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NITROAZINES

24.* STABLE ANIONIC σ-ADDUCTS OF CONDENSED NITROTRIAZINES

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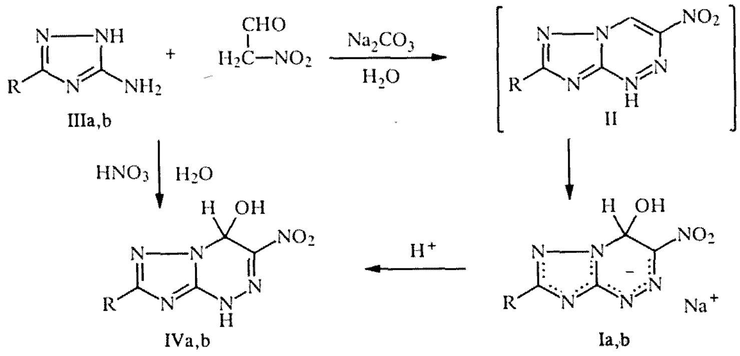
Stable anionic σ-adducts of azolo-ring condensed 1,2,4-traizines with water were synthesized, and their x-ray structural analysis was carried out.

The formation of anionic σ-adducts is often a key stage in nucleophilic substitution reactions as well as various transformations in the aromatic and heteroaromatic series. Information on their stereochemical structure allows the mechanism of these reactions to be revealed, and an understanding of the nature of the transition state to be reached. At the present time, the amount of data on the molecular structure of cyclohexadienate σ-adducts, based on x-ray structural measurements, is small [2-5]. As far as anionic σ-adducts – derivatives of nitroazaaromatic systems – are concerned, products of the addition of O-, C-, N-, and P-nucleophiles to nitropyridine, nitropyrimidine, and their derivatives have been described [6]. Most of such compounds are unstable; they were therefore investigated using the solutions. The adducts were only successfully isolated in the solid form in some cases; this mainly relates to the reaction with C-nucleophiles. The scanty published data on x-ray structural measurements are probably explained by the difficulty in the isolation of the anionic σ-adducts in the crystalline state [7-11].

We synthesized, isolated, and characterized anionic σ-adducts with the hydroxy group at the sp^3-hybridized carbon atom – sodium salts of 6-nitro-7-hydroxy-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazine (Ia,b). Utilizing a previously developed method for the isolation of condensed nitrotriazines [12, 13], we attempted to isolate 6-nitro-1,2,4-triazolo[5,1-c][1,2,4]triazines (II) by the condensation of the diazotriazoles (IIIa,b) with nitroacetaldehyde in the presence of sodium carbonate. However, the anionic σ-adducts (Ia,b) were isolated with the yields of 50-60% instead of the expected compounds (II).



I—IV a R = H, b R = CH3

The formation of the compounds (Ia,b) evidently proceeds as a result of the addition of water to the nitrotriazines (II) having a raised π-deficiency.

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*For Communication 23, see [1].

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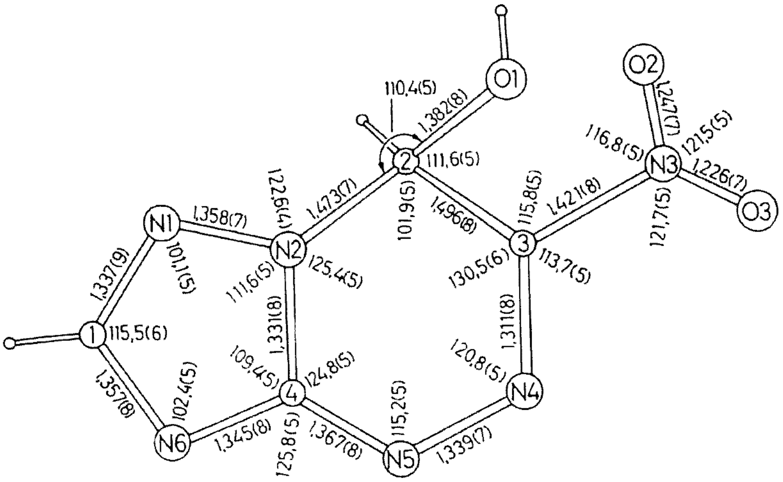

Fig. 1. Structure of the molecule of compound (Ia).

The anionic σ-adducts (Ia,b) are red crystalline substances which are readily soluble in water, DMSO, and DMF, and are stable on heating to 200°C.

In the PMR spectra of the compounds (Ia,b), the proton in the germinal unit appears in the form of a broad singlet on account of the spin–spin interaction with the proton of the hydroxy group, and changes into a sharp singlet when D_2O is added. The IR spectra contain characteristic bands corresponding with the stretching vibrations of the nitro and hydroxy groups. It should be noted that, in contrast to the σ-adducts of nitropyrimidine [14], the bands of the symmetrical and nonsymmetrical stretching vibrations of the nitro group do not undergo a large high-frequency shift. This indicates the lower contribution of the nitro group to the delocalization of charge in the triazolo[5,1-c][1,2,4]triazine condensed system, although the shortening of the $C-NO_2$ bond length in the compound (Ia) (1.421 Å) by comparison, for example, with 2-phenyl-6-nitro-7-amino-1,2,4-triazolo[5,1-c][1,2,4]triazine (1.440 Å) [13] is comparable with the shortening of the bond length with the formation of the σ-complex from trinitroanisole ($C-NO_2$ 1.387 Å in the p-position and 1.439 Å in the o-position) against 1.462 Å in the starting compound [7, 8].

When the anionic σ-adducts (Ia,b) are treated with dilute sulfuric acid, the 4-N-protonation occurs with the formation of the 2-R-6-nitro-7-hydroxy-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazines (IVa,b). The last are also formed with low yields by the reaction of the diazotriazoles (IIIa,b) with nitroacetaldehyde in an acidic medium. The spectral characteristics and melting temperatures of the adducts (IVa,b) agree with the data for the compounds previously obtained by the reaction of diazotriazoles with nitromalonic dialdehyde [15].

X-Ray Structural Investigation. The structure of the compound (Ia), which crystallizes in the form of the hydrate, is ionic and consists of the organic anion $C_4H_3N_6O_3^-$, the cation Na^+, and water molecules, bound in the crystal by hydrogen bonds. The anion (cf. Fig. 1) consists of the planar triazole ring and the triazine fragment ring-condensed to it at the $N_{(2)}-C_{(4)}$ bond. The $C_{(2)}$ atom has the tetrahedral configuration and diverges from the plane of the remaining five atoms by 0.130 Å (Table 1). The dihedral angle between mean plane of the triazole ring and five atoms of the triazine ring (excluding $C_{(2)}$) equals, in all, 1.5°, i.e., the system of 10 atoms of the condensed rings is practically planar. Analysis of the distribution of the bond lengths in the molecule indicates the significant delocalization of the electron density in the chain $N_{(1)}C_{(1)}N_{(6)}C_{(4)}N_{(5)}N_{(4)}C_{(3)}$.

The coordination of the cation in the structure is distorted octahedral (Table 2), including the oxygen atom of the water molecule, and three oxygen atoms and two nitrogen atoms of the organic anion. The Na-O distances are in the range 2.335-2.598 Å. The Na-N distances are in the range 2.487-2.494 Å, i.e. they are typical of octahedral sodium cations [16].

The are two protons present in the structure which are capable of forming hydrogen bonds – the hydrogen atom of the hydroxyl group in the organic anion and the hydrogen atom in the water molecule having the crystallographic symmetry C_2. Both atoms participate in the formation of hydrogen bonds of the length 2.650 Å [$O_{(1)}-HN_{(5)}$, (x, −y, −1/2+z), OHN 166°] and 3.17 Å [$O_{(W)}-HN_{(4)}$, (x, y, z), OHN 148°]. According to the classification [17] of water molecules participating in the hydrogen bonds, the molecule of water pertains to the class C. The coordinates of the atoms and their temperature factors are presented in Table 3.

TABLE 1. Equations of the Planes Ax + By + Cz = D of Planar Fragments of the Molecule (Ia) and Deviations from Them (Å)

Planes*	Atoms							
1	$N_{(1)}$ 0,001	$N_{(2)}$ 0,005	$N_{(6)}$ 0,009	$C_{(1)}$ -0,007	$C_{(4)}$ 0,009	$C_{(2)}^{**}$ -0,130	$N_{(5)}^{**}$ 0,019	
2	$O_{(2)}$ 0,004	$O_{(3)}$ 0,004	$N_{(3)}$ -0,012	$C_{(3)}$ 0,003				
3	$N_{(2)}$ 0,001	$N_{(4)}$ 0,005	$N_{(5)}$ 0,009	$C_{(3)}$ -0,007	$C_{(4)}$ -0,009	$C_{(2)}^{**}$ -0,130	$O_{(1)}^{**}$ 0,019	$H_{(2)}^{**}$ 0,554

Planes*	*A*	*B*	*C*	*D*
1	-5,459	6,523	2,814	-1,394
2	-7,490	5,993	4,568	-2,237
3	-5,459	6,523	2,814	-1,394

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*The planes form dihedral angles between each other comprising 10.4° for 1/2 and 1.5° for 1/3.

**The atoms are not included in the calculation of the equation of the corresponding planes.

TABLE 2. Coordination of the Na Cation in the Structure [presented are the Na- ... X distances (Å) and the Angles for Na ... XNa ... X (°)]

Atoms	Na...X	$O_{(2)}$	$O_{(3)}$	$O_{(w)}$	$N_{(1)}$	$N_{(6)}$
$O_{(1)}$ (1-*x*, -*y*, -*z*)	2,335	169,6	94,7	88,2	93,2	93,7
$O_{(2)}$ (1-*x*, -*y*, -*z*)	2,598		95,7	96,0	77,4	86,0
$O_{(3)}$ (*x*, *y*, *z*)	2,404			72,2	158,9	85,9
$O_{(W)}$ (*x*, *y*, *z*)	2,465				88,5	158,1
$N_{(1)}$ (1/2 + *x*, 1,2-*y*, 1/2 + *z*)	2,487					113,1
$N_{(6)}$ (1/2 + *x*, 1,2-*y*, *z*)	2,494					

EXPERIMENTAL

The IR spectra were recorded on the UR-20 instrument using mineral oil. The UV spectra of aqueous solutions were obtained on the Specord UV-vis spectrometer. The PMR spectra were obtained on the Bruker WP-80 (80 MHz instrument using DMSO-d_6 and TMS as the internal standard.

Sodium Salt of 6-Nitro-7-hydroxy-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazine (Ia)($C_4H_3N_6O_3Na$). To the cooled solution of 0.84 g (10 mmole) of 5-amino-1,2,4-triazole in 1.6 ml of nitric acid (d = 1.4) and 10 ml of water at 0°C are added 1.27 g (10 mmole) of the potassium slat of nitroacetaldehyde and 5 g of sodium carbonate in 15 ml of water at 0°C. The mixture is stirred for 3 h at 0°C, and the residue is filtered off rapidly. The $T_{decomp} > 200°C$ (from water). The IR spectrum was as follows: 3525 cm^{-1} (OH), 1520 cm^{-1}, and 1350 cm^{-1} (NO_2). The UV spectrum [λ_{max} (log ε)] was as follows: 215 nm (3.10) and 420 nm (3.90). The PMR spectrum was as follows: 7.30 ppm (1H, br. s, 7-H) and 8.20 ppm (1H, s, 2-H). The yield was 1.2 g (60%).

Sodium Salt of 2-Methyl-6-nitro-7-hydroxy-4,7-dihydro-1,2,4-triazolo[5,1-c]triazine (Ib)($C_5H_5N_6O_3Na$). This is obtained analogously. It has the $T_{decomp} > 200°C$ (from water). The IR spectrum was as follows: 3520 cm^{-1} (OH), 1520 cm^{-1}, and 1345 cm^{-1} (NO_2). The UV spectrum [λ_{max} (log ε)] was as follows: 215 nm (3.12) and 419 nm (3.92). The PMR spectrum was as follows: 2.25 ppm (3H, s, CH_3) and 7.28 ppm (1H, br. s, 7-H). The yield was 1.1 g (50%).

6-Nitro-7-hydroxy-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazine (IVa)($C_4H_4N_6O_3$). A. Compound (Ia) (2.06 g, 10 mmole) is mixed with 15 ml of 30% H_2SO_4. After 30 min, the mixture is filtered, and the product is crystallized from

TABLE 3. Atomic Coordinates ($\times 10^4$, and $\times 10^3$ for H Atoms) and Parameters of Anisotropic Temperature Factors ($\times 10^3$) in the Form T - $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12} + \ldots)]$

Atoms	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Na	6043(1)	3568(4)	1613(2)	31(2)	59(2)	28(1)	-1(1)	6(1)	-2(1)
$O_{(1)}$	3343(2)	-596(6)	-2005(3)	32(3)	9(3)	24(2)	-4(2)	6(2)	2(2)
$O_{(2)}$	4419(3)	2879(8)	-1419(4)	31(3)	81(4)	38(3)	16(3)	6(2)	-9(3)
$O_{(3)}$	4992(3)	2334(8)	236(4)	24(3)	98(4)	28(3)	-2(3)	-5(2)	-16(3)
$O_{(W)}$	5000(0)	2435(11)	2500(0)	33(4)	67(5)	32(4)	0(0)	11(3)	0(0)
$N_{(1)}$	1718(3)	8(7)	-1635(4)	32(3)	45(3)	23(3)	1(3)	-1(3)	-3(2)
$N_{(2)}$	2433(3)	331(7)	-984(4)	24(3)	45(3)	19(3)	3(2)	6(2)	-3(2)
$N_{(3)}$	4423(3)	2170(8)	-516(4)	23(3)	29(4)	31(3)	1(3)	9(2)	-4(3)
$N_{(4)}$	3716(3)	810(8)	615(4)	26(3)	50(3)	25(3)	-4(2)	6(2)	-4(3)
$N_{(5)}$	3071(3)	84(8)	877(4)	29(3)	52(3)	23(3)	-1(2)	6(2)	-4(3)
$N_{(6)}$	1721(3)	-732(8)	114(4)	21(4)	55(5)	27(4)	-2(4)	7(3)	-12(4)
$C_{(1)}$	1316(4)	-647(11)	-925(5)	28(4)	60(4)	29(4)	-3(3)	4(3)	-7(3)
$C_{(2)}$	3125(3)	884(10)	-1405(5)	13(3)	42(4)	31(5)	1(3)	5(2)	-1(2)
$C_{(3)}$	3726(4)	1227(10)	-389(5)	27(4)	54(4)	17(3)	1(3)	2(3)	-6(3)
$C_{(4)}$	2439(4)	-125(9)	37(5)	21(3)	46(4)	27(3)	1(3)	13(3)	-2(3)
$H_{(1)}$	80(2)	-118(7)	-119(4)						
$H_{(2)}$	298(3)	203(5)	-183(3)						
$H_{(O(1))}$	319(3)	-27(5)	-274(3)						
$H_{(W)}$	474(4)	150(8)	200(5)						

water. It has the mp > 300°C. The IR spectrum was as follows: 3150-3500 cm^{-1} (NH, OH), 1540 cm^{-1}, and 1350 cm^{-1} (NO_2). The UV spectrum [λ_{max} (log ε)] was as follows: 202 nm (3.35) and 340 nm (3.84). The PMR spectrum was as follows: 7.00 ppm (1H, d, J = 8 Hz, 7-H), 8.04 ppm (1H, s, 2-H), 8.15 ppm (1H, d, J = 8 Hz, OH), and 12.62 ppm (1H, s, NH). The yield was 1.66 g (90%).

B. To the cooled solution of 0.84 g (10 mmole) of 5-amino-1,2,4-triazole in 1.6 ml of nitric acid (d = 1.4) and 10 ml of water at 0°C are added 1.27 g (10 mmole) of the potassium salt of nitoracetaldehyde in 15 ml of water. After 3 h of mixing at 0°C, 0.2 g (11%) of (IVa) is filtered off.

2-Methyl-6-nitro-7-hydroxy-4,7-dihydro-1,2,4-triazolo[5,1-c][1,2,4]triazine (IVb $C_5H_6N_6O_3$). This is obtained analogously to (IVa). It has the mp 280-282°C. The IR spectrum was as follows: 3050-3400 cm^{-1} (NH, OH), 1543 cm^{-1}, and 1350 cm^{-1} (NO_2). The UV spectrum [λ_{max} log ε)] was as follows: 203 nm (3.35) and 341 nm (3.90). The PMR spectrum was as follows: 2.30 ppm (3H, s, CH_3), 7.10 ppm (1H, d, J = 8 Hz, 7-H), 8.20 ppm (1H, d, J = 8 Hz, OH), and 12.60 ppm (1H, s, NH). The yield was 90% by the method A, and 7% by the method B.

X-Ray Structural Investigation of the Adduct (Ia). The crystals of (Ia) are monoclinic, a = 19.445(7), b = 6.965(3), and c = 12.686(5) Å; β = 102.39(3)°; V = 1505 $Å^3$; Z = 8; the space group C2/c. The x-ray diffraction experiment was carried out on the Sinteks $P\bar{1}$ diffractometer with a graphite monochromator, the λ_{CuK}, the $\theta/2\theta$-scanning, $2 < 2\theta < 120°$, and 817 reflections with $F^2 > 3\sigma$. The structure was interpreted by thee direct method and specified by the method of least squares with the full-matrix anisotropic approximation to R = 0.076 (R_w = 0.082).

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