IR SPECTRA AND STRUCTURE OF 2-ARYL-3-HYDROXYPYRIDINES

B. E. Zaitsev, K. M. Dyumaev,
V. I. Kuz'min, and L. D. Smirnov

UDC 547.823'828:543.422.7

The IR spectra of methyl, chloro, and phenyl derivatives of 3-hydroxypyridines in CCl_4 solutions and in the crystalline state were studied. A comparison of the frequencies, half widths, and integral intensities of the bands of the stretching vibrations of the hydroxyl groups in the spectra of solutions of the 3-hydroxypyridine derivatives in CCl_4 with the characteristic OH bands in the spectra of phenols demonstrates that 3-hydroxypyridines exist practically completely in the hydroxy form in dilute CCl_4 solutions. The shift in the OH bands in the spectra of 2-phenyl-3-hydroxypyridine derivatives indicates that the OH group forms a π-hydrogen bond with the phenyl ring. The presence also of a band of a free OH group is evidence for the existence of s-cis and s-trans conformers relative to the C—O bond.

The IR spectra of 3-hydroxypyridine derivatives have not received sufficient study. As a consequence of the low solubility of 3-hydroxypyridines, little effort has been devoted to the study of the IR spectra in inert organic solvents [1]. In the present paper, we have studied the spectra of a number of 3-hydroxypyridine derivatives in the crystalline state and have measured the frequencies and integral intensities of the absorption bands of the hydroxyl groups of solutions of these compounds in CCl_4. The results are compared with the properties and structure of the 3-hydroxypyridines.

There is no single opinion regarding the structure of 3-hydroxypyridines [2]. A number of authors assume that 3-hydroxypyridines exist only in the hydroxy form [2]. Other authors assume that the 3-hydroxypyridines can exist in the pyridone form [2]. By virtue of the characteristic nature of the absorption bands of the stretching vibrations of the OH groups (hydroxy form) and of the C=O bond (pyridone form) with respect to frequency and intensity, the method of vibrational spectroscopy makes it possible to unambiguously solve a number of problems involving the structure of 3-hydroxypyridines and, in particular, makes it possible to ascertain their structure in solutions of inert organic solvents. Under these conditions, a characterization of the hydroxy form is a model based on phenol and its methyl derivatives, for which $\nu_{OH} = 3612\ cm^{-1}$ in CCl_4 and $J_{OH} = 1.20 \cdot 10^4$ liter/mole $\cdot$ cm^2 [4, 5]. It is apparent from Table 1 that the IR spectra of solutions of 2-methyl-, 2-chloro-, and 2-aryl-3-hydroxypyridines in CCl_4 contain bands of the valence hydroxyl groups at 3545-3610 cm^{-1}, while there are no absorption bands in the carbonyl group (1620-1800 cm^{-1}) and N—H group (3300-3500 cm^{-1}) regions. The measured integral intensity of the OH bonds ranges from 0.9 to 1.2. The half width of the band ranges from 22.2 to 30 cm^{-1}. The frequencies in the spectra of 3-hydroxypyridines are consequently very close to those in the spectra of phenols. This makes it possible to conclude that the isolated 3-hydroxypyridine molecules exist practically completely in the hydroxy form in very dilute solutions in CCl_4. The ν_{OH} bands in the spectra of 2-chloro- and 2-aryl-3-hydroxypyridines are doublets ($\Delta\nu = 35\text{-}40\ cm^{-1}$), and the high-frequency band is at least one order of magnitude weaker in intensity than the low-frequency component (Fig. 1b). Only one band is observed in the spectra of methyl derivatives of 3-hydroxypyridine (Fig. 1a), and its frequency is equal to the frequency

---

Institute of Chemical Physics, Academy of Sciences of the USSR. Scientific-Research Institute of Organic Intermediates and Dyes, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 187-190, February, 1972. Original article submitted April 15, 1970.

TABLE 1. Frequencies (ν_{OH}), Half Widths ($\Delta\nu_{1/2}$), and Integral Intensities (J_{OH}), of the Bands of the Stretching Vibrations of the Hydroxyl Groups

Compound	ν_{OH}, cm^{-1}	$\Delta\nu_{1/2}$, cm^{-1}	$J_{OH}\cdot10^{-4}$ liter/mole·cm^2 accord. to Burzhen	$J_{OH}\cdot10^{-4}$ liter/mole·cm^2 accord. to Ramsay	$\Delta\nu_{CH} = \nu_{OH}^{free} - \nu_{OH}^{bond}$, cm^{-1}
Phenol	3609 3612	—	1,20 1,00	—	—
3-Hydroxypyridine	3595	—	—	—	—
2-Methyl-3-hydroxypyridine	3595	28,2	0,86	0,87	—
2,6-Dimethyl-3-hydroxypyridine	3603	25,5	—	—	—
2,4,6-Trimethyl-3-hydroxypyridine	3608	25	0,9	0,91	—
2-Phenyl-3-hydroxypyridine	3500 3500	—	—	—	38
2-(4-Methylphenyl)-3-hydroxypyridine	3559 3600	24,4	1,1	1,06	39
2-(4-Ethylphenyl)-3-hydroxypyridine	3550 3590	22,5	1,2	1,1	40
2-(4-tert-Butylphenyl)-3-hydroxypyridine	3545 3585	22,2	1,11	1,08	39
2-(2,4,6-Trimethylphenyl)-3-hydroxypyridine	3522 3587	21,0	1,2	—	65
2-(4-Methoxyphenyl0-3-hydroxypyridine	3546 3585	25,5 —	0,9 —	1,0 —	39 —
2-(3-Nitro-4-tert-butylphenyl)-3-hydroxypyridine	3560	30	1,1	1,0	40
2-Chloro-3-hydroxypyridine	3530 3595	25,4	1,6	1,5	65
2-(3-Nitro-4-ethylphenyl)-3-hydroxypyridine	3545 3558	—	—	—	—
2-(3-Nitro-4-isopropylphenyl)-3-hydroxypyridine	3542 3557	—	—	—	—
2-Hydroxydiphenyl	—	—	—	—	42
o-Vinylphenol	—	—	—	—	55
o-Ethynylphenol	—	—	—	—	114

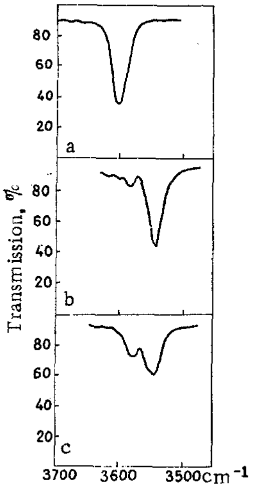


Fig. 1

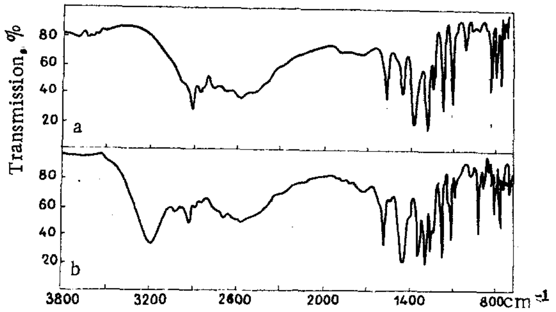
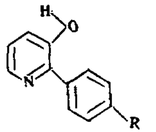


Fig. 2

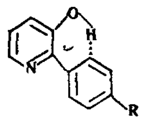
Fig. 1. Bands of the stretching vibrations of the OH groups in CCl_4 solution: a) 2,4,6-trimethyl-3-hydroxypyridine; b) 2-(4-methylphenyl)-3-hydroxypyridine; c) 2-(3-nitro-4-tert-butylphenyl)-3-hydroxypyridine.

Fig. 2. IR spectra in the crystalline state: a) 2-(4-tert-butylphenyl)-3-hydroxypyridine; b) 2-(3-hydroxy-4-ethylphenyl)-3-hydroxypyridine.

of the high-frequency component in the spectra of the 2-chloro- and 2-aryl-3-hydroxypyridine derivatives. The observed splitting of the ν_{OH} band should be ascribed to s-cis and s-trans orientation of the OH groups relative to the phenyl ring:



s-trans-form
$\nu \sim 3585$ cm^{-1}



s-cis-form
$\nu \sim 3550$ cm^{-1}

An intramolecular hydrogen bond is formed in the cis form through interaction of the hydroxyl hydrogen atom with the π-electron system of the phenyl ring or with the chlorine atom. In the trans form, ν_{OH} corresponds to a free OH group and, as expected, lies in the ν_{OH} region of alkyl derivatives of 3-hydroxypyridine. The increased intensity (J_{OH}) for 2-aryl-3-hydroxypyridines as compared with the methyl derivatives of hydroxypyridine is also evidence in favor of the formation of a hydrogen bond, since its formation is usually accompanied by an increase in the band intensity. The explanation of the observed splitting of the ν_{OH} band in the spectra of 2-phenyl-3-hydroxypyridine derivatives is in agreement with a great deal of data on the π-hydrogen bond [6-8]. The magnitude of $\Delta\nu_{OH}$ in the spectra of the studied 2-aryl-3-hydroxypyridines differs by only 2-3 cm^{-1} from $\Delta\nu_{OH}$ in 2-hydroxydiphenyl (Table 1). This is an additional confirmation of the similarity of the π-electron structures of 2-aryl-3-hydroxypyridines and 2-arylphenols.

Since the formation of an intramolecular π-hydrogen bond requires orientation of the O–H bond approximately perpendicular to the plane of the benzene ring, it can be assumed that the phenyl and pyridine rings in 2-aryl-3-hydroxypyridines are not coplanar. The introduction of a nitro group into the meta position of the phenyl ring of 2-aryl-3-hydroxypyridine leads to intensification of the high-frequency band (Fig. 1c). This is probably evidence for hindrance of the nitro group to the formation of a π-hydrogen bond. The increase in the intensity (J_{OH}) in 2-chloro-3-hydroxypyridine is almost twice that in 2-aryl-3-hydroxypyridine and attests to a stronger hydrogen bond in the first case.

The absorption at 2400-3200 cm^{-1} in the spectra of 2-phenyl-3-hydroxypyridine derivatives in the crystalline state (Fig. 2a) corresponds to the stretching vibrations of the hydroxyl group. The pronounced shift of the ν_{OH} bands as compared with the spectra of solutions attests to strong intermolecular hydrogen bonding. A number of individual bands, which are probably due to different types of hydrogen bonds, can be isolated in the indicated region. In all cases, the bands of the stretching vibrations of the CH_2, CH_3, and CH groups are overlapped by the bands of associated OH groups, although the components of the ν_{CH_2}, ν_{CH_3}, and ν_{CH} absorption maxima can nevertheless be isolated in a number of spectra. When there is an OH group in the meta position of the phenyl ring, a very intense maximum at 3170-3190 cm^{-1} is distinctly isolated in the ν_{OH} region (Fig. 2b).

A doublet with an intense component at 1584 cm^{-1} and a weak component at 1604 cm^{-1} is observed in the spectra of all of the 3-hydroxypyridine derivatives at 1580-1610 cm^{-1}. When an OH group is introduced into the para position of the phenyl ring of 2-aryl-3-hydroxypyridine, the intensity ratio changes sharply: the band at 1608 cm^{-1} becomes intense, while the band at 1580 cm^{-1} is weakened sharply. This may serve as an indication of an increase in the conjugation of the phenyl ring with the pyridine ring.

The stretching vibrations of the C–O bonds are usually characterized by an intense band at 1250-1400 cm^{-1}. The band of the deformation vibrations of the CH_2 and CH_3 groups are overlapped by the vibrations of the aromatic rings and the stretching vibrations of the C–O bond. Many bands, the intensities of which change markedly in the various compounds, are observed in the region of the deformation vibrations of the aromatic CH bond. The absorption of methyl derivatives of 3-hydroxypyridine at 400-700 cm^{-1} can be used to determine the number of CH_3 groups.

The authors thank Academician N. M. Émanuél for his constant interest in this research.

EXPERIMENTAL

The studied compounds (Table 1) were synthesized by known methods. The IR spectra of KBr pellets and CCl_4 solutions were recorded with a UR-20 spectrophotometer. The solution concentration was $3 \cdot 10^{-3}$-$5 \cdot 10^{-4}$ M, and the layer thickness was 5-50 mm. The transmission of the solvent in the region of hydroxyl group absorption was no less than 25%. The slightly soluble substances were prepared as saturated solutions, and the solutions were then evaporated to determine the concentrations. The integral intensity (J_{OH}) was determined by the Burzhen method and the Ramsay method [9] with three to four measurements each. The intensity is expressed in practical units (10^4 liter/mole · cm^2). The accuracy of the frequency measurements in the region of an NaCl prism was ±2 cm^{-1} compared with ±5 cm^{-1} with an LiF prism. The accuracy in the intensity measurements was ±10%.

LITERATURE CITED

1. D. Heinert and A. E. Martell, J. Am. Chem. Soc., 81, 3933 (1959).
2. L. Paolini, M. L. Tosato, and M. C. Gnitti, Theoret. Chim. Acta, 14, 221 (1969).
3. D. Albert, Heterocyclic Chemistry, London (1959), p. 56.
4. G. M. Barrow, J. Phys. Chem., 59, 1129 (1955).
5. K. Ingold and D. Taylor, Can. J. Chem., 39, 474 (1961).
6. A. W. Baker and A. T. Shulgin, J. Am. Chem. Soc., 80, 5358 (1958).
7. W. West, J. Am. Chem. Soc., 81, 1616 (1959).
8. M. Oki and H. Jwamurd, Bull. Chem. Soc., Japan, 34, 1395 (1961).
9. D. A. Ramsay, J. Am. Chem. Soc., 74, 72 (1952).