

INVESTIGATIONS IN THE BENZAZOLE AND NAPHTHAZOLE SERIES

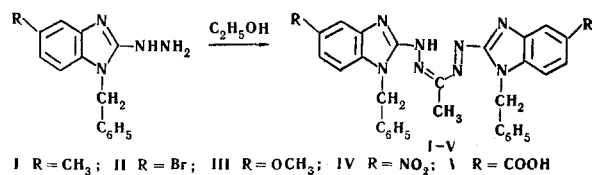
XXIX.* 1,5-BIS(1'-BENZYL-5'-R-BENZIMIDAZOLYL)- 3-METHYLFORMAZANS

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1,5-Bis(1'-benzylbenzimidazolyl)-3-methylformazans containing methyl, bromo, methoxy, nitro, and carboxy groups in the benzene rings are obtained by autooxidation in alcohol of 5-substituted 2-hydrazinobenzimidazoles. The nature of these substituents has only a slight effect on the color of the formazans and their salts but significantly affects the color of their complexes with metals.

In an investigation of the problems of the structure and color of 1,5-bis(benzimidazolyl)formazans, their salts, and complexes with metals it was found that the substituent on the heterocyclic nitrogen atom has a slight effect on the color [2-5]. We have obtained the following formazans by the previously described autooxidation method [2] in order to study the effect of substituents in the benzene ring of benzimidazole on the structure and color of the formazans and their derivatives:



The starting substituted hydrazino derivatives [1] were dissolved as bases in alcohol, and the solutions were allowed to stand at room temperature in air. The color of the solution deepened to an intensely violet color, and crystals of formazans I-IV were isolated in 2 to 3 days. The hydrazine containing a carboxyl group was oxidized considerably more slowly (20-25 days) and only with the addition of a small amount of pyridine to decrease the acidity of the medium, similar to the situation for 2-hydrazinobenzimidazole [2].

The formazans obtained, like 1,5-bis(1'-benzylbenzimidazolyl)-3-methylformazan, are amphoteric and form hydrochlorides and sodium salts in solution which have, as was previously shown, the cyanin structure [4]. It is characteristic that the substituent in the 5 position of benzimidazole has only a slight effect on the color of both formazan itself and its salt (Table 1).

Compounds I-V complex instantaneously in solutions of most metallic ions. The nature of the substituent appreciably affects the color of the complexes. Electron-donating substituents increase the bathochromic effect of complexes with Ni²⁺, Zn²⁺, Co²⁺, and Ce³⁺, while electron-accepting substituents decrease the bathochromic effect.

EXPERIMENTAL

The absorption spectra were obtained with an SF-10 spectrophotometer.

*For Communication XXVIII see [1].

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TABLE 1. Spectral Characteristics of 1,5-Bis(1'-benzyl-5'-R-benzimidazolyl)-3-methylformazans

Comp.	R	λ_{max} , nm			λ_{max} (nm) of complexes with metals			
		alcohol	alcoholic NaOH	alcoholic HCl	Ni ²⁺	Zn ²⁺	Co ²⁺	Ce ³⁺
I	CH ₃	530	584,620	596,630	636,700	610,656	620,690	590,628
II	Br	538	574,612	584,622	632,690	592,650	608,682	572,620
III	OCH ₃	550	586,628	620,650	654,720	616,672	638,710	610,650
IV*	NO ₂	558	575,615	575,615	620,678	585,644	596,574	—
V	COOH	542	576,610	580,616	640,690	578,616	630,690	574,614

*Does not form a complex with Ce.

TABLE 2. 1,5-Bis(1'-benzyl-5'-R-benzimidazolyl)-3-methylformazans

Comp.	R	mp	Empirical formula	Found, %			Calc., %			Yield, %
				C	H	N	C	H	N	
I	CH ₃	157—158	C ₃₂ H ₃₀ N ₈ · H ₂ O	70,42	5,77	20,83	70,56	5,92	20,58	38
II	Br	199—200	C ₃₀ H ₂₄ Br ₂ N ₈	54,77	4,10	16,88	54,89	3,68	17,07	42
III	OCH ₃	160—161	C ₃₂ H ₃₀ N ₈ O ₂ · H ₂ O	67,02	5,58	19,10	66,46	5,59	19,42	40
IV	NO ₂	162—163	C ₃₀ H ₂₄ N ₁₀ O ₄ · H ₂ O	59,92	4,30	23,42	59,53	4,31	23,11	45
V	COOH	249—250	C ₃₂ H ₂₆ N ₈ O ₄	65,07	4,93	19,49	65,52	4,47	19,10	35

1,5-Bis(1'-benzyl-5'-methylbenzimidazolyl)-3-methylformazan (I). 1-Benzyl-5-methyl-2-hydrazinobenzimidazole [1.2 g (0.01 mole)] was dissolved in 100 ml of ethanol. The solution became red-violet in several hours, and green crystals of I with a metallic luster were filtered after 2-3 days. They were soluble in alcohol, benzene, carbon tetrachloride, and acetone, and insoluble in water. Compounds II-IV were similarly obtained.

1,5-Bis(1'-benzyl-5'-carboxybenzimidazolyl)-3-methylformazan (V). 1-Benzyl-5-carboxy-2-hydrazinobenzimidazole [2.8 g (0.01 mole)] was dissolved in 100 ml of ethanol and 3 ml of pyridine was added. The solution became violet after several days, and a violet precipitate was precipitated with water after 1 month. This was purified by reprecipitation with water from alcohol. The product was soluble in dioxane, dimethylformamide, alcohol, and acetone, and insoluble in water, ether, chloroform, and carbon tetrachloride.

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