INVESTIGATIONS OF BENZAZOLES AND NAPHTHAZOLES

XXXII.* SYNTHESIS, STRUCTURE, AND PROPERTIES OF UNSYMMETRICAL FORMAZANS CONTAINING A 5-BENZIMIDAZOLE RESIDUE

L. P. Sidorova, N. P. Bednyagina,
and T. A. Kuznetsova

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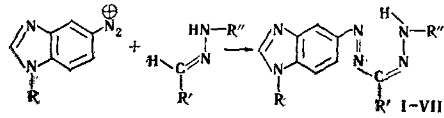
1-(5-Benzimidazolyl)-5-phenylformazans, which are isomers of the previously obtained 1-(2-benzimidazolyl)-5-phenylformazans, and 1-(5-benzimidazolyl)-5-(2-benzimidazolyl)formazans, which are isomers of 1,5-bis(2-benzimidazolyl)formazans, were synthesized. In contrast to their isomers, the benzimidazole ring in the formazans obtained is connected to the formazan chain at the 5 position rather than at the 2 position, and this leads to substantial differences in the properties, structures, and chromaticities of the isomeric formazans. The imidazole ring in 1-(5-benzimidazolyl)-5-phenylformazans is far removed from the chain and cannot participate in amino⇌imino tautomerism, in connection with which, the indicated formazans behave like 1,5-diphenylformazans and do not form complexes with metal ions in the cold. For the same reasons, 1-(5-benzimidazolyl)-5-(2-benzimidazolyl)formazans differ from the isomeric symmetrical 1,5-bis(2-benzimidazolyl)formazans by a hipsochromic shift of the long-wave maximum of the spectrum and are similar (with respect to their spectrophotometric characteristics and complexing properties) to the unsymmetrical 1-(2-benzimidazolyl)-5-phenylformazans. Conclusions regarding the state of the hydrogen bond of the formazan chain were drawn on the basis of the IR spectral data.

For the further study of the problems of the interrelationship between the structure and chromaticity of formazans and in order to search for ligands that have maximum color contrast during complexing, we have synthesized 1-(5-benzimidazolyl)-5-phenylformazans (I-IV) and 1-(5-benzimidazolyl)-5-(2-benzimidazolyl)formazans (V-VIII) that contain a benzimidazole ring joined to the formazan grouping at the 5 position (Table 1).



I R=H, R'=R''=C_6H_5; II R=H, R'=CH_3, R''=C_6H_5; III R=$C_6H_5CH_2$, R'=R''=C_6H_5;
IV R=$C_6H_5CH_2$, R'=CH_3, R''=C_6H_5; V R=H, R'=C_6H_5; VI R=H, R'=CH_3;
VII R=$C_6H_5CH_2$, R'=C_6H_5; VIII R=$C_6H_5CH_2$, R'=CH_3; V-VIII R''= 2-benzimidazolyl

Compounds I-IV are isomers of unsymmetrical 1-(2-benzimidazolyl)-5-phenylformazans [2]. The imidazole ring of I-IV is separated from the formazan chain by a phenyl group and owing to this is not capable of participating in the amino⇌imino tautomerism characteristic for 1-(2-benzimidazolyl)formazans [3]. This leads to weakening of the complexing properties of I-IV (complexes are not formed in the cold when metal salt solutions are added) and renders them similar to 1,5-diphenylformazan.

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*See [1] for communication XXXI.

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TABLE 1. Spectra of Formazans and Their Complexes

Compound	Elec. spectra, λ_{max}, nm (alcohol)				IRspectra, ν_{NH}, cm^{-1} (0.5% soln. in chloroform)*
	formazan	Na salt	Ni complex	Cu complex	
I	494	—	—	—	3470, 3331
II	420	520	—	—	3469, 3366
III	496	—	—	—	3333
IV	418	520	—	—	3368
V	480	550	634	654	3465, 3303
VI	470	528	630	648	3429
VII	486	556	664	682	3460, 3320
VIII	480	534	660	670	3450

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* ν_{NH} of benzimidazole is found at 3470 cm^{-1}.

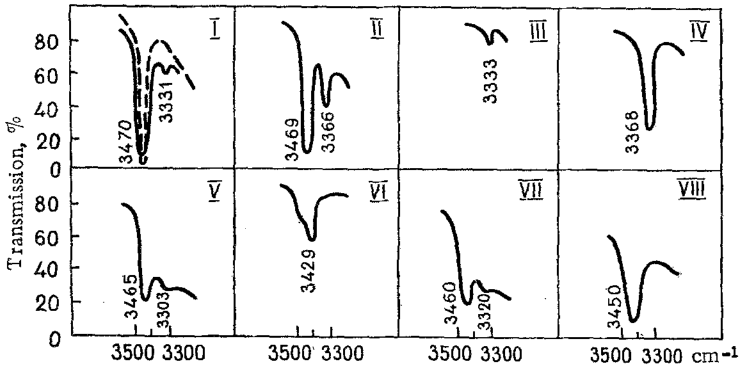

Fig. 1. IR spectra of I-VIII (0.5% solutions in chloroform). (The dashed line is the spectrum of benzimidazole.)

Like 1,5-diphenyl-3-methylformazan, II and IV, which contain a methyl group in the meso position, are capable of forming sodium salts. Like triphenylformazan, I and III (with a phenyl group in the meso position) have a chelate ring and are not converted to anions when they are made alkaline. An examination of the IR spectra of I-IV (Table 1), which are substituted and unsubstituted in the imidazole ring, makes it possible to assign the band at 3470 cm^{-1} to the stretching vibrations of the N—H bond in the imidazole ring, which is confirmed by comparison with the IR spectrum of unsubstituted benzimidazole. The band at 3330-3360 cm^{-1} should be assigned to ν_{NH} of the formazan grouping. Compounds II and III have intense ν_{NH} formazan bands, which attests to the absence of a hydrogen bond in the formazan ring of these compounds. The low-intensity band of I and III at 3330 cm^{-1} indicates a weaker chelate ring than in triphenylformazan, the IR spectra of which does not contain this band. In fact, it is scarcely possible to speak about strict uniformity of the bonds in the chelate formazan ring for unsymmetrical formazans in which there are substituents of different electron-acceptor character in the 1- and 5-positions.

Compounds V-VIII are isomers of symmetrical 1,5-bis(2-benzimidazolyl)formazans. Withdrawal of the imidazole ring from the formazan chain with retention of its ability to participate in coordination with metals induces an increase in the coloration of the formazan by 70-80 nm as compared with 1,5-bis(2-benzimidazolyl)formazans and thus ensures the maximum contrast in the color during complexing. In structure and color, V-VIII prove to be closer to unsymmetrical 1-(2-benzimidazolyl)-5-phenylformazans, but their complexes with metals of the 3d series are 35-40 nm more deeply colored. One ν_{NH} band at 3400 cm^{-1} is observed in the IR spectra of substituted and unsubstituted formazans V-VIII (Fig. 1). Thus V-VIII have an imino structure [3] while in the IR spectra of V and VI there is superimposition of the ν_{NH} bands of unsubstituted benzimidazole and the imino form of formazan (Table 1). The band at 3300 cm^{-1} in the spectra of V-VII (a phenyl group in the meso position) can be ascribed to ν_{NH} vibrations of the amino form of formazan [3].

EXPERIMENTAL

5(6)-Aminobenzimidazole Dihydrochloride. This was obtained by the reaction of 1,2,4-triaminobenzene with formic acid and had mp 315-317° (dec.) [4].

TABLE 2. Characteristics of the Synthesized Formazans

Compound	mp, °C	Crystallization solvent	Empirical formula	Found, %			Calc., %		
				C	H	N	C	H	N
I	184—185	Ethanol	$C_{20}H_{16}N_6$	70,30	5,03	24,76	70,56	4,74	24,7
II	110—112	Isopropanol	$C_{15}H_{14}N_6$	64,38	5,30	29,3	64,73	5,07	30,2
III	185—186	Ethanol	$C_{27}H_{22}N_6$	75,10	5,17	20,02	75,33	5,15	19,52
IV	174—175	Isopropanol	$C_{22}H_{20}N_6$	71,80	5,67	23,07	71,72	5,47	22,81
V	156—158	Aq. ethanol	$C_{28}H_{22}N_8 \cdot H_2O$	68,85	5,10	22,8	68,81	4,95	22,92
VI	158—160	Isopropanol	$C_{23}H_{20}N_8 \cdot 1/2\,H_2O$	66,38	5,26	26,3	66,2	5,07	26,84
VII	106—107	Ethanol	$C_{35}H_{28}N_8$	74,68	5,27	19,66	74,97	5,03	20,0
VIII	128—130	Isopropanol	$C_{30}H_{26}N_8 \cdot 1/2\,H_2O$	70,62	5,19	22,07	70,84	5,36	22,07

1-Benzyl-5-aminobenzimidazole. A 3 g (0.01 mole) sample of 1-benzylamino-2,4-dinitrobenzene was reduced with hydrazine hydrate on Raney nickel by the method in [5]. The resulting solution of triamine was filtered, and the filtrate was refluxed for 4 h with 98% formic acid (distilled over B_2O_3) and evaporated. The residual resin was dissolved in HCl (1:1), the solution was boiled with charcoal, and 1-benzyl-5-aminobenzimidazole was isolated from the solution with 2 N NaOH. The product was purified by repeated reprecipitation from hydrochloric acid solution by the addition of alkali to give 60% of a product with mp 122°. Found: C 75.53; H 5.86; N 19.25%. $C_{14}H_{13}N_3$. Calculated: C 75.41; H 5.87; N 18.83%.

1-(1-Benzyl-5-benzimidazolyl)-3,5-diphenylformazan (III). A diazonium salt solution prepared from 1 g of 1-benzyl-5-aminobenzimidazole, 6 ml of HCl (1:1), and 0.48 g of $NaNO_2$ was added to a cooled solution of 0.883 g (4.5 mole) of benzaldehyde phenylhydrazone in 10 ml of ethanol and 6 ml of pyridine. The mixture was neutralized with 2 N NaOH to pH 7-8, and the red-brown precipitate of III was crystallized from ethanol.

Compounds I-VIII were similarly obtained by azo coupling of the diazonium salts of 5-aminobenzimidazole and 1-benzyl-5-aminobenzimidazole with the appropriate aryl- and 2-benzimidazolyl hydrazones: I was obtained in alcohol–pyridine; II, VI, IV, and VIII were obtained in isopropyl alcohol; and V and VII were obtained in alcoholic alkali. The yields were 65-80%. The characteristics of the formazans obtained are presented in Table 2.

The IR spectra of thin films of solutions of the compounds were recorded with a UR-20 spectrophotometer from 3200 to 3500 cm^{-1} using LiF prisms.

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