Picrylamino-substituted Heterocycles. II. Furazans (1,2)

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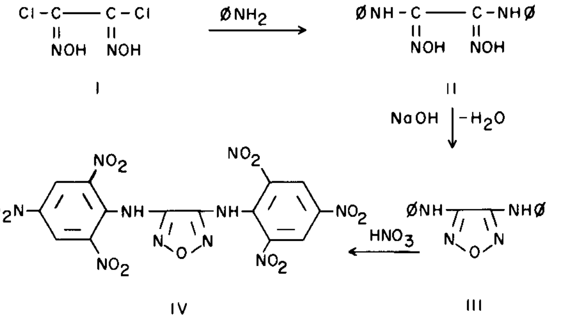
This paper describes the synthesis of the various picrylamino- and nitro-substituted furazans and bifurazanyls. Except for 3,4-bis(picrylamino)furazan, which was obtained by nitrating 3,4-dianilinofurazan, the picrylaminofurazans were prepared by condensing the appropriate aminofurazan with picryl fluoride in the presence of triethylamine. The various aminofurazans were oxidized with peroxytrifluoroacetic acid to the corresponding nitro derivatives.

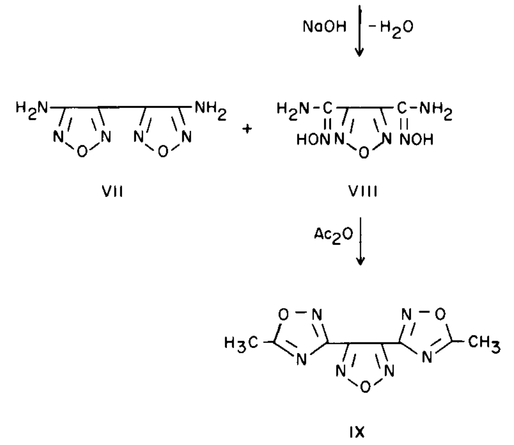
The picrylamino- and nitro-substituted furazans have been synthesized and evaluated as potential high explosives as part of our continuing effort in the field of picrylamino-substituted heterocycles. It was found that dichloroglyoxime could be used as the primary starting material for the synthesis of most of the members of this series.

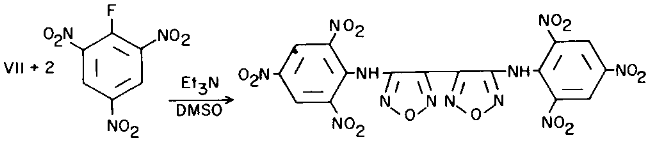
Treatment of dichloroglyoxime (I) with aniline in tetrahydrofuran gave dianilinoglyoxime (II) which, when heated with sodium hydroxide in ethylene glycol, was converted to 3,4-dianilinofurazan (III). Nitration of III with concentrated nitric acid produced 3,4-bis(picrylamino)furazan (IV).

Dicyanoglyoxime (V), obtained from the reaction of dichloroglyoxime with aqueous potassium cyanide, reacted with two molecules of hydroxylamine to yield 1,4-diamino-1,2,3,4-tetraoximinobutane (VI) (3). The diaminotetraoxime, when heated with aqueous sodium hydroxide, was dehydrated to a mixture of 4,4′-diamino-3,3′-bifurazanyl (VII) and furazan-3,4-dicarboxamidoxime (VIII). The structure of VIII was confirmed by its reaction with acetic anhydride to form 3,4-bis(5-methyl-1,2,4-oxadiazol-3-yl)furazan (IX). The proton magnetic resonance spectrum of IX in carbon tetrachloride consists of a singlet at $\delta = 2.72$ p.p.m.

Treatment of VII with two equivalents of picryl fluoride (X) in the presence of triethylamine in dimethyl sulfoxide gave 4,4′-bis(picrylamino)-3,3′-bifurazanyl (XI). When X was treated with an excess of VII in the presence of triethylamine in dimethyl sulfoxide, 4-amino-4′-picrylamino-3,3′-bifurazanyl (XII) was obtained. 4-Nitro-4′-picrylamino-3,3′-bifurazanyl (XIII) resulted when XII was subjected to oxidation by peroxytrifluoroacetic acid. Oxidation of VII with peroxytrifluoroacetic acid gave the sensitive explosive 4,4′-dinitro-3,3′-bifurazanyl (XIV).







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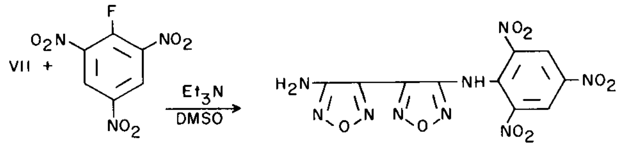

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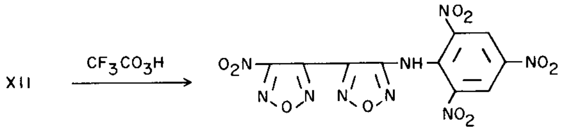

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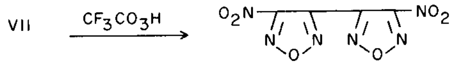

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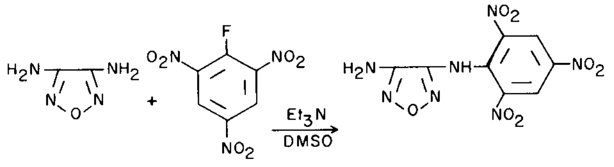
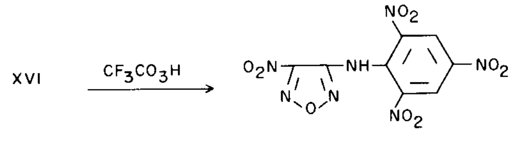


XV X XVI



XVII

3,4-Diaminofurazan (XV) (4), obtained by dehydrating diaminoglyoxime, was treated with an equivalent amount of X in the presence of triethylamine in dimethyl sulfoxide to give 3-amino-4-picrylaminofurazan (XVI). XVI was converted to 3-nitro-4-picrylaminofurazan (XVII) by oxidation with peroxytrifluoroacetic acid.

When Parker treated XV with peroxytrifluoroacetic acid, 3-amino-4-nitrofurazan was obtained (4). Although a large excess of oxidant was employed, no 3,4-dinitrofurazan could be isolated.

The physical and explosive properties of the picrylamino- and nitro-substituted furazans are summarized in Table I, and the proton magnetic resonance data for these compounds are tabulated in Table II.

EXPERIMENTAL (5)

Dianilinoglyoxime (II).

Dichloroglyoxime (6) (15.7 g., 0.10 mole) and aniline (37.2 g., 0.40 mole) were dissolved in 200 ml. of tetrahydrofuran and the resulting solution was refluxed for 3 hours. The aniline hydrochloride was removed from the cooled reaction mixture by filtration and the filtrate was boiled with Norite. After the Norite had been removed by filtration, the solution was diluted with petroleum ether (b.p. 30-60°) until no more product precipitated. The solid was collected by filtration and dried to give 25.6 g. (95%) of crude dianilinoglyoxime, m.p. 205° dec. The crude product was crystallized from ethanol to give 9.2 g. of pure material, m.p. 217° dec. [lit. (7) m.p. 218° dec.]. It was found that the crude product was sufficiently pure for the preparation of 3,4-dianilinofurazan.

3,4-Dianilinofurazan (III).

Dianilinoglyoxime (13.5 g., 0.05 mole) was added to a solution of 2.0 g. (0.05 mole) of sodium hydroxide in 150 ml. of ethylene glycol and the resulting mixture was heated at 140° for 2 hours. The solution was cooled to 25° and poured into 500 ml. of ice and water. The solid was collected by filtration and crystallized from ethanol-water to yield 4.64 g. (37%) of 3,4-dianilinofurazan, m.p. 221-222°.

Anal. Calcd. for $C_{14}H_{12}N_4O$: C, 66.65; H, 4.79; N, 22.21. Found: C, 66.65; H, 4.87; N, 21.90.

3,4-bis(Picrylamino)furazan (IV).

3,4-Dianilinofurazan (2.00 g., 0.00794 mole) was added slowly to 25 ml. of concentrated nitric acid at 25°. After the mixture was stirred at 25° for 30 minutes, it was gradually heated to 90° and held at this temperature for 2 hours. The mixture was cooled with an ice bath to 0° and the crystals were collected by filtration, washed repeatedly with water, and dried to give 3.55 g. (86%) of 3,4-bis(picrylamino)furazan, m.p. 250° dec. Recrystallization of the product from acetone-ethanol did not raise its melting point.

Anal. Calcd. for $C_{14}H_6N_{10}O_{13}$: C, 32.20; H, 1.16; N, 26.82. Found: C, 32.49; H, 1.40; N, 26.45.

Dicyanoglyoxime (V) (3).

A solution of potassium cyanide (58.5 g., 0.90 mole) in 300 ml. of water was cooled to below 0° with an ice-salt bath and dichloroglyoxime (31.4 g., 0.20 mole) was added at such a rate that the temperature did not exceed 10°. After the dichloroglyoxime had dissolved, the cooling bath was removed, and the dark mixture was allowed to warm to 20°. The mixture was filtered and the filtrate was acidified to *p*H 2 with concentrated sulfuric acid while being cooled with an ice bath, then chilled to 0°. The dark solid which crystallized from the solution was collected by filtration and dissolved in 200 ml. of hot water. The resulting dark solution was treated with Norite and filtered while hot. The filtrate was cooled to 0° and the hydrated product was collected by filtration and dried in a vacuum desiccator over silica gel to yield 17.0 g. (61%) of dicyanoglyoxime, m.p. 141° dec. [lit. (3) m.p. 145° dec.].

TABLE I

Physical and Explosive Properties of the Picrylamino- and Nitro-substituted Furazans

Compound	m.p.	Thermal Stability (a)	Crystal Density (g./ml.)	Impact Sensitivity (b)
3,4-bis(Picrylamino)-furazan	250° dec.	230°	1.86	71 cm.
3-Nitro-4-picrylamino-furazan	181° dec.	180°	1.81	60 cm.
4,4′-bis(Picrylamino)-3,3′-bifurazanyl	315° dec.	310°	1.81	79 cm.
4-Nitro-4′-picrylamino-3,3′-bifurazanyl	120°	160°	1.77	---- (c)
4,4′-Dinitro-3,3′-bifurazanyl	85°	250°	1.85	12 cm.

(a) Determined by differential thermal analysis at 10°/minute except that for 4,4′-dinitro-3,3′-bifurazanyl, which was determined by differential scanning calorimetry with a sealed sample container.

(b) Determined with the LASL Type 12 machine (2.5 kg. weight, sample on sandpaper). The 50% points of several common explosives are: PETN, 11 cm.; RDX, 23 cm.; TNT, 160 cm.

(c) Sufficient material for complete impact sensitivity determination was not prepared; however, several samples failed to detonate at 50 cm. while a violent reaction occurred at 100 cm.

TABLE II

Proton Magnetic Resonance Data for the Picrylamino- and Nitro-substituted Furazans (a)

Compound	δ (p.p.m.)		Ratio
	N-H	Ar-H	(Ar-H/N-H)
3,4-bis(Picrylamino)-furazan	9.88	9.25	2 : 1
3-Nitro-4-picrylamino furazan	10.33	9.25	2 : 1
4,4′-bis(Picrylamino)-3,3′-bifurazanyl	10.35	9.25	2 : 1
4-Nitro-4′-picrylamino-3,3′-bifurazanyl	10.27	9.25	2 : 1

(a) Determined with a Varian A-60A spectrometer as dioxane solutions using tetramethylsilane as an internal standard.

1,4-Diamino-1,2,3,4-tetraoximinobutane (VI) (3).

A mixture of hydroxylamine (0.80 mole) and dicyanoglyoxime (27.6 g., 0.20 mole) in 350 ml. of water was heated at 60° for 1.5 hours. The reaction mixture was cooled with an ice bath and the solid was removed by filtration, washed with water, and dried. The yield of 1,4-diamino-1,2,3,4-tetraoximinobutane was 16.3 g., m.p. 180-181° dec. [lit. (3) m.p. 181-182° dec.]. The filtrate was carefully acidified with hydrochloric acid to *p*H 5 to give an additional 15.2 g. of product, m.p. 179-180° dec. The combined yield was 31.5 g. (77%).

4,4′-Diamino-3,3′-bifurazanyl (VII) and Furazan-3,4-dicarboxamidoxime (VIII).

1,4-Diamino-1,2,3,4-tetraoximinobutane (17.7 g., 0.087 mole) was added to a solution of sodium hydroxide (3.5 g., 0.087 mole) in 50 ml. of water in a soda bottle. The mixture was heated to its boiling point with an oil bath, the bottle was capped, and the bath temperature was raised to 135° for 1.5 hours, the oil bath was removed and the mixture was removed and the mixture was allowed to cool to room temperature. The bottle was opened and the crystals were collected by filtration, washed with water, and dried to yield 2.95 g. (20%) of pure 4,4′-diamino-3,3′-bifurazanyl, m.p. 305° dec.

Anal. Calcd. for $C_4H_4N_6O_2$: C, 28.58; H, 2.40; N, 49.99. Found: C, 28.25; H, 2.36; N, 50.09.

The filtrate was carefully acidified with hydrochloric acid to *p*H 6 and placed in the refrigerator overnight. The product which crystallized from the solution was collected by filtration and recrystallized from water to give 5.54 g. (34%) of furazan-3,4-dicarboxamidoxime, m.p. 177-178° dec.

Anal. Calcd. for $C_4H_6N_6O_3$: C, 25.81; H, 3.25; H, 45.15. Found: C, 25.68; H, 3.27; N, 45.18.

3,4-bis(5-Methyl-1,2,4-oxadiazol-3-yl)furazan (IX).

A mixture of furazan-3,4-dicarboxamidoxime (1.86 g., 0.01 mole) and acetic anhydride (25.5 g., 0.25 mole) was refluxed for 6 hours, then poured into 150 ml. of water. After the excess acetic anhydride was hydrolyzed, the solution was cooled with an ice bath while sodium hydroxide (16.0 g., 0.40 mole) was added with stirring. The resulting mixture was stored at 0° overnight. The product was collected by filtration and recrystallized twice from methanol-water to yield 0.52 g. (22%) of 3,4-bis(5-methyl-1,2,4-oxadiazol-3-yl)furazan, m.p. 79°.

Anal. Calcd. for $C_8H_6N_6O_3$: C, 41.03; H, 2.58; N, 35.89. Found: C, 40.63; H, 2.61; N, 35.59.

4,4′-bis(Picrylamino)-3,3′-bifurazanyl (XI).

Picryl fluoride (8) (3.00 g., 0.013 mole) was added to a solution of 4,4′-diamino-3,3′-bifurazanyl (0.84 g., 0.005 mole) and triethylamine (1.8 ml., 0.013 mole) in 15 ml. of anhydrous dimethyl sulfoxide, and the resulting solution, protected from moisture, was heated at 70° for 3 hours. The solution was diluted with 200 ml. of ethanol and the product was precipitated by adding 200 ml. of water to the rapidly stirred solution. The crude product was collected by filtration, washed first with water and then with ethanol, and dried. The crude material was recrystallized from acetone-ethanol to give 1.80 g. of 4,4 -bis(picrylamino)-3,3′-bifurazanyl, m.p. 315° dec.

Anal. Calcd. for $C_{16}H_6N_{12}O_{14}$: C, 32.55; H, 1.02; N, 28.48. Found: C, 32.60; H, 1.36; N, 28.35.

The filtrate was concentrated until more product began to crystallize, then chilled in the freezer. A second crop of 0.65 g., m.p. 314° dec., was obtained. The combined yield was 2.45 g. (83%).

4-Amino-4′-picrylamino-3,3′-bifurazanyl (XII).

Picryl fluoride (8) (1.15 g., 0.005 mole) was added to a solution of 4,4′-diamino-3,3′-bifurazanyl (1.26 g., 0.0075 mole) and triethylamine (0.7 ml., 0.005 mole) in 50 ml. of anhydrous dimethyl sulfoxide, and the resulting solution, protected from moisture, was heated at 65° for 2 hours. The solution was diluted with 100 ml. of ethanol, then 400 ml. of water was added with rapid stirring. The precipitated solid was collected by filtration, washed with water, and dried. The material was stirred with 350 ml. of methylene chloride for 30 minutes and the undissolved 4,4′-diamino-3,3′-bifurazanyl was removed by filtration. The filtrate was evaporated to dryness under reduced pressure and the residue was crystallized from methanol-water to yield 1.04 g. (56%) of 4-amino-4′-picrylamino-3,3′-bifurazanyl, m.p. 222-223°.

Anal. Calcd. for $C_{10}H_5N_9O_8$: C, 31.67; H, 1.33; N, 33.24. Found: C, 31.57; H, 1.50; N, 33.41.

4-Nitro-4′-picrylamino-3,3′-bifurazanyl (XIII).

To a slurry of 90% hydrogen peroxide (2.0 ml., 0.073 mole) in 60 ml. of methylene chloride, trifluoroacetic anhydride (16.5 g., 0.078 mole) was added dropwise with stirring at 5-10° (9). After the exothermic reaction had subsided, 4-amino-4′-picrylamino-3,3′-bifurazanyl (1.00 g., 0.00264 mole) was added and the mixture was gently refluxed for 20 hours. The resulting solution was cautiously neutralized with aqueous sodium bicarbonate and the layers were separated. The aqueous layer was extracted with 20 ml. of methylene chloride and the combined extracts were washed with aqueous sodium bisulfite, then dried over anhydrous magnesium sulfate. The solution was evaporated to dryness under reduced pressure and the residue was crystallized from methanol-water to give 0.65 g. of slightly impure product, m.p. 113-117°. A stream of air was passed over the filtrate, thereby concentrating it to yield a second crop of 0.20 g. of 4-nitro-4′-picrylamino-3,3′-bifurazanyl, m.p. 120°.

Anal. Calcd. for $C_{10}H_3N_9O_{10}$: C, 29.35; H, 0.74; N, 30.81. Found: C, 28.93; H, 0.87; N, 30.51.

The combined yield was 0.85 g. (79%). The infrared spectra of the two crops were identical. The melting point of the first crop could be raised to 120° by chromatographing it over silica gel with chloroform.

4,4′-Dinitro-3,3′-bifurazanyl (XIV).

To a slurry of 90% hydrogen peroxide (2.5 ml., 0.091 mole) in 50 ml. of methylene chloride, trifluoroacetic anhydride (20.2 g., 0.096 mole) was added dropwise with stirring at 5-10° (9). After the exothermic reaction had subsided, 4,4′-diamino-3,3′-bifurazanyl (0.84 g., 0.005 mole) was added and the mixture was gently refluxed for 20 hours. The resulting solution was worked up as described for the preparation of XIII. The residue obtained from the evaporation of the methylene chloride extracts was dissolved in the minimum amount of acetone and the solution was injected into the preparative gas chromatograph in 0.5 ml. portions. The column employed was packed with 30% silicon rubber on 60-80 mesh acid-washed Chromosorb W and was 20′ by 3/8″. The column temperature was 140° and the flow rate was 200 ml./minute. The product collected was crystallized from hexane to yield 0.40 g. (35%) of 4,4′-dinitro-3,3′-bifurazanyl, m.p. 85°.

Anal. Calcd. for $C_4N_6O_6$: C, 21.06; H, 0.00; N, 36.85. Found: C, 21.01; H, 0.25; N, 36.78.

3,4-Diaminofurazan (XV) (4).

Diaminoglyoxime (10) (11.8 g., 0.10 mole) was added to a solution of sodium hydroxide (4.0 g., 0.10 mole) in 50 ml. of water in a soda bottle. The mixture was heated to its boiling point with an oil bath, the bottle was capped, and the bath temperature was raised to 165°. After the mixture had been heated at 165° for 4 hours it was allowed to cool to room temperature, then chilled with an ice bath. The vessel was opened cautiously and the solid was collected by filtration. The product was recrystallized twice from water to give 2.00 g. (20%) of 3,4-diaminofurazan, m.p. 180°.

Anal. Calcd. for $C_2H_4N_4O$: C, 24.00; H, 4.03; N, 55.98. Found: C, 23.99; H, 4.02; N, 55.90.

3-Amino-4-picrylaminofurazan (XVI).

Picryl fluoride (8) (2.31 g., 0.01 mole) was added to a solution of 3,4-diaminofurazan (4) (1.00 g., 0.01 mole) and triethylamine (1.4 ml., 0.01 mole) in 15 ml. of anhydrous dimethyl sulfoxide, and the resulting solution, protected from moisture, was heated at 65° for 2 hours. The solution was diluted with 100 ml. of ethanol, then 400 ml. of water was added with rapid stirring. The product separated as a black tar. The solvent mixture was carefully decanted and the tar was dissolved in boiling acetone. After the solution had been treated with Norite, it was diluted with an equal volume of ethanol, concentrated until crystallization began to occur, then chilled in the freezer. The crystalline material was collected by filtration and dried to give 0.37 g. of 3-amino-4-picrylaminofurazan, m.p. 220° dec.

Anal. Calcd. for $C_8H_5N_7O_7$: C, 30.88; H, 1.62; N, 31.51. Found: C, 31.03; H, 1.25; N, 31.07.

The boiling filtrate was diluted with water until it became cloudy and was cooled in the freezer. A second crop of 0.60 g., m.p. 218° dec., was obtained. The combined yield was 0.97 g. (31%).

3-Nitro-4-picrylaminofurazan (XVII).

To a slurry of 90% hydrogen peroxide (2.0 ml., 0.073 mole) in 40 ml. of methylene chloride and 20 ml. of ethyl acetate was added trifluoroacetic anhydride (16.5 g., 0.078 mole) dropwise with stirring at 5-10° (9). After the exothermic reaction had subsided, 3-amino-4-picrylaminofurazan (1.00 g., 0.032 mole) was added and the mixture was refluxed gently for 20 hours. The resulting solution was worked up as described for the preparation of XIII. The residue obtained from the evaporation of the methylene chloride extracts was chromatographed over silica gel with benzene. The eluate was concentrated to about 100 ml., heptane (25 ml.) was added, and the concentration was continued until crystallization began to occur. After the solution had been chilled in the freezer, the crystals were collected by filtration and dried to yield 0.46 g. (42%) of 3-nitro-4-picrylaminofurazan, m.p. 181° dec.

Anal. Calcd. for $C_8H_3N_7O_9$: C, 28.16; H, 0.89; N, 28.74. Found: C, 28.01; H, 0.83; N, 28.56.

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