INVESTIGATIONS IN THE BENZAZOLE AND NAPHTHAZOLE SERIES

XXXVI.* SYNTHESIS, STRUCTURE, AND PROPERTIES OF UNSYMMETRICAL 1-[4(7)-BENZIMIDAZOLYL]FORMAZANS

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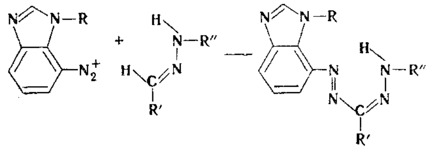
1-[4(7)-Benzimidazolyl]-5-phenyl- and 1-[4(7)-benzimidazolyl]-5-(2-benzimidazolyl)formazans, which are isomers of the previously obtained 1-(2-benzimidazolyl)-5-phenyl- and 1,5-di(2-benzimidazolyl)formazans, were synthesized. Structural problems (tautomerism and hydrogen bonding) of the new formazans are discussed.

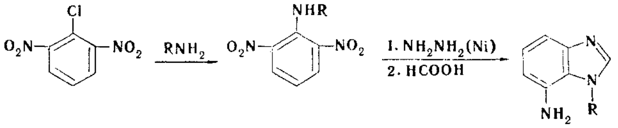
1-[4(7)-Benzimidazolyl]-5-phenylformazans (I-III) and 1-[4(7)-benzimidazolyl]-5-(2-benzimidazolyl)-formazans (IV-VIII) were obtained by the azo coupling of diazonium salts of 4(7)-aminobenzimidazole (VIII) and 1-benzyl-7-aminobenzimidazole (IX) with the appropriate arylhydrazones and 2-benzimidazolylhydrazones.



I–VII

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′=CH_3, R″=C_6H_5; IV R=H, R′=C_6H_5; V R=H, R′=CH_3; VI R=$C_6H_5CH_2$, R′=C_6H_5; VII R=$C_6H_5CH_2$, R′=CH_3; IV—VII R″= 1-benzyl-2-benzimidazolyl

Compound VIII was obtained via the method in [2], while IX was obtained from 2,6-dinitrochlorobenzene (X) [3]:



X XI IX

IX, XI R=$CH_2C_6H_5$

In the investigation of I-VII, it was necessary to ascertain the effect of the NH group of benzimidazole on hydrogen bonding in the formazan ring and on the properties of the formazans.

The imidazole ring in I-III is separated from the formazan chain by the phenyl ring and, in contrast to the isomeric 1-(2-benzimidazolyl)-5-phenylformazans, is therefore incapable of participating in amine–imine tautomerism [4,5]. An examination of the IR spectra of I-III (Table 1) makes it possible to assign the band at 3430-3450 cm^{-1} to the stretching vibrations of the N−H bond in the imidazole ring and the band at 3360 cm^{-1} to ν_{N-H} of the formazan grouping. It is interesting that formazan I, with a phenyl group at-

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*See [1] for communication XXXV.

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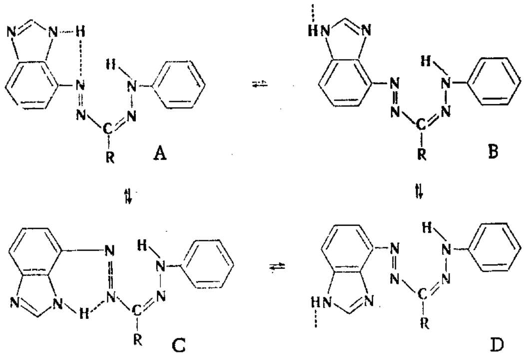
TABLE 1. Characteristics of the Synthesized Compounds

Comp.	mp, °C	Empirical formula	Found, %			Calc., %			λ_{max}, nm (alcohol)	IR spectra, ν_{N-H}, cm^{-1} (chloroform)
			C	H	N	C	H	N		
I	161—163	$C_{20}H_{16}N_6$	71,31	4,8	23,92	70,56	4,74	24,7	456	3448, 3345
II	99—101	$C_{15}H_{14}N_6 \cdot 1/2H_2O$	62,82	5,39	22,10	62,70	5,26	29,25	434	3434, 3364
III	153—155	$C_{22}H_{20}N_6$	71,29	5,33	23,14	71,72	5,48	22,81	440	3360
IV	202—204	$C_{28}H_{22}N_8$	71,33	4,79	23,70	71,47	4,71	23,82	500	3460
V	193—194	$C_{23}H_{20}N_8$	67,36	5,06	27,03	67,50	5,2	27,2	490	3470, 3439
VI	146—148	$C_{35}H_{28}N_8$	75,08	5,09	19,45	74,97	5,03	19,99	510	3470
VII	150—152	$C_{30}H_{26}N_8 \cdot 1/2H_2O$	70,85	5,41	21,74	70,84	5,36	22,07	500	3455

tached to the C_3, has an intense band at 3345 cm^{-1}, which is evidence for the absence of hydrogen bonding in the formazan ring, in contrast to triphenylformazan, which has a strong chelate ring and for which the ν_{NH} band does not appear at all.

By virtue of the peculiarities of the three-dimensional structures of I and II and the possible tautomeric transition of the hydrogen in the benzimidazole ring, one might have assumed the possibility of both intramolecular (A, C) and intermolecular (B, D) hydrogen bonds. Since dilution of the chloroform solution of I, II during investigation of ν_{NH} does not result in its disappearance or in a change in the character of the band at 3440 cm^{-1}, structures with intramolecular hydrogen bonds (A, C) are most probable.



$R = CH_3, C_6H_5$

Compounds I and II instantaneously form complexes with divalent ions of metals of the 3-d series at room temperature. The formation of complexes with solutions of metal salts under similar conditions is not observed for III, which contain a 1-substituted benzimidazole ring, which is evidence for the participation of the benzimidazole hydrogen in complexing. Thus I and II are unusual new bidentate formazans, similar to 1-(2-benzazolyl)-5-[o-hydroxy(carboxy)phenyl)]- and 1-phenyl-5-[o-hydroxy(carboxy)phenyl]-formazans [6,7]. Considering the bidentate properties of I and II, structure A can be considered to be the most probable of the two structures with intramolecular hydrogen bonds (A, C). The absence of a hydrogen bond in the formazan ring of I can apparently be explained by "competition" of the hydrogen of the benzimidazole ring with the hydrogen of the formazan chain for the formation of an intramolecular hydrogen bond with N_1 of the formazan ring (A).

Compounds IV-VII are isomers of the symmetrical 1,5-di(2-benzimidazolyl)formazans. One ν_{NH} band at 3440-3470 cm^{-1} is observed in the IR spectra of IV-VII. Thus IV-VII have an imino structure [5] with a hydrogen attached to the basic nitrogen of the 2-benzimidazolyl grouping. The ν_{NH} bands of the unsubstituted benzimidazole ring and the imino form of formazan are superimposed in the spectra of IV and V. A certain resolution of the N−H band is observed for formazan V for ν_{NH} 3470 and 3435 cm^{-1}. A comparison of these bands with ν_{NH} of formazans VI and VII, which contain a nitrogen-substituted benzimidazole ring, makes it possible to assign the high-frequency band at 3470 cm^{-1} to ν_{NH} of the imino form of formazan (Table 1).

Removal of one of the imidazole rings from the formazan chain causes an increase in the color of IV-VII by 40-50 nm as compared with 1,5-di(2-benzimidazolyl)formazans. Compounds IV-VII instantaneously form complexes with divalent ions of metals of the 3-d series at room temperature. Like I and II, formazans IV and V are capable of manifesting bidentate properties with the participation of the benzimidazole hydrogen in complexing.

EXPERIMENTAL

4(7)-Aminobenzimidazole (VIII) Dihydrochloride. This compound was obtained by the reaction of 1,2,3-triaminobenzene with formic acid [2]. The heavy rose needles did not have a sharp melting point. Found: N 20.8; Cl 34.1%. $C_7H_7N_3 \cdot 2HCl$. Calculated: N 20.4; Cl 34.5%.

2-Benzylamino-1,3-dinitrobenzene (XI). An 8-g sample of sodium acetate (anhydrous) was added to 8 g of X [3] dissolved in ethanol. The mixture was cooled, 8 ml of benzylamine was gradually added, and the resulting mixture was refluxed for 1 h on a water bath and poured into 200 ml of hot water. The aqueous mixture was cooled to precipitate bright-yellow XI. The product crystallized satisfactorily from ethanol to give a substance with mp 92-94°. Found: C 57.64; H 4.21; N 15.98%. $C_{13}H_{11}N_3O_4$. Calculated: C 57.14; H 4.05; N 15.38%.

1-Benzyl-7-aminobenzimidazole (IX). A 3-g (0.01 mole) sample of XI was dissolved in 100 ml of ethanol and reduced with hydrazine hydrate over Raney nickel via the method in [8]. The resulting solution of 2-benzylamino-1,3-diaminobenzene was filtered, and the compound in solution was subjected to closure with 98% HCOOH (distilled over B_2O_3) for 8 h. The solution was evaporated, and the resin was dissolved in HCl (1:1). The solution was boiled with charcoal for 15-20 min. Base IX was isolated from the solution by the addition of 2 N NaOH and precipitated as white flakes. The product darkened and resinified on contact with air. After brief air drying, it was diazotized to obtain the formazan.

1-[4(7)-Benzimidazolyl]-3-methyl-5-phenylformazan (II). A 10-g sample of sodium acetate and a diazonium solution, obtained from 7.5 mmole of the dihydrochloride of VIII, 9 ml of HCl (1:1), and 0.7 g of $NaNO_2$ in 5 ml of H_2O, were added to a cooled solution of 1 g (7.5 mmole) of acetaldehyde phenylhydrazone in 30 ml of ethanol. The solution was neutralized with 2 N NaOH to give a yellow-brown precipitate of II. Compounds I, III, and IV were similarly obtained by azo coupling of the diazonium salts of VIII and IX with the appropriate arylhydrazones and 2-benzimidazolylhydrazones; I was prepared in alcohol–pyridine and was obtained in low yield; III, V, and VII were prepared in ethanol with sodium acetate, and IV and VI were prepared in alcoholic alkali media and were obtained in 60-70% yield. All of the formazans crystallized readily from ethanol, aqueous ethanol, and isopropyl alcohol. The characteristics of the formazans obtained are presented in Table 1.

The IR spectra of solutions of the compounds were recorded. The measurements were made with a UR-20 spectrophotometer from 3200 to 3500 cm^{-1} with an LiF prism.

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