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Dense Energetic Compounds of C, H, N, and O Atoms IV Nitro and Azidofurazan Derivatives

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ABSTRACT

Both diaminofurazan **5** *(DAF) and diaminoazofurazan* **6** *(DAAF) were converted to 5-(4-amino-1,2,5-oxadiazol-3-yl)-1H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazolium inner salt* **8** *(AMOTO) (25 and 91%) in oxidations with iodobenzene diacetate and to dinitroazoxyfurazan* **13** *(DNAF) (4 and 15%) in oxidations with a mixture of ammonium persulfate and hydrogen peroxide in concentrated sulfuric acid. The intermediacy of diaminoazoxyfurazan* **7** *was supported by its conversion under similar treatment to DNAF (60%). Further oxidation by ammonium persulfate converted AMOTO* **8** *to 5,5'[azobis-(1,2,5-oxadiazole-4,3 - diyl)]bis[1H(1,2,3)triazolo - [4,5-c][1,2,5]oxadiazolium]bis(inner salt)* **10**. *Diazidofurazan* **19** *(tentative assignment) was obtained from DAF* **5** *by tetrazotization followed by treatment with sodium azide. Aminoazido-azofurazan* **16** *was obtained from diazotized DAAF by treatment with sodium azide and was converted to AMOTO* **8** *by an elimination of nitrogen at 25°C. Similar treatment converted tetrazotized DAAF to diazidoazofurazan* **9** *and 5-(4-azido-1,2,5-oxadiazol-3-yl) - 1H -[1,2,3]-triazolo[4,5-c][1,2,5]-oxadiazolium inner salt* **15** *(AZOTO) after evolution of nitrogen. Aminofurazan-2-ONN-azoxyazidofurazan* **17** *(AAAF) was obtained from diazotized diaminoazoxyfurazan* **7** *by treatment with sodium azide. Excellent calculated detonation properties were obtained for DNAF* **13**, *AZOTO* **15**, *and AAAF* **17**.

INTRODUCTION

A density (d) greater than 2.0 g/cc, a detonation velocity (D) near 10 mm/μs, and a detonation pressure (P_{CJ}) over 400 kbar were desired to advance a superior performance as an explosive and/or a propellant from solid state energetic material composed of carbon, hydrogen, nitrogen, and oxygen atoms [1]. Reasonably accurate (±2 to 5%) calculations of d, D, and P_{CJ} values afforded a facile preliminary evaluation of each proposed candidate [2]. A superior performance also needed an efficient balance for intramolecular combustion to carbon oxides, water, and nitrogen [3]. A candidate must show a suitable insensitivity to light, heat, impact, shock, friction, and static charge and resistance to degradation on storage [3].

These properties in insensitive energetic nitroheterocyclic derivatives [4], such as 2,6-dipicrylbenzo[1,2-*d*][4,5-*d'*]bistriazole-4,8-dione **1** dec 430°C [5,6] and tacot **2** dec 378°C [7–9], were presumably augmented by a distinctly characteristic contribution from the *v*-triazole ring. More recently, a similar contribution to stabilization from the furazan ring in 5-(4-nitro-1,2,5-oxadiazol-3-yl)-1*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazolium inner salt **3** [10] (NOTO), a rare example of an energetic liquid composed of C, N, and O atoms exclusively, was recognized [11]. In contrast, dinitrofuroxan **4** (a furazan-*N*-oxide) was dangerously explosive and extreme caution was advised in its handling [12].

The present investigation was undertaken for further examination of furazan derivatives as energetic molecules. Convenience in synthesis was brought about by an improved preparation of the starting material, diaminofurazan **5** (DAF) [11,13].

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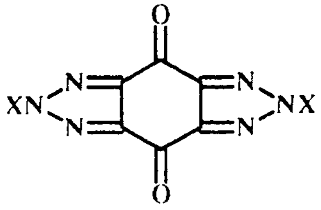
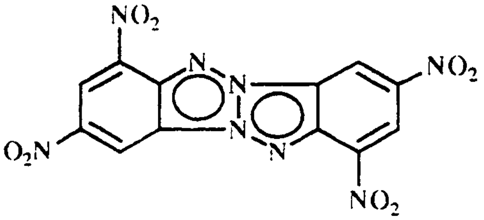
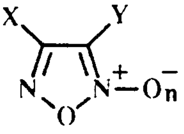


1 X = 2,4,6-$(NO_2)_3C_6H_2$

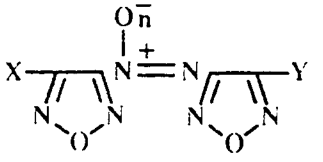


2

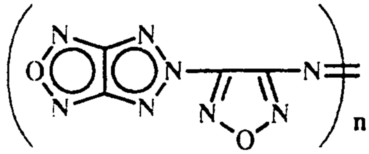
3 X = NO_2
8 X = NH_2
15 X = N_3
18 X = N = $P(OC_2H_5)_3$



4 n = 1, X = Y = NO_2
5 n = 0, X = Y = NH_2
14 n = 0, X = NH_2, Y = N_3
19 n = 0, X = Y = N_3

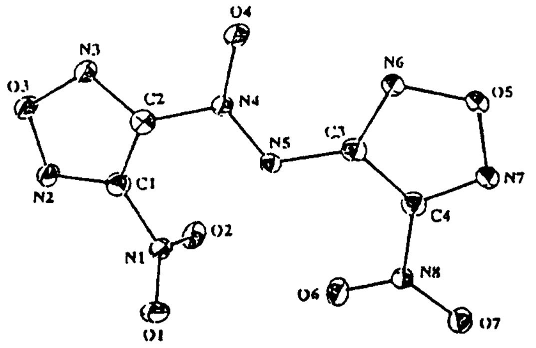


6 n = 0, X = Y = NH_2
7 n = 1, X = Y = NH_2
9 n = 0, X = Y = N_3
13 n = 1, X = Y = NO_2
16 n = 0, X = NH_2, Y = N_3
17 n = 1, X = NH_2, Y = N_3

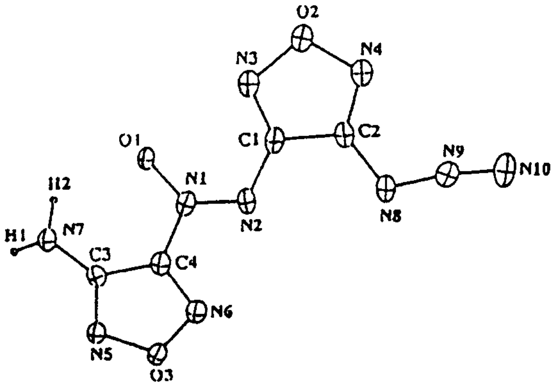


10 n = 2
12 n = 1

11



13 Ortep plot



17 Ortep plot

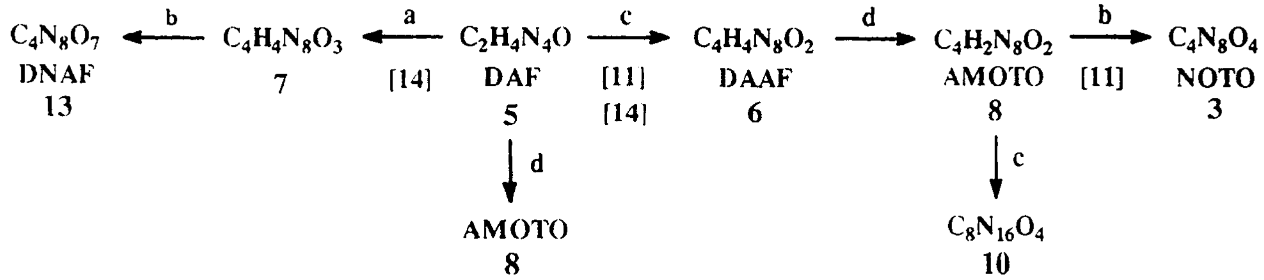
As previously reported, the versatile DAF was oxidized to diaminoazofurazan **6** (DAAF) by treatment with aqueous ammonium persulfate [11,14] and to diaminoazoxyfurazan **7** by treatment with hydrogen peroxide in concentrated sulfuric acid [14].

RESULTS AND DISCUSSION

Nitrofurazan Derivatives (Scheme 1)

DAAF **6** was oxidized by treatment with iodobenzene diacetate to 5-(4-amino-1,2,5-oxadiazol-3-yl)-1*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazolium inner salt **8** [10] (AMOTO) [11], needed for conversion by oxidation in a mixture of hydrogen peroxide and ammonium persulfate in concentrated sulfuric acid to NOTO **3** [11]. This oxidation **6** → **8** bypassed handling of diazidoazofurazan **9**, an unstable intermediate in an alternative synthesis of AMOTO **8** [11]. By a similar treatment with iodobenzene diacetate, DAF **5** was less efficiently converted to AMOTO **8**, presumably *via* the intermediacy of DAAF.

Oxidation by treatment with ammonium per-



a) H_2SO_4, H_2O_2. b) $(NH_4)_2S_2O_8$, H_2O_2, H_2SO_4. c) $(NH_4)_2S_2O_8$. d) $C_6H_5I(O_2CCH_3)_2$.

SCHEME 1

sulfate converted AMOTO **8** to 5,5′[azobis(1,2,5-oxadiazole-4,3-diyl)]bis[1*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]-oxadiazolium]bis(inner salt) **10** [10]. This is a tentative identification, supported by the detection of three nonequivalent carbon atoms, as shown by three ^{13}C NMR signals at δ 165.71, 157.34, and 150.19, and an absence of ^1H NMR signals. Infrared absorption bands, mass spectroscopy data for fragments detected, and elemental analyses were consistent with the assigned structure. There was no detection of an alternative oxidation to NOTO **3** [11] or to difurazano-1,3*a*,4,6*a*-tetraazapentalene **11** [11], a structure limited in principle to two ^{13}C NMR signals. Presumably, an intermediate nitrene **12** underwent dimerization to the inner salt **10** without competition from an intramolecular cyclization to the tetraazapentalene [15]. An impure unstable complex $\mathbf{10}\cdot C_6H_6$ (tentative identification) was obtained when attempts to recrystallize the inner salt **10** from benzene were unsuccessful; the compound **10** was readily recovered from the complex by warming.

Oxidation of diaminoazoxyfurazan **7** to dinitroazoxyfurazan **13** (DNAF) was brought about by treatment with a mixture of hydrogen peroxide and ammonium persulfate in concentrated sulfuric acid. The structure of DNAF, confirmed by an X-ray crystallographic analysis, is shown by the **13** Ortep plot [16]. Similar oxidations of DAF and DAAF less efficiently gave DNAF. Although DNAF gave a violent explosion with flame when struck by a hammer, it showed thermal stability over 270°C and gave calculated detonation properties: d 1.91 g/cc, D 9.78 mm/μs, P_{CJ} 456 kbar.

Azidofurazan Derivatives (Scheme 2)

Most azidofurazan derivatives were sensitive to heat, shock, and friction. Diazonium and tetrazonium salts prepared *in situ* from DAF **5** were converted by treatment with sodium azide to aminoazidofurazan **14** [17] and diazidofurazan **19** (tentative identification), a highly sensitive yellow oil. Similar treatment converted DAAF **6** to aminoazidoazofurazan **16** and diazidoazofurazan **9**. Thermolysis at 25°C converted the monoazide **16** to AMOTO **8** and the diazide **9** to 5-(4-azido-1,2,5-oxadiazol-3-yl)-1*H*-[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazolium inner salt [10] **15** (AZOTO), mp 103–104°C, with thermal stability over 160°C [11]. Further confirmation of the structure of AZOTO was brought about by its conversion to 5-[4-triethylphosphorimino-1, 2, 5-oxadiazol-3-yl]-1*H*-[1, 2, 3]triazolo[4,5*c*]-[1,2,5]oxadiazolium inner salt **18**. Diazotization followed by treatment with sodium azide converted diaminoazoxyfurazan **7** to aminofurazan-2-*ONN*-azoxyazidofurazan **17** (AAAF), a structure confirmed by an X-ray crystallographic analysis and shown in the **17** Ortep plot. Stable azidofurazan derivatives AZOTO **15** and AAAF **17** gave excellent calculated values for detonation properties d (g/cc), D (mm/μs), and P_{CJ} (kbar): **15** 1.81, 9.7, 451; **17** 1.74, 9.4, 426.

EXPERIMENTAL

Instruments included the following: Perkin-Elmer 1600 series FT-IR, Hewlett-Packard 5985 (70 ev) GC-MS, and Varian-Gemini 300 NMR. Solvents were removed by rotary evaporation under reduced pressure unless otherwise indicated. Melting and decomposition points were determined on a Mel-Temp II apparatus and were uncorrected. Elemental analyses were obtained from Galbraith Laboratories, Inc. (Knoxville, TN) and Midwest Micro Lab (Indianapolis, IN). Iodobenzene diacetate was obtained from the Sigma-Aldrich Chemical Company. *Caution*: All of the nitro and azido compounds should be treated as dangerously explosive.

AMOTO 8

DAF **5** (0.50 g, 5 mmol) was added to iodobenzenediacetate (4.40 g, 14 mmol) in acetone (50 mL). After having been stirred at 25°C for 1 hour, the mixture was stirred for 1 hour at 56°C. The solvent was evaporated and the residue was washed with

$$\underset{\mathbf{19}}{C_2N_8O} + \underset{\mathbf{14}}{C_2H_2N_6O} \xleftarrow[\text{[17]}]{\text{a}} \underset{\substack{\text{DAF}\\ \mathbf{5}}}{C_2H_4N_4O} \xrightarrow[\text{[14]}]{\text{b}} \underset{\mathbf{7}}{C_4H_4N_8O_3} \xrightarrow{\text{a}} \underset{\substack{\text{AAAF}\\ \mathbf{17}}}{C_4H_2N_{10}O_3}$$

$$\underset{\substack{\text{DAAF}\\ \mathbf{6}}}{C_4H_4N_8O_2} \xrightarrow{\text{a}} \underset{\mathbf{16}}{C_4H_2N_{10}O_2} \left(\xrightarrow{\text{c}} \underset{\substack{\text{AMOTO}\\ \mathbf{8}}}{C_4H_2N_8O_2}\right) + \underset{\mathbf{9}}{C_4N_{12}O_2} \left(\xrightarrow{\text{c}} \underset{\substack{\text{AZOTO}\\ \mathbf{15}}}{C_4N_{10}O_2}\right)$$

a) HONO/NaN_3. b) H_2SO_4, H_2O_2. c) heat/$-N_2$. d) $(NH_4)_2S_2O_8$, H_2O_2.

SCHEME 2

pentane (2 × 10 mL) and purified by column chromatography (silica gel,pentane/dichloromethane, 1:2) to give AMOTO **8** as yellow needles (0.12 g, 25%), mp 132–133°C (Ref. [11], mp 132–133°C). IR and NMR values agreed with authentic data [11].

DAAF **6** (0.70 g, 3.6 mmol) was added to iodobenzenediacetate (1.57 g, 4.9 mmol) in acetone (50 mL). The mixture was stirred at 25°C for 1 hour and the solvent was removed. The residue was washed with pentane (2 × 10 mL) and purified by column chromatography (silica gel, pentane/dichloromethane, 1:2) to give AMOTO **8** as yellow needles (0.63 g, 91%), mp 132–133°C (Ref. [11], mp 132–133°C). IR and NMR values agreed with authentic data [11].

5,5′-[Azobis(1,2,5-oxadiazole-4,3-diyl)]bis[1H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazolium]bis-(inner salt) 10

AMOTO **8** (1.0 g, 5 mmol) was added to an aqueous solution of ammonium persulfate (7.5 g in 50 mL of water). The mixture was stirred at 70°C for 1 hour and extracted with dichloromethane (3 × 50 mL). The extract was washed with water (50 mL), dried (magnesium sulfate), and evaporated. The residue was purified chromatographically (silica gel, pentane/dichloromethane, 1:1) to obtain the inner salt **10** as light brown needles (0.36 g, 38%), mp 100–102°C (dec). IR (KBr): ν/cm^{-1} 1596 (C=N–O), 1044 (furazan ring). ^{13}C NMR (DMSO-d_6): δ 165.71, 157.34, 150.19. EI-MS *m/z* (%): 68 (4), 54 (6), 52 (6), 42 (1), 38 (5), 30 (100). Anal. calcd for $C_8N_{16}O_4$: C, 25.00; N, 58.33. Found: C, 25.08; N, 57.61.

Attempted recrystallization from benzene gave instead an impure complex tentatively identified as **10**·C_6H_6 and obtained as dark orange needles, mp 78–83°C (dec). IR (KBr): ν/cm^{-1} 1583–607 multiple absorptions were a composite of bands otherwise obtained from the inner salt **10** and benzene. ^{1}H NMR (DMSO-d_6): δ 7.34 (benzene) ^{13}C NMR (DMSO-d_6): δ 165.76, 157.39, and 150.23 (corresponded to the three bands assigned to the inner salt **10**) and 128.28 (benzene). Anal. calcd for $C_{14}H_6N_{16}O_4$: C, 36.37; H, 1.31; N, 48.48. Found: C, 35.06; H, 1.19; N, 47.82. The authentic inner salt **10** was recovered from the complex by heating.

DNAF 13

Diaminoazoxyfurazan **7** (2.12 g, 10 mmol) in concentrated sulfuric acid (25 mL) was added to a stirred mixture of hydrogen peroxide (30%, 30 mL) and ammonium persulfate (25.0 g) at 10–20°C. The mixture was stirred at 50°C for 5 hours and added to ice-cold water (200 mL). A yellow precipitate was isolated, washed with ice-cold water, and dried to give DNAF **13** as light yellow needles (1.65 g, 60%), mp 110–112 °C (hexane/dichloromethane). IR (KBr): ν/cm^{-1} 1572 (C=N–O), 1518 and 1351 (NO_2), 1036 (furazan ring). ^{13}C NMR (acetone-d_6): δ 156.96, 154.68, 153.17, 149.29. EI-MS *m/z* (%): 272 (M$^+$, 0.12), 68 (4), 54 (3), 46 (37), 30 (100). Anal. calcd for $C_4N_8O_7$: C, 17.66; N, 41.18; O, 41.16. Found: C, 17.78; N, 40.49; O, 41.09. A violent explosion with flame was brought about by a hammer blow on DNAF. When heated by an oil bath, a sample contained in a tube boiled at 270°C and condensed on the cooler wall. As shown by IR, tlc, and mp data, the condensate was identical with authentic DNAF.

DAF **5** [11] (1.0 g, 10 mmol) in concentrated sulfuric acid (25 mL) was added to a stirred mixture of hydrogen peroxide (30%, 30 mL) and ammonium persulfate (45.0 g) at 10–20°C. The mixture was stirred at 50°C for 2 hours, added to ice-cold water (200 mL), extracted with pentane (4 × 50 mL), dried (Na_2SO_4), and evaporated to leave DNAF **13** as a light yellow solid (50 mg, 4%), mp 101–103°C. IR values agreed with the authentic data for DNAF.

DAAF **6** [11] (1.0 g, 5 mmol) in concentrated sulfuric acid (13 mL) was added to a stirred mixture of hydrogen peroxide (30%, 15 mL) and ammonium persulfate (13.0 g) at 10–20°C. The mixture was stirred at 70°C for 2 hours, added to ice-cold water (100 mL), extracted with hexane (3 × 30 mL), dried ($MgSO_4$), and evaporated to leave

DNAF **13** as a light yellow solid (0.2 g, 15%), mp 103–105°C. IR values agreed with the authentic data for DNAF.

Aminoazidofurazan **14** *and Diazidofurazan* **19**

A solution of DAF **5** (3.0 g, 30 mmol) in concentrated sulfuric acid (10 mL) at 0–5°C was added to a solution of sodium nitrite (2.1 g, 30 mmol) in concentrated sulfuric acid (30 mL) at 5°C. The mixture was diluted with glacial acetic acid (40 mL) and treated with aqueous sodium azide (3.0 g in 60 mL of water) at 5°C. After having been stirred for 30 minutes, the reaction mixture was poured onto ice (200 g) and extracted with ether (3 × 50 mL). Evaporation gave aminoazidofurazan **14** (1.2 g, 31%), mp 86–87.5°C (Ref. [17], mp 86.5–87.5°C) and the diazide **19** (tentative assignment) as a pale yellow viscous liquid (0.6 g). The liquid was highly sensitive to friction and gave a violent explosion with flame upon scratching with a glass rod. IR (NaCl): ν/cm^{-1} 2301, 2148 (N_3), 1558 (C=N–O), 1018 (furazan ring). Elemental and ^{13}C NMR analyses were not attempted.

Diazidoazofurazan **9** *and Azidoaminoazofurazan* **16**

A solution of sodium nitrite (2.0 g) in concentrated sulfuric acid (30 mL) was added at −10°C to a solution of DAAF **6** [14] (2.0 g, 10 mmol) in concentrated sulfuric acid (14 mL). At 0°C, the mixture was diluted with glacial acetic acid (44 mL), treated with a solution of sodium azide (2.0 g) in water (30 mL), and stirred for 30 minutes. After the mixture had been mixed with crushed ice (500 g), a yellow solid separated and was isolated by filtration and purified by chromatography (silica gel, pentane/dichloromethane, 2:1) to give diazidoazofurazan **9** as yellow platelets (0.62 g, 25%) dec 68°C [11] followed by the azidoamine **16** as a yellow solid (0.60 g, 26%), mp 99–102°C (dec). IR (KBr): ν/cm^{-1} 3471 and 3319 (NH_2), 2247, 2163, and 2130 (N_3), 1622 (C=N–O). ^{1}H NMR (DMSO-d_6): δ 6.87. ^{13}C NMR (DMSO-d_6): δ 157.55, 155.78, 149.29, 148.51. Elemental analyses were precluded since the azide **16** was converted on storage at 25°C for 4 days to AMOTO **8**, identical with an authentic sample [11]. The diazide **9** was similarly converted to AZOTO **15**, identical with an authentic sample [11].

AAAF **17**

A solution of sodium nitrite (1.0 g, 15 mmol) in concentrated sulfuric acid (15 mL) was added to a stirred solution of diaminoazoxyfurazan **7** [14] (1.1 g, 5 mmol) in concentrated sulfuric acid (10 mL) at 0–5°C. While the mixture was kept at 0–5°C, it was diluted with glacial acetic acid (25 mL), treated with a solution of sodium azide (1.0 g, 15 mmol) in water (20 mL), stirred for 45 minutes, and poured onto ice (500 g). A yellow precipitate was isolated, washed with ice-cold water, and purified by chromatography (silica gel, pentane/dichloromethane, 1:1) to give AAAF **17** as bright yellow needles (0.83 g, 70%), mp 149–151°C (dec). IR (KBr): ν/cm^{-1} 3424 and 3308 (NH_2), 2330, 2264, and 2139 (N_3). ^{1}H NMR (DMSO-d_6): δ 7.04. ^{13}C NMR (DMSO-d_6): δ 153.54, 151.78, 151.03, 149.22. Anal. calcd for $C_4H_2N_{10}O_3$: C, 20.17; H, 0.84; N, 58.82. Found: C, 20.58; H, 0.76; N, 58.17.

5-[4-Triethylphosphorimino-1,2,5-oxadiazol-3-yl]-1H-[1,2,3]triazolo[4,5-c][1,2,5]oxadiazolium inner salt **18**

A solution of triethyl phosphite (0.34 g, 2 mmol) in dichloromethane (5 mL) was added at 25°C to a solution of AZOTO **15** [11] (0.44 g, 2 mmol) in dichloromethane (20 mL). The mixture was stirred for 30 minutes and evaporated. The residue was purified by chromatography (silica gel, pentane/dichloromethane, 4:1) to give the inner salt **18** as a yellow solid (0.57 g, 77%), mp 27–28°C. IR (KBr): ν/cm^{-1} 1594 (C=N–O), 1030 (furazan ring). Anal. calcd for $C_{10}H_{15}N_8O_5P$: C, 33.52; H, 4.24; N, 31.27. Found: C, 33.69; H, 4.30; N, 30.99.

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