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THE CHEMISTRY OF FURAZANO-[3,4-*b*]PYRAZINE.* 7.** PROPERTIES OF 5,6-DIAMINO- AND 5,6-DIHYDRAZINO-FURAZANO[3,4-*b*]PYRAZINE

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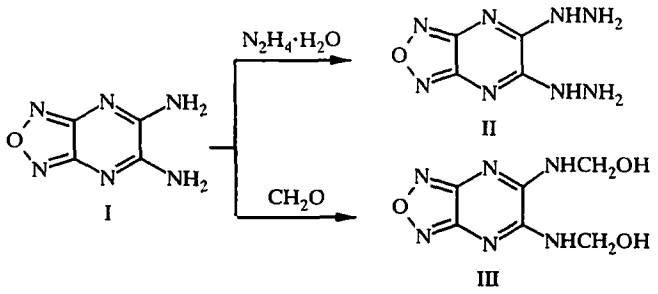
The reactions of 5,6-diamino- and 5,6-dihydrazinofurazano[3,4-b]pyrazine that produce polycyclic or highly reactive compounds are reviewed. The furazan ring has a deactivating effect on the amine functions of these compounds.

The construction of planar polycondensed molecules based on furazano[3,4-*b*]pyrazine is a promising although little studied path to the synthesis of highly reactive and variously biologically active compounds. In continuation of studies on the chemistry of furazano[3,4-*b*]pyrazine [1-12], we report several reactions of 5,6-diaminofurazano[3,4-*b*]pyrazine (I) [2, 6, 11] and 5,6-dihydrazinofurazano[3,4-*b*]pyrazine (II) [2, 6] that produce polycondensed compounds.

The furazan ring is a strong electron acceptor. Therefore, reacting it with amines considerably reduces their reactivity. As a result, diamine I does not react with such electrophiles as alkyl and aryl halides, haloketones, diethyl carbonate, dichloroglyoxime, and 1,1'-thiocarbonyldiimidazole, does not form stable salts of strong acids, and does not give normal acylation products. On the other hand, the distinct electron-accepting properties enhance nucleophilic attack on the pyrazine ring, as a result of which substitution of the amino group by a hydrazino group that is rather untypical of aromatic compounds becomes possible:

Scheme 1



* Dedicated to Professor Henk van der Plas on his 70th birthday.

** For No. 6, see [1].

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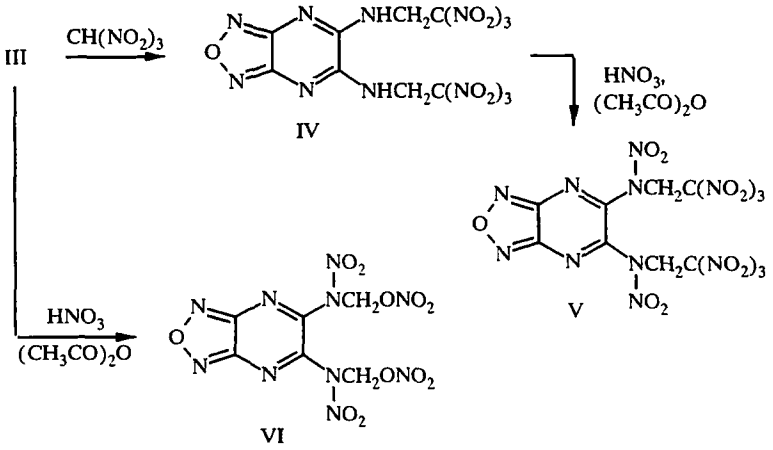
The increased "acidity" of amine I also stabilizes α-aminocarbinol III. It is interesting that only the monoaminocarbinol derivative (according to the literature [13]) could be isolated from the reaction of diaminofurazan with formaldehyde. Bis-α-aminocarbinol of diaminofurazan could not be isolated pure owing to its high reactivity. It polymerized as soon as it formed.

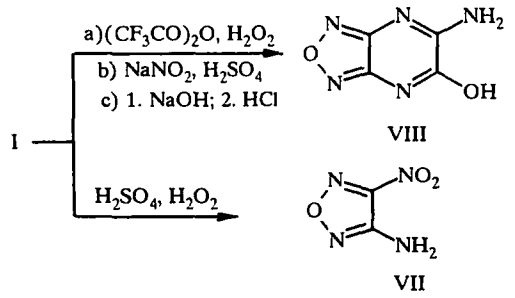
The reaction of bisaminocarbinol III with trinitromethane produces the Mannich base IV, which was further nitrated into V. Amino alcohol III undergoes nitration at both the oxygen and nitrogen atoms to give the nitroxymethylnitramine VI (Scheme 2).

Scheme 2



Oxidation of diamine I under mild conditions is accompanied by deamination of one of the amino groups (a). Exhaustive oxidation (Caro acid) destroys the pyrazine ring and produces 3-amino-4-nitrofurazan (VII). The only product of nitrosation (b) or hydrolysis (c) (1 equiv. of NaOH) of I is 5-amino-6-hydroxyfurazano[3,4-*b*]-pyrazine (VIII) [1, 7] (Scheme 3).

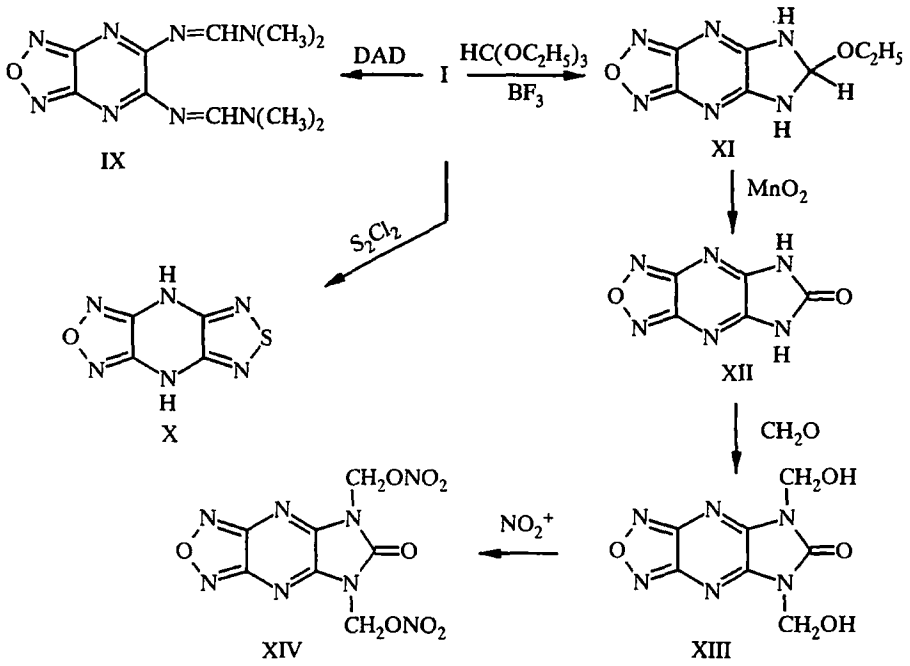
Scheme 3



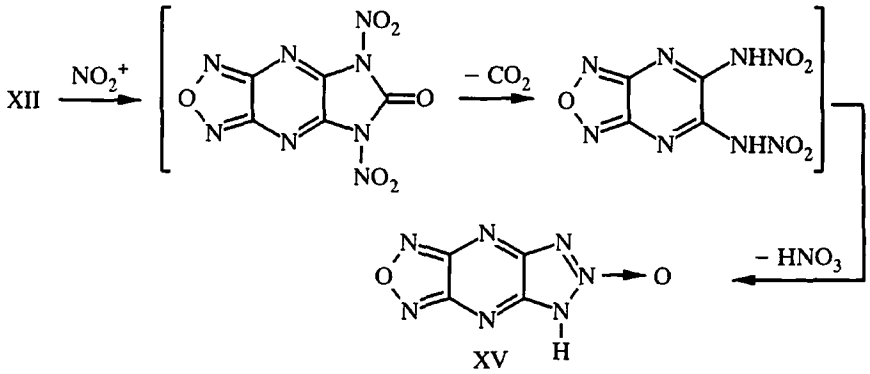
Such a strong electrophile as the dimethylformamide diethyl acetal (DAD) reacts with diamine I to give the corresponding amidine IX. The reaction of diamine I with sulfur monochloride leads to cyclization to thiadiazole X. The reaction of I with orthoformic ester that gives the cyclic derivative XI occurs in the presence of Lewis acids.

The ethoxy derivative XI is oxidized in the presence of manganese dioxide into imidazolone XII. Its oxymethylation and subsequent nitration lead to formation of the dinitrate XIV (Scheme 4). Investigations have demonstrated that imidazolone XII is not nitrated and remains unchanged in a sulfuric/nitric acid mixture (20 h at 20°C) or in a mixture of nitric acid and trifluoroacetic anhydride (20 h at 4°C). Only traces of 1,2,3-triazolo[4,5-*e*]-furazano[3,4-*b*]pyrazine-6-oxide (XV) [2, 8, 11] are observed in the reaction mixture. These may be formed according to Scheme 5.

Scheme 4



Scheme 5

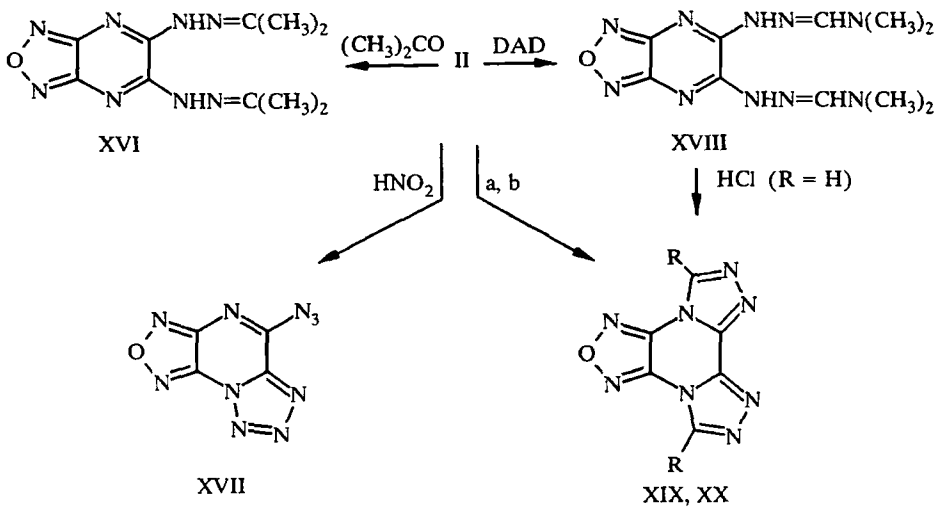


Dihydrazine II readily reacts with ketones to give the corresponding hydrazones XVI. A study of nitrosation of II found that the single reaction product is 7-azidofurazano[3,4-*b*]tetrazolo[1,2-*d*]pyrazine (XVII) [2, 5] (Scheme 6)

The amidrazone XVIII, which is prepared by condensation of dihydrazine II with dimethylformamide diethyl acetal, cyclizes upon thermolysis (200°C) or boiling in hydrochloric acid solution to give the tetracyclic derivative XIX. A one-step method for preparing XIX by boiling dihydrazine II in solution of formic acid was developed in order to simplify the synthesis. The reaction with acetic anhydride proceeds analogously to give the corresponding methyl derivative XX (Scheme 6).

An X-ray structure analysis of the derivative XIX was performed in order to confirm the structure. The results indicate that the molecule is planar, d_{calc} = 1.73 g/cm^3, and the relative index of aromaticity is relatively high (J_a = 56) [4]. Figure 1 shows a general view of XIX. Tables 2 and 3 list the structural characteristics. The packing of molecules in the crystal reveals the occurence of a weak intermolecular hydrogen bond $C_{(8)}$–H···$N_{(9)}$ ($C_{(8)}$ ···$N_{(9)}$ = 3.26 Å; H···$N_{(9)}$ = 2.20 Å; $C_{(8)}$–H···$N_{(9)}$ = 166.7°).

Scheme 6



a = HCOOH, XIX R = H; b = $(CH_3CO)_2O$, XX R = CH_3

Nitration of XIX by a mixture of trifluoroacetic anhydride and nitric acid produces 4,9-dioxo-5,8-dinitro-1,2,4-triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]pyrazine (XXI) (Scheme 7).

Nitramide XXI is unstable. It quantitatively converts to the corresponding amide XXII upon recrystallization from aqueous acetone or heating. Such instability is apparently characteristic of this class of triazoles. In particular, according to the literature, nitration of 6,7-diphenyl-1,2,4-triazolo[4,3-*b*]1,2,4-triazine gives the triazolotriazinone XXIII as the principal product [14].

Oxidation of XX by $KMnO_4$ in acidic medium successively forms the monocarboxylic acid XXIV and then the dicarboxylic acid XXV, a part of which decarboxylates during the reaction to produce the monocarboxylic acid XXVI (Method A) (Scheme 8).

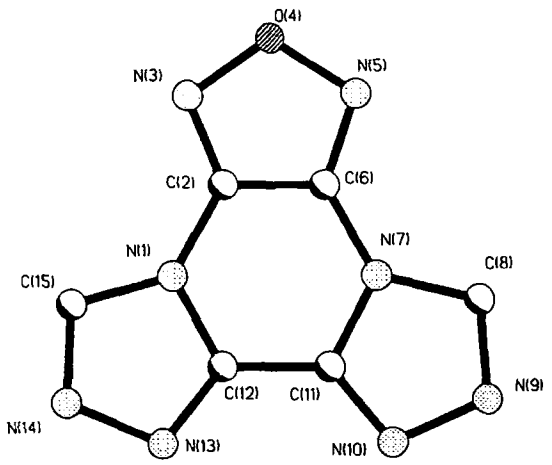


Fig. 1. General view of molecule of compound XIX.

TABLE 1. Characteristics of Compounds III-XXVI

Compound	Empirical formula	mp, °C	IR spectrum, ν, cm^{-1}		PMR spectrum, δ, ppm	Yield, % (method)
			furazan	other groups		
III	$C_6H_8N_6O_3$	260...265 (dec.)	1022	3100; 3400 (NH, OH)	4,89 (4H, q, CH_2); 6,07 (2H, t, OH); 8,58 (2H, t, NH)	92
IV	$C_8H_6N_{12}O_{13}$	174...175 (dec.)	1027	1298; 1600 (NO_2); 3350 (NH)	5,62 (4H, s, CH_2); 8,95 (2H, s, NH)	67
V	$C_8H_4N_{14}O_{17}$	94...95	1038	1295; 1592 (NO_2)	7,11 (4H, s, CH_2)	79
VI	$C_6H_4N_{10}O_{11}$	110...112	1040	1280; 1670 (NO_2); 3050 (CH_2)	6,75 (4H, s, CH_2)	82
IX	$C_{10}H_{14}N_8O$	214...216	1000	1620 (C=N)	3,12 and 3,30 (12H, s, s, CH_3); 8,60 (2H, s, CH)	64
X	$C_4H_2N_6OS$	>260			11,71 (2H, s, NH)	23
XI	$C_7H_8N_6O_2$	175...177	995	1675 (C=N); 3100 (NH)	1,16 (3H, m, CH_3); 3,56 (2H, q, CH_2); 6,60 (1H, s, CH) 10,44 (2H, s, NH)	88
XII	$C_5H_2N_6O_2$	>250	1000	1620 (C=N); 1755; 1780 (C=O) 3480; 3620 (NH)	11,60 (2H, s, NH)	61
XIII	$C_7H_6N_6O_4$	150...155	1020	1615 (C=N); 1755 (C=O); 3430 (OH)	5,31 (4H, s, CH_2); 7,07 (2H, s, OH)	73
XIV	$C_7H_4N_8O_8$	161...162	980	1287; 1670 (ONO_2); 1795 (C=O) 3045 (CH_2)	5,07 (4H, s, CH_2)	86
XVI	$C_{10}H_{14}N_8O$	260...261	965	1730; 1582 (C=N) 3180, 3340, 3550 (NH)	2,03 and 2,19 (12H, s, s, CH_3); 9,8 (2H, s, NH)	81
XVIII	$C_{10}H_{14}N_{10}O$	>200 (dec.)	1000	1620 (C=N); 3220, 3325 (NH)	2,81 and 2,99 (12H, s, s, CH_3); 7,97 (2H, s, CH)	92
XIX	$C_6H_2N_8O$	>300	1002	1590, 1618 (C=N); 3100 (CH)	10,02 (2H, s, CH)	100 (A), 76 (B)
XX	$C_8H_6N_8O$	250...257	990	1590, 1610 (C=N)	2,89 (3H, s, CH_3)	93
XXI	$C_6N_{10}O_7$	140 (dec.)	1004	1290 (NO_2); 1600 (C=N); 1790 (C=O)	—	61
XXII	$C_6H_2N_8O_3$	>300	1000	1740 (C=O); 3470, 3530, 3620 (NH)	12,29 (2H, s, NH)	92
XXIV	$C_8H_4N_8O_3$	218...220	1020	1730 (C=O); 3500 (OH)	2,80 (3H, s, CH_3); 13,10 (1H, s, OH)	31
XXV	$C_8H_2N_8O_5$	270...280	1015	1730 (C=O); 3510 (OH)	13,15 (2H, s, OH)	18 (A), 23 (B)
XXVI	$C_7H_2N_8O_3$	280...282		—	9,95 (1H, s, OH)	28

TABLE 2. Bond Lengths (d) in Molecule of I

Bond	d, Å	Bond	d, Å
$N_{(1)}$–$C_{(2)}$	1,40(2)	$O_{(4)}$–$N_{(5)}$	1,37(1)
$C_{(2)}$–$N_{(3)}$	1,37(1)	$N_{(5)}$–$C_{(6)}$	1,30(2)
$N_{(3)}$–$O_{(4)}$	1,37(1)	$C_{(2)}$–$C_{(6)}$	1,40(1)
$O_{(4)}$–$N_{(5)}$	1,37(1)	$C_{(6)}$–$N_{(7)}$	1,38(2)
$N_{(1)}$–$C_{(12)}$	1,36(1)	$N_{(7)}$–$C_{(8)}$	1,39(1)
$N_{(1)}$–$C_{(15)}$	1,40(1)	$N_{(7)}$–$C_{(11)}$	1,36(2)
$C_{(2)}$–$C_{(6)}$	1.40(1)	$N_{(10)}$–$C_{(11)}$	1,30(2)
$C_{(12)}$–$N_{(13)}$	1,31(2)	$C_{(11)}$–$C_{(12)}$	1,48(1)
$N_{(13)}$–$N_{(14)}$	1,39(1)	$N_{(9)}$–$N_{(10)}$	1.39(2)
$N_{(14)}$–$C_{(15)}$	1,40(2)	$C_{(8)}$–$N_{(9)}$	1,32(2)
$N_{(7)}$–$C_{(8)}$	1,39(1)		

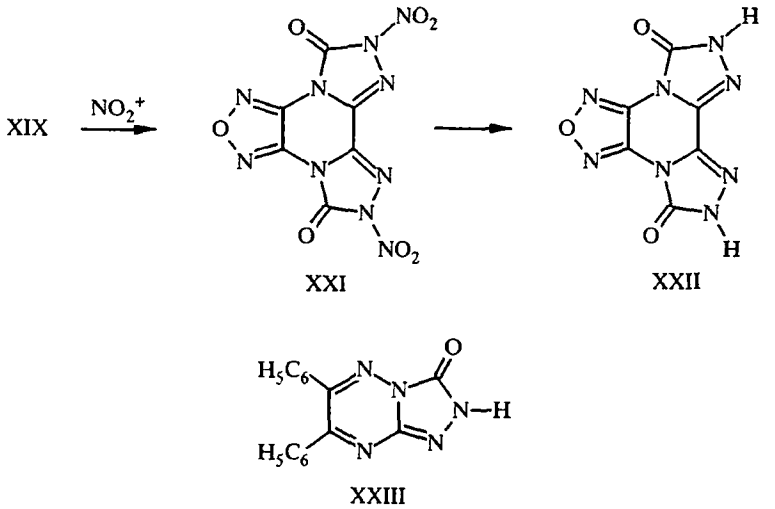
TABLE 3. Bond Angles (ω) in Molecule of I

Angle	ω, deg.	Angle	ω, deg.
$N_{(3)}$–$O_{(4)}$–$N_{(5)}$	113,6(8)	$N_{(1)}$–$C_{(15)}$–$N_{(14)}$	108,1(8)
$C_{(2)}$–$N_{(3)}$–$O_{(4)}$	102,2(9)	$O_{(4)}$–$N_{(5)}$–$C_{(6)}$	103,8(9)
$N_{(1)}$–$C_{(2)}$–$N_{(3)}$	128,6(9)	$C_{(2)}$–$C_{(6)}$–$N_{(7)}$	119,5(8)
$N_{(1)}$–$C_{(2)}$–$C_{(6)}$	119,7(10)	$C_{(2)}$–$C_{(6)}$–$N_{(5)}$	108,7(10)
$N_{(3)}$–$C_{(2)}$–$C_{(6)}$	111.7(10)	$C_{(6)}$–$N_{(7)}$–$C_{(11)}$	122,7(9)
$C_{(12)}$–$N_{(1)}$–$C_{(15)}$	103,9(9)	$C_{(8)}$–$N_{(7)}$–$C_{(11)}$	104,6(9)
$C_{(12)}$–$N_{(1)}$–$C_{(2)}$	121,4(9)	$N_{(7)}$–$C_{(11)}$–$N_{(10)}$	113,2(10)
$N_{(1)}$–$C_{(12)}$–$N_{(13)}$	112,7(9)	$N_{(7)}$–$C_{(11)}$–$C_{(12)}$	117,7(9)
$N_{(1)}$–$C_{(12)}$–$C_{(11)}$	118,9(10)	$C_{(11)}$–$N_{(10)}$–$N_{(9)}$	104,2(9)
$C_{(12)}$–$N_{(13)}$–$N_{(14)}$	104,6(8)	$C_{(8)}$–$N_{(9)}$–$N_{(10)}$	110,5(9)
$N_{(13)}$–$N_{(14)}$–$C_{(15)}$	110,7(8)	$N_{(7)}$–$C_{(8)}$–$N_{(9)}$	107,6(10)

TABLE 4. Coordinates of Nonhydrogen Atoms in Molecule of I

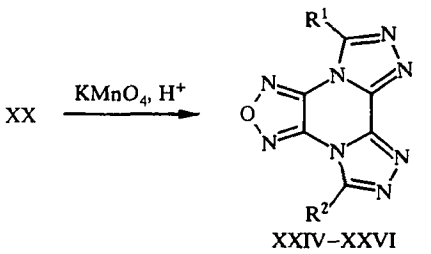
Atom	x	y	z
$N_{(1)}$	1,1857(08)	0,2126(00)	0,3538(09)
$C_{(2)}$	1,5131(09)	0,0268(17)	0,2675(08)
$N_{(3)}$	1,2726(11)	-0,1174(18)	0,2497(10)
$O_{(4)}$	1,1616(12)	-0,2548(15)	0,1498(09)
$N_{(5)}$	0,9772(10)	-0,1929(16)	0,1070(10)
$C_{(6)}$	0,9723(11)	-0,0159(15)	0,1801(09)
$N_{(7)}$	0,8269(11)	0,1232(17)	0,1840(10)
$C_{(8)}$	0,6362(12)	0,1218(16)	0,1148(11)
$N_{(9)}$	0,5609(13)	0,2942(17)	0,1581(10)
$N_{(10)}$	0,6972(13)	0,4129(14)	0,2568(10)
$C_{(11)}$	0,8517(12)	0,3039(18)	0,2686(11)
$C_{(12)}$	1,0436(14)	0,3504(16)	0,3594(12)
$N_{(13)}$	1,0991(13)	0,5104(17)	0,4510(11)
$N_{(14)}$	1,2889(14)	0,4731(18)	0,5104(11)
$C_{(15)}$	1,3423(15)	0,3005(18)	0,4542(12)

Scheme 7



Dicarboxylic acid XXV is also formed by condensation of dihydrazine II with trichloroacetic acid chloride (Method B).

Scheme 8



XXIV R^1 = COOH, R^2 = Me; XXV $R^1 = R^2$ = COOH;
XXVI R^1 = COOH, R^2 = H

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 580B instrument in vaseline oil. PMR spectra were recorded on a Bruker WH-90/DS (90 MHz) spectrometer using DMSO-d_6 solutions and TMS as internal standard. Mass spectra were measured on a VS-50AET (70 eV) spectrometer. The purity of the products was monitored by TLC on Silufol UV-254 plates and by HPLC on a DuPont 850 chromatograph with a Zorbax SIL (4.6×250 mm) column. Derivatograms were recorded on an OD-102 MOM (Hungary) derivatograph. The heating rate was 5 deg/min. The sample mass was 50-80 mg. Elemental analyses for C, H, N, and S were performed on a Carlo-Erba instrument.

X-ray Structure Studies. Single crystals of XIX, $C_6H_2N_8O$ are monoclinic: a = 7.204(4), b = 6.419(2), c = 8.562(3) Å; β = 100.94(4)°; V = 388.7(5) Å^3; M = 202.15; d_{calc} = 1.73 g/cm^3; space group $P2_1$; Z = 2. The intensities of 673 independent reflections were measured on a Syntex $P2_1$ diffractometer (θ/2θ-scanning, Cu Kα-radiation, graphite monochromator, $2\theta_{max}$ = 150°). A total of 613 reflections with $I > 2\sigma(I)$ were used in the calculations. The structure was solved by direct methods and refined by isotropic least-squares methods up to R = 0.088. Tables 1-3 contain the bond lengths and angles and atomic coordinates.

5,6-Di(hydroxymethylamino)furazano[3,4-*b*]pyrazine (III). 5,6-Diaminofurazano[3,4-*b*]-pyrazine I (7.60 g, 0.05 mol) [6] in a mixture of water (5 ml) and formaldehyde solution (37%, 20 ml) was stirred for one day. The solid was filtered off and washed with water (3×20 ml). Colorless crystals of compound III were obtained after drying for one day over P_2O_5. The crystals are poorly soluble in organic solvents. Found, %: C 33.55; H 3.56; N 40.03. $C_6H_8N_6O_3$. Calculated, %: C 33.96; H 3.77; N 39.62.

This method was also used to prepare the di(hydroxymethyl) derivative XIII.

5,6-Di(trinitroethylamino)furazano[3,4-*b*]pyrazine (IV). 5,6-Di(hydroxymethylamino)furazano[3,4-*b*]-pyrazine III (4.24 g, 0.02 mol) in aqueous nitroform (30 ml, 20%, 0.05 mol) was stirred for one day. The solid was filtered off and washed with water (3×10 ml). Yellow crystals of the product were recrystallized from dioxane and dried over KOH. Found, %: C 20.52; H 1.42; N 34.72. $C_8H_6N_{12}O_{13}$. Calculated, %: C 20.08; H 1.25; N 35.15.

N,N'-Di(trinitroethyl)-5,6-di(nitramino)furazano[3,4-*b*]pyrazine (V). The solid 5,6-di(trinitroethyl-amino)furazano[3,4-*b*]pyrazine IV (4.78 g, 0.01 mol) was added over 5 min to mixture of acetic anhydride (40 ml) and anhydrous HNO_3 (20 ml) at 10°C. The mixture was held for 2 h at 15-20°C and then poured in water–ice (200 g) mixture. The solid was filtered off and washed with water (3×30 ml). The crystals were dried and purified by column chromatography (SiO_2, CH_2Cl_2 eluent). Found, %: C 17.25; H 0.82; N 33.98. $C_8N_4N_{14}O_{17}$. Calculated, %: C 16.90; H 0.70; N 34.51. The temperature at which extensive decomposition starts (T_{dec}) is 146°C.

N,N'-Di(nitroxymethyl)-5,6-di(nitramino)furazano[3,4-*b*]pyrazine (VI). Solid aminoalcohol III (10.6 g) was added over 5 min to mixture of acetic anhydride (60 ml) and anhydrous HNO_3 (30 ml) at 10-12°C. The mixture was stirred for 2 h at 15-20°C. The mixture was poured into water–ice mixture. The solid was filtered off and washed with water. The dry product was recrystallized from aqueous acetone. Found, %: C 18.42; H 1.15; N 35.37. $C_6H_4N_{10}O_{11}$. Calculated, %: C 18.37; H 1.02; N 35.71. T_{dec} = 106°C. The nitroxymethyl derivative XIV was also prepared under these conditions.

5,6-Di(N,N'-dimethylaminomethyleneamino)furazano[3,4-*b*]pyrazine (IX). Suspension of diamine I (0.76 g, 0.005 mol) in dimethylformamide diethyl acetal (4 ml) was stirred for 2 h. The solid was filtered off and washed with water (10 ml). The product was recrystallized from ethanol. Found, %: C 43.41; H 5.24; N 43.02. $C_{10}H_{14}N_8O$. Calculated, %: C 42.75; H 5.34; N 42.75.

4,8-Dihydro-1,2,5-thiadiazolo[3,4-*b*]-1,2,5-oxadiazolo[3,4-*e*]pyrazine (X). Suspension of diamine I (1.52 g, 0.01 mol) in dimethylformamide (20 ml) was treated with sulfur monochloride (2.4 ml, 0.03 mol). The mixture was heated for 10 min at 70°C, cooled, and poured onto ice (50 g). The product was extracted with ethyl acetate and purified by column chromatography (SiO_2, ethyl acetate eluent). Found, %: C 26.02; H 1.05; N 45.84; S 17.61. $C_4H_2N_6OS$. Calculated, %: C 26.37; H 1.11; N 46.13; S 17.16.

6-Ethoxy-5,6-dihydrofurazano[3,4-*b*]imidazo[4,5-*e*]pyrazine (XI). Suspension of diamine I (4.5 g, 0.03 mol) in orthoformic ester (20 ml) and BF_3 etherate (0.2 ml) was heated for 20 min to distill the volatile fraction (bp = 65-70°C). The reaction mixture was cooled. The solid was filtered off and washed with ether. The product was recrystallized from ethanol. Found, %: C 40.31; H 3.75; N 40.03. $C_7H_8N_6O_2$. Calculated, %: C 40.38; H 3.85; N 40.38.

5,6-Dihydrofurazano[3,4-*b*]imidazo[4,5-*e*]pyrazin-6-one (XII). Solution of ethoxy derivative XI (2.3 g, 0.011 mol) in acetone (100 ml) containing MnO_2 (20 g) was stirred for 6 h at room temperature. The solid was filtered off and washed with acetone (30 ml). Acetone was removed. The solid was recrystallized from water. Mass spectrum, *m/z*: 178 (M^+), 148 (M - NO). Found, %: C 33.44; H 1.28; N 46.80. $C_5H_2N_6O_2$. Calculated, %: C 33.70, H 1.12, N 47.19.

5,6-Di(dimethylmethylenehydrazino)furazano[3,4-*b*]pyrazine (XVI). Solution of hydrazino derivative II (1.0 g, 0.005 mol) in acetone (20 ml) and water (100 ml) was boiled for 5 min and cooled. The solid was filtered off and washed with water. Mass spectrum, *m/z*: 262 (M^+), 247 (M - CH_3), 206 [M - N=C(CH_3)$_2$]. Found, %: C 46.03, H 5.58, N 42.58. $C_{10}H_{14}N_8O$. Calculated, %: C 45.80; H 5.34; N 42.75.

5,6-Di(N,N-dimethylaminomethylenehydrazino)furazano[3,4-*b*]pyrazine (XVIII). Suspension of hydrazino derivative (0.91 g, 0.05 mol) in ethanol (40 ml) was treated with the N,N-dimethylformamide diethyl acetal (3.46 g, 0.013 mol). After 20 min the solid was filtered off and washed with ethanol. The solid was recrystallized from ethanol and dried at room temperature. Found, %: C 41.57; H 5.76; N 49.40. $C_{10}H_{14}N_{10}O$. Calculated, %: C 41.10; H 5.48; N 49.95.

1,2,4-Triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]pyrazine (XIX). A. Compound XVIII (0.29 g, 0.001 mol) was boiled for 30 min in 5% hydrochloric acid (20 ml). The solution was cooled. The solid was filtered off and washed with water.

B. Mixture of hydrazino derivative II (1.82 g , 0.01 mol), 85% formic acid (13 ml), and BF_3 etherate (3 drops) was refluxed for 1 h and cooled. The solid was filtered off. The filtrate was treated with water (25 ml), heated until the formed precipitate dissolved, and slowly cooled. The crystals were filtered off, washed with water, and dried over alkali. Mass spectrum, *m*/z: 202 (M^+). Found, %: C 35.71; H 0.90; N 55.14. $C_6H_2N_8O$. Calculated, %: C 35.64; H 0.99; N 55.45.

4,9-Dimethyl-1,2,4-triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]pyrazine (XX). Mixture of hydrazino derivative (0.546 g, 0.0033 mol), glacial acetic acid (4 ml), acetic anhydride (4 ml), and BF_3 etherate (2 drops) was boiled for 1 h. Water (5 ml) was added. The mixture was slowly cooled. The crystals were filtered off, washed with water, and dried over alkali. Found, %: C 42.10; H 2.46; N 48.18. $C_8H_6N_8O$. Calculated, %: C 41.74; H 2.61; N 48.69.

4,9-Dioxo-5,8-dinitro-1,2,4-triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]-pyrazine (XXI). Tetracyclic derivative XIX (0.2 g, 0.001 mol) was added to mixture of trifluoroacetic anhydride (6.5 ml) and anhydrous HNO_3 (3 ml) at 0°C. The mixture was held at 20°C for 4 h. The solid was filtered off, washed with water, and dried over P_2O_5. Found, %: C 22.75; N 43.24. $C_6N_{10}O_7$. Calculated, %: C 22.22; N 43.21.

4,9-Dioxo-1,2,4-triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]pyrazine (XXII). Solution of nitramide XXI (0.33 g, 0.001 mol) in acetone (10 ml) was boiled and water (2 ml) was added. The mixture was cooled. The solid was filtered off, washed with water (2×5 ml), and dried. Found, %: C 30.35; H 0.93; N 47.44. $C_6H_2N_8O_3$. Calculated, %: C 30.78; H 0.86; N 47.86.

4-Methyl-9-carboxy-1,2,4-triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[[3,4-*b*]pyrazine (XXIV). Solution of dimethyl derivative XX (4.52 g, 0.02 mol), potassium permanganate (25 g), and concentrated H_2SO_4 (5 ml) in water (50 ml) was heated at 80-85°C for 4 h. Solution was decolorized by addition of oxalic acid and filtered. The product was extracted from the precipitate by acetone. The acetone solution was evaporated. The product was recrystallized from water. Found, %: C 36.6; H 1.7; N 42.9. $C_8H_4N_8O_3$. Calculated, %: C 36.9; H 1.6; N 43.1.

4,9-Dicarboxy-1,2,4-triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]pyrazine dihydrate (XXV). A. Dicarboxylic acid XXV was prepared analogously to monocarboxylic acid XXIV by increasing the reaction time up to 8 h.

B. The dihydrazine derivative II (1.82 g, 0.01 mol) in trichloroacetyl chloride (5.5 ml, 0.05 mol) was refluxed for 1 h and cooled. The mixture was poured onto ice. The solid was filtered off. The product was extracted from the precipitate by hot acetone. The acetone solution was evaporated. The product was recrystallized from water. Found, %: C 29.07; H 1,71; N 33.92. $C_8H_2N_8O_5 \cdot 2H_2O$. Calculated, %: C 29.45; H 1.84; N 34.35.

4-Carboxy-1,2,4-triazolo[3,4-*d*]-1,2,4-triazolo[3,4-*f*]furazano[3,4-*b*]pyrazine (XXVI). Carboxylic acid XXVI was prepared analogously to monocarboxylic acid XXIV by increasing the reaction time up to 14 h. Found, %: C 33.8; H 0.9; N 45.3. $C_7H_2N_8O_3$. Calculated, %: C 34.2; H 0.8; N 45.5.

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