INVESTIGATIONS IN THE BENZAZOLE AND NAPHTHAZOLE SERIES

XXVI. Steric Effects in Unsymmetrical Halogen-Containing Benzimidazole Formazans*

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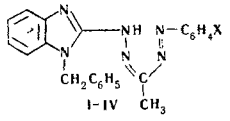
1-[1'-Benzylbenzimidazolyl]-5-halogenophenyl-3-methylformazans with the halogen (chlorine or bromine) in the para or ortho positions have been synthesized. In a comparative study of the reactions of the ortho and para halogen-containing isomers, steric hindrance due to a halogen in the ortho position of the phenyl radical has been observed in the formation of tetrazolium salts and nickel and copper complexes, and in the capacity of phototropic transformations.

To elucidate the influence of a substituent in the ortho position of the phenyl ring on the structure and properties of formazan, we have synthesized the following benzimidazole formazans:



I X = *p*-Cl;
II X = *o*-Cl;
III X = *p*-Br;
IV X = *o*-Br

It was shown previously [2] that the halogen-free 1-[1'-benzylbenzimidazolyl]-3-methyl-5-phenylformazan has a nonchelate structure with the predominance in carbon tetrachloride solution of the tautomeric form with the hydrogen on a nitrogen atom of the benzimidazole ring. This tautomeric imino form is characterized in the UV spectrum by the frequency of the stretching vibrations of the NH group, 3445 cm^{-1}. The formazans containing a methyl group in the para or ortho position of the phenyl ring have the same band, ν_{NH}, at 3445 cm^{-1} and similar absorption spectra in the visible region [3], the influence of the ortho-methyl group appearing only in complex formation with nickel and in the higher frequency of the absorption band of the complex of the ortho-methyl isomer.

The para-chloro and para-bromo benzimidazolyl formazan derivatives investigated (I and III) have an analogous ν_{NH} band at 3449 cm^{-1} in the IR spectra in carbon tetrachloride solution, but, unlike the ortho-tolyl formazan [3], the ortho-chloro and ortho-bromo derivatives II and IV exhibit no bands whatever in this region.

The absence of bands of N—H stretching vibrations is apparently caused by the screening of this group by the halogen in the ortho position of the phenyl but not by intramolecular chelation (N—H ··· N), which is accompanied by a considerable bathochromic effect [2], while the spectra in the visible region of the para and ortho halogen-containing isomers are similar (Table 1).

The isomeric para and ortho halogen-containing formazans are affected to a similar small extent by the solvent, and on passing from a nonpolar solvent (benzene) to a polar one (nitrobenzene) or from a proton-donating solvent (ethanol) to a proton-accepting one (dioxane) their color changes only slightly. On passing to the anion, a bathochromic shift of 50–56 nm is found in all the formazans.

However, the bathochromic effect of complex formation with various metals is different for the para and the ortho isomers. While with zinc the isomers give similarly colored complexes, with copper the complexes of the para isomers have absorption bands with frequencies 20–24 nm lower than the complexes with the ortho isomers. The influence of a halogen in the ortho position appears particularly strong in complex formation with nickel and, apparently, depends on the volume of the halogen (in II the hypsochromic effect in comparison with I is 76 nm, and in IV and III it is 89 nm).

The influence of the ortho halogen appears clearly in the formation of tetrazolium salts. The para halo-

*For part XXV, see [1].

Table 1

Spectral Characteristics of the 1-[1'-Benzylbenzimidazolyl]-5-halogenophenyl-3-methylformazans (V)

Compound	IR spectra, ν_{NH}, cm^{-1}	Absorption spectra in the visible region, λ_{max}, nm								
		V					complexes of V with metal ions (in ethanolic solutions			
		benzene	nitrobenzene	dioxane	ethanol	ethanol + NaOH	Ni^{2+}	Cu^{2+}	Zn^{2+}	Co^{2+}
I	3449	466	478	468	466	522	640	646	514	664; 520
II	None	466	476	468	468	516	564	622	520	670; 476
III	3449	468	478	466	476	526	640	650	518	674; 490
IV	None	468	476	464	474	528	558	628	516	670; 480

Table 2.

1-[1'-Benzylbenzimidazolyl]-5-halogenophenyl-3-methylformazans

Compound	Mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %
			C	H	N	halogen	C	H	N	halogen	
I	185—186	$C_{22}H_{19}N_6Cl \cdot C_2H_5OH$	63.76	5.76	18.32	7.84	64.20	5.68	18.73	7.90	77
II	101—102		63.96	5.29	18.84	7.96					60
III	190—191	$C_{22}H_{19}N_6Br \cdot C_2H_5OH$	58.43	5.05	17.10	16.18	58.42	5.10	17.03	16.20	75
IV	87—88		58.43	4.63	17.30	16.08					58

Table 3

Complexes of the Formazans I–IV with Ni^{2+}

Formazan forming the complex	Mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %
			C	H	N	halogen	C	H	N	halogen	
I	247—248	$(C_{22}H_{18}N_6Cl)_2Ni$	60.79	4.30	19.53	8.37	61.20	4.22	19.49	8.23	95
II	210—211		61.10	4.49	19.52	8.25					90
III	255—256	$(C_{22}H_{18}N_6Br)_2Ni$	55.75	4.20	17.64	17.28	55.67	3.83	17.70	16.84	92
IV	204—205		55.62	3.94	17.32	16.68					88

gen-containing formazans I and III readily form the corresponding tetrazolium salts with bromosuccinimide, while the ortho isomers II and IV on treatment with bromosuccinimide resinify and decompose with the formation of products of as yet unknown structure. Hindrance from the direction of an ortho nitro group has been found in the aryl formazan series [4], but in this case the tetrazolium salts were formed, although more slowly than from the corresponding para nitro formazans.

Finally, the ortho effect of a halogen appears in the phototropic isomerization of the formazans. As shown previously [2] in carbon tetrachloride solution on irradiation with sunlight benzimidazole formazans are converted into blue isomers (presumably dimers). The introduction of halogen into the para position of the phenyl radical accelerates this reaction, and in 1×10^{-4} M solutions I and III undergo phototropic transformations in only a few minutes. In contrast to this, the ortho isomers are incapable of undergoing phototropic transformations.

EXPERIMENTAL

1-[1'-Benzylbenzimidazolyl]-5-halogenophenyl-3-methylformazans (I–IV). A solution of a diazonium salt obtained from 0.01 mole of the appropriate amine, 5 ml of HCl (1:1), and 0.01 mole of $NaNO_2$ in 6 ml of water was added to a solution of 0.01 mole of acetaldehyde 1-benzylbenzimidazol-2-ylhydrazone in 150 ml of ethanol initially cooled to 0° C, the temperature being kept between 5 and 7° C. Then the reaction mixture was brought to pH 6 with 2 N NaOH solution. It was kept in the cold for 40 min and was then treated with 200 ml of water and the red precipitate that deposited was filtered off and recrystallized from ethanol (Table 2).

Nickel complexes of the formazans I–IV (V–VIII). Hot ethanolic solutions of 0.002 mole of a formazan and 0.002 mole of $Ni(NO_3)_2 \cdot 6H_2O$ were mixed. On cooling, a brown precipitate with a metallic luster of the corresponding complex deposited. It was filtered off and was washed on the filter several times with ethanol and with water to eliminate nickel ions (Table 3).

Tetrazolium salts. A solution of 0.001 mole of a formazan in 30 ml of chloroform was treated with 0.003 mole of bromosuccinimide in 50 ml of chloroform. The addition of absolute ether precipitated a yellow solid. For purification it was dissolved in a small amount of chloroform, boiled with carbon, and precipitated with ether.

2-[1'-Benzylbenzimidazolyl]-3-(p-chlorophenyl)-5-methyltetrazolium bromide (IX). Found, %: C 55.17; H 3.79; N 17.37. Calculated for $C_{22}H_{18}N_6ClBr$, %: C 54.92; H 3.77; N 17.47. Mp 150–151° C.

2-[1'-Benzylbenzimidazolyl]-3-(p-bromophenyl)-5-methyltetrazolium bromide (X). Found, %: C 44.09; H 3.09; Br 40.28%. Calculated for $C_{22}H_{18}N_6Br_2 \cdot HBr$, %: C 44.59; H 3.15; Br 39.56.

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