IR SPECTRA AND STRUCTURES OF 3-HYDROXYQUINOLINE, 4-HYDROXYISOQUINOLINE, AND THEIR DERIVATIVES

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From an examination of the frequencies, integral intensities, and half-widths of the absorption bands of the stretching vibrations of the hydroxyl groups in the IR spectra, it was concluded that 3-hydroxyquinoline, 4-hydroxyisoquinoline, and their derivatives exist in the phenol form in dilute CCl_4 solutions. Strong intermolecular hydrogen bonds, which are destroyed on dilution, exist in 3-hydroxyquinoline, 4-methyl-3-hydroxyquinoline, 4-hydroxyisoquinoline, and 1-chloro-3-methyl-4-hydroxyquinoline at concentrations above 10^{-2} M in CCl_4. From an examination of the values of halo derivatives of 3-hydroxyquinoline and 4-hydroxyisoquinoline, it was concluded that an intramolecular hydrogen bond of the OH...Hal type is present in these compounds. The shift in the OH band increases in the order $Cl < Br < I$. Weak bands of a free OH group that pertain to the s-trans form are observed in the spectrum. Strong intramolecular hydrogen bonds exist in 3-nitro-4-hydroxyisoquinoline and 3-piperidinomethyl-4-hydroxyisoquinoline.

The electronic spectra have been used to show that 3-hydroxyquinoline and 4-hydroxyisoquinoline exist in four forms (neutral, dipolar, cationic, and anionic), depending on the pH of the medium [1]. The structures of these compounds in solutions in organic solvents have not been examined. Important information regarding the structures of derivatives of 3-hydroxyquinoline and 4-hydroxyisoquinoline can be obtained from the IR spectra. However, the IR spectra of these compounds have received very little study. The frequencies of the stretching vibrations of the hydroxyl groups (ν_{OH}) in the crystalline state are presented only in [2], and the ν_{OH} values in the CCl_4 are indicated for two compounds. The intensities and shapes of the ν_{OH} bands were not presented. We have studied the IR spectra of 3-hydroxyquinoline, 4-hydroxyisoquinoline, and a number of their derivatives in CCl_4 solutions and in the crystalline state.

Structure

It is apparent from an examination of the IR spectra of solutions of 3-hydroxyquinoline, 4-methyl-3-hydroxyquinoline, 4-hydroxyisoquinoline, and 1-chloro-3-methyl-4-hydroxyisoquinoline in CCl_4 that they are characterized by a narrow absorption band at 3592-3601 cm^{-1} (ν_{OH}) (Fig. 1 and Table 1) and a broad intense band at 2400-3200 cm^{-1}, which vanishes on dilution (Fig. 1). No bands are observed in the region of the absorption of the valence vibrations of the N−H or C=O groups in very dilute solutions. The IR spectra of solutions of halo derivatives of 3-hydroxyquinoline and 4-hydroxyisoquinoline are similar to those described above. In this case, however, the bands of the stretching vibrations of the OH groups that are not tied up in an intermolecular hydrogen bond are shifted by 60-126 cm^{-1} to the low frequency region (Fig. 2). This is readily explained by intramolecular hydrogen bonding (IHB) of the OH...Hal type, as in ortho-substituted phenols [3]. Since the ν_{OH} values of saturated and aromatic hydroxy derivatives are quite close, and one frequency is insufficient for characterizing the nature of the OH group, one must also use the integral intensity (I_{OH}) and the band half-width ($\Delta\nu_{1/2}{}^{a}$), which are, like the frequencies, also characteristic [4]. It is known that I_{OH} of phenols ranges from $0.9 \cdot 10^4$ liter/mole · cm^2 to $1.2 \cdot 10^4$ liter/mole · cm^2,

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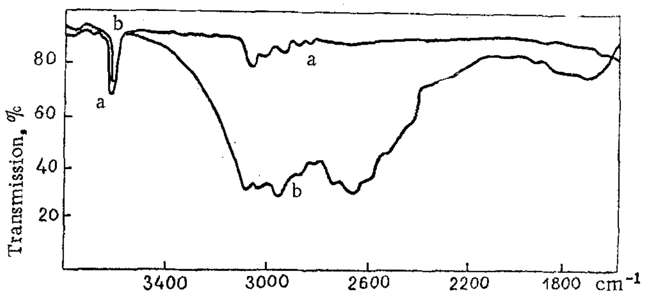

Fig. 1. IR spectra of solutions of 4-methyl-3-hydroxyquinoline in CCl_4: a) c = $4.19 \cdot 10^{-3}$ M (l = 2 cm); b) c = $1.38 \cdot 10^{-3}$ M (l = 1 cm).

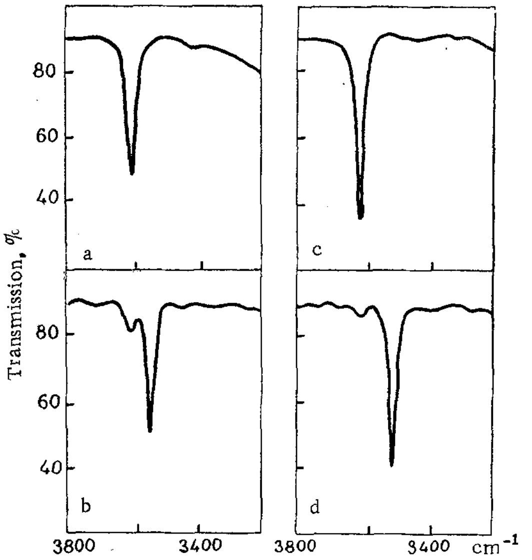

Fig. 2.

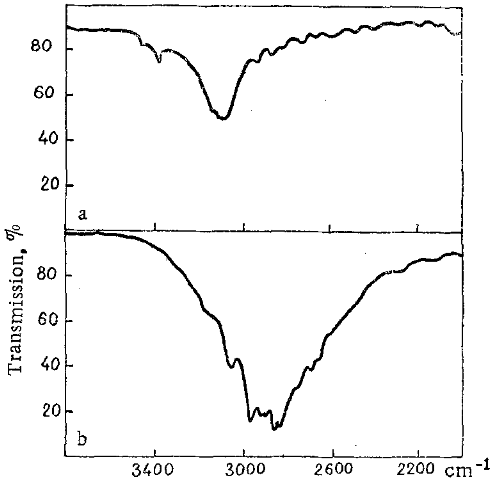

Fig. 3.

Fig. 2. Absorption bands (ν_{OH}) of halo dervatives of 3-hydroxyquinoline and 4-hydroxyisoquinoline in CCl_4: a) 3-hydroxyquinoline; b) 4-chloro-3-hydroxyquinoline; c) 1-chloro-3-methyl-4-hydroxyisoquinoline; d) 3-bromo-4-hydroxyisoquinoline.

Fig. 3. IR spectra of CCl_4 solutions: a) 3-nitro-4-hydroxyisoquinoline (c = $8.7 \cdot 10^{-3}$M, l = 5 cm); b) 3-piperidinomethyl-4-hydroxyisoquinoline (c = $8.62 \cdot 10^{-3}$ M, l = 4.99 cm).

while $\Delta\nu_{1/2}{}^{a} = 18.0$ cm^{-1} [4]. The I_{OH} and $\Delta\nu_{1/2}{}^{a}$ values of the absorption bands of the 3-hydroxyquinoline and 4-hydroxyisoquinoline derivatives are close to those observed for phenols (Table 1). This is evidence in favor of the aromatic nature of the OH group in neutral forms of the compounds under consideration. Thus 3-hydroxyquinoline, 4-hydroxyisoquinoline, and their derivatives exist in neutral (phenolic) forms in dilute CCl_4 solutions.

Some information on the structures of the 3-hydroxyquinoline and 4-hydroxyisoquinoline derivatives can be obtained from an examination of the IR spectra in the crystalline state, in which broad, intense ν_{OH} bands of markedly associated OH groups are observed at 2300-2500 cm^{-1}. The most intense band in the 1000-1400 cm^{-1} region is the band from 1333 to 1380 cm^{-1}, which is probably related to the stretching vibrations of the C—O bonds.

The intervals of the vibrational frequencies of the quinoline and isoquinoline rings in the spectra of the investigated compounds (Table 2) are basically in agreement with the intervals found for a number of trisubstituted quinolines and isoquinolines [5].

TABLE 1. Frequencies (ν_{OH}), Half-Widths ($\Delta\nu_{1/2}{}^{a}$), and Integral Intensities (I_{OH}) of the Absorption Bands of the Stretching Vibrations of the OH Group in Solutions of 3-Hydroxyquinoline and 4-Hydroxyisoquinoline Derivatives in CCl_4.

Compound	ν_{OH}, cm^{-1}	$\Delta\nu_{1/2}{}^{a}$, cm^{-1}	$I_{OH} \cdot 10^{-4}$, liter/mole · cm^2
3-Hydroxyquinoline	3592 s	32,4	—
4-Methyl-3-hydroxyquinoline	3593 s	34,6	0,9
4-Chloro-3-hydroxyquinoline	3533 s 3593 w	—	—
4-Bromo-3-hydroxyquinoline	3515 s 3570 w	—	—
4-Iodo-3-hydroxyquinoline	3482 s 3574 w 3605 w	25	1,1
4-Hydroxyisoquinoline	3600 s	—	—
1-Chloro-3-methyl-4-hydroxyisoquinoline	3601 s	33,4	1,35
3-Iodo-4-hydroxyisoquinoline	3500 s 3591 w	22	0,95
3-Bromo-4-hydroxyisoquinoline	3465 s 3605 w	26	1,10
1,3-Diiodo-4-hydroxyisoquinoline	3475 s	26	1,50
1,3-Dibromo-4-hydroxyisoquinoline	3498 s	—	—
3-Nitro-4-hydroxyisoquinoline	3090 s	—	—
3-Piperidinomethyl-4-hydroxyisoquinoline	2600—3200	—	—

Note: s is strong, and w is weak.

TABLE 2. Vibrational Frequencies (ν, cm^{-1}) of the Rings of 3-Hydroxyquinoline and 4-Hydroxyisoquinoline Derivatives from 1350 to 1630 cm^{-1}.

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8
3-Hydroxyquinoline	1603	1585	—	—	1475		1420	1384
4-Methyl-3-hydroxyquinoline	1621	1582	1540	1522	1460		1419	1381
4-Chloro-3-hydroxyquinoline	1620	1591	1570	1507	1473	1447	—	1386
4-Bromo-3-hydroxyquinoline	1616	—	1568	1509	1482*	1441	—	1371
4-Iodo-3-hydroxyquinoline	1602	—	1562	1504	—	1434	1415*	1370
3-Hydroxyquinoline methiodide	1616	1592 1581	—	1535	1486	1439	1422	1381
4-Hydroxyisoquinoline	1630	1585	—	1525	1482	1450	1412	1382*
1-Chloro-3-methyl-4-hydroxyisoquinoline	1625	1582	—	1501	—	1450	1430*	1382
3-Bromo-4-hydroxyquinoline	1624	1584	1564*	1500	1485*	1445	1414c	1375*
3-Iodo-4-hydroxyquinoline	1620	1579	1565*m	1502	1481	1445	1414c	—
1,3-Dibromo-4-hydroxyisoquinoline	1630	1583	—	1524	1483	1450	1413	1380
1,3-Diiodo-4-hydroxyisoquinoline	1612	—	1562 1540	1498	—	1447	1420	1376

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* The bands are overlapped.

TABLE 3. $\Delta\nu_{OH}$ Values of o-Halo Derivatives of 3-Hydroxyquinoline, 4-Hydroxyisoquinoline, Phenol, and 2-Naphthol

Compound	$\Delta\nu_{OH}$, cm^{-1}
2-Chlorophenol	58[3]
2-Bromophenol	74[3]
2-Iodophenol	91[3]
3-Bromo-2-naphthol	66[8]
4-Chloro-3-hydroxyquinoline	60
4-Bromo-3-hydroxyquinoline	80
4-Iodo-3-hydroxyquinoline	107
3-Bromo-4-hydroxyisoquinoline	91
3-Iodo-4-hydroxyisoquinoline	126

As pointed out above, the IR spectra of solutions of 3-hydroxyquinoline and 4-hydroxyisoquinoline derivatives in CCl_4 are characterized by a broad, intense band at 2400-3200 cm^{-1} and a narrow band at $\sim$3600 cm^{-1}. The low-frequency region of absorption of the solutions is to a great degree similar to the absorption region in the spectra of the compounds in the crystalline state. This makes it possible to assume that the character of the association in concentrated solutions and in the crystal state is similar.

The low-frequency absorption region vanishes at dilutions of up to 10^{-3} to 10^{-4} M, while the intensity of the band at $\sim$3600 cm^{-1} is increased correspondingly (Fig. 1). The 2400-3200 cm^{-1} absorption region is consequently due to OH groups that are bonded by intermolecular hydrogen bonds of the $OH \cdots N\leqslant$ type. As shown in [6], similar changes are detected in the IR spectrum of 3-hydroxypyridine in CCl_4. The intermolecular hydrogen bond energy (E) was estimated from the formula [7]

$$E=\frac{10^2}{K}\cdot\frac{\Delta\nu_{OH}}{\nu_{OH}},$$

where K=1.7, and $\Delta\nu \simeq 600$ cm^{-1}.

The E values obtained ($\sim$10 kcal/mole) are somewhat higher than those in known phenol–pyridine systems [7]. This is due to the greater acidic character of the OH group in 3-hydroxyquinolines.

Two ν_{OH} bands are observed in the spectra of dilute solutions of 3-hydroxyquinoline and 4-hydroxyisoquinoline derivatives – one for a free OH group (3580-3600 cm^{-1}) and one for an OH group tied up in an intramolecular hydrogen bond (OH...Hal) (3465-3533 cm^{-1}) (Table 1). The first band corresponds to an s-trans orientation and the second to an s-cis orientation of the hydroxy group relative to the halogen atom. The difference ($\Delta\nu_{OH}$) between the free and bonded ν_{OH} bands ranges from 60 to 126 cm^{-1} (Table 3) and increases in the order Cl < Br < I. The $\Delta\nu_{OH}$ values in the spectra of halo derivatives of 3-hydroxyquinoline and 4-hydroxyisoquinoline are 2-14 cm^{-1} and 21-33 cm^{-1} higher, respectively, than in the spectra of o-halophenols and o-bromonaphthols [8]. This is also explained by the greater acidic character of the OH group in 3-hydroxyquinolines and 4-hydroxyisoquinolines.

When there is a nitro group in the ortho position relative to the OH group in 3-hydroxyquinoline and 4-hydroxyisoquinoline, a band at $\sim$3100 cm^{-1}, which is related to an IHB of the OH...ONO type, is observed in the IR spectra of solutions of these compounds (Fig. 3). This band is 150-200 cm^{-1} lower than $\nu_{OH...ONO}$ in the spectra of 2-nitro-3-hydroxypyridine [6].

An especially strong IHB bond of the $OH...N\langle$ type was observed in 3-dialkylaminomethyl-4-hydroxyisoquinoline and 4-dialkylaminomethyl-3-hydroxyquinoline. Thus the IR spectrum of a solution of 3-piperidinomethyl-4-hydroxyisoquinoline in CCl_4 contains one broad, intense band of valence vibrations of the OH group at 2600-3200 cm^{-1}, which does not change on dilution to $\sim 10^{-4}$ M (Fig. 3).

EXPERIMENTAL

The synthesis of several of the compounds studied is described in [9]. The IR spectra of CCl_4 solutions ($1.0\text{-}4.0\cdot 10^{-3}$ M, layer thickness 5-50 mm) and in the crystalline state (KBr pellets) were recorded with a UR-20 spectrophotometer. The integral intensities were calculated by the Burzhen method. The accuracy in the measurement of the frequencies in the NaCl and LiF prism regions was ± 2 cm^{-1} and ± 5 cm^{-1}, respectively, while the accuracy in the measurement of the intensities was ± 10%.

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