\text{H}_2\text{N}_8\text{O}_2$ : C, 24.74; H, 1.03; N, 57.73. Found: C, 24.93; H, 1.04; N, 57.34.

*5-[4-Nitro-(1,2,5)oxadiazoly]-5H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole (NOTO) 1*

A solution of the amine 13 (0.60 g, 3.1 mmol) in concentrated sulfuric acid (7.80 g) was added to a suspension of hydrogen peroxide (30%, 4.80 g) and ammonium persulfate (3.90 g) at 18–25



°C with stirring. The reaction mixture was stirred for 2 h at 30–35 °C. It was then diluted with ice-water (50 mL) and extracted with dichloromethane (3 × 40 mL). The organic extracts were washed with aqueous sodium carbonate (10%, 3 × 15 mL) and dried (MgSO<sub>4</sub>). Evaporation of the solvent gave a viscous liquid product which on column chromatography (neutral aluminum oxide, pentane/dichloromethane 19:1) afforded NOTO 1 0.21 g (31%) as a yellow-orange oil bp 160–165 °C (determined in a melting point capillary tube). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 165.91, 153.60, 146.19. Anal. calcd for C<sub>4</sub>N<sub>8</sub>O<sub>4</sub>: C, 21.44; N, 50.00. Found: C, 21.62; N, 49.45.

*5-[4-Triphenylphosphorimino-(1,2,5)oxadiazoly]-5H[1,2,3]triazolo[4,5-c][1,2,5]oxadiazole 9*  
To a solution of triphenylphosphine (0.27 g, 1.0 mmol) in tetrahydrofuran (15 mL) 0.03 g of water was added. The azide 5 (0.22 g, 1.0 mmol) was added at room temperature, the reaction mixture was stirred for 12 h at room temperature, and the solvent was removed by evaporation. The residue recrystallized from ether/petroleum ether to give the phosphinimine 9 as orange needles 0.11 g (24%) mp 177–178 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.56–7.86 (m); <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 166.02, 153.60, 133.02, 132.91, 129.05, 128.88, 127.64, 126.30. Anal. calcd for C<sub>22</sub>H<sub>15</sub>N<sub>8</sub>O<sub>2</sub>P: C, 58.15; H, 3.33; N, 24.67. Found: C, 57.91; H, 3.34; N, 24.23.

An adaptation of a general procedure for the reduction of an azido group to an amino group by treatment with one equivalent of triphenylphosphine in the presence of a slight excess of water in tetrahydrofuran [16] was unsuccessful when applied to the azide 5 and led instead to an intractable mixture in which neither a primary amine nor triphenylphosphine oxide were detected.

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