NITROAZINES.

3.* NITROACETONITRILE IN THE SYNTHESIS OF NITROAZINES

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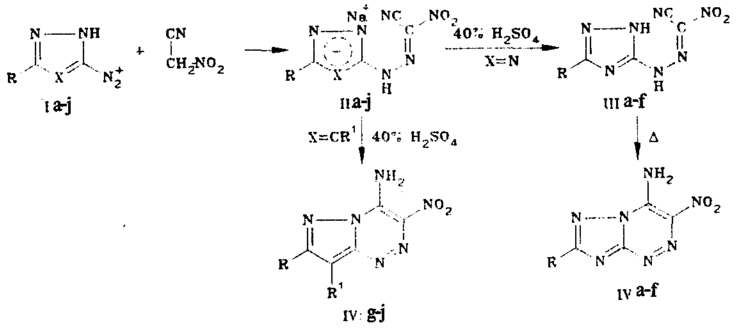
Azolo-annelated nitro-1,2,4-triazines have been obtained by the cyclization, thermally or under the action of acids, of the products of the coupling of diazopyrazoles or diazo-1,2,4-triazoles with nitroacetonitrile.

Compounds containing a nitro group in a triazine ring have scarcely been studied. This is due to the difficulty of their synthesis by traditional methods [2], although the introduction of a nitro group into a triazine ring not only powerfully changes the chemical properties of the compound but also enhances its physiological activity [3].

It has been shown previously [4] that the nitro-1,2,4-triazine ring can be constructed from diazoazoles and nitroacetic ester, the interaction of which leads to the formation of 6-nitro-4,7-dihydroazolo[5,1-c][1,2,4]triazin-7-ones. Continuing these investigations, we have considered the possibility of using another bifunctional nitro synthon — nitroacetonitrile — for constructing a 1,2,4-triazine ring containing a nitro group.

On the reaction of the 1,2,4-triazolediazonium compounds (Ia-f) and the pyrazolediazonium compounds (Ig-j) with nitroacetonitrile in the presence of an excess of sodium acetate or carbonate, the corresponding azolylhydrazones of nitroglyoxylonitrile were obtained in the form of the sodium salts (IIa-j). When compounds (IIa-f) were treated with a 40% solution of sulfuric acid, the free triazolylhydrazones (IIIa-f) were isolated:



(For an explanation of the symbols, see footnote to Table 1)

The IR spectra of compounds (IIa-j) and (IIIa-f) showed absorption bands of amino, nitro, and cyano groups. The hydrazone nature of the products was indicated by their electronic spectra (Table 1), which were typical for similar arylhydrazones [5], including the phenylhydrazone of nitroglyoxylonitrile [λ_{max} (log ε) 400 nm (3.95); 270 nm (3.30)], and differed from the spectra of their aza analogs [6].

In the mass spectra of compounds (IIIa-f) (Table 2), the peaks of the molecular ion (M^+) having intensities between 3.6 and 8.0% of the total ion current (W_M) were recorded. By analogy with the triazenes [7], the benzazolylazoketoximes [8] and formazane derivatives [9, 10], M^+ represented two tautomers: A (hydrazine form) and B (azo form), which are

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*For communication 2, see [1].

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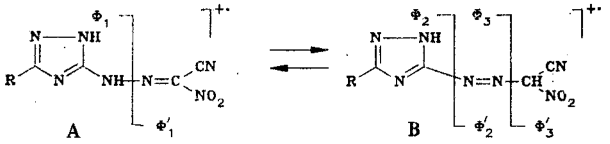
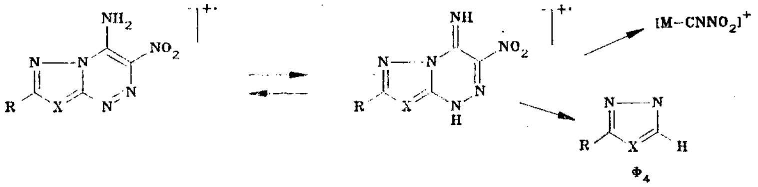
characterized by fragmentation pathways specific for each of them (Table 2). The formation of the ions Φ_1, Φ_1', and also Φ_2, Φ_2', Φ_3, and Φ_3' confirmed this conclusion:



The possibility of the existence of prototropic isomers with the participation of the 1,2,4-triazole ring is excluded [11]. The presence of a nitro group in the molecule is characterized by the $[M - NO]^+$, $[M - NO_2]^+$, and $[M - HNO_2]^+$ ions [12]. The appearance of the last-mentioned ion is connected with the manifestation of the "ortho effect" [13] and presupposes that the configuration of M^+ in the form of the anti isomer. In the mass spectra of compound (IIIe, f) the maximum peaks are those of the 103 and 104* ions ($[Ph - CN]^+$ and $[4\text{-}Py - CN]^+$, respectively) arising from the fragmentation of the ions Φ_1 and Φ_2.

Since we were interested in the possibility of obtaining condensed derivatives of nitrotriazine, we investigated the behavior of the hydrazones (II) and (III) under the conditions for the cyclization of δ-amino nitriles [14]. It was established that the sodium salts of the pyrazolylhydrazones (IIg-j) underwent cyclization smoothly in an acidic medium. Their treatment with a 40% solution of sulfuric acid gave the 7-amino-6-nitropyrazolo[5,1-c][1,2,4]-triazines (IVg-j). The capacity for forming a triazine ring in the hydrazones investigated obviously depends on the acceptor properties of the azole fragment. In contrast to the pyrazolyl derivatives (IIg-j), the standard cyclization conditions [14] proved to be ineffective for the hydrazone derivatives of the 1,2,4-triazoles (IIIa-f). The reaction did not take place when the compounds were boiled in alcohols, acetic acid, and solutions of mineral acids and alkalis. When the thermal stabilities of compounds (IIIa-f) were studied by thermogravimetry, it was found that an endothermic process took place at 190-220°C with no change in the weight of the sample. The preparative performance of thermolysis (boiling in decalin for 3 h or heating in silicone oil) gave the 7-amino-6-nitro-1,2,4-triazolo[5,1-c][1,2,4]triazines (IVa-f) (Table 1).

The IR spectra of the cyclization products showed absorption bands corresponding to the vibrations of a nitro group and lacked a signal in the region of absorption of a nitrile group, which confirmed that cyclization had taken place with the participation of this group. Fragmentation under the action of electronic impact of the cyclic products (IV) (Table 3) differed substantially from the breakdown of the corresponding hydrazones (III) and was characterized by the following features: 1) as a rule, a high stability to electron impact (in the majority of cases, the values of W_M were between 14.7 and 21.7%, apart from the derivatives (IVg) and (IVj); in the case of the latter, new fragmentation pathways due to the breakdown of the ethoxycarbonyl group appeared); 2) the direct (without isomerization [12]) elimination of the nitro group from M^+; and 3) the ejection of a $CNNO_2$ particle, and also the formation of the common ion Φ_4 directly from M^+, which is evidence in favor of the existence of M^+ in the imino form.



Also, in the case of compound (IVe), the ions $C_6H_5^+$ (77) and $C_6H_5CN^+$ (103) were recorded in the mass spectrum. In the mass spectrum of (IVj), according to high-resolution mass spectrometry the peak of the 180 ion consisted of two fragments: 80% of a fragment with the composition $[M - NCNO_2]^+$ and 20% of a fragment with the composition $[M - COOC_2H_4]^+$, which was confirmed by t peaks of the fragmentary ions 136 (10%) - $[M - NCNO_2 - OC_2H_4]^+$, 135 (7%) - $[M - NCNO_2, - OC_2H_5]$ 108 (40%) - $[M - NCNO_2, - COOC_2H_4]^+$.

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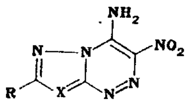
*The numbers characterizing the ions give the m/z values.

TABLE 1. Characteristics of the Azolylhydrazones of Nitroglyoxylonitrile (IIa-j*) and (IIIa-f) and of the 7-Amino-6-nitroazolo[5,1-c][1,2,4]triazines (IVa-j)



Compound†	R	mp,‡°C	IR spectrum, cm⁻¹				Electronic spectrum, λmax, nm (log ε)	Found, %			Analytical formula	Calculated, %			Yield, %
			$\nu^{as}_{NO_2}$	$\nu^{s}_{NO_2}$	ν_{NH}	ν_{CN}		C	H	N		C	H	N	
IIa	H	234—235	1470	1280	3220	2230	294 (3,40); 407 (4,00)	22,0	1,7	43,8	$C_4H_2N_7NaO_2 \cdot H_2O$	21,6	1,7	43,7	93
IIb	CH_3	200—201	1470	1290	3270	2225	293 (3,30); 407 (4,02)	27,7	2,0	45,5	$C_5H_4N_7NaO_2$	27,6	1,8	45,2	85
IIc	C_2H_5	185—187	1470	1270	3175	2212	291 (3,38); 407 (3,98)	31,3	2,7	42,0	$C_6H_6N_7NaO_2$	31,0	2,6	42,4	90
IId	SCH_3	250—252	1470	1280	3150	2215	285 (3,40); 414 (4,09)	24,4	2,0	39,5	$C_5H_4N_7NaO_2S$	24,1	1,6	39,3	58
IIe	C_6H_5	>300	1470	1290	3170	2220	293 (3,90); 410 (4,10)	42,7	2,4	34,8	$C_{10}H_6N_7NaO_2$	43,0	2,1	35,1	80
IIg	H	>300	1470	1300	3295	2212	263 (3,90); 305 (4,10); 419 (4,00)	29,4	1,7	41,2	$C_5H_3N_6NaO_2$	29,7	1,5	41,6	80
IIh	CH_3	>270	1470	1300	3300	2215	410 (4,10)	33,0	2,5	38,5	$C_6H_5N_6NaO_2$	33,3	2,3	38,9	73
IIi	H	>300	1470	1300	3300	2240, 2220		31,2	1,2	43,0	$C_6H_2N_7NaO_2$	31,6	0,9	43,0	54
IIj	H	>300	1470	1300	3200	2210	409 (4,12)	35,5	2,8	30,6	$C_8H_7N_6NaO_4$	35,0	2,9	30,6	62
IIIa	H	200—202	1500	1310	3140	2218	274 (3,40); 412 (4,00)	26,5	2,1	54,0	$C_4H_3N_7O_2$	26,5	1,7	54,1	90
IIIb	CH_3	188—189	1505	1310	3140	2220	277 (3,29); 415 (4,02)	30,5	2,2	50,0	$C_5H_5N_7O_2$	30,8	2,6	50,3	90
IIIc	C_2H_5	178—180	1500	1310	3150	2230	280 (3,38); 415 (4,00)	34,1	3,6	47,2	$C_6H_7N_7O_2$	34,5	3,4	47,0	85
IIId	SCH_3	268—270	1500	1320	3120	2240	280 (3,40); 414 (4,09)	26,0	2,5	43,4	$C_5H_5N_7SO_2$	26,4	2,2	43,2	80
IIIe	C_6H_5	>300	1505	1325	3160	2230	273 (4,00); 420 (4,10)	46,7	3,1	37,8	$C_{10}H_7N_7O_2$	46,7	2,7	38,1	90
IIIf	4-Pyridyl	>300	1505	1330	3222	2192	270 (3,99); 421 (4,12)	41,8	2,6	43,1	$C_9H_6N_8O_2$	41,9	2,3	43,4	80
IVa	H	278—280	1510	1350	3460		350 (3,98); 303 (3,85)	26,4	1,7	54,4	$C_4H_3N_7O_2$	26,5	1,7	54,1	76
IVb	CH_3	280—281	1515	1345	3430		340 (4,00); 303 (3,80)	31,0	2,6	50,4	$C_5H_5N_7O_2$	30,8	2,6	50,3	65
IVc	C_2H_5	142—143	1520	1345	3450		351 (4,01); 291 (3,85)	35,0	3,5	47,0	$C_6H_7N_7O_2$	34,5	3,4	47,0	76
IVd	SCH_3	>270	1525	1350	3380, 3160		353 (4,08); 277 (3,80)	26,1	2,4	43,5	$C_5H_5N_7O_2S$	26,4	2,2	43,2	80
IVe	C_6H_5	>300	1525	1350	3460, 3160		351 (4,00); 272 (4,30)	46,8	3,0	38,0	$C_{10}H_7N_7O_2$	46,7	2,7	38,1	98
IVf	4-Pyridyl	>300	1525	1345	3450, 3280		352 (3,98); 272 (4,25)	41,7	2,6	43,1	$C_9H_6N_8O_2$	41,9	2,3	43,4	90
IVg	H	218—221	1555	1330	3431, 3273		370 (4,10); 214 (4,20)	33,1	2,4	46,4	$C_5H_4N_6O_2$	33,3	2,2	46,7	80
IVh	CH_3	240—242	1500	1320	3450		380 (4,14); 214 (4,20)	36,9	3,2	43,5	$C_6H_6N_6O_2$	37,1	3,1	43,3	90
IVi	H	>270	1505	1320	3400		378 (4,12); 220 (4,15)	35,0	1,7	48,0	$C_6H_3N_7O_2$	35,1	1,5	47,8	85
IVj	H	>300	1505	1325	3410		375 (4,20); 220 (4,25)	38,5	3,5	33,0	$C_8H_8N_6O_4$	38,1	3,3	33,3	80

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*Compound (IIf) was not isolated.

†(IIa-e), (IIIa-f), and (IVa-f), X = N; (IIg, h) and (IVg, h), X = CH; (IIi) and (IVi), X = CCN; (IIj) and (IVj), X = $CCOOC_2H_5$.

‡Compound (IIa) from methanol; compound (IIb, d) and (IIIa-c) from n-propanol; (IIc, e, g, h), (IIIe), and (IVg) from ethanol; (IIi-j) and (IVa-d), from water; (IIId) from butanol–heptane (1:1); (IIIf) and (IVe-f) from DMFA–water (3:1); (IVh) from butanol; (IVi, j) from DMFA.

TABLE 2. Mass Spectra of the Triazolylhydrazones (IIIa-f)

Compound	m/z values (intensities of the peaks, % of the maximum)*												
	M^+	$[M-NO]^+$	$[M-NO_2]^+$	$[M-HNO_2]^+$	Φ_1^+	$\Phi'_1{}^+$	Φ_2^+	$[\Phi_2+H]^+$	$\Phi'_2{}^+$	Φ_3^+	$\Phi'_3{}^+$	$[\Phi'_3-NO_2]^+$	W_M
IIIa	181 (42)	151 (39)	135 (32)	134 (13)	83 (36)	98 (6)	68 (65)	69 (100)	113 (8)	96 (12)	85 (13)	67 (10)	3,6
IIIb	195 (88)	165 (10)	149 (59)	148 (12)	97 (6)	98 (5)	82 (11)	83 (8)	113 (5)	110 (7)	85 (5)	67 (100)	6,4
IIIc	209 (52)	179 (7)	163 (10)	162 (5)	111 (14)	98 (5)	96 (30)	97 (16)	113 (5)	124 (6)	85 (11)	67 (100)	4,6
IIId	227 (100)	197 (15)	181 (5)	180 (15)	129 (13)	98 (5)	114 (16)	115 (17)	—	142 (5)	85 (12)	67 (13)	8,0
IIIe	257 (41)	227 (5)	211 (17)	210 (17)	159 (8)	—	144 (5)	145 (6)	113 (5)	—	85 (10)	67 (9)	4,4
IIIf	258 (88)	229 (5)	212 (8)	211 (10)	160 (18)	98 (5)	—	146 (7)	—	—	85 (5)	67 (5)	4,2

*Peaks with intensities ⩾5%) are given.

TABLE 3. Mass Spectra of the 7-Amino-6-nitroazolo[5,1-c][1,2,4]triazines (IVa-c, e-h, j)

Compound	m/z values (intensities of the peaks, % of the maximum*										
	M^+	$[M-NO_2]^+$	$[M-NO_2, -H]^+$	$[M-NO_2CN]^+$	$[M-NO_2, -HCN]^+$	Φ_4^+	$[C_2N_4H_2]^+$	$[C_2N_3H_2]^+$	$[C_2N_3H]^+$	$[C_2N_2H]^+$	W_M
IVa	181 (100)	135 (75)	134 (8)	109 (5)	108 (10)	68 (20)	82 (5)	68 (20)	67 (7)	53 (54)	21,7
IVb	195 (100)	149 (28)	—	123 (7)	122 (11)	82 (7)	82 (7)	68 (17)	67 (82)	53 (24)	16,3
IVc	209 (100)	163 (23)	162 (6)	137 (11)	136 (12)	96 (14)	82 (7)	68 (37)	67 (8)	53 (48)	14,8
IVe	257 (100)	211 (27)	—	185 (5)	184 (14)	144 (7)	—	68 (8)	—	53 (17)	14,7
IVg	180 (100)	134 (11)	—	108 (6)	107 (43)	67 (27)	—	67 (27)†	66 (40)†	53 (100)	8,6
IVh	194 (100)	148 (7)	—	122 (5)	121 (12)	81 (9)	—	67 (5)†	66 (93)†	53 (36)	17,2
IVj	252 (24)	134 (5)	—	180 (100)	—	159 (11)	—	67 (19)†	66 (10)†	53 (40)	4,3

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*The peaks with intensities ⩾ 5% are given.

†The ions $[C_3H_2H_3]^+$ and $[C_3N_2H_2]^+$, respectively.

TABLE 4. Coordinates of the Atoms ($\times 10^4$) and Their Equivalent Temperature Factors ($\times 10$) $B_{eq} = 4/3\Sigma_i\Sigma_j B_{ij} a_i a_j$

Atoms	x	y	z	Beq	Atoms	x	y	z	Beq
$O_{(1)}$	2459 (5)	-1277 (15)	8041 (4)	67 (3)	$C_{(2)}$	3906 (6)	974 (18)	8637 (6)	41 (4)
$O_{(2)}$	3309 (4)	−184 (13)	7554 (4)	65 (3)	$C_{(3)}$	3666 (6)	1142 (18)	9748 (6)	44 (4)
$O_{(3)}$*	663 (4)	2746 (11)	1874 (4)	72 (4)	$C_{(4)}$	4574 (6)	2140 (15)	10083 (5)	43 (3)
$N_{(1)}$	2852 (4)	54 (14)	9112 (5)	49 (4)	$C_{(5)}$	5104 (6)	2787 (17)	10496 (6)	40 (5)
$N_{(2)}$	3032 (5)	484 (15)	9682 (4)	48 (3)	$C_{(6)}$	5724 (6)	3325 (17)	10264 (6)	46 (5)
$N_{(3)}$	4083 (5)	1350 (13)	9253 (4)	35 (3)	$C_{(7)}$	6222 (6)	3973 (16)	10674 (5)	48 (4)
$N_{(4)}$	4673 (4)	1966 (13)	9453 (4)	35 (3)	$C_{(8)}$	6092 (6)	4115 (17)	11307 (6)	56 (5)
$N_{(5)}$	3969 (5)	1636 (15)	10281 (4)	45 (4)	$C_{(9)}$	5480 (6)	3576 (17)	11550 (6)	68 (6)
$N_{(6)}$	2988 (5)	−434 (17)	8036 (5)	53 (4)	$C_{(10)}$	4988 (6)	2929 (18)	11149 (5)	56 (5)
$N_{(7)}$	4329 (4)	1301 (13)	8184 (4)	42 (5)	$C_{(11)}$*	1111 (6)	2783 (15)	1463 (5)	67 (6)
$N_{(8)}$*	1551 (5)	1377 (16)	1427 (5)	57 (4)	$C_{(12)}$*	1554 (6)	-357 (16)	1832 (6)	76 (6)
$C_{(1)}$	3254 (6)	253 (18)	8621 (5)	43 (4)	$C_{(13)}$*	2074 (6)	1446 (15)	929 (6)	76 (6)

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*Atoms of the DMFA solvate molecule.

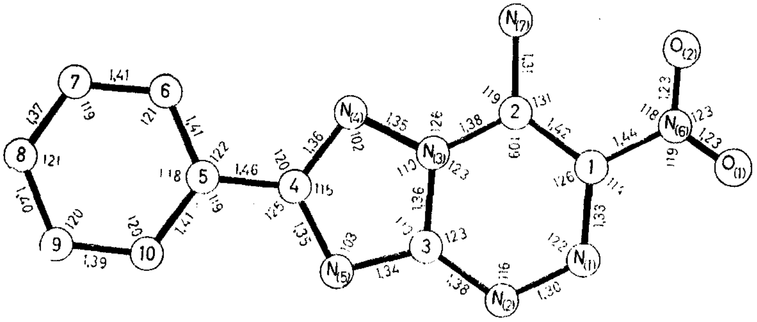

Fig. 1. Bond lengths and valence angles in compound (IVe).

In the case of triazolylhydrazones (IIIa-f), condensation with the participation of the nitrile group may take place either at the $N(_1)$ or at the $N(_4)$ atom of the triazole with the formation of [5,1-c] or [4,3-c] isomers. To determine the nature of the annelation of the rings, an X-ray structural analysis was performed for the case of compound (IVe), which crystallized in the form of a 1:1 solvate with DMFA (Fig. 1 and Table 4).

The solvate exhibited a structure consisting of molecules of (IVe) and of DMFA linked with one another in the crystal by $N(_7)$—N...$O(_3)$DMFA...H—$N(_7)$ intermolecular hydrogen bonds, forming layers with parallel planes (ac010). The $N(_7)$...$O(_3)$ (1/2 + x, 1/2 − y, 1 − z) and $N(_7)$...$O(_3)$ (1/2 − x, 1/2 − y, 1/2 + z) distances were 2.80 and 2.86 Å, respectively. Furthermore, the hydrogen atom at the $N(_7)$ atom apparently participates in the form of an intramolecular hydrogen bond with the $O(_2)$ atom of the nitro group, as is indicated by the $N(_7)$...$O(_2)$ distance of 2.86 Å. The molecule of (IVe) is planar, the maximum deviation from the mean plane for the $C(_2)$ atom being 0.03 Å. The dihedral angle between the $C(_1)$—$C(_4)$, $N(_1)$—$N(_5)$ plane and the planes of the $C(_5)$—$C(_{10})$ phenol ring and of the nitro group are, respectively, 0.4 and 9.6°, so that the molecule exhibits considerable conjugation, leading to an equilibrium of the bond lengths in the heterocyclic system. In actual fact, the $C(_2)$—$N(_7)$ (1.31 Å), the $N(_1)$—$C(_1)$ (1.33 Å), and the $N(_2)$—$C(_3)$ (1.38 Å) bonds are substantially shortened and the $N(_1)$—$N(_2)$ (1.30 Å) and $C(_1)$—$C(_2)$ (1.42 Å) bonds are lengthened in comparison with the usual values for $C(sp^2)$—N(1.44 Å), N=N (1.25 Å), and C=C (1.336 Å) bonds [15].

The geometric parameters of the DMFA solvate molecule are the usual ones, the lengths of the $N(_8)$—$C(_{11})$, $N(_8)$—$C(_{12})$, $N(_8)$—$C(_{13})$, and $C(_{11})$—$O(_3)$ bonds being 1.33, 1.49, 1.50, and 1.26 Å, respectively; the $N(_8)C(_{11})O(_3)$ valence angle is 121°, the configuration of the nitrogen atom plane-trigonal and the sum of the valence angles 360°.

The shortening of the C—NH_2 bond to 1.31 Å as compared, for example, with 3-aminopyridine [16] (1.384 Å), 2-aminopyridine [17] (1.35 Å), or 2-aminopyridazine [18] (1.34 Å) indicates considerable conjugation of the amino group with the ring and the possibility of the manifestation of amino-imino tautomerism [19]

The electronic spectra of the cyclic products (IVa-f) are similar (Table 1), which indicates a similar nature of the linkage of the triazole and triazine rings in these compounds.

EXPERIMENTAL

UV spectra were recorded on a Specord UV-vis instrument (in ethanol), and IR spectra on a UR-20 instrument (in paraffin oil). Mass spectra were obtained on a Varian MAT-311 A spectrometer under the standard conditions for the working of the instrument [12]. The X-ray structural investigation was performed on a Syntex PI diffractometer, λ Cu K_α, Ni filter, the intensities of 880 reflections with $F \geqslant 3\sigma$ being measured with the introduction of an empirical correction for absorption. The crystals of the 1:1 solvate of compound (IVe) with DMFA were orthorhombic: *a* 20.364(5); b 7.011(2); c 21.245(5) Å; d_{calc} 1.44 g/cm³; z = 8; space group Pbcn. The structure was interpreted by the direct method with refinement by the method of least squares in the anisotropic block-diagonal approximation to R = 0.085. The coordinates of the atoms and their temperature factors are given in Table 4.

Sodium Salts of Azolylhydrazones of Nitroglyoxylonitrile (IIa-j). A solution of 0.8 g (11 mmole) of $NaNO_2$ in 5 ml of water was added over 15 min to a cooled solution of 10 mmole of an amino azole in 1.6 ml of nitric acid (d 1.4) and 10 ml of water at 0°C. The mixture was left at this temperature for 10 min and was then added in portions to a cooled solution of 0.86 g (10 mmole) of nitroacetonitrile and 40 mmole of sodium acetate or carbonate in 20 ml of water. The mixture was stirred at 20°C for 3 h and then the precipitate formed was filtered off, crystallized, and dried in vacuum at 130°C over P_2O_5.

Triazolylhydrazones of Nitroglyoxylonitrile (IIIa-f).* A suspension of 10 mmole of a hydrazone (II) in 10 ml of 40% H_2SO_4 was stirred for 10 min, and the resulting precipitate was filtered off, crystallized, and dried in vacuum at 100-120°C over P_2O_5.

7-Amino-6-nitropyrazolo[5,1-c][1,2,4]triazines (IVg-j). A suspension of 10 mmole of the sodium salt of one of the pyrazolylhydrazones (IIg-j) in 10 ml of 40% H_2SO_4 was stirred for 10 min, and the resulting compound (IVg, h, i, or j) was filtered off. Ether was used to extract additional amounts of compounds (IVg and h) from the filtrate.

7-Amino-6-nitro-1,2,4-triazolo[5,1-c][1,2,4]triazines (IVa-f). A suspension of 10 mmole of one of the hydrazones (IIIa-f) in 20 ml of silicone oil was heated at 200°C (or the compound was boiled in 20 ml of decalin) for 3 h, and the product was filtered off, carefully washed with heptane, and crystallized.

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*The 2-phenyl- and 2-(4-pyridyl)triazolylhydrazones (IIIe, f) were isolated in the nonsalt form when the coupling reaction of the corresponding triazolediazonium compounds with nitroacetonitrile was carried out in a sodium acetate medium.

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NITROAZINES.

4.* POLAROGRAPHIC BEHAVIOR OF 5-NITROPYRAZOLO[3,4-b]PYRIDINES AND THE ESR SPECTRA OF THEIR ELECTROCHEMICALLY GENERATED FREE RADICALS

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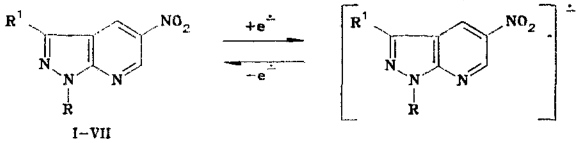
1-Methyl- and 1-phenyl-substituted derivatives of 5-nitropyrazolo[3,4-b]pyridines are reduced at a dropping mercury electrode in a single one-electron wave with the formation of radical anions in interval of potentials from −0.94 to −1.06 V. Compounds unsubstituted at the $N_{(1)}$ nitrogen atom give an additional polarographic wave at $E_{1/2}$ = −1.4 V due to the reduction of the deprotonated form (anion). The potentials and HFS constants of the ESR spectra of the corresponding electrochemically generated free radicals are given.

Among derivatives of pyrazolo[3,4-b]pyridine are found substances which are capable of inhibiting cAMP [2, 3] and which also exhibit bactericidal, analgesic, and antiinflammatory activities [4, 5]. The biological activity of many classes of compounds is said to be connected with their capacity for forming donor–acceptor complexes with biological substrates and of interfering in redox processes of metabolism [6]. It is therefore a matter of interest to study the behavior of compounds of this type under redox conditions, and also the structures of their free radicals.

With the aim of studying the redox characteristics of the 5-nitropyrazolo[3,4-b]pyridines, in the present work we have performed the polarographic reduction of compounds (I-VII), which have been studied previously [7]. The presence of a polynitrogen heterocyclic residue in the pyrazolone[3,4-b]pyridine molecules suggested the possibility of the formation of stable radicals on their reduction.

In the polarographic reduction of the 5-nitropyrazolo[3,4-b]pyridines, the one-electron wave of the primary process — the formation of radical anions — was clearly distinguishable:



I-VII

I, III R=H; II, IV R=CH_3, V—VII R=C_6H_5; I, II, V R¹=H; III, IV, VII R¹=CH_3; VI R¹=C_6H_5

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*For Communication 3, see [1].

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