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RESEARCHES ON TETRAZOLE AND s-TRIAZOLE FORMAZANS

III. Synthesis and Properties of 1-(4'-α-Pyridyl-s-triazolyl)-5-arylformazans*

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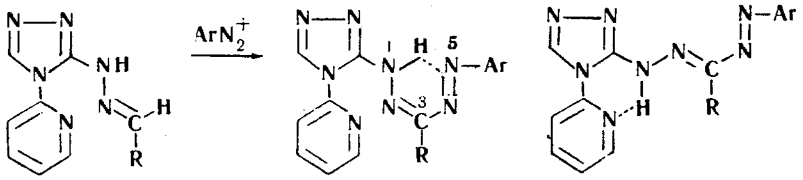
The synthesis and properties of some formazans, with the 4-(α-pyridyl)-1,2,4-triazole group at N_1 in the formazyl group, are described. It is shown that the presence of the α-pyridyl group results in weakening of the intramolecular bonding in the formazyl group.

Continuing research on the relationships between structure and properties of formazans, 1-[4'-(α-pyridyl)-1,2,4-triazolyl]-5-arylformazans (II) have been synthesized by diazo coupling aryldiazonium salts with 3-hydrazone-4-(α-pyridyl)-1,2,4-triazoles (I):



I II III

$R = CH_3$, C_6H_5, $p\text{-}C_6H_4NO_2$; $Ar = C_6H_5$, $p\text{-}C_6H_4NO_2$, $p\text{-}C_6H_4N(CH_3)_2$

It has already been shown [1–3] that the colors of the compounds and the strength of the intramolecular hydrogen bond depend on the nature of the groups at N_1, N_5, and C_3; the strongest hydrogen bonding is when there is an aromatic group at C_3. In that case, the hydrogen of the imino group closes a stable 6-membered quasi-heteroatomic (chelate) ring, and a band characteristic of the NH group is absent from the IR spectra.

It might have been expected that the nitrogen atom in the pyridine ring of compounds II, having a basic character, would compete with the N_5 nitrogen atom for possession of the proton, and that the compound would tend to go over into the trans-anti form III (cf. [4]). In other words, the presence of two prototropic centers (at N of α-pyridine and at N_5 of the formazyl group) would be expected to lead to weakening of the intramolecular hydrogen bond in the formazyl ring, and to the appearance of a ν NH band in the IR spectrum. These assumptions were confirmed: the crystals of the compounds prepared (see table) are red, λ_{max} is at 420–480 mμ ($CHCl_3$ solutions), while with both triarylformazans [5], and our recently described formazans containing the phenyltetrazole group, λ_{max} lies at 480–560 mμ [2, 3]; further, the IR spectra of all the compounds prepared have clear-cut absorption bands at 3160–3200 cm^{-1} which can be ascribed to NH group valence vibrations (free or connected with the comparatively weak hydrogen bond).

An interesting relationship between structure and color can be noted. Compounds with a methyl group at C_3 are more colored than the corresponding compounds with phenyl at C_3. This is in accord with views regarding participation of C_3 aryl in conjugation with the formazyl ring. Correspondingly, the ν NH values are greater also for the methyl derivatives than for the aryl ones, which indicates the high stability of the NH bond in the latter. Prominent is the considerable bathochromic shift of λ_{max}, brought about by introducing the NO_2 group at the para position in the phenyl group at N_5 (compounds IV and VII), and also the almost complete lack of effect of introduction of phenyl at C_3 (compound IX). A bathochromic and somewhat smaller shift is brought about by introducing the Me_2N group, as can be seen by comparing λ_{max} of compounds V and VIII with λ_{max} for compounds III and VI.

All the formazans prepared (see table) are soluble in ethanolic alkali (pH 8–9), to give dark bluish-violet solutions (sodium salt formation). Ethanolic hydrogen chloride solutions are pale yellow (hydrochloride formation). They all exhibit positive solvatchromism. With Cu^{2+} and Ni^{2+} salts they give crystalline complexes, whose structures are at present being studied.

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* For Part II see [1].

1-(4'-α-Pyridyl-s-triazolyl) formazans II

Compound number	R	Ar	Mp °C (solvent)	Appearance	Formula	Found, %		Calculated, %		λ_{max} ($\varepsilon \cdot 10^{-4}$), mμ	νNH, cm^{-1}	Yield, %
						C	H	C	H			
III	CH_3	C_6H_5	199—201 (benzene)	Orange-yellow needles	$C_{15}H_{14}N_8$	59.12	4.81	58.81	4.61	422 (2.37)	3444 (NH free) 3216 (NH bound)	83
IV	CH_3	p-$C_6H_4NO_2$	214—215 (Me_2CO)	Reddish-brown needles	$C_{15}H_{13}N_9O_2$	51.20	4.02 N 36.29	51.28	3.73 N 35.89	482 (2.62)	3172	50
V	CH_3	p-$C_6H_4N(CH_3)_2$	232—233 (EtOH)	Red prisms	$C_{17}H_{19}N_9$	58.37	6.03	58.45	5.48	476 (2.31)	3208	62
VI	C_6H_5	C_6H_5	159—161 (water-EtOH 2:1)	Dark red needles	$C_{20}H_{16}N_8$	65.24	4.55	65.21	4.38	428 (0.83)	3189	67
VII	C_6H_5	p-$C_6H_4NO_2$	233—234 (dioxane)	Orange-yellow minute crystals	$C_{20}H_{15}N_9O_2$	58.52	3.98 N 30.82	58.12	3.73 N 30.50	547 (1.69)	3169	60
VIII	C_6H_5	p-$C_6H_4N(CH_3)_2$	212—213 (MeOH)	Reddish-orange plates	$C_{22}H_{21}N_9$	63.86	4.82	64.21	5.14	474 (0.31)	3161	47
IX	p-$C_6H_4N_2$	C_6H_5	204—206 (MeOH)	Orange-red filamentous crystals	$C_{20}H_{15}N_9O_2$	57.65	3.42 N 30.23	58.12	3.73 N 30.50	427 (1.32)	3160	86

Experimental

Acetaldehyde 4-α-pyridyl-s-triazolyl-5-hydrazone. This was prepared from 2.0 g of the hydrazine (mp 213°–214° C [6]), and 1.0 ml acetaldehyde in 15 ml EtOH. Colorless prisms ex benzene. Yield 1.5 g (65%), mp 141°–142° C. Found: N 41.80%. Calculated for $C_9H_{10}N_6$: N 41.55%.

1-(4'-α-Pyridyl-s-triazolyl)-5-p-nitrophenyl-3-methylformazan (IV). 0.4 g (0.002 mole) acetaldehyde pyridyltriazolylhydrazone was mixed with 10 ml EtOH, and 0.2 g NaOH in 5 ml water added. The solution was then cooled to 0° C, and a solution of diazotized p-nitroaniline added (0.25 g p-nitroaniline, 1.2 ml conc. HCl, 0.16 g $NaNO_2$, 5 ml water). The reddish-brown precipitate was filtered off, yield 0.35 g (50%). Recrystallized from acetone. Formazans III and IV were prepared similarly.

1-(4'-α-Pyridyl-s-triazolyl)-3,5-diphenylformazan (VI). 0.6 g (0.002 mole) benzaldehyde 4-α-pyridyl-s-triazolyl-5-hydrazone (mp 214°–215° C) was dissolved in 30 ml EtOH, 0.2 g NaOH, and 10 ml water, and after cooling to 0°–4° C, the phenyldiazonium compound prepared from 0.19 g aniline, 4 ml water, 0.8 ml conc. HCl, and 0.14 g $NaNO_2$ added. After stirring for 30 min, 120 g ice was added, and the mixture then left overnight. The orange-yellow needles which separated were filtered off, washed with water, and dried in air. Recrystallized from aqueous EtOH (2:1), and vacuum-dried at 110° C for 7 hr. Formazans VII and VIII were prepared by the same method.

1-(4'-α-Pyridyl-s-triazolyl)-5-phenyl-3-p-nitrophenylformazan (IX). 1 g p-nitrobenzaldehyde 4-α-pyridyl-s-triazolylhydrazone (mp 219°–220° C) was dissolved in 100 ml pyridine, and coupled at 0°–4° C with diazotized aniline (0.32 g aniline, 6 ml water, 1 ml conc. HCl, 0.28 g $NaNO_2$). On standing the formazan began to separate; the mixture was left overnight, the orange-red precipitate filtered off, and recrystallized from 500 ml MeOH.

It should be mentioned that the formazans burned with difficulty during the elementary analyses. Apparently this is due to the presence of two heterocyclic rings, and a large number of nitrogen atoms in the compounds.

The IR spectra were measured with an IKS-14 instrument, in a paste with vaseline, LiF prism. The visible region spectra were determined with a SF-10 spectrophotometer in $CHCl_3$ solution, concentration 10^{-4} M.

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