IR SPECTRA OF PYRIMIDINECARBOXYLIC ACIDS AND SOME PROBLEMS INVOLVING THEIR STRUCTURE

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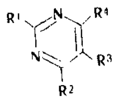
The IR spectra of solid pyrimidinecarboxylic acids and of solutions of them in dioxane and chloroform were obtained. It is demonstrated that the frequencies of the stretching vibrations of the carboxyl C=O groups of acids that are not capable of tautomerism correlate linearly with their acidity constants.

Previously some of us synthesized a series of substituted pyrimidinecarboxylic acids and studied the effect of substituents and the position of the carboxyl groups in the pyrimidine ring on the acid properties [1, 2]. It seemed of interest to study them in greater detail, particularly by IR spectroscopy, and this was the aim of the present study.

One of the chief peculiarities of pyrimidine derivatives is the possibility of tautomeric transformations [3, 4]. We will first consider the spectra of pyrimidinecarboxylic acids that cannot produce tautomeric forms (I-IX, Table 1). The stretching vibrations of the O–H groups of KBr pellets of the samples (Fig. 1) appear at 2600-3200 cm^{-1} and should be ascribed to associated molecules. The IR spectra of chloroform solutions of these acids in a number of cases make it possible to conclude that intramolecular hydrogen bonds (IHB) are present in the molecules. Thus for 5-carboxy derivatives (III-V) in dilute $CHCl_3$ solutions that practically exclude intermolecular association ($c \approx 10^{-3}$ M), the ν_{OH} absorption is recorded near 3512

TABLE 1



Compound	R¹	R²	R³	R⁴	$\nu_{C=O}$, cm^{-1}		ν_{O-H}, cm^{-1}	pK_a
					dioxane	chloroform	(chloroform)	
I	COOH	H	H	H	1745, 1749	1747, 1786	3363	2,99
II	COOH	H	Br	H	1746, 1748	1766, 1788	3395, 3505	2,80
III	H	H	COOH	H	1738	1731, 1747	—	3,16
IV	C_2H_5S	H	COOH	H	1735	1704, 1742	3512	3,39
V	Cl	H	COOH	Cl	1749, 1754	—	—	3,10
VI	H	COOH	H	H	1737, 1760	1768, 1780	3358, 3508	2,98
VII	H	COOH	H	COOH	1742, 1757	1786	—	2,74
VIII	H	COOH	H	Cl	1740, 1760	1780	3360, 3500	2,80
IX	Cl	COOH	H	Cl	1703, 1736, 1755	1712, 1760, 1783	3400, 3500	2,81
X	OH	H	COOH	OH	1750	—	—	4,32
XI	SH	H	COOH	OH	1756	1807	—	3,87
XII	H	H	COOH	NH_2	1642	—	—	5,62
XIII	H	COOH	H	SH	1749	1709	—	3,02
XIV	H	COOH	H	OH	1705	1711	—	2,83
XV	OH	COOH	H	OH	1702, 1727	1711	—	2,62
XVI	OH	COOH	NO_2	OH	1715, 1738	1713, 1757	—	2,53
XVII	SH	COOH	H	OH	1713	1712, 1806	—	2,72

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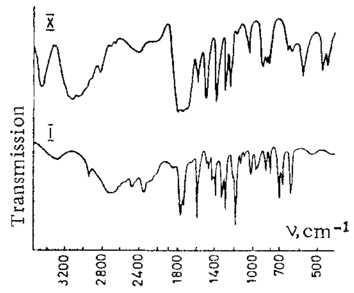


Fig. 1. IR spectra of pyrimidinecarboxylic acids (KBr pellets).

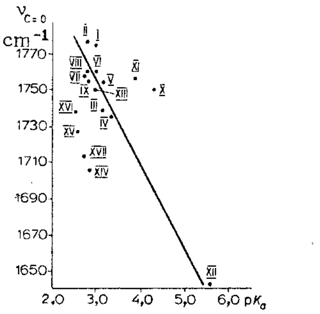
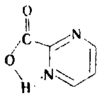
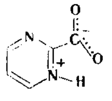


Fig. 2. Dependence of the frequencies of the stretching vibrations of the carbonyl groups of the acids on their pK_a values.

cm^{-1}, i.e., in the usual region of absorption of the O−H stretching vibrations of carboxylic acid monomers [5]. However, the ν_{OH} band is recorded at ~3363 cm^{-1} for pyrimidine-2-carboxylic acid (I) under the same conditions, which attests to the presence of an IHB [5] with one of the ring nitrogen atoms (A). It should be noted that the contribution of a structure with complete transfer of a proton to the nitrogen atom (B) is apparently insignificant, since the absorption band at ~3150 cm^{-1} that is usually associated with vibrations of the $\overset{+}{N}$−H bond [6] does not appear.


A


B

Two absorption bands of the O−H stretching vibrations are observed for the 4- and 6-carboxy derivatives (VI-IX) in dilute $CHCl_3$ solutions – one in the region of vibrations of free O−H groups (~3500 cm^{-1}), and the other in the region of associated IHB (~3360-3400 cm^{-1}) – which is apparently due to the possibility of different spatial orientations of the interacting elements of these molecules.

The bands of the carbonyl group stretching vibrations in KBr pellets are recorded at 1690-1730 cm^{-1}. When the compounds are dissolved in dioxane and $CHCl_3$, these bands are shifted to higher frequencies, and this shift is due to cleavage of the intermolecular hydrogen bonds. The splitting of the bands of the carbonyl absorption that is observed for most of the investigated acids in both the solid state and in solutions can be explained in the first case mainly by the effect of the crystal lattice field and in the second case by the presence of rotational isomers and IHB [7]. The appearance of carbonyl absorption for I, II, and VI-IX in the usual region of $\nu_{C=O}$ vibrations of acids rather than in the region of absorption of the carboxylate ion [7] also indicates that the O−H. . .N IHB does not lead to the formation of inner salts (B).

Four to five bands, the intensities of which differ for different compounds, are recorded at 1400-1620 cm^{-1} (Fig. 1). They may be affiliated with ring vibrations [3], but the C−O stretching vibrations and O−H deformation (planar) vibrations [7] fall here. The vibrations below 1400 cm^{-1} should be related [8] to the different forms of deformation vibrations, breathing vibrations of the ring, etc.

Pyrimidinecarboxylic acids with substituents of the OH, NH_2, and SH type (X-XVII), which are capable of tautomeric transformations, can be placed in a second group. Because of their low solubilities, we were unable to obtain the IR spectra of chloroform solutions of these compounds, and the assignment of the ν_{X-H} vibrations (X = O, N, S) of KBr pellets of the samples is not completely reliable. It can be assumed that 4-amino-5-carboxylic acid XII is in the amino form, since the relatively intense bands at 3203 and 3346 cm^{-1} should be related to the symmetrical and antisymmetrical [8] stretching vibrations of the amino group.* An IHB of the $-\mathrm{OH}\cdots\mathrm{O}{=}\mathrm{C}\begin{smallmatrix}\diagup \\ \diagdown \mathrm{O{-}H}\end{smallmatrix}$ form is extremely likely for X. This is attested to by the rather narrow band at ~3470 cm^{-1} (Fig. 1).

The regions of carbonyl absorption of the ketone forms of hydroxypyrimidines and $\nu_{C=O}$ of the carboxyl group overlap (see [3, 6]). To solve the problem of the predominant structure of these compounds, we used the method of correlation analysis. The dependence of the frequencies of the $\nu_{C=O}$ stretching vibrations of the pyrimidinecarboxylic acids† on their acidity constants (pK_a) is shown in Fig. 2. The corresponding correlation equation has the form

$$\nu_{C=O} = (1871 \pm 7.5) - (40.6 \pm 2.26)\,\mathrm{p}K_a, \quad r = 0.969; \quad \Delta S = 5.859.$$

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*The broad band that ranges between 3100 and 2500 cm^{-1} corresponds to the absorption of the O−H groups.

†The $\nu_{C=O}$ frequencies of dioxane solutions of the acids were used. The highest-frequency components were adopted for the split bands.

The points for X, XI, and XIV-XVII deviate markedly from the linear dependence,* and all of them are affiliated with compounds capable of tautomerism. This is apparently the result of the substantial changes in the molecular structure that occur during these sorts of transformations. It is interesting that, judging from the correlation in Fig. 2, only the hydroxy-substituted acids form tautomeric forms.

EXPERIMENTAL

The IR spectra were recorded with a UR-20 spectrometer with KBr, NaCl, and LiF prisms. The spectra of chloroform solutions of the compounds were recorded in 10-20-mm-thick demountable cuvettes, while the spectra of dioxane solutions were recorded in permanently installed 0.1-1.0-mm-thick cuvettes. The solvents and the KBr were purified by the methods in [9, 10].

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*Allowance for them in the statistical treatment brings about pronounced deterioration in the correlation parameters ($r = 0.553$, $\Delta S = 24.836$.