STUDY OF THE STRUCTURES OF INDAZOLES, PYRAZOLO[3,4-b]PYRIDINES, AND PYRAZOLO[3,4-b]PYRAZINE BY IR SPECTROSCOPY

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It is shown on the basis of a study of the IR spectra of indazoles, pyrazolopyridines, and pyrazolopyrazine in the solid state and of their N-deutero-substituted derivatives and hydrochlorides at room temperature and at the temperature of liquid nitrogen that these heterocycles exist in a tautomeric form in which the labile hydrogen atom is localized on the nitrogen atom of the pyrazole ring. It was established that 6-aminopyrazolopyridine exists in the crystalline state in the amino form and that it is protonated at the ring nitrogen atom rather than at the amino group. The applicability of the temperature-shift method for the detection not only of $\gamma\text{NH}$ bands but also of $\gamma\text{ND}$ bands is demonstrated.
Few data on the IR and UV spectra and the structures of condensed pyrazoles and closely related compounds have been published. In particular, the tautomeric forms of some of them in solution and in the crystalline state have been determined [1-4], and the spectra and structures of natural purines and their derivatives have been studied [5-7]. In [7-9] it was shown that one of the several possible tautomeric forms predominates for many hydroxy, amino, and mercapto derivatives of purines and their salts in the solid state. Some of the regularities found in the spectra of purines can be used for the interpretation of the spectra of condensed pyrazoles.

The first results of a study of the IR spectra in the solid state of indazole and its derivatives (I-III), pyrazolo[3,4-b]pyridines (IV-X), and pyrazol[3,4-b]pyrazine (XI), as well as their hydrochlorides (Ia-Xla), are reported below:

\[
\begin{align*}
\text{I, II} & \quad \text{III} & \quad \text{IV-VI} \\
\text{Cl} & \quad \text{Cl'} & \quad \text{R'} \\
\text{X} & \quad \text{VII-IX} & \quad \text{XI} \\
\end{align*}
\]

\[\text{R} = \text{H}; \quad \text{II} \quad \text{R} = \text{CH}_3; \quad \text{IV} \quad \text{R} = \text{H}; \quad \text{V} \quad \text{R} = \text{NH}_2; \quad \text{VI} \quad \text{R} = \text{N}\left(\text{CH}_3\right)_2; \quad \text{VII} \quad \text{R} = \text{R'} = \text{H}; \quad \text{VIII} \quad \text{R} = \text{CH}_3, \quad \text{R'} = \text{H}; \quad \text{IX} \quad \text{R} = \text{R'} = \text{CH}_3
\]

The method of temperature shift of the bands of the N-H deformation vibrations [10, 11], deuterium substitution, and a comparison with the spectra of model heterocyclic compounds [12] were used for the interpretation of the IR spectra of the condensed pyrazoles.

The assignment of the frequencies associated with the vibrations of the NH and NH$_2$ groups and the skeleton of the molecules is presented in Table 1.

It is known that the bands of stretching vibrations of CH, NH, NH$_2$, ND, NH$_2$, and ND$_2$ groups are found at 2000-3400 cm$^{-1}$. A broad intense absorption band at 2500-3300 cm$^{-1}$, which has a complex structure, is observed in the spectra of all of the investigated compounds. It undoubtedly is related to the NH stretching vibration, and its structure and position constitute evidence for the presence of strong intermolecular hydrogen bonds in crystals of the condensed pyrazoles. The IR spectra of pyrazolopyridine (VI) and its hydrochloride and N-deutero derivative are presented in Fig. 1 as an example.

A broad band with a maximum at about 2500 cm$^{-1}$, which is related to the stretching vibration of the NH bond, appears, as a rule, in the spectra of the hydrochlorides.

In addition, intense bands at about 3150, 3300, and 3400 cm$^{-1}$, which are shifted on deuteration to 2300 and 2560 cm$^{-1}$, are observed in the spectrum of 6-aminopyrazolo[3,4-b]pyrid-