RESEARCH ON BENZ- AND NAPHTHAZOLES

XIII. 1-Benzazolyl-3, 5-diphenylformazans*

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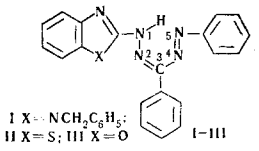
Heterocyclic analogs of triphenylformazan have been synthesized: 1-(1'-benzylbenzimidazolyl)-3,5-diphenylformazan (I), 1-benzothiazolyl-3,5-diphenylformazan (II), and 1-benzoxazolyl-3,5-diphenylformazan (III). On a basis of the study of IR and UV spectra, the hypothesis has been put forward that I lacks a chelate ring while II and III have chelate rings with a weak intramolecular hydrogen bond. Ease of complex formation with many metals and a capacity for the formation of tetrazolium salts have been noted.

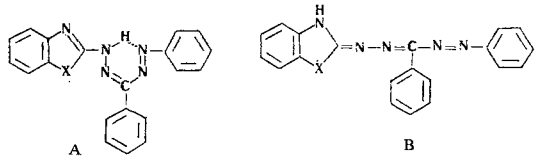
The present communication describes the synthesis and gives some information on the structure and properties of unsymmetrical formazans of the benzazole series which represent heterocyclic analogs of triphenylformazan.



I X = $NCH_2C_6H_5$; II X = S; III X = O I–III

The formazans obtained, like triphenylformazan, may either have the structure of a chelate with an intramolecular hydrogen bond or exist in the open form, the latter being theoretically capable of tautomerization (with the hydrogen on N_1, N_5, or the N atom of the heterocycle).

The IR spectra of the formazans (in CCl_4 solution) showed that formazan I has the band of NH stretching vibrations in the 3445 cm^{-1} region, while in the formazans II and III the ν_{NH} band in this region is absent. On this basis, it may be assumed that the formazan I has the open structure (with possible passage of the hydrogen atom to the more basic nitrogen of the heterocycle) (B) and formazans II and III have the chelate structure (A)



A B

The spectral characteristics of the formazans (Table 1) confirm this conclusion: the formazan I exhibits considerable positive solvatochromy, while the formazans II and III, like triphenylformazan, are little affected by the solvating influence of the solvent. However, the chelate ring in II and III is unstable, and proton-accepting solvents (acetone and dioxane) are capable of opening the ring as a consequence of which the coloration of the formazan becomes more intense. The instability of the chelate is also indicated by the fact that in an ethanolic alkaline medium the formazans II and III, like the formazan I, readily form deeply colored sodium salts, while triphenylformazan which has a stable chelate ring, does not change its coloration in alcoholic alkali.

The 1-benzazolyformazans also differ from triphenylformazan in their capacity for complex formation. While triphenylformazan forms complexes with metals only on being heated with metal salts [2], the formazans I–III form deeply colored complexes which can be isolated in the crystalline state when ethanolic solutions of the formazan and a metal salt ($Ni(NO_3)_2$, $ZnCl_2$, $CuCl_2$, etc.) are mixed in the cold.

In order to elucidate the influence of the position of the heterocycle in the molecule on the properties of the formazan, we obtained 3-benzothiazolyl-1, 5-diphenylformazan (IV) which has been described previously [3]. In this compound, as in triphenylformazan, and unlike the formazan II, the color of an ethanolic solution does not deepen on basification, and no complex formation takes place in the cold when solutions of metal salts are added. Its IR spectrum lacks the band of the stretching vibrations of an NH group (in the 3450–3100 cm^{-1} region). Thus, the formazan IV has a chelate ring with a strong hydrogen bond. Obviously the symmetry of the molecules of formazans having similar substituents on nitrogen atoms 1 and 5 strengthens the hydrogen bond.

Like triphenylformazan, [4], on reaction with bromosuccinimide, compounds I–II give tetrazolium salts which are reconverted into the initial formazans by the action of reducing agents. The tetrazolium salt obtained from formazan III is unstable and rapidly changes into a colorless product of as yet unknown structure.

EXPERIMENTAL

Benzaldehyde 1-benzyl-2-benzimidazolylhydrazone was obtained by heating 0.01 mole of 1-benzyl-2-hydrazinobenzimidazole in 30 ml of ethanol with 0.01 mole of benzaldehyde. Yield 90%. Mp 197–198° (from ethanol). Found, %: C 77.33; H 5.57. Calculated for $C_{21}H_{18}N_4$, %: C 77.26; H 5.56.

1-(1'-Benzylbenzimidazolyl)-3,5-diphenylformazan (I). To a cooled solution of 1.6 g (0.005 mole) of benzaldehyde 1-benzyl-2-benzimidazolylhydrazone in a mixture of 15 ml of pyridine and 16 ml of methanol was added the diazonium solution obtained from 0.005 mole of aniline, 6 ml of HCl (1 : 1), and 0.35 g of $NaNO_2$ in 5 ml of water, the temperature being kept at 0–5°. The mixture was kept at this temperature for 40 min, after which 200 ml of water was added and it was left overnight in the refrigerator. This gave dark green lustrous rhombic crystals (dark red under the microscope) with mp 95–98° (from methanol). Found, %: C 73.77; H 5.65; N 19.18. Calculated for $C_{27}H_{22}N_6 \cdot {}^1/_2CH_3OH$, %: C 73.90; H 5.41; N 18.82. When I was recrystallized from a mixture of petroleum ether (low-boiling) and

*For part XXII, see [1].

Spectral Characteristics of 1-Benzazolyl-3, 5-diphenylformazans

Compound	X	UV spectra λ_{max}, nm	Visible region of the spectrum λ_{max}, nm* in the following solvents							Complexes, λ_{max}		
			benzene	nitrobenzene	chloroform	acetone	dioxane	ethanol	ethanolic NaOH	Zn	Ni	Cu
I	$NCH_2C_6H_5$	245, 305	456	474	466	460	462	474	540	614	626	642
II	S	230, 295	484	486	476	460	470	470	526	616	630	646
III	O	245, 290	470	460	456	426	440	430	504	592	606	630

*Triphenylformazan has λ_{max}, nm: in benzene 494, in nitrobenzene 498, in ethanol 488, in ethanolic alkali 488; 3-benzothiazolyl-1,5-diphenylformazan (IV) has λ_{max}, nm: in benzene 440, in nitrobenzene 446, in ethanol 430, in ethanolic alkali 432.

n-heptane, the compound was obtained without solvent of crystallization. Mp 70–72°. Found, %: C 75.18; H 5.25; N 19.52. Calculated for $C_{27}H_{22}N_6$, %: C 75.32; H 5.15; N 19.52.

Benzaldehyde benzothiazolylhydrazone and benzaldehyde benzoxazolylhydrazone were obtained as described previously [5].

1-Benzothiazolyl-3,5-diphenylformazan (II). The diazonium solution obtained from 0.01 mole of aniline, 8 ml of HCl (1 : 1), and 0.7 g of $NaNO_2$ in 7 ml of H_2O was added to a cooled solution of 2.54g (0.01 mole) of benzaldehyde benzothiazolylhydrazone in 170 ml of methanol and 4 ml of concentrated HCl. The solution was neutralized with 2 N NaOH to pH 6 and left in the refrigerator after which the lustrous green crystals of II were filtered off. Mp 183–185° (from methanol). Yield 77%. Found, %: C 66.78; H 4.22; S 9.51; N 19.49. Calculated for $C_{20}H_{15}N_5S$, %: H 4.23; S 8.95; N 19.59.

1-Benzoxazolyl-3,5-diphenylformazan (III). This was obtained similarly. Yield 60%. Dark brown plates (red under the microscope) with mp 155–156° (from methanol). Found, %: C 70.66; H 4.62; N 20.74. Calculated for $C_{20}H_{15}N_5O$, %: C 70.36; H 4.42; N 20.52.

3-Benzothiazolyl-1,5-diphenylformazan (IV) was obtained by Seyhan's method [3]. Orange crystals with mp 184–185° (from methanol) (literature: 185–186°). Found, %: C 67.20; H 4.20; S 8.90. Calculated for $C_{20}H_{15}N_5S$, %: C 67.20; H 4.23; S 8.97.

2-(1'-Benzylbenzimidazolyl)-3,5-diphenyltetrazolium bromide. A solution of 0.44 g (0.001 mole) of the formazan in 20 ml of chloroform was treated with 0.5 g (0.0032 mole) of bromosuccinimide in 40 ml of chloroform. The color of the mixture changed from dark red to light brown. When absolute either was added, a yellow-green precipitate deposited. For purification, the compound was dissolved in a small amount of chloroform and precipitated with ether. Yield 70%. Mp 109–110°. Found, %: Br 27.82. Calculated for $C_{27}H_{21}BrN_6 \cdot HBr$, %: Br 27.12.

2-Benzothiazolyl-3,5-diphenyltetrazolium bromide. This was obtained similarly to the preceding compound. Mp 180–182°. Yield 80%. Found, %: Br 38.95, Calculated for $C_{20}H_{14}BrN_5S \cdot 2HBr \cdot H_2O$, %: Br 38.96.

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