INVESTIGATIONS IN THE BENZAZOLE AND NAPHTHAZOLE SERIES

XXIV. The Structure of Unsymmetrical Formazans of the Benzazole Series*

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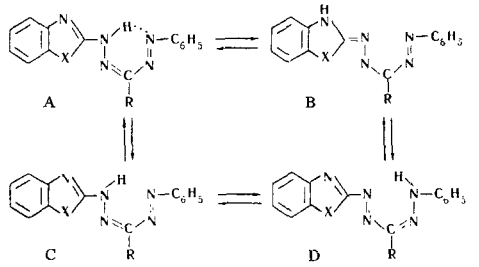
The structure of the chelate ring and the tautomerism of unsymmetrical 1-benzazolylformazans depends on the nature (basicity) of the heterocycle and on the nature of the substituent (methyl, phenyl) in position 3. Analogs of 3-methyl-1, 5-diphenylformazan containing 1-benzylbenzimidazolyl, benzothiazolyl, or benzoxazolyl groups have an open structure of the formazan chain without an intromolecular hydrogen bond (IHB) while in the case of a benzimidazolylformazan the tautomeric form with hydrogen attached to the heterocyclic nitrogen atom predominates in solution. Of the analogs of triphenylformazan, 1-(1'-benzylbenzimidazolyl)-3, 5-diphenylformazan also has an open structure, but 1-benzoxazolyl-3, 5-diphenylformazans have a chelate structure with a weak IHB. Conclusions have been drawn from the IR and UV spectra and from determinations of the ionization constants of the formazans. In the formazans of the benzimidazole series, the phenomenon of the photoisomerization of the red form of the formazan into a blue form when solutions in carbon tetrachloride are irradiated with visible light has been found. It has been shown that the blue form produced is a dimer of the formazan.

It is known that triphenylformazans have a chelate structure and that diphenyl-3-alkylformazans do not have a strong IHB [2–6].

In this paper we consider the influence of the nature of the heterocycle in position 1 (benzimidazole, benzothiazole, benzoxazole) and of the substituent in postion 3 (methyl, phenyl) on the structure of the formazan group in a number of 1-benzazolyl-5-phenylformazans that we have obtained previously.

The formazans I–VI may exist in tautomeric (B, C, D) or chelate (A) forms.



I X=NCH$_2$C$_6$H$_5$, R=CH$_3$; II X=NCH$_2$C$_6$H$_5$, R=C$_6$H$_5$; III X=S, R=CH$_3$; IV X=S, R=C$_6$H$_5$; V X=O, R=CH$_3$; VI X=O, R=C$_6$H$_5$

Information on the structure of the formazans is given by their IR spectra, particularly the position and intensity of the ν_{NH} bond, which appears in the 3450–3100 cm^{-1} region in the nonchelate [6] and is absent from the chelate formazans [4, 9]. In carbon tetrachloride solution, ν_{NH} appears clearly in I (3450 cm^{-1}), II (3445 cm^{-1}), III (3450 and 3360 cm^{-1}) and V (3450 and 3370 cm^{-1}), while in IV and VI these bands are practically absent. Thus, only IV and VI possess a chelate ring but it is weaker than in the triphenylformazans and partially opens in a proton-accepting solvent, dioxane, which is shown by the appearance in dioxane solution of the ν_{NH} band in the 3200 cm^{-1} region for IV and the 3210 cm^{-1} region for VI. Consequently, in the formazans of the benzothiazole and benzoxazole series the same features are observed as in the arylformazans: the formazans with methyl in position 3 have an open structure and those with phenyl a chelate structure. A phenyl group in position 3 favors the formation of the chelate, since it enters into conjugation with the formazan ring. Conversely, in the 1-benzimidazolylformazans, regardless of the substituent in position 3, the formazan group is open. Apparently, in the case of II, the influence of the more basic imidazole ring is shown more strongly than the influence of the phenyl in position 3.

A consideration of the UV and visible spectra (Fig. 1) leads to the same conclusions. Compounds I–VI each have two maxima in the UV region, characterizing the phenyl and benzazole rings, and a maximum in the visible region relating to the chromophoric grouping. The chelate compounds IV and VI are more deeply colored than the open-chain compounds III and V. This is due to the fact that the closure of the chelate ring increases the degree of conjugation in the system, which leads to a bathochromic shift of the absorption maximum of the long-wave π-electronic transition. Compounds I and II, in spite of the different substituents in position 3, have the same position of the physical maximum.

Compounds I–III and V may exist in forms B, C, and D. The question of the tautomerism of the amine-imine type, B $\rightleftarrows$ C, is part of the general problem of the tautomerism of heterocyclic amines. The state of the amine-imine equilibrium [11, 12] depends on the basicity of the heterocycle and the acceptor nature of the substituent of the extracyclic nitrogen. The higher the basicity of the heterocycle, the more probable is a shift in the direction of the imino form [13]. In compounds I, III, and V, having a similar structure, and in II, IV, and VI, correspondingly, the shift in the tautomeric equilibrium must depend only on the influence of the heterocycle, and since the basicity of benzimidazole is considerably greater than that of benzothiazole and benzoxazole [14], the tendency to a transition to the B form must be higher in I and II. In actual fact, when the UV spectra of I and II are compared with the UV spectrum of the "model" 2-amino-1-benzylbenzimidazole and 1-benzyl-2-imino-3-methylbenzimidazoline [15–17] the similarity of the spectra of I and II to that of the "imino model" is established.

*For part XXIII, see [1].

Compound	λ_{max}, anal., nm	pH	d_1	d	d_M	$\log \frac{d_1-d}{d-d_M}$	pK_a (mean)
I	520	11.6	1.137	0.550	0.475	0.89	12.5
II	540	12.2	1.640	1.250	0.790	−0.07	12.1
III	500	10.0	1.525	1.338	0.287	−0.75	9.1
		9.4	1.525	1.225	0.287	−0.50	
		9.0	1.525	0.890	0.287	−0.08	
IV	520	11.6	2.162	1.900	0.875	−0.529	11.1
		9.7	2.162	0.912	0.875	1.53	
V	490	10.4	1.775	1.550	0.287	−0.75	9.7
		9.0	1.775	1.363	0.287	0.73	
VI	490	11.6	1.025	0.762	0.400	−0.14	11.2
		10.7	1.025	0.625	0.400	0.25	

A comparison of the UV spectra of III with the spectra of 2-amino-benzothiazole and 2-imino-3-methylbenzothiazoline [18, 19] gives no clear picture. 2-Aminobenzothiazole has an absorption maximum at 262 nm, 2-imino-3-methylbenzothiazole has maxima at 266 and 305 nm, and III (Fig. 1) at 272, 305 (shoulder), and 445 nm. At the same time, the IR spectrum of III has two ν_{NH} bands. This indicates that III (and apparently V) exist in solution in the form of a mixture of tautomeric forms.

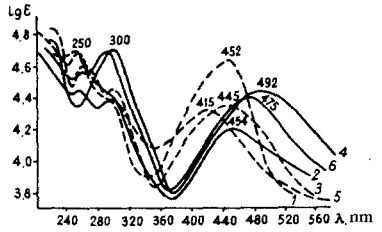


Fig. 1. Electronic spectra of the formazans I–VI (in n-heptane). The numbers of the spectral curves correspond to the numbers of the formazans.

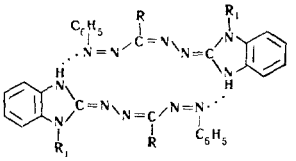
The structure of the formazan group and the strength of the IHB can also be characterized by the ease of detachment of a proton. To characterize the acidic properties of compounds I–VI, we determined their ionization constants (table) by the spectrophotometric method [20, 21], which proved to be extremely convenient since the conversion into the anion is accompanied by a large bathochromic effect.

As was to be expected, the acidity constants I and II scarcely depend on those of III and IV and of V and VI definitely do depend on the nature of the substituent in position 3 (table), while the chelate compounds IV and VI differ from the nonchelate III and V by a decrease in the acidity by two orders of magnitude, i. e., the hydrogen, being bound by an intramolecular hydrogen bond, exhibits a smaller capacity for ionization. However, the benzimidazolylformazans proved to be the least acidic, in spite of their open structure, which is explained by their imine structure (more difficult ionization of the hydrogen, which is attached to a basic imidazole ring).

Thus, the IR and UV spectra and the ionization constants show that, in dependence on the heterocyclic residue in position 1 and the substituent in position 3, benzazolylformazans have the following structures: I and II) B; IV and VI) A; III and V) mixtures of isomers.

For I and II we found a photoisomerization phenomenon. When solutions of I and II in carbon tetrachloride (or chloroform) were irradiated with visible light, a gradual change of the color of the solution of from red to blue was observed, but no paramagnetic properties appeared. Phototropic transformations on the irradiation of benzene solutions in visible light are known in the triphenylformazan series [2, 4], and in this case there is a color change in the opposite direction, the red chelate form changing to a yellow nonchelate form (while in the IR spectrum of the solution the ν_{NH} band appears at 3290 cm^{-1}.

Since in our case it is not a heightening but a deepening of the color that is observed and the initial formazan has structure B, it may be assumed that here there is either the formation of form A or of the dimer E with a plane 16-membered porphyrin-like ring.



E

The features of the UV and IR spectra refute form A and confirm structure E. In actual fact, such a considerable deepening of the color (190 nm) (Fig. 2) indicates the appearance of a strong chromophore differing from the six-membered chelate ring. In just the same way, in the IR spectrum one could expect, by analogy with the formazans of the benzothiazole and benzoxazole series [10], only slight changes in the 1600–700 cm^{-1} region and the disappearance of the ν_{NH} band in the 3450–3100 cm^{-1} region on intramolecular chelation. In actual fact, in the IR spectrum of a solution of the blue isomer (Fig. 3) there are marked changes in the 1600–700 cm^{-1} region as compared with I and II. The spectrum is scarcely resolved, which is characteristic for molecules with a high degree of symmetry. The dimeric structure of the blue isomer is indicated by the disappearance of ν_{NH} in the 3450 cm^{-1} region, which is characteristic for the red form, and the appearance of two strong bands at 3170 and 3090 cm^{-1} the positions of which do not depend on the concentration. The appearance of this doublet of bands, in which the low-frequency band is stronger than the high-frequency one, is also observed in the IR spectra of dimers of amides.

The blue dimeric form is unstable, and when the polar solvents ethanol and dioxane are added to a solution in carbon tetrachloride the initial red coloration is restored.

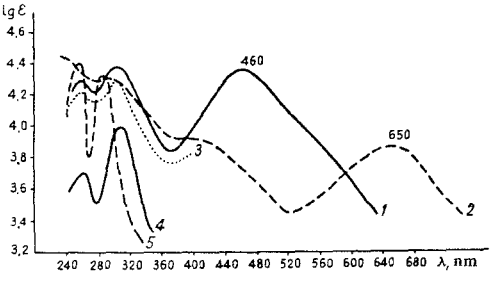


Fig. 2. UV spectra: 1) II in the red form (in carbon tetrachloride); 2) II in the blue form (in carbon tetrachloride); 3) I (in dioxane); 4) 1-benzyl-2-imino-3-methylbenzimidazoline (in dioxane); 5) 2-amino-1-benzyl-benzimidazole (in dioxane).

The study of the phototropism of the benzazolylformazans will be continued.

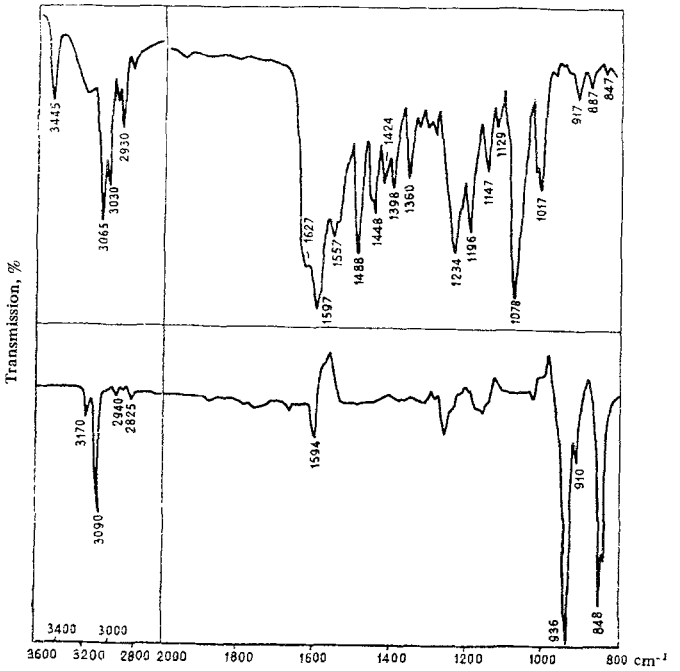


Fig. 3. IR spectra of the formazan II in the red and blue forms (in carbon tetrachloride).

EXPERIMENTAL

1-Benzoxazolyl-3-methyl-5-phenylformazan (V). A diazonium solution obtained from 0.02 mole of aniline, 20 ml of HCl (1 : 1), and 1.4 g of sodium nitrite in 15 ml of water was added to a solution of 3.5 g (0.02 mole) of acetaldehyde benzoxazolylhydrazone [8] in 200 ml of isopropanol cooled to 5° C. Coupling was carried out at 5–10° C, and the mixture was neutralized with 2 N NaOH to pH 6 and left to stand for 3 hr. Yield 82%. Red crystals, mp 160–162° C (dil ethanol). Found, %: C 64.59; H 4.67. Calculated for $C_{15}H_{13}N_5O$, %: C 64.57; H 4.62.

1-Benzylbenzimidazolyl-3-methyl-5-phenylformazan (I) was obtained similarly. Yield 65%. Large dark red crystals, mp 163–165° C (methanol). Found, %: C 71.50; H 5.42; N 23.19. Calculated for $C_{22}H_{20}N_6$, %: C 71.72; H 5.47; N 22.81.

1-Benzothiazolyl-3-methyl-5-phenylformazan (III) was obtained similarly. Yield 80%. Yellow-orange crystals, mp 108–110° C (dil methanol). Found, %: C 57.59; H 5.04; N 21.91. Calculated for $C_{15}H_{13}N_5S \cdot H_2O$, %: C 57.55; H 4.79; N 22.35.

The synthesis of **II, IV,** and **VI** has been described previously [1].

The IR spectra were taken on a UR-10 instrument, the UV spectra on an SF-4 instrument, and the visible spectra on an SF-10 instrument.

The ionization constants were determined by a method described previously [21]. A working concentration of the formazan solutions of $2 \cdot 10^{-5}$ M was used. The optical density was determined on an SF-10 recording spectrophotometer and the pH of the mixture was determined on a PL-VI laboratory-type pH-meter. The values of the selected analytical wavelengths and of the optical densities of solutions of the ionic (d_I) and neutral (d_N) forms and of a mixture at the corresponding pH values and the calculated pK_a values are given in the table.

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