SPECTRAL CHARACTERISTICS OF THE BANDS OF NH GROUPS AND STRUCTURE OF 2-THIOXOBENZAZOLINES IN SOLVENTS WITH LOW POLARITIES

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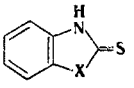
The IR spectra of five 2-thioxo-benzazolines in carbon tetrachloride (2500-3500 cm^{-1}) and chloroform (3200-3500 cm^{-1}) are examined. Analysis of the spectral parameters of the absorption band of the unassociated NH groups showed that the high proton-donor capacity of the hydrogen atom of the thioamide group of 2-thioxobenzoxazoline is evidently associated with the high electronegativity of the oxygen atom. The existence of intermolecular hydrogen bonds with a degree of dissociation of 0.3 in carbon tetrachloride and 0.1 in chloroform was established by means of the concentration dependence of the spectra. A change with time in the integral coefficient of the absorption band of the unassociated NH groups was observed in solutions in carbon tetrachloride; this is explained by interaction of the 2-thioxobenzazolines with carbon tetrachloride. The IR spectra, a table of the spectral characteristics, the dependence of the relative integral intensity on the concentration, and the dependence of the optical density of the absorption band of free NH groups on time are presented.

In a continuation of our research [1] on amine—imine tautomerism in the benzazolylhydrazone series we have studied the IR spectra of solutions of five 2-thioxobenzazolines in carbon tetrachloride and chloroform in the region of the stretching vibrations of NH bonds. The available literature data [2] from the IR spectra of these compounds contain primarily information regarding the frequencies of the NH and C=S groups in the crystalline state. 2-Thioxobenzazolines with the general formula



I X=NCH_3^*; II X=$CH_2C_6H_5$; III X=NC_6H_5; IV X=S; V X=O

can serve as model compounds for elucidation of the effect of the character of the heteroring on the state of the NH bond and are also convenient subjects for the study of the hydrogen bonds, the properties of which are always of interest. We recorded the IR spectra of freshly prepared solutions in the region of the stretching vibrations of the NH bond in order to investigate the character and degree of association in solutions of the investigated thioamides and the dependence of the spectral parameters of the absorption bands of the unassociated NH groups on the character of the heteroring and the medium.

Analysis of the spectral parameters (Table 1) shows that the nature of the substituent attached to the nitrogen atom of the benzimidazole ring has an appreciable effect only on the magnitude of the relative integral intensity. Compounds I-IV react in the same way to the change in the polarity of the medium that occurs on passing from carbon tetrachloride to the more polar chloroform; the half-width and integral intensity are almost doubled in this case, and the shift in the absorption maximum to the low-frequency region does not exceed 14 cm^{-1}. The NH group of 2-thioxobenzoxazoline (V) has the most unusual character in the manifestation of spectral properties. The absorption band of the stretching vibrations of this group has the greatest half-width and intensity in the indicated solvents. The position of the absorp-

*In view of its low solubility in the indicated solvents, it is not possible to measure the spectral characteristics of the absorption band of the NH group of unsubstituted 2-thioxobenzimidazoline (X = NH).

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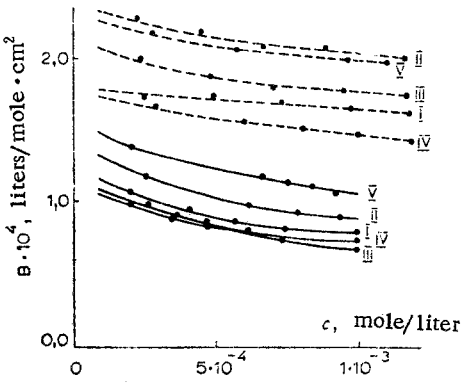


Fig. 1

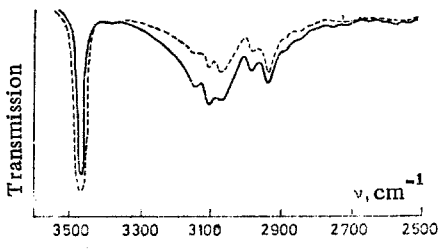


Fig. 2

Fig. 1. Dependence of the relative integral intensity of the absorption band of the NH groups on the concentration in $CHCl_3$ (---) and CCl_4 (——) solutions (the numbers of the curves in the figure correspond to the numbers of the compounds).

Fig. 2. IR spectra of I in CCl_4: ——) $c = 9.073 \cdot 10^{-4}$ mole/liter and l = 20.09 mm; ---) $c = 3.629 \cdot 10^{-4}$ and l = 49.95 mm.

tion maximum rather than the intensity and half-width, as we observed for I-IV, has the greatest sensitivity to an increase in the polarity of the solvent. This spectral behavior of V is evidently associated with the higher electronegativity of the oxygen atom in the benzoxazole ring, owing to which the polarity of the NH bond and its proton-donor capacity increase with the development of a formal positive charge on the nitrogen atom.

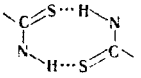
The dependence of the relative integral intensity on the concentration presented in Fig. 1 shows that all of the investigated compounds are associated in carbon tetrachloride and chloroform by means of intermolecular hydrogen bonds. The behavior of the broadened absorption bands due to the vibrations of associated NH groups, the intensity of which depends on the concentration, serves as an additional confirmation of this in the spectra of solutions in carbon tetrachloride below 3200 cm^{-1}. The spectrum of I, which illustrates the effect of dilution, is presented in Fig. 2. The spectra of the remaining 2-thioxobenzazolines are similar. According to [3], the self-association of heterocyclic thioamides is associated with the formation of  complexes, although when there are electronegative atoms such as oxygen and nitrogen atoms in the thioamide molecule, one cannot exclude the possibility of the formation of hydrogen bonds of the NH...O and NH...N type. Hydrogen bonds with the participation of a sulfur atom are usually classified as weak hydrogen bonds; however, the self-associates of thioamides exist in sufficiently dilute solutions, the concentration of which does not exceed $5 \cdot 10^{-4}$ mole/liter. By determination of the relative integral intensities at concentrations of 10^{-4} and 10^{-3} mole/liter by extrapolation and assuming that virtually unassociated molecules exist in 10^{-4} mole/liter solutions, one can approximately calculate the percentage of associated molecules at 10^{-3} mole/liter from the intensity ratio. It turns out that ~30% of the total amount of dissolved molecules participate

TABLE 1. Spectral Characteristics of I-V

Compound	CCl_4			$CHCl_3$		
	ν_{NH}, cm^{-1}	$\Delta\nu_{NH^{1/2}}$, cm^{-1}	$B \cdot 10^4$, liter/mole·cm^2	ν_{NH}, cm^{-1}	$\Delta\nu_{NH^{1/2}}$, cm^{-1}	$B \cdot 10^4$, liter/mole·cm^2
I	3465	18,5	1,07	3453	34,0	1,78
II	3462	19,0	1,20	3450	34,5	2,30
III	3460	18,0	1,03	3446	35,0	1,99
IV	3406	18,0	1,02	3393	34,5	1,73
V	3455	24,0	1,43	3437	42,5	2,23

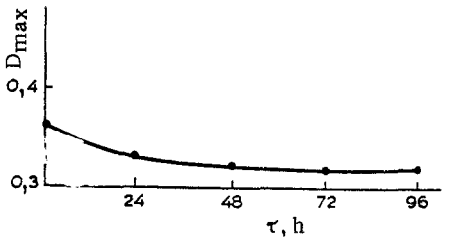


Fig. 3. Dependence of the optical density of the absorption band of the free NH group of I with time in CCl_4.

in hydrogen bonding in carbon tetrachloride, as compared with no more than 10% in chloroform solutions.

It should be noted that a change in the integral coefficient of absorption of the band of the free NH groups with time is observed when solutions in carbon tetrachloride are allowed to stand (Fig. 3). Similar changes with time are recorded in the spectra of the remaining compounds of the investigated series. In connection with the fact that the decrease in the intensity of the absorption of free NH groups is not accompanied by the appearance of bands that characterize the SH group, it is evidently not associated with the tautomeric conversion of the thiones to the thiol form but is due to interaction of the 2-thioxobenzazolines with the products of photochemical decomposition of carbon tetrachloride, since it is known [4] that amines are capable of forming complexes with carbon tetrachloride under ordinary conditions with subsequent transformations of the resulting complexes as a result of photochemical reactions.

EXPERIMENTAL

The IR spectra of solutions of the 2-thioxobenzazolines in carbon tetrachloride (2500-3500 cm^{-1}) and chloroform (3200-3500 cm^{-1}) were recorded with a UR-20 spectrometer. Series of concentrations ranging from 10^{-3} to $2 \cdot 10^{-4}$ mole/liter in 10-50 mm layers were used in the recording of the spectra. The accuracy in the measurement of the ν_{NH} frequencies was ±2 cm^{-1}. The relative integral intensity was determined by the method of Wilson and Wells; the range of integration in this case was three to four half-widths. The accuracy in the measurement of the relative integral intensities was 5-7%. The area under the absorption curves was calculated from the Simpson formula.

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