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STRUCTURE AND ABSORPTION SEPCTRA OF 3-PHENYL-4-HYDROXYISOQUINOLINE

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It was shown by IR spectroscopy that 3-phenyl-4-hydroxyisoquinoline exists in the hydroxy form in solution in organic nonpolar solvents. The splitting of the ν_{OH} band in the IR absorption spectra was assigned to the S-cis and S-trans orientations of the OH group relative to the phenyl ring. An intramolecular hydrogen bond is formed in the cis form of 3-phenyl-4-hydroxyisoquinoline due to interaction of the hydroxyl hydrogen atom with the π-electron system of the phenyl ring. An interpretation of the first two absorption maxima in the electronic spectra of the neutral and ionic forms of the 4-hydroxyisoquinoline and 3-phenyl-4-hydroxyisoquinoline molecules is given within the framework of the MO method and the Pariser–Parr–Pople approximation. It is shown that the introduction of a phenyl group in the 3 position of 4-hydroxyisoquinoline, protonation of the ring nitrogen atom, the ionization of the exocyclic β-hydroxyl group affect the energy of the upper occupied molecular orbital, leaving the lower vacant molecular orbital of 4-hydroxyisoquinoline almost unchanged.

In our previous paper [1] we demonstrated by UV spectroscopy that the 3-phenyl-4-hydroxyisoquinoline (II) molecule, like the 4-hydroxyisoquinoline (I) molecule, exists, depending on the polarity of the solvent, in neutral (N) and dipolar (D) forms in neutral media and in cationic (C) and anionic (A) forms in acid and alkaline media, respectively.

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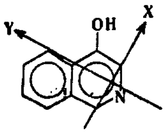
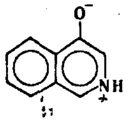


(N)



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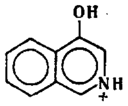

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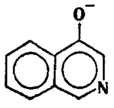
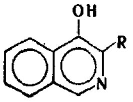


(A)

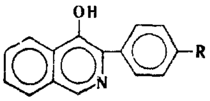
On the basis of the use of perturbation theory (PT) within the framework of the Hückel MO method and the transition energy of the long-wave absorption band, we calculated the angle of rotation, and the length of the bond between the planes of the phenyl ring and the heteorring and its degree of double bond character for 3-phenyl-4-hydroxyisoquinoline [1]. We also determined the energy of conjugation of the phenyl group with the π system of 4-hydroxyisoquinoline [1].

The solution of the following problems constituted the basis of the present research: 1) the study of the IR spectra of II; 2) the quantum-chemical interpretation of the electronic absorption spectra of the neutral and ionic forms of I and II; 3) an experimental and theoretical study of the effect of a phenyl group, protonation of the ring nitrogen atom, and ionization of the β-hydroxyl group on the electronic absorption spectra of I and II, respectively.

The IR spectra of mineral oil and hexachlorobutane suspensions and CCl_4, $CHCl_3$, and CH_2Cl_2 solutions of the investigated 4-hydroxyisoquinolines (Figs. 1 and 2, Table 1) show the absence of absorption bands of N-H and C=O valence vibrations. The presence of a narrow intense band in the spectra of solutions in organic nonpolar solvents at 3550-3580 cm^{-1}, which are related to the stretching vibrations of the O-H bond, proves the presence of the hydroxy form (N). The complete absence of absorption bands at 3500-3600 cm^{-1} and the broad band at 2200-3000 cm^{-1}, which is overlapped by C-H vibrations (in the crystalline state), indicated a very strong intermolecular association [2, 3] of the OH···N$\lessdot$ type.

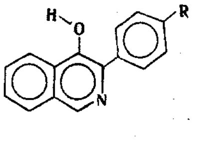


(A)



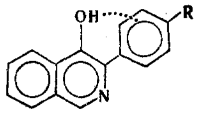
(B)

Two bands — a strong band at 3540-3560 cm^{-1} and a less intense band at 3600-3615 cm^{-1} — are observed in the spectra of 3-aryl-4-hydroxyisoquinolines (Table 1); the latter band is at least one order of magnitude weaker in intensity than the former (Figs. 1 and 2). The observed splitting of the band can be ascribed to the S-cis and S-trans orientation of the OH group relative to the phenyl ring, as demonstrated for 2-phenyl-3-hydroxypyridine [4].



S-trans form

$\nu_{OH} \sim 3615—3600$ cm^{-1}



S-cis form

$\nu_{OH} \sim 3560—3540$ cm^{-1}

An intramolecular hydrogen bond is formed in the cis form due to interaction of the hydroxyl hydrogen atom with the π-electron system of the phenyl ring. The ν_{OH} band in the

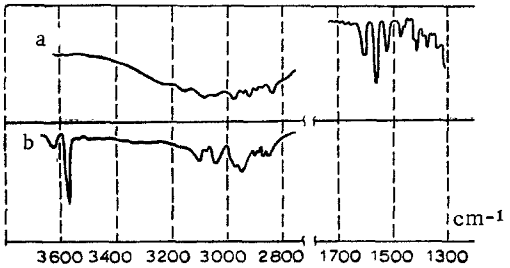


Fig. 1. IR spectra of III: a) in hexachlorobutane; b) in CH_2Cl_2 solution.

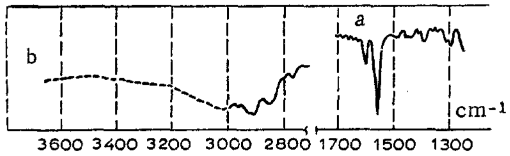


Fig. 2. IR spectra of IV: a) in CH_2Cl_2 solution; b) in hexachlorobutane.

TABLE 1. Frequencies of the Stretching Vibrations of the Hydroxyl Group of 4-Hydroxyisoquinoline Derivatives in Various Solvents (cm^{-1})

Compound	Type of compound	R	CCl_4			$CHCl_3$					CH_2Cl_2		
			ν_{free}	ν_{assoc}	$\Delta\nu$	ν_{free}	ν_{assoc}	$\Delta\nu$	$\Delta\nu_{1/2}$	$I \cdot 10^4$	ν_{free}	ν_{assoc}	$\Delta\nu$
I	A	H	3600	—	—	3598	—	—	—	—	—	—	—
II	A	C_6H_5	—[a]	3560	—	3630[a]	3558[a]	72	—	—	—[a]	3560	—
III	B	OCH_3	3608	3553	55	3611	3548	63	38,5	2,42	3609	3549	60
IV	B	CH_3	—[a]	3552	—	3598	3552	46	38,3	2,23	—	—	—
V	B	C_2H_5	—[a]	3553	—	—[a]	3548	—	38,6	2,68	3610	3548	62
VI	B	Br	—[a]	3564	—	3602	3560	42	32,3	1,92	—	—	—
VII	B	NO_2	—	—	—	3590	—[b]	—	—	—	—	—	—
VIII	A (methiodide)	C_6H_5	—	—	—	3615[b]	3538	77	—	—	—	—	—

[a] In benzene; inexact measurements. [b] The band is practically absent.

TABLE 2. Calculated and Experimental Data on the Electronic Absorption Spectra of 4-Hydroxyisoquinoline and 3-Phenyl-4-hydroxyisoquinoline

Compound and its form	Calcd.				Exptl.	
	ΔE_n, eV	f_n	α_n, °	$A_n(i \to j)$	ΔE_n^{max}, eV	$\lg \varepsilon_n^{max}$
IN	3,93 4,14	0,216 0,144	−3 41	0,728 (6→7); 0,555 (6→8) 0,639 (6→7); 0,607 (6→8)	3,74* 3,89*	3,65 3,62
IC	3,84 4,15	0,258 0,117	−3 49	0,816 (6→7); 0,463 (6→8) 0,528 (6→7); 0,693 (6→8)	3,63* 3,76*	3,93 3,86
IA	3,79 3,96	0,265 0,127	−5 49	0,788 (6→7); 0,539 (6→8) 0,588 (6→7); 0,684 (6→8)	3,60* 3,84*	3,83 3,75
IB	3,69	0,290	−6	0,833 (6→7); 0,470 (6→8)	3,50	3,71
IIN	3,89 4,11	0,264 0,239	−25 76	0,856 (9→10) 0,852 (9→11)	3,64 4,09	3,81 3,90
IIC	3,82 4,08	0,325 0,251	−15 88	0,822 (9→10) 0,807 (9→11)	3,54 4,10	3,98 3,68
IIA	3,69 4,01	0,278 0,264	−29 53	0,914 (9→10) 0,939 (9→11)	3,49 4,71	3,97 4,02
IIB	3,63	0,346	−21	0,842 (9→10)	3,22	3,89

*Shoulder.

spectrum of the trans form is close to that in the spectrum of unsubstituted 4-hydroxyisoquinoline (3600 cm^{-1}) and corresponds to the stretching vibrations of the free hydroxyl group [3].

The explanation of the splitting of the ν_{OH} band in the spectra of 3-aryl-4-hydroxyisoquinolines is in agreement with a great deal of data on the π-electron bonding in 2-hydroxydiphenyls [5-7] and 2-vinylphenols [8, 9], in the IR spectra of which the ν_{OH} band appears as a doublet. This was also confirmed by means of the PMR spectra in the case of protonation of 3-phenyl ketones [10]. The position of the doublet band in the IR spectra of 3-aryl-4-hydroxyisoquinolines (Table 1) is close to the position in the spectrum of 2-hydroxydiphenyl [6]: 3603-3608 (free) and 3552-3576 cm^{-1} (associated).

It is apparent from the data in Table 1 that the maximum difference $\Delta\nu = \nu_{OH}$ (free) − ν_{OH} (associated is reached when there are donor substituents in the phenyl ring (III-V). Correspondingly, the $\Delta\nu_{1/2}$ and I_{OH} values for the band corresponding to the S-cis form also attain maximum values. These values decrease when the electron-acceptor character of the substituent increases. Since the energy of the hydrogen bond depends on these values, it may be concluded that the OH...π bond weakens as the acceptor character of the substituent increases. According to the data in [6], the energy of this type of bond is 0.5-1.2 kcal/mole, i.e., it is weaker than other hydrogen bonds. The appearance of practically one band in the spectrum of VII (R = NO_2) at 3583 cm^{-1} constitutes evidence in favor of the predominant existence of a free OH group (the S-trans form), and this is also confirmed by the more intense absorption in the UV region for this compound as compared with other 3-aryl-4-hydroxy-

TABLE 3. E_{UOMO} and E_{LVMO} Values of I and II (in eV) Calculated by the PPP and PT HMO Methods

Compound and its form	I N	I C	I A	I B	II N
E_{UOMO} PPP	−8,84	−8,87	−8,56	−8,58	−8,65
E_{LVMO} PPP	−1,99	−2,09	−1,92	−2,03	−2,01
E_{UOMO} PT HMO	−8,08	−8,11	−7,97	−8,01	−7,99

isoquinolines [1]. The effect of a nitro group should not be so sharply expressed if the phenyl ring deviates from the plane of the molecule, since the UV spectra of the other 3-aryl-4-hydroxyisoquinolines are similar to one another.

In the calculation of the angle of rotation between the planes of the phenyl ring and the heteroring in II [1] we proceeded from the assumption that the maximum of the long-wave absorption band in the electronic spectra of I and II is due primarily to transition of π-electrons from the upper occupied molecular orbital (UOMO) to the lower vacant MO (LVMO) of these compounds.

It follows from an examination of the $A_n(i \to j)$ coefficients (Table 2) as components of the eigenvectors of the configuration interaction matrix that the transition energy (ΔE_1) of the electronic absorption spectra of the neutral and ionic forms of the I and II molecules is actually due mainly to the singlet-singlet UOMO→LVMO (6 → 7) π-electron transition, which is polarized relative to the X axis at angles from −3 to −6° and from −15 to −29°, respectively.

In the observed absorption spectra of the neutral, cationic, and anionic forms of I (Table 2) the first two maxima (ΔE_1^{max} and ΔE_2^{max}) in the long-wave region are resolved weakly and represent the shoulders of one rather wide absorption band. An analysis of the calculated $A_n(i \to j)$ coefficients for the ΔE_1 and ΔE_2 transitions of I explains this fact by means of the large contribution to ΔE_1 and ΔE_2 of both the transition of a π electron from the UOMO to the LVMO and transition from the UOMO to the second vacant MO (VMO), respectively (Table 2).

It was apparent from the $A_n(i \to j)$ values for the ΔE_1 and ΔE_2 transitions of the N, C, and A forms of II that ΔE_1 is due primarily to transition of a π electron from the UOMO ($i = 0$) to the LVMO ($j = 10$), while ΔE_2 is due primarily to transition from the UOMO to the second VMO ($j = 11$). The ΔE_1^{max} and ΔE_2^{max} values are therefore well resolved in the observed absorption spectra of the N, C, and A forms of II.

It follows from an analysis of the coefficients of expansion of the UOMO with respect to the atomic orbitals that the oxygen atom of the β-hydroxyl group makes the maximum contribution (25-36%) to the UOMO → LVMO transition for the neutral and ionic forms of I and II.

It follows from an examination of the UOMO and LVMO energies calculated by the Pariser—Parr—Pople (PPP) and perturbation theory Hückel MO (PR HMO) [1] methods (Table 3) that the introduction of a phenyl group in the 3 position, protonation of the ring nitrogen atom, and ionization of the exocyclic β-hydroxyl group have an appreciable effect on the E_{UOMO} value, leaving the E_{LVMO} value of I almost unchanged. Protonation of the nitrogen atom increases the absolute value of E_{UOMO} of I, whereas ionization of the β-hydroxyl group lowers it; the latter effect on E_{UOMO} is stronger than the former. The results of the calculation of the E_{UOMO} values of I and II by the PPP and PT HMO methods are close (Table 3).

EXPERIMENTAL

The IR spectra of mineral oil and hexachlorobutane suspensions and CCl_4, $CHCl_3$, and $CHCl_2$ solutions ($3 \cdot 10^{-3}$-$5 \cdot 10^{-4}$ mole; layer thickness 5-50 mm) of the compounds were recorded with a UR-20 spectrometer. The transmission of the solvent in the region of absorption of the hydroxyl group was no less than 25%. In the case of slightly soluble compounds saturated solutions were prepared and subsequently evaporated to determine the concentrations. The integral intensity (I_{OH}) was determined by the Ramsay method from three to four measurements. The intensity is expressed in practical units (10^4 liters/mole·cm^2). The accuracy in the measurement of the frequencies in the range of an NaCl prism was ±2 cm^{-1}, as compared with ±5 cm^{-1} in the range of an LiF prism. The accuracy in the measurement of the intensities was ±10%.

TABLE 4. Parameters (in eV) of the Heteroatoms for the Calculation

Atom (r)	I_r	γ_{rr}	r–s bond	β_{rs}
C	11,16	11,13	$\mathrm{C}\cdots\mathrm{C}$	−2,39
$\dot{\mathrm{N}}$	14,12	12,34	$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$	−2,58
$\dot{\mathrm{N}}^+$	15,12	12,34	$\mathrm{C}\overset{\cdots}{-}\mathrm{N}$	−2,58
OH(C—OH)	30,79	21,30	C—OH	−1,53
O^-(C—O^-)	29,79	21,30	C—O^-	−1,70

The neutral and ionic forms of I and II were calculated by the self-consistent field (SCF) MO LCAO PT method within the Pariser—Parr—Pople (PPP) approximation with allowance for the contribution of 25 singly excited configurations by a modified program, the algorithm of which is described in [11]. Experimental data on the interatomic distances and bond angles for benzene and 8-hydroxyquinoline [12] were used in the postulation of the geometry of I and II. The C-OH, C-O^-, and C-C bond lengths were assumed to be equal to 1.37, 1.34, and 1.47-1.48 Å, respectively. It was assumed that the C-O and C-C bonds divide the external angle in half.

The calculated parameters [the ionization potential (I) and the one-center coulombic (γ) and resonance (β) integrals] are presented in Table 4. In the determination of the numerical values of I, γ, and β for the nitrogen and oxygen atoms we investigated the effect of a change in the I, γ, and β values on the shift of the maximum of the long-wave absorption band ($\Delta E_{1\max}$) in the electronic absorption spectra of the neutral and ionic forms of 3-hydroxypyridine. As a result we ascertained that the ΔE_1 shift depends markedly on the change in the I value, while variation of β and γ has a slight effect on the ΔE_1 value. We used the values [13] $I_o = 37.93$ and $\gamma_{oo} = 23.04$ eV as the starting I_o and γ_{oo} values for the hydroxyl group oxygen atom. The $\beta_{CX} = k_{CX}\beta_{CC}$ ratios that we previously found for the corresponding 3-hydroxypyridines [14] were used to find the β_{CX} values for the C-OH and C-O^- bonds and the "single" C-C bond connecting the benzene ring to the heteroring.

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