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CHEMISTRY OF FURAZANO[3,4-*b*]PYRAZINE
6.* 1,2,3-TRIAZOLO[4,5-*b*]FURAZANO[3,4-*b*]PYRAZINES

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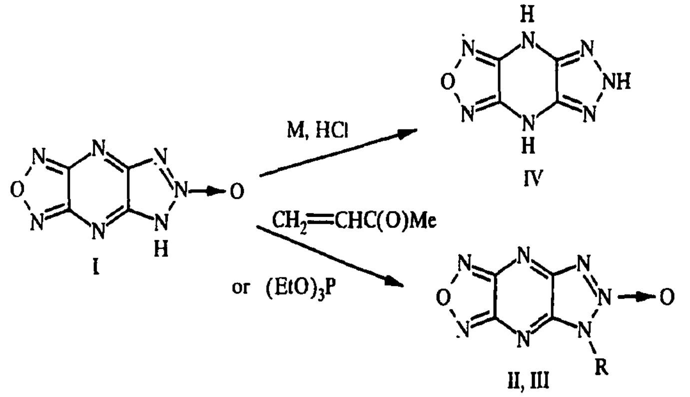
The reduction of 1,2,3-triazolo[4,5-e]furazano[3,4-b]pyrazine 6-oxide was investigated. By means of data from x-ray crystallographic analysis it was shown that there is a relation between the aromaticity and the structure of the obtained triazoles.

The construction of planar polycondensed molecules based on the furazano[3,4-*b*]pyrazine fragment has proved a promising direction of investigation. Compounds with unique energy characteristics have been created on their basis [2-5].

While continuing our papers on the chemistry of furazano[3,4-*b*]pyrazine [1, 5-11], we are reporting on the reactions of 1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]pyrazine 6-oxide (I) [1, 5, 11], leading to high-energy compounds. We established that the addition of methyl vinyl ketone to the N-oxide (I) led to 5-(3-oxobutyl-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]pyrazine 6-oxide (II), the destructive nitration of which should lead to the trinitromethyl derivative.



II R = $CH_2CH_2C(O)Me$; III R = Et

However, the investigations showed that the oxobutyl derivative (II) is converted quantitatively into the N-oxide (I) by the action of the nitration mixture ($HNO_3-H_2SO_4$) at various reaction temperatures (−5 to 30°C).

During an attempt at the deoxygenation of the N-oxide (I) with triethyl phosphite we unexpectedly obtained not the reduction product but the alkylation product — compound (III).

4,6,8H-1,2,3-Triazolo[4,5-*e*]furazano[3,4-*b*]dihydropyrazine (IV) was obtained by the reduction of the N-oxide (I) with aluminum, zinc, or magnesium in hydrochloric acid or ammonium chloride solution.

X-ray crystallographic analysis showed (Fig. 1) that compound (IV) has a symmetrical planar molecule and has a high density (1.91 g/cm^3). One of the hydrogen atoms is attached to the $N_{(2)}$ atom of the triazole ring, while the other two are localized at the nitrogen of the pyrazine ring.

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*For communication 5, see [1].

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TABLE 1. Characteristics of the Synthesized Compounds

Compound	Empirical formula	mp, °C	IR spectrum, ν, cm^{-1}	PMR spectrum, δ, ppm	Yield, %
II	$C_8H_7N_7O_3$	123...124	980 (furazan); 1635 (N—O); 1710 (C=O)	2,11 (3H, s, CH_3); 3,22 (2H, t, CH_2); 4,60 (2H, t, CH_2)	67
III	$C_6H_5N_7O_2$	145...146	990 (furazan); 1633 (N—O); 1610 (C=N)	1,44 (3H, s, CH_3); 4,88 (2H, q, CH_2)	81
IV	$C_4H_3N_7O$	250...255 decomp.	1007 (furazan); 3190, 3270 (NH)	10,40 (1H, s, NH); 12,31 (2H, s, NH)	94
V	$C_{11}H_{10}N_{14}O_2$	220...230 decomp.	1002 (furazan); 3220 (NH)	2,07 (6H, s, CH_3); 10,67 (4H, s, NH)	80
VI	$C_6H_5N_7O_2$	280...285 decomp.	1000 (furazan); 1735 (C=O); 3190 (NH)	2,60 (3H, s, CH_3); 11,51 (2H, s, NH)	81
VII	$C_7H_9N_7O_4$	142...143	1000 (furazan); 3270, 3440 (OH)	5,07 (4H, d, CH_2); 5,33 (2H, d, CH_2); 6,71 (2H, t, OH); 6,89 (1H, t, OH)	82
VIII	$C_5H_2N_8O_4$	110...111	1007 (furazan); 1668, 1285 (ONO_2); 3050 (CH_2)	7,15 (2H, s, CH_2)	82
IX	$C_5H_3N_7O_2$	125...126	1030 (furazan); 1615 (C=N); 3340 (OH)	6,00 (2H, s, CH_2); 7,17 (1H, s, OH)	85
XI	C_4HN_7O	170...175 decomp.	950 (furazan); 1620, 1550 (C=N); 3140 (NH)	9,87 (1H, s, NH)	92

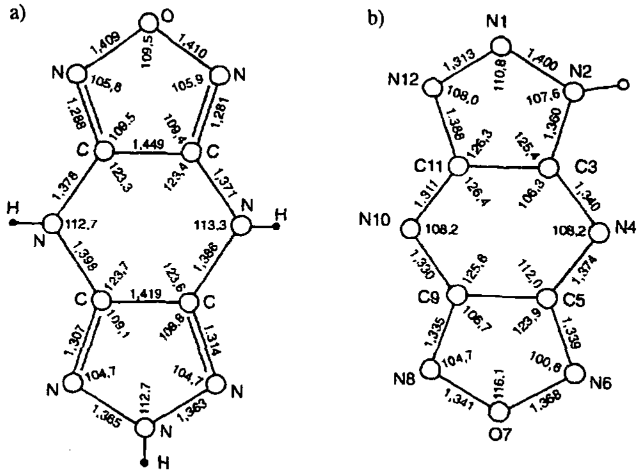


Fig. 1. Structures of compounds (IV) (a) and (XI) (b).

Study of the properties of the dihydropyrazine (IV) showed that the nitrogen atom $N_{(2)}$ of the triazole ring has the highest nucleophilicity. It is this atom that enters into reaction with acetone and leads to the condensation product 2,2-bis(4,6,8H-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]dihydro-6-pyrazinyl)propane (V):

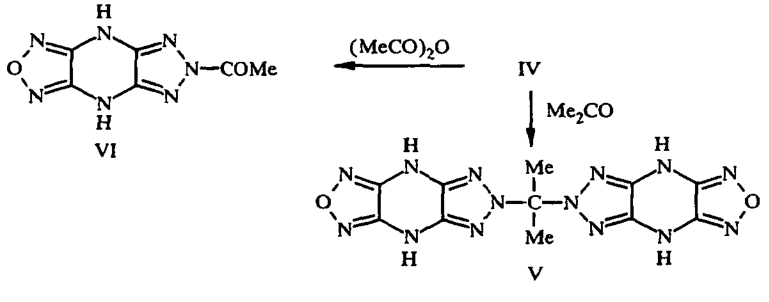
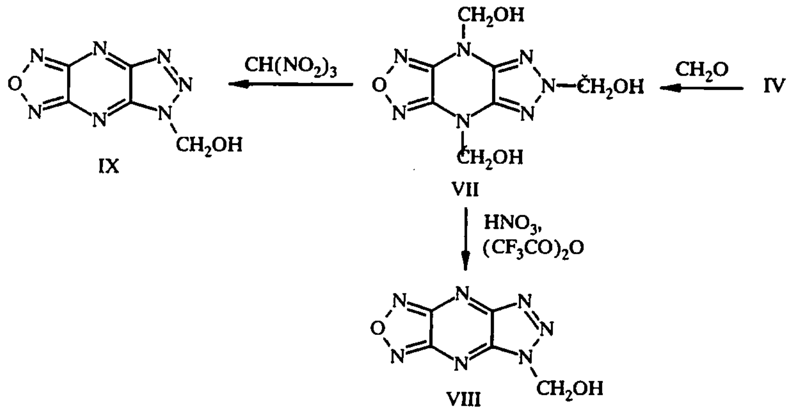


TABLE 2. Coordinates of the Nonhydrogen Atoms in the Molecule of (XI)

Atom	*x*	y	*z*
$N_{(1)}$	0,097(1)	0,333(1)	0,0600(3)
$N_{(2)}$	0,316(1)	0,250(1)	0,0898(3)
$C_{(3)}$	0,314(1)	0,267(1)	0,1743(4)
$N_{(4)}$	0,484(1)	0,207(1)	0,2289(3)
$C_{(5)}$	0,406(1)	0,255(1)	0,3076(3)
$N_{(6)}$	0,532(1)	0,215(1)	0,3773(4)
$O_{(7)}$	0,383(1)	0,301(1)	0,4356(3)
$N_{(8)}$	0,178(2)	0,388(1)	0,4066(4)
$C_{(9)}$	0,183(2)	0,355(1)	0,3246(5)
$N_{(10)}$	0,017(1)	0,419(1)	0,2702(3)
$C_{(11)}$	0,089(1)	0,369(1)	0,1952(4)
$N_{(12)}$	-0,038(1)	0,401(1)	0,1215(4)

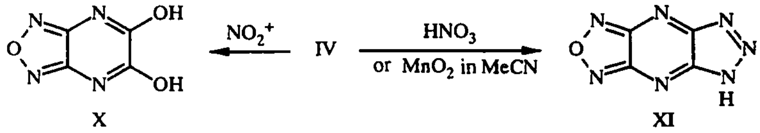
The triazole (IV) is only acylated at one NH group, giving 6-acetyl-4,6,8H-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]dihydropyrazine (VI). The structures of compounds (V, VI) are supported by the data from the PMR spectra, according to which the hydrogen atoms in them are equivalent, thereby eliminating the structures with the substituents in the pyrazine ring.

The use of the stronger electrophile formaldehyde in the Henry reaction leads to the trimethylol derivative (VII), which is easily oxidized by nitrating mixtures with the formation of the nitrate (VIII) and is converted by the action of nitroform into monomethylol derivative (IX).



IX VII VIII

Numerous attempts at the nitration of the triazole (IV) by various nitrating agents (mixtures of nitric acid with sulfuric acid, acetic or trifluoroacetic anhydrides) were unsuccessful — the triazole ring was destroyed, and the dihydroxy derivative (X) was formed; treatment with nitric acid (*d* 1.4 g/cm^3) at 0°C led to the formation of 5H-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]pyrazine (XI). Oxidation of the triazole (IV) to (XI) was observed during the action of manganese dioxide in acetonitrile:



X XI

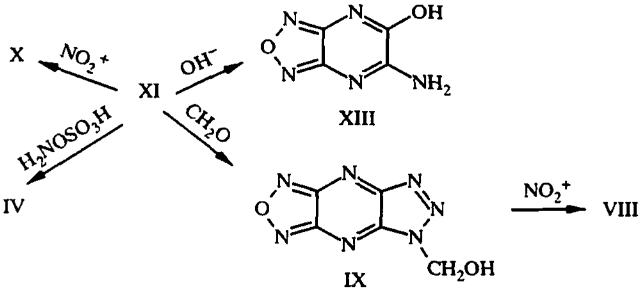
X-ray crystallographic analysis showed that compound (XI), like the triazole (IV), has a planar structure, and the hydrogen atom is localized at the $N_{(1)}$ atom of the triazole ring. However, on account of the loss of the symmetry of the molecule the compound has a lower density (1.83 g/cm^3), which can be explained by ineffective packing of the molecules in the crystal.

By means of the data from x-ray crystallographic analysis using Bird's method [12] we calculated the aromaticity index (Ia) of the nonaromatic triazole (IV) (containing 16 π-electrons) and of the aromatic derivative formed during its oxidation (containing 14 π-electrons). In the transition from the structure (IV) (Ia = 49) to the structure (XI) (Ia = 63) the peripheral bonds are equalized, and the length of the formal single bonds $O_{(1)}-N_{(1)}$ and $C_{(1)}-N_{(2)}$ is reduced, while that of the double bond is increased so much that it becomes practically equal to the $C_{(1)}-N_{(2)}$ bond. This can explain the ease of dehydrogenation of the nonaromatic triazole (IV) and its derivatives.

The nitration of compound (XI), like that of the triazole (IV), led only to the quantitative formation of the dihydroxy derivative (X) even under mild conditions (trifluoroacetyl nitrate at −10°C). This can probably be explained by the instability of the nitramine that forms.

We also established that compound (XI) exhibits weak acidic characteristics, forming unstable sodium and potassium salts in an alkaline medium. Concentrated solutions of these salts decompose fully to the aminohydroxy derivative (XIII) [9] after 2 h at 20°C.

The monomethylol derivative (XI), the nitration of which gives the nitrate (VIII), was easily obtained by hydroxymethylation.



We note that in reaction with the triazole (XI) hydroxylaminesulfonic acid, unexpectedly exhibiting reducing characteristics, gave the triazole (VI) instead of the expected amination product.

EXPERIMENTAL

The PMR spectra were recorded on a Bruker WH-90 Spectrometer in DMSO-d_6 with TMS as internal standard. The IR spectra were recorded on a Perkin-Elmer 580 B spectrometer in Nujol. The purity of the products was monitored by TLC on Silufol UV-254 plates and also by HPLC on a Du Pont 850 chromatograph with a Zorbax SIL column (4.6 × 250 mm). The mass spectra were obtained on a VS-50AET spectrometer at 70 eV.

X-ray Crystallographic Investigation. The single crystals of compound (XI) were rhombic: a = 5.4315(8), b = 6.775(1), c = 16.151(3), Z = 4, d_{calc} = 1.83 g/cm^3, space group $P2_12_12_1$. The unit cell parameters and the intensities of 720 independent reflections with $F > 2\sigma(F)$ were measured on a Syntex $P2_1$ automatic four-circle diffractometer (λCuKα, graphite monochromator, $\theta/2\theta$ scan, $2\Theta_{max}$ = 150°C). The structure was interpreted by the direct method with the MULTAN software and was refined by least-squares treatment in anisotropic approximation to R = 9.2%. The coordinates of the nonhydrogen atoms are given in Table 2.

A separate paper will be devoted to the x-ray crystallographic investigation of the triazole (IV).

5-(3-Oxobutyl)-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]pyrazine 6-Oxide (II). To 2.0 g (0.011 mole) of 1,2,3-triazole[4,5-*e*]furazano[3,4-*b*]pyrazine 6-oxide (I) [1, 5, 11] we added 15 ml of ether and then 1.4 g (0.02 mole) of methyl vinyl ketone. The mixture was kept at room temperature for 2 h and, after the addition of 10 ml of hexane, at −15°C for 1 h. The filtered precipitate was crystallized from a 2:1 mixture of ether and hexane. Found %: C 38.92; H 2.65; N 39.02. $C_8H_7N_7O_3$. Calculated %: C 38.56; H 2.83; N 39.35.

5-Ethyl-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]pyrazine 6-Oxide (III). A solution of 0.53 g (0.003 mole) of compound (I) in 10 ml of ethanol was boiled with 1.0 g (0.005 mole) of triethyl phosphite for 1 h. To the reaction mixture we then added 5 ml of water. The precipitate was filtered off and recrystallized from aqueous acetone. Mass spectrum (m/z): 207 (M^+); 177 (M − NO); 163, 149, 133. Found %: C 34.98; H 2.65; N 47.12. $C_6H_5N_7O_2$. Calculated %: C 34.78; H 2.42; N 47.34.

4,6,8H-1,2,3-Triazolo[4,5-*e*]furazano[3,4-*b*]dihydropyrazine (IV). To a solution of 3.6 g (0.02 mole) of compound (I) in mixture of 10 ml of concentrated hydrochloric acid and 10 ml of water with cooling we added in small portions 3.0 g of powdered aluminum, while keeping the temperature in the range of 30-40°C. At the end of the reaction (when the aluminum had completely dissolved) the precipitate was filtered off and washed with water (3 × 10 ml). The triazole (IV) can be recrystallized from dioxane. Mass spectrum (m/z): 165 (M^+); 135 (M−NO); 107 ($M-NO-N_2$). Found %: C 29.25; H 1.95; N 59.03. $C_4H_3N_7O$. Calculated %: C 29.10; H 1.83; N 59.39.

2,2-Bis(4,6,8H-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]dihydro-6-pyrazinyl)propane (V). We boiled 1.65 g (0.01 mole) of the triazole (IV) in a mixture of 20 ml of acetone and 10 ml of water for 20 min. The mixture was cooled, and the separated crystals were filtered off. Found %: C 35.27; H 2.72; N 52.83. $C_{11}H_{10}N_{14}O_3$. Calculated %: C 35.68; H 2.70; N 52.97.

6-Acetyl-4,6,8H-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]dihydropyrazine (VI). A mixture of 0.5 g (0.003 mole) of compound (IV) and 0.1 g of sodium acetate in 3 ml of acetic anhydride was heated at 70°C for 4 h, 1 ml of water was added, and the mixture was cooled to 20°C. The precipitate was filtered off and recrystallized from dioxane. Mass spectrum (m/z): 207 (M^+); 165 ($M-CH_3CO$); 135 ($M-CH_3CO-NO$). Found %: C 34.66; H 2.65; N 47.03. $C_6H_5N_7O_2$. Calculated %: C 34.79; H 2.43; N 47.33.

4,6,8-Tri(hydroxymethyl)-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]dihydropyrazine (VII). In an ultrasonic bath we dispersed 1.65 g (0.01 mole) of compound (IV) in a mixture of 4 ml of 37% formalin and 2 ml of water for 10 min. The mixture was then stirred for 24 h. The precipitate was filtered off and washed with water (3 × 5 ml). The product was dried over phosphorus pentoxide. Found %: C 32.75; H 3.48; N 38.05. $C_7H_9N_7O_4$. Calculated %: C 32.94; H 3.53; N 38.43.

3-Nitroxymethyl-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]pyrazine (VIII). To a nitrating mixture consisting of 4.6 ml of trifluoroacetic anhydride and 2 ml of anhydrous nitric acid at −30°C we added 1.27 g (0.005 mole) of compound (VII). The mixture was stirred at 0°C for 1 h and poured onto ice. The precipitate was filtered off, washed with water, and recrystallized from aqueous acetone. Found %: C 25.45; H 0.63; N 46.89. $C_5H_2N_8O_4$. Calculated %: C 25.21; H 0.84; N 47.06.

5-Hydroxymethyl-1,2,3-triazolo[4,5-*e*]furazano[3,4-*b*]pyrazine (IX). A mixture of 1.27 g (0.005 mole) of compound (VII) and 8.5 ml of a 20% aqueous solution of nitroform (0.015 mole) was stirred at room temperature for 24 h. The precipitate was filtered off, washed with water, and dried over alkali. Found %: C 31.01; H 1.72; N 50.29. $C_5H_3N_7O_2$. Calculated %: C 31.09; H 1.55; N 50.79.

5H-1,2,3-Triazolo[4,5-*b*]furazan[3,4-*b*]pyrazine (XI). Over 5 min we added 3.3 g (0.02 mole) of the triazole (IV) in portions to nitric acid (*d* 1.4 g/cm³) cooled to −10°C. The temperature was raised to 20°C, and the mixture was kept for 20 min. The reaction mass was then cooled to −20°C, and the precipitate was filtered off and recrystallized from water. Mass spectrum (m/z): 163 (M^+); 133 (M−NO); 105 ($M-NO-N_2$). Found %: C 29.32; H 0.41; N 59.97. C_4HN_7O. Calculated %: C 29.45; H 0.62; N 60.12.

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