INVESTIGATIONS IN THE BENZAZOLE AND NAPHTHAZOLE SERIES

XXI. Structure and Properties of 1-Benzazolyl-3-methyl-5-tolylformazans

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1-Benzazolyl-3-methyl-5-(p- or o-)tolylformazans (benzazolyl residues: 1-benzylbenzimidazole, benzothiazole, benzoxazole) have been synthesized and their structures have been studied by IR and UV spectroscopy. It has been found that in solutions the formazans are present in the open form and do not contain a chelate ring. Formazans containing an o-tolyl residue do not differ in respect of the structure of the formazan chain from their p-tolyl isomers, but in solutions of the complexes with nickel and copper the influence of the ortho methyl group is shown in the higher coloration of the complex of the ortho isomer than of the para isomer.

Continuing our study of formazans of the benzazole series, we have synthesized unsymmetrical formazans of the benzimidazole, benzothiazole, and benzoxazole series containing a p- or o-tolyl residue:

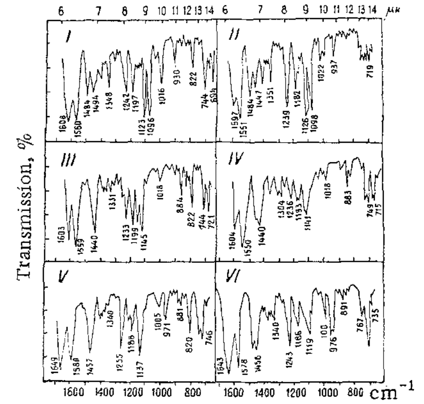
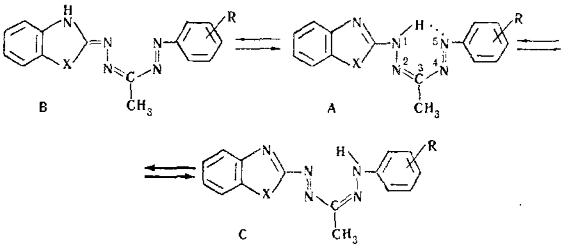


Fig. 1. IR spectra of the formazans I–VI (in paraffin oil).



	X	R		X	R
I	$NCH_2C_6H_5$	p-CH_3	IV	S	o-CH_3
II	$NCH_2C_6H_5$	o-CH_3	V	O	p-CH_3
III	S	p-CH_3	VI	O	o-CH_3

The object of the work was to establish the structural features of the formazans by IR and UV spectroscopy and to study their behavior in complex formation in dependence on the nature of the heteroatom and the position of the methyl group in the phenyl ring (taking into account the possibility of steric hindrance in the ortho isomers).

The IR spectra of the formazans of the benzimidazole series have been studied previously. The assignments of the main absorption bands were made, including those for the formazan I, and its open structure was established. The IR spectra of the formazans I–VI in the crystalline state (3500–2000 cm^{-1} region, mull in perfluorohydrocarbon) are poorly resolved and have no ν_{N-H} bands. It is remarkable that the solvent of crystallization present in I (ethanol) and in V (water) does not appear in the IR spectra. To explain this phenomenon, further investigations of the nature of these compounds (clathrate compounds or associates with a strong hydrogen bond) are required. Solutions of the formazans in carbon tetrachloride studied in the same region (Fig. 2) gave well-resolved spectra. In all formazans, besides ν_{C-H} of aliphatic bonds (2925-2920 cm^{-1}) and ν_{C-H} of aromatic bonds (3060-3030 cm^{-1}), strong bands of ν_{N-H} completely identical for the para and ortho isomers appear clearly (I and II–3445; III and IV–3435 and 3340; V and VI–3440 and 3355 cm^{-1}). Thus, according to the IR spectra all six formazans are present in solution in the open form. The presence of two ν_{NH} bands in the formazans of benzothiazole and benzoxazole is perhaps due to the presence of two tautomeric forms in the solutions. The similarity of the spectra of the para and ortho isomers indicates the absence of a steric influence of the ortho methyl group on the state of the formazan skeleton.

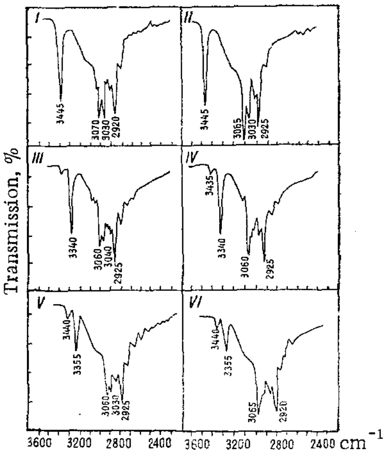


Fig. 2. IR spectra of the formazans I–VI (in carbon tetrachloride solution).

The IR spectra of the crystalline formazans I–VI (Fig. 1) have two strong bands at 1640–1600 and 1580–1550 cm^{-1} belonging to the stretching vibrations $\nu_{C=C}$ of the benzene rings and $\nu_{C=N}$ of the formazan

Table 1

UV Spectra of the Formazans in Dioxane Solution

Compound	I	II	III	IV	V	VI
λ_{max}, nm (log ε)	254 (3.96) 300 (3.89)	254 (4.13) 302 (4.07)	272 (4.05) 310 (3.70) (shoulder)	272 (4.15) 305 (3.99) (shoulder)	250 (4.15) 288 (3.95)	250 (4.30) 288 (4.10)

group. In the IR spectrum of the formazans I and II there are bands at 1484 cm^{-1} (absent from those of the formazans III–VI); these bands may be assigned to the deformation vibrations δ-CH_2 of the benzyl residue. In the 1450–1440 cm^{-1} region in all the formazans there are strong bands of δ-CH_3 deformation vibrations. Bands of the absorption of the paraffin oil may also be present in this region of the spectrum (usually 1465 and 1375 cm^{-1}).

In the region of the stretching vibrations $\nu_{C—N}$ of the aromatic bonds in all the formazans there are several bands (1350–1180 cm^{-1}); these bands characterize the benzazole ring. The stretching vibrations $\nu_{C—N}$ of the aliphatic bonds are expressed in I and II by two bands at 1126, 1098, and at 1123, 1096 cm^{-1}. Of these bands, 1098 cm^{-1} in I and 1096 cm^{-1} in II are probably due to the stretching vibrations of the bond of the heterocyclic nitrogen and the carbon of the benzyl group, since this band is not present in spectra of the formazans III–VI which have only one band (1145–1120 cm^{-1}) in this region. All the para methyl isomers differ from the ortho isomers by the presence of a band of the nonplanar deformation vibrations $\delta_{C—H}$ of two adjacent hydrogen atoms in the benzene ring at 822–820 cm^{-1}.

The structures of the formazans in solutions were studied by means of their electronic absorption spectra. The UV region of the spectra of the compounds (Table 1) is characterized by two absorption maxima. The spectra of the para and ortho isomers have similar positions of the maxima, but the ortho isomers are distinguished by a somewhat greater intensity. The nature of the spectrum depends on the nature of the heteroatom.

In the visible region of the spectra of the formazans I–VI there are three maxima (table 2). The benzimidazole formazans possess the deepest coloration and the benzoxazole formazans, as reported previously [3], a higher coloration.

It is known that 3-methyl-1,5-diphenylformazan exists in the form of a red or a yellow isomer according to the nature of the solvent [4, 5]. To elucidate the possibility of the same phenomenon for the formazans I–VI we recorded the absorption spectra in the visible region in various solvents. As can be seen from the figures of Table 2, the formazans exhibit some positive solvatochromism. The bathochromic shift of the absorption maximum on passing from a nonpolar solvent (benzene) to a polar one (nitrobenzene) is less than 20 nm in the majority of them. On passing from a proton-donating solvent (ethanol) to a proton-accepting one (dioxane), large shifts in the absorption maximum again take place. Thus, the appearance in solutions of isomeric (or tautomeric) forms differing considerably from one another in color (as is the case, for example, for the 1-(1'-phenyltetrazolyl)-5-nitrophenylformazans [6]), was not observed. The differences in the color of the ortho and para isomers is slight, which indicates the absence of an influence of the ortho methyl group on the chromophoric system of the dyes and is in agreement with the IR spectra.

As we have shown for substituted triphenylformazans [7], formazans with a chelate structure do not change their color when an ethanolic solution is made alkaline, while formazans having an open azohydrazone group form deeply colored sodium salts. With all the formazans considered here, a marked deepening of the coloration by more than 100 nm was observed

Table 2

Spectral Characteristics of the 1-Benzazolyl-3-methyl-5-(p- or o-)tolylformazans

Compound	Mp, °C	λ_{max}, nm (10^{-4}) in solvents							Absorption of the complexes in ethanolic solution, nm		
		benzene	nitrobenzene	chloroform	acetone	dioxane	ethanol	ethanolic NaOH	Ni^{2+}	Cu^{2+}	Zn^{2+}
I*	121–124	448 (4.75)	462 (6.40)	452 (3.47)	454 (4.26)	460 (4.01)	460 (2.33)	546 (3.06)	626	640	506
II	85–87	466 (3.91)	464 (3 38)	460 (3.77)	460 (3.77)	460 (3.77)	456 (3.58)	532 (4.41)	562	616	508
III	136–137	416 (1.89)	412 (1.07)	422 (1.61)	404 (2.65)	420 (2.46)	414 (2.59)	516 (5.37)	616	646	500
IV	81–87	418 (1.70)	427 (1.84)	418 (1.40)	410 (1.62)	410 (2.46)	414 (2.28)	520 (4.48)	558	622	500
V**	115–116	400 (2.09)	420 (3.35)	410 (1.51)	400 (4.19)	412 (2.19)	400 (2.20)	494 (3.77)	588	624	470
VI	80–82	414 (2.04)	432 (1.40)	410 (1.74)	404 (1.97)	405 (2.98)	400 (2.15)	490 (3.60)	520	600	464

*Contains C_2H_5OH of crystallization.

**Contains water of crystallization.

in an alkaline medium (Table 2). This also indicates the absence of a chelate ring with a strong intramolecular hydrogen bond from the formazans I–VI. However, the question of in which of the three possible tautomeric forms (A, B, or C) the formazans I–VI exist requires additional study.

In order to compare the complex-forming capacity of the formazans, the behavior of compounds I–VI in ethanolic solutions on the addition of an excess of a metal salt was studied spectroscopically. The metal ions used were Ni^{2+}, Cu^{2+}, and Zn^{2+} ($Ni(NO_3)_2$, $CuCl_2$, and $ZnCl_2$). The complexes of the formazan I with nickel and copper have been described previously [8].

The features of the change in the coloration on complex formation for the formazans I, III, and V in comparison with II, IV, and VI are interesting (Table 2). While the positions of the absorption maxima of the o- and p-tolyl isomers are the same for the complexes with zinc, the Ni complexes of the ortho isomers have a coloration 60 nm higher than the corresponding para isomers. For the copper complexes, this difference in the coloration of the ortho and para isomers amounts to 24 nm. Thus, the spatial influence of a methyl group in the ortho position of the phenyl ring is shown in complex formation. A study of the structure of the complexes will permit an explanation of the cause of this feature.

EXPERIMENTAL

The synthesis of 1-(1'-benzyl-2'-benzimidazolyl)-3-methyl-5-tolylformazan (I) and of 1-benzothiazolyl- and 1-benzoxazolyl-3-methyl-5-p-tolylformazans (III and V) has been described previously [3].

1-(1'-Benzylbenzimidazolyl)-3-methyl-5-o-tolylformazan (II) was obtained from acetaldehyde 1-benzylbenzimidazolylhydrazone and an o-toluenediazonium salt by analogy with previous work [9]. Yield 60–70%. Orange-brown needles from dilute ethanol. Found, %: C 72.47; H 6.00; N 21.61. Calculated for $C_{23}H_{22}N_6$, %: C 72.25; H 5.76; N 22.00.

1-Benzothiazolyl-3-methyl-5-o-tolylformazan (IV) was obtained similarly from acetaldehyde benzothiazolylhydrazone. Yield about 60%. Lustrous dark orange needles from dilute ethanol. Found, %: C 62.67; H 4.92; N 22.45; S 10.74. Calculated for $C_{16}H_{15}N_5S$, %: C 62.13; H 4.85; N 22.66; S 10.36.

1-Benzoxazolyl-3-methyl-5-o-tolylformazan (VI) was obtained similarly. Yield about 50%. Orange needles from dilute ethanol. Found, %: C 65.07; H 5.04; N 24.09. Calculated for $C_{16}H_{15}N_5O$, %: C 65.52; H 5.11; N 23.88.

The IR spectra of the crystalline formazans were recorded on an IKS-14 spectrometer (NaCl prism, samples in the form of mulls in paraffin oil). The IR spectra of 1% solutions in carbon tetrachloride were recorded in the 3500–2000 cm^{-1} region (LiF prism) on a UR-10 instrument. The electronic spectra were recorded on an SF-4 instrument and, in the visible region, on an SF-10 spectrophotometer.

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