INVESTIGATIONS IN THE FIELD OF BENZAZOLES AND NAPHTHAZOLES

XXII. Synthesis of Unsymmetrical Formazans of the Benzazole Series Containing Sulfo Groups and a Spectrophotometric Study of the Complexes Formed by Them*

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1-(Alkyl benzimidazolyl)-, 1-benzothiazolyl- and 1-benzoxazolyl-3-methyl-5-phenylformazans containing sulfo groups (in the meta or para position) in the phenyl residue have been synthesized. It has been established that some of them can be used as analytical reagents.

Arylformazans containing sulfo groups are widely used as analytical reagents [1, 2].

We have synthesized unsymmetrical formazans of the benzimidazole, benzothiazole, and benzoxazole series containing sulfo groups and suitable for the photometric determination of metal ions in aqueous solutions. The synthesis was effected by the azo-coupling of diazotized sulfanilic and diazotized metanilic acids with acetaldehyde benzazolylhydrazones.

As can be seen from the table, the color of the formazans obtained depends on the nature of the heterocycle to a greater extent than on the position of the sulfo group and deepens in the following sequence: benzoxazole–benzothiazole–benzimidazole. In an alkaline medium the color of the solutions deepens from yellow-orange (400–470 nm) to red-violet (500–540 nm). The benzothiazole and benzoxazole formazans containing sulfo groups in the meta positions (VI) and (VIII) possess the greatest solubility in water. Thus, the solubility of the formazan VIII is 1–1.5% at 16°C. All the formazans are readily soluble in water at pH 10–12 in the form of their salts (sodium, potassium, ammonium).

When metal salts are added to solutions of the formazans, deeply colored solutions of complex compounds are formed: from deep blue to blue-green for copper and nickel and red-violet for zinc.

It has been established spectroscopically that the pH limits within which the complexes of nickel, copper, and zinc with the formazans I, II, VI, and VIII exist depend only on the metal ion and are practically independent of the nature of the heteroatom in the formazan. The nickel complexes exist over the widest pH range (4–11.5). The copper complexes are stable between pH 3 and 7. The nickel complexes have a very narrow range—pH 6–9.

In order to determine the possibility of using it as an analytical reagent for the Cu^{2+} ion, 1-(1'-benzylbenzimidazolyl)-3-methyl-5-p-sulfophenylformazan (I) was studied in more detail. With the bivalent copper ion the formazan I forms a compound an aqueous solution of which is colored deep blue or grayish according to the ratio of the reactants. The appearance of the color on complex formation takes place instantaneously and the coloration remains unchanged for several hours. The sensitivity of the reaction is $5 \cdot 10^{-7}$ mole/ml. The maximum absorption of the complex is in the range from 582 to 610 nm, and the formazan itself has practically no absorption in this range. The molar absorption coefficient calculated at $\lambda = 582$ nm is 3000 and at $\lambda = 610$ nm it is 2750. Within the range of concentrations of copper of $2 \cdot 10^{-6}$ to $6 \cdot 10^{-6}$ g and above the solutions obey the Lambert-Bouguer-Beer Law. The investigations carried out show that the formazan I can be used as an analytical reagent for copper. The determination of copper under the given conditions is interfered with by zinc, nickel, cobalt, manganese, and cadmium ions.

1-Benzoxazolyl-3-methyl-5-m-sulfophenylformazan (VIII) is no less promising.

EXPERIMENTAL

1-(1'-Benzylbenzimidazolyl)-3-methyl-5-p-sulfophenylformazan (I). The diazonium solution prepared from 0.95 g (5.5 mmole) of sulfanilic acid, 0.38 g (5.5 mmole) of sodium nitrite, and 25 ml of 2 N HCl was added to a solution of 1.32 g (5 mmole) of acetaldehyde 1-(1'-benzylbenzimidazolyl)-hydrazone obtained by the method of Rybakova and Bednyagina [3] in 60 ml of ethanol cooled to 3–5° C. The solution was brought to pH 3–4 with 2 N NaOH, whereupon the formazan precipitated; then it was filtered off, washed on the filter with hot water until chloride ions had been eliminated from the filtrate, and dried at 100° C.

The formazans II, III, and IV were obtained similarly. According to the results of elementary analysis and their spectral characteristics, compounds I–IV consisted of pure formazans sparingly soluble in ethanol, acetone, chloroform, and benzene and readily soluble in pyridine and dimethylformamide. They form brown microcrystalline powders with various tinges.

Acetaldehydes of benzothiazolylhydrazone and benzoxazolylhydrazone were obtained as described previously [4].

1-Benzothiazolyl-3-methyl-5-sulfophenylformazans (V, VI) and 1-benzoxazolyl-3-methyl-5-sulfophenylformazans (VII, VIII) were obtained similarly, but after the azo-coupling reaction the products were precipitated at different pH values of the medium: the formazans V and VIII at pH 5–5.5 and the formazans VI and VII at pH 2–3. In the case of compound VII, the solution was first brought to a weakly alkaline pH and then 2 N HCl was added to pH 2–3. In the preparation of VI, the reaction solution was evaporated to 1/3 bulk. The formazan VIII was crystallized from ethanol, giving nodules of yellow microcrystals. The formazans of the benzothiazole and benzoxazole series consisted of yellow or orange microcrystalline powders.

The study of the properties of the formazan I and its complex with Cu^{2+} was carried out photometrically on an FEK-56 photocolorimeter with filters nos. 7 and 8 at pH 6; the visible region of the spectrum was recorded on an SF-10 instrument.

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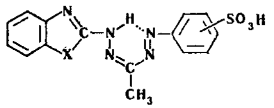
*For part XXI, see [5].

1-Benzazolyl-3-methyl-5-p- (or m-)sulfophenylformazans



Compound	X	Position of the sulfo group	Mp, °C	λ_{max}, nm (in water)					Empirical formula	Found, %			Calculated, %			Yield, %
				neutral medium	pH>12	solutions of the complexes*				C	H	S	C	H	S	
						$Ni(NO_3)_2$	$CuCl_2$	$ZnCl_2$								
I	N—$CH_2C_6H_5$	para	192—195	478	534	624	628	—	$C_{22}H_{20}N_6O_3S$	58.58	4.46	6.87	58.91	4.49	7.15	63
II	N—$CH_2C_6H_5$	meta	202—204	470	538	624	628	510	$C_{22}H_{20}N_6O_3S \cdot {}^1/_2H_2O$	57.82	4.67	6.70	57.75	4.63	7.01	80
III	N—CH_3	para	213—215	470	528	624	632	—	$C_{16}H_{16}N_6O_3S \cdot H_2O$	49.33	4.75	7.95	49.22	4.64	8.21	60
IV	N—CH_3	meta	208—210	478	544	624	630	—	$C_{16}H_{16}N_6O_3S \cdot H_2O$	48.77	4.40	8.10	49.22	4.64	8.21	61
V	S	para	206—208	432	530	610	630	—	$C_{15}H_{13}N_5O_3S_2 \cdot {}^1/_2H_2O$	47.19	3.77	16.42	46.86	3.67	16.68	70
VI	S	meta	218—220	418	520	606	624	474	$C_{15}H_{13}N_5O_3S_2$	47.48	3.52	16.91	47.98	3.48	16.71	50
VII	O	para	229—231	426	500	592	614	—	$C_{15}H_{13}N_5O_4S \cdot H_2O$	47.74	4.00	8.75	48.16	3.88	9.06	67
VIII	O	meta	227—229	404	508	592	608	468	$C_{15}H_{13}N_5O_4S \cdot 2H_2O$	45.45	3.94	8.03	45.56	4.33	8.11	50

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* Obtained by the addition of an excess of a solution of the metal salt to a solution of the formazan.

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