RESEARCH ON BENZ- AND NAPHTHAZOLES

XX. Synthesis of 2-Hydrazinonaphth[2, 1-d]Thiazole and Derived Formazans*

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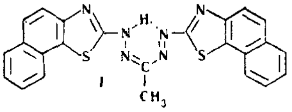
The synthesis of 2-hydrazinonaphth[2, 1-d]thiazole is effected, and its ability to undergo autoxidation in ethanol solution to give 1, 5-di(naphth[2, 1-d]thiazolyl-2)-3-methylformazan is established. Unsymmetrical 1-naphth[2, 1-d]thiazolyl-5-tolyl-3-aryl(or methyl) formazans are obtained by coupling a p-tolyldiazonium compound with the appropriate 2-hydrazinonaphth[2, 1-d]thiazole hydrazones.

In continuation of the research into heterocyclic hydrazino derivatives and their capacity to autooxidize in solutions of primary alcohols with formation of formazans, we synthesized for the first time 2-hydrazinonaphth [2, 1-d] thiazol and studied certain of its properties.

It has been prepared by two routes: hydrazinolysis of 2-chloronaphth[2, 1-d]thiazole and 2-methylmercaptonaphth[2, 1-d]thiazole. Of these, the second is preferred, as it does not necessitate carrying out the reaction under pressure.

Like 1-alkyl-2-hydrazinobenzimidazole [1] and 2-hydrazinonaphth[2, 1-d]imidazole [2], 2-hydrazinonaphth[2, 1-d]thiazole dissolved in ethanol autooxidizes in air, to give 1, 5-di(naphth[2, 1-d]thiazolyl-2)-3-methylformazan (I) (Table 1). The formazan I is a crystalline compound with a green metallic glitter, slightly soluble in most organic solvents. In some solvents (benzene, $CHCl_3$, nitrobenzene, and dioxane), it gives red solutions, ** in others (ethanol, acetone, dimethylformamide, alcoholic alkali) blue ones. IR spectroscopy data (lack of an absorption band corresponding to ν_{NH}*** valance vibrations) show that crystals of I contain a stable intra- or intermolecular hydrogen bond. Special study is required to determine whether solvatochromism in solutions is due to association with the solvent, or to conversion of isomers (like the yellow and red forms of 1, 5-diphenyl-3-methylformazan [4, 5]).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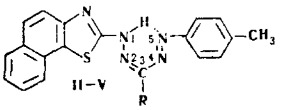
II–V

R=CH_3 (II); C_6H_5 (III); p-$C_6H_4NO_2$ (IV), 3,4-$C_6H_3(OCH_3)_2$ (V)

With aldehydes 2-hydrazinonaphth[2, 1-d]thiazole readily gives hydrazones (Table 2). Diazo coupling of p-tolyldiazonium chloride with these hydrazones gives the unsymmetrical formazans II–IV.

Unsymmetrical naphthothiazolylformazans are deeply colored crystalline compounds, slightly soluble in organic solvents. The state of the formazan ring depends on the substituent at position 3: IR data show that the 3 derivative II does not have a chelate ring, while the 3-aryl substituted compounds III–V are chelate compounds. The nature of the substituent in the benzene ring at position 3 (electron-accepting nitro group IV or electron-donating methoxy group V) does not have a large effect on the absorption spectrum in the visible region, or on the intramolecular or intermolecular hydrogen bonding.

All the formazans prepared readily form complexes with ions of many metals in solution, and are of potential interest as new ligands.

EXPERIMENTAL

Naphth[2, 1-d]thiazol-2-one (VI). A well ground mixture of 7.6 g (0.036 mole) β-amino-α-thionaphthol (prepared as described in [6]) and 5 g (0.16 mole) urea was melted in a porcelain beaker, at 220–225° for 15 min. The melt was extracted with alkali, the alkaline solution purified with active charcoal, then brought to pH 7 with AcOH. A precipitate of VI was obtained, yield 2.7 g (36%). Soluble in EtOH and dimethylformamide, mp 231–232°. Found: N 6.52; S 15.95%, calculated for $C_{11}H_7NOS$: N 6.96; S 15.96%.

2-Chloronaphth[2, 1-d]thiazole (VII). 1.5 g (0.008 mole) VI and 10 ml $POCl_3$ were heated together in a sealed tube for 4 hr at 170–180°, then excess $POCl_3$ distilled off, and the residue carefully decomposed with water. The reaction products were neutralized with 30% NaOH, the precipitate filtered off, and washed with water, yield 1.25 g (76.6%), prisms, mp 74–76° (ex aqueous EtOH). Found: Cl 15.47; N 6.42; S 14.56%, calculated for $C_{11}H_6ClNS$: Cl 16.13; N 6.28; S 14.59%.

Naphth[2, 1-d]thiazol-2-thione (VIII). 14.5 g β-amino-α-thionaphthone was heated for 6 hr with 8 ml CS_2 in 50 ml dry pyridine. Then the products were poured into water, and acidified with AcOH. The oil thrown out solidified on standing. The solid was filtered off and washed with water. Yield 14 g (96%). It was purified by recrystallization from an alkaline solution of AcOH, mp 219–221° (ex EtOH).

2-Methylmercaptonaphth[2, 1-d]thiazole (IX). 2.2 g (0.01 mole) VIII was dissolved in 30 ml EtOH and 3 ml 30% NaOH, then 2 ml MeI added, and the mixture left for 24 hr at room temperature. The colorless precipitate of IX was filtered off, washed with water, and recrystallized from EtOH. Yield of pure product 0.9g (39%). Long needles, mp 68–69° (ex EtOH). Found: N 6.40; S 28.58%, calculated for $C_{12}H_9NS_2$: N 6.05; S 27.72%.

2-Hydrazinonaphth[2, 1-d]thiazole (X). a) 3.5 g VII was refluxed for 6 hr with 20 ml hydrazine hydrate. After cooling the solid was filtered off and washed with water, yield 1.7 g (50%). After recrys-

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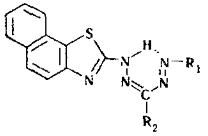
*For Part XIX see [3].

**λ_{max} in benzene and dioxane 520, in nitrobenzene and $CHCl_3$ 544 nm.

***The IR spectrum of formazan II has a band at 3320 cm^{-1}.

Table 1

Naphth[2, 1-d]thiazole Formazans



Compound	R	R_1	Mp, °C	λ_{max}, nm (in EtOH) Neutral solution	λ_{max}, nm (in EtOH) HCl, pH 1—2	λ_{max}, nm (in EtOH) NaOH, pH 10—12	Formula	Found, % N	Found, % S	Calculated, % N	Calculated, % S
I	CH_3	Naphthothiazolyl	253—254	614, 654	558	630, 654	$C_{24}H_{16}N_6S_2$*	17.48	14.26	18.39	14.17
II	CH_3	$C_6H_4CH_3$-*p*	190—192 (ex EtOH)	440	412	546	$C_{20}H_{17}N_5S$	19.49	9.08	19.48	8.92
III	C_6H_5	$C_6H_4CH_3$-*p*	189—191 (ex EtOH)	492	480	550	$C_{26}H_{19}N_5S$	16.72	7.77	16.15	7.39
IV	$C_6H_4NO_2$-*p*	$C_6H_4CH_3$-*p*	225—227 (ex BuOH)	496	494	558	$C_{25}H_{18}N_6O_2S$	17.76	6.68	18.02	6.87
V	$C_6H_3(OCH_3)_2$-3,4	$C_6H_4CH_3$-*p*	181—183 (ex BuOH)	508	490	552	$C_{27}H_{23}N_5O_2S$	15.19	6.72	14.53	6.63

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*Found: C 63.96; H 3.66%, calculated: C 63.69; H 3.58%.

Table 2

2-Hydrazinonaphth[2, 1-d]thiazole Hydrazones

Compound	Aldehyde	Mp, °C	Appearance of the crystals under the microscope	Formula	Found, % N	Found, % S	Calculated, % N	Calculated, % S
XI	Acetaldehyde	241—243	Colorless needles	$C_{13}H_{11}N_3S$	17.64	12.85	17.41	13.28
XII	Benzaldehyde	251—252	Yellowish needles	$C_{17}H_{13}N_3S$	13.81	11.28	14.42	11.00
XIII	p-Nitro benzaldehyde	305	Red needles	$C_{17}H_{12}N_4O_2S$	16.53	9.14	16.60	9.50
XIV	3,4-Dimethoxy-benzaldehyde	229—231	Needles	$C_{20}H_{17}N_3O_2S$	11 30	8.83	11.56	8.75

talizing from a large volume of EtOH it formed prisms, mp 208–209°. Found: S 14.70%, calculated for $C_{11}H_9N_3S$: S 14.78%.

b) 5.6 g IX and 20 ml hydrazine hydrate were refluxed together for 4–4 1/2 hr, yield 1.8 g (35%), prisms mp 208–210° (ex aqueous dimethylformamide).

1, 5-Di(naphth[2, 1-d]thiazolyl-2)-3-methylformazan (I). 1 g hydrazine X was dissolved in 60 ml hot EtOH, and the solution allowed to stand in air at room temperature. After 24 hr the solution turned dark blue, and after a few days a precipitate of minute crystals of I formed, and was filtered off yielding 0.5 g, mp 253–254°. Its solubility in organic solvents was low; it formed minute crystals with a metallic glitter.

2-Hydrazinonaphth[2, 1-d]thiazole hydrazones (XI-XIV). Prepared by heating together for 30 min equimolecular amounts of hydrazine X and the aldehyde in dimethylformamide-EtOH.

Preparation of unsymmetrical 1-(naphth[2, 1-d]thiazolyl-2)-3-alkyl(aryl)-5-p-tolylformazans (II–V). A solution of p-tolyldiazonium compound prepared from 0.012 g p-toluidine was added to a solution of 0.01 mole of the desired hydrazone in EtOH containing 1–2 ml 30% NaOH at 1–3°. The coupling was carried out in alkaline solution, and the solution was reddish violet. If the reaction mixture became acid during reaction, a few drops of 30% NaOH solution were immediately added to make it strongly alkaline. The products were left (solution pH 9–10) for 24 hr in a refrigerator, then with cooling brought to pH 6–7 with 2 N HCl. The resultant precipitate of formazan was filtered off, washed with water, and dried.

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