STUDY OF THE STRUCTURE OF BENZAZOLYLHYDRAZONES BY IR SPECTROSCOPY

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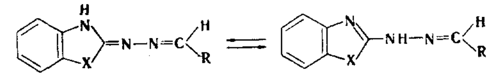
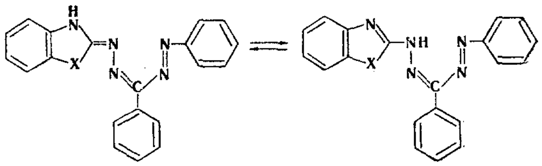
Benzazolylhydrazones may exist in amino and imino tautomeric forms in carbon tetrachloride and chloroform solutions. The investigated hydrazones are associated in carbon tetrachloride solutions through intermolecular hydrogen bonds.

The IR spectra of benzazolylhydrazones in the crystalline state have been interpreted [1] and the spectra of solutions of them have not been studied. We have investigated a number of benzazolylhydrazones and formazans by IR spectroscopy in order to follow the effect of the character of the ring heteroatom and the nature of the "aldehyde" fragment on the state of the tautomeric equilibrium A ⇌ B.



III-VIII



IX-XII

III X=$NCH_2C_6H_5$, R=C_6H_5; IV X=O, R=C_6H_5; V X=S, R=C_6H_5; VI X=$NCH_2C_6H_5$, R=CH_3; VII X=O, R=CH_3; VIII X=S, R=CH_3; IX X=$NCH_2C_6H_5$; X X=O; XI X=S; XII complex of formazan with Co^{2+}.

Special attention was directed to ν_{NH} and $\nu_{C=N}$, which are the most sensitive frequencies to the structural changes under investigation. Data from the IR spectra of benzimidazole (I) and benzaldehyde phenylhydrazone (II) were used for the reliable assignment of the ν_{NH} frequencies of the ring and exocyclic secondary amino groups.

The spectra of IV, V, VII, and VIII in CCl_4 (Fig. 1 and Table 1) above 3000 cm^{-1} contain two absorption bands of a free amino group, although the amino group is characterized by only one maximum [2]. The presence of two bands may constitute evidence for the tautomeric equilibrium A ⇌ B, and, in analogy with the absorption of I, the high-frequency absorption can be assigned to vibrations of the ring amino group, and the low-frequency absorption can be assigned to the exocyclic amino group. Another peculiarity of the spectra in this range is the presence of a band at ~3200 cm^{-1}, which characterizes a bonded amino group. The remaining frequencies at 2600-3500 cm^{-1} should be assigned to the ν_{CH} frequency of the benzene and benzazole rings [5]. From the data in [3, 4], one may assume the formation of hydrogen bonds primarily between the ring amino group of one molecule and the "pyridine" nitrogen atom of the benzazole ring of another molecule. This is confirmed by the fact that the relative intensity of the band of the bonded NH group is lowest when absorption of only the ring amino group is present in the spectrum.

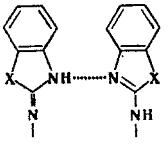


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TABLE 1. IR Spectra at 3300-3500 cm^{-1}

Compound	CCl_4		$CHCl_3$	
	ν_{NH}, cm^{-1}	$\Delta\nu_{NH}{}^{1/2}$, cm^{-1}	ν_{NH}, cm^{-1}	$\Delta\nu_{NH}{}^{1/2}$, cm^{-1}
I	3480	11	3470	23
II	3345	22	3340	23
III	3470	17	3465	25
			3330	vw
IV	3455	34	3455	35
	3355	22	3350	23
V	3440	25	3430	35
	3340	19	3335	25
VI	3470	18	3460	28
			3330	vw
VII	3465	27	3455	w
	3385		3360	35
	3365			
VIII	3450	20	3430	w
	3370		3340	24
	3350			
IX	3445	40	3445	42
			3300	vw
X	3350	42	3340	45
XI	3445	20	3425	w
	3340	18	3330	27

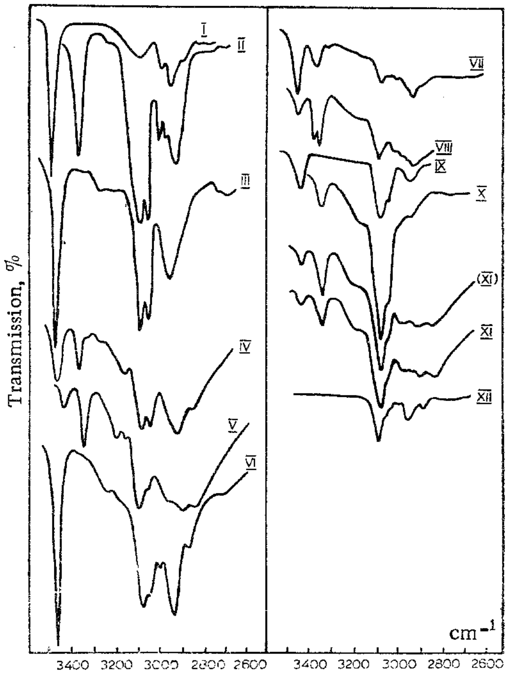

Fig. 1. IR spectra of I-XII in carbon tetrachloride: I) saturated solution, l 50 mm; II) $4.7 \cdot 10^{-3}$ M, l 50 mm; III) $2.1 \cdot 10^{-3}$ M, l 50 mm; IV) $8.3 \cdot 10^{-4}$ M, l 50 mm; V) $9.3 \cdot 10^{-4}$ M, l 50 mm; VI) $2.3 \cdot 10^{-3}$ M, l 50 mm; VII) $6.5 \cdot 10^{-4}$ M, l 50 mm; VIII) 10^{-3} M, l 50 mm; IX) $1.7 \cdot 10^{-3}$ M, l 10 mm; X) $2.4 \cdot 10^{-3}$ M, l 50 mm; XI) $1.9 \cdot 10^{-3}$ M, l 20 mm; XI) $9.3 \cdot 10^{-4}$ M, l 50 mm; XII) saturated solution, l 10 mm.

The intermolecular character of the hydrogen bonds in solutions of hydrazones III-VIII in CCl_4 is proved by the fact that the relative intensity of the band of the bonded amino group falls when the temperature is raised or when the solutions are diluted, whereas the relative intensity of the band of free amino groups increases.

When CCl_4 is replaced by chloroform, the absorption bands of the free amino groups in the spectra of III and VI, which contain benzimidazole rings, are broadened and shifted to the low-frequency region. One should note the appearance in the spectra of chloroform solutions of these compounds of low-intensity absorption with a maximum at ~3330 cm^{-1}, which is absent in the spectra of CCl_4 solutions. Broadening and a low-frequency shift of the maxima of these bands are also observed in the spectra of the benzothiazolylhydrazones. The ratio of the areas of the absorption bands of the free NH groups of V changes only slightly (0.5 in CCl_4 and 0.4 in $CHCl_3$).

A different pattern is observed in the spectra of the benzoxazolylhydrazones. Thus the ratio of the areas of the high-frequency and low-frequency bands in the spectra of IV is 0.7 in chloroform and 1.3 in carbon tetrachloride, regardless of the concentration, and this indicates a substantial change in the ratio of the tautomers in this case. The presence of two absorption bands of a C=N bond at 1668 and 1647 cm^{-1} in the spectrum of IV, the relative intensity of which depends on the CCl_4 to $CHCl_3$ ratio, is a confirmation of this (Fig. 3). However, in the spectra of hydrazones that contain benzimidazole and benzothiazole rings the transition from carbon tetrachloride to chloroform causes only an insignificant shift of the frequencies of the stretching vibrations of the C=N groups, which is apparently due to a change in the polarity of the medium.

The effect of the nature of the "aldehyde" fragment is manifested spectrally as slight changes in the position of the bands under discussion and in the half widths, as well as in the asymmetry or splitting of the absorption bands of the exocyclic amino group; this is probably assoicated with syn and anti isomerism.

An assumption regarding the existence of similar tautomerism in formazans of the benzazole series has been previously expressed [6]. In this connection, it is interesting to compare the IR spectra of hydrazones

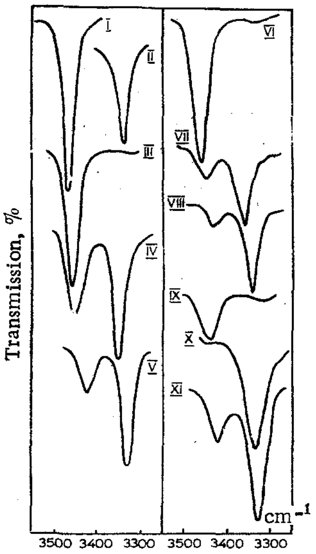

Fig. 2

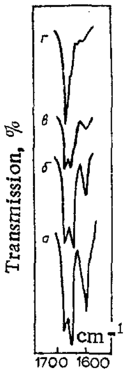

Fig. 3

Fig. 2. IR spectra of I-XI in chloroform: I) $3.3 \cdot 10^{-3}$ M, l 10 mm; II) $1.1 \cdot 10^{-2}$ M, l 10 mm; III) $2.7 \cdot 10^{-3}$ M, l 10 mm; IV) $3 \cdot 10^{-3}$ M, l 20 mm; V) $3.2 \cdot 10^{-3}$ M, l 20 mm; VI) $3.5 \cdot 10^{-3}$ M, l 10 mm; VII) $3.1 \cdot 10^{-3}$ M, l 10 mm; VIII) $3.3 \cdot 10^{-3}$ M, l 10 mm; IX) 10^{-3} M, l 20 mm; X) 10^{-2} M, l 20 mm; XI) $5.3 \cdot 10^{-3}$ M, l 20 mm.

Fig. 3. IR spectra of hydrazone IV in CCl_4–$CHCl_3$. Compositions of the mixtures and concentrations: a) 100% $CHCl_3$, 0% CCl_4, $3 \cdot 10^{-3}$ M; b) 80% $CHCl_3$, 20% CCl_4, $2.4 \cdot 10^{-3}$ M; c) 40% $CHCl_3$, 60% CCl_4, $1.5 \cdot 10^{-3}$ M; d) 0% $CHCl_3$, 100% CCl_4, saturated solution; l 1 mm.

III-VIII and formazans IX-XII. The spectrum of formazan XI in carbon tetrachloride is similar to the spectrum of hydrazone V, but the half widths and the positions of the maxima of the bands of the free amino groups remain virtually unchanged. The small low-frequency shift of the absorption bands of the ring NH group of formazan IX, its asymmetry, and the increase in the half width can be explained by steric factors [7].

Taking into account the high tendency of benzoxazolylhydrazones to undergo tautomeric transformations, one might expect a more profound change in the structure of 1-benzoxazolyl-3,5-diphenylformazan (X) as compared with hydrazone IV. In fact, the spectrum of this formazan has only one absorption band of a free NH group, whereas the spectrum of hydrazone IV has two frequencies (the ring and exocyclic amino groups). The frequency at 3350 cm^{-1} (free NH group) in the spectrum of formazan X makes it possible to assign this absorption to vibrations of an exocyclic amino group. The spectra of 1-benzazolyl-3-methyl-5-phenylformazans were presented in [6] and are analogous to the spectra of the corresponding hydrazones VI-VIII.

The self-association of formazans IX-XI in carbon tetrachloride solutions, which was previously described only for 1-(1-benzylbenzimidazolyl)-3,5-diphenylformazan [1] shows up in the IR spectra in the form of absorption of bonded amino groups at ~3200 cm^{-1}, the intensity of which decreases as the concentration decreases, whereas the intensity of the absorption of the free amino groups increases correspondingly in this case (Fig. 1).

EXPERIMENTAL

The investigated compounds were synthesized by N. V. Serebryakova and G. N. Lipunova [8, 9].

The IR spectra of 5-50-mm thick layers of $5 \cdot 10^{-4}$–$5 \cdot 10^{-3}$ M solutions of the compounds were recorded with a UR-20 double-beam IR spectrometer. The accuracies in the measurements of the frequencies were ±2 cm^{-1} and ±5 cm^{-1} in the region of NaCl and LiF prisms, respectively, and the accuracy in the measurement of the half widths was ±5 cm^{-1}. The areas under the contours of the absorption bands were calculated from the Simpson formula, and the range of integration was 3-5 half widths.

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OXIDATION OF VINYL DERIVATIVES OF BENZIMIDAZOLE-2-THIONE

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N-Vinylbenzimidazole-2-sulfonic acid, 2-benzimidazolyl vinyl sulfoxide, and 2-benzimidazolyl vinyl sulfone were obtained in high yields by the action of concentrated hydrogen peroxide and acetyl hydroperoxide on N- and S-monovinyl derivatives of benzimidazole-2-thione. N-Vinyl-2-benzimidazolone and a complex mixture of polymeric products are formed in the oxidation of N,S-divinyl-2-mercaptobenzimidazole. It is shown that the reactivity of the sulfur atom depends on the number of vinyl groups and their orientation with respect to the heteroatoms.

We have previously reported [1] the synthesis of 2-benzimidazolyl vinyl sulfide (I) and N,S-divinyl-2-mercaptobenzimidazole (II) and their transformations involving the double bond of the vinyl group. In the present research we have studied the oxidation of I and II, as well as benzimidazole-2-thione (III) and N-vinylbenzimidazole-2-thione (IV), in order to obtain new water-soluble vinyl monomers containing oxidized sulfur.

It is known [2] that di(2-benzimidazolyl) disulfide is isolated in the oxidation of thione III with 10% hydrogen peroxide, whereas benzimidazole-2-sulfonic acid (V) is obtained by the action of 30% H_2O_2 in glacial acetic acid or in sodium hydroxide solution.

When we used 78% hydrogen peroxide in glacial acetic acid or 70% acetyl hydroperoxide in ether for the oxidation of III we were unable to isolate the above-indicated disulfide, but sulfonic acid V was obtained in quantitative yield. Oxidation of thione III in acetone gives benzimidazole-2-sulfonic acid (VI), the structure of which is confirmed by the presence of the absorption bands of a SO_2H group in its IR spectrum. The literature data [2-4] on the melting point of acid V are contradictory, apparently in connection with the formation of various hydrated forms of this compound. According to the results of elementary analysis, acids V and VI, which we isolated in the present research, are stable monohydrates with mp ~200 and 157°, respectively. The IR spectrum of V contains an intense absorption band at 1043 cm^{-1} and a doublet at 1200 cm^{-1}, which are characteristic for hydrated sulfonic acids [5]. The bands of the stretching vibrations of the C—H bonds and associated NH and OH groups are superimposed at 2400-3600 cm^{-1}. It was also established by potentiometric titration of an

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