STRUCTURE OF 2,3- AND 2,5-DIHYDROXYPYRIDINES

V. T. Grachev, B. E. Zaitsev,
K. M. Dyumaev, L. D. Smirnov,
and M. R. Avezov

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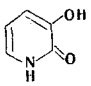
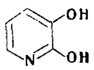
On the basis of an analysis of the UV and IR spectra, it was established that 2,3- and 2,5-dihydroxypyridines exist in different forms in neutral, acid, and alkaline media. The electronic absorption spectra of the neutral forms of the molecules and the distribution of the π-electron charges in them were calculated by means of the Pariser–Parr–Pople (PPP) MO method. A comparison of the results of the calculations with the experimental UV spectroscopic data demonstrated that the calculations correctly predict the number of $\pi \to \pi^*$ absorption bands in the accessible region of the UV spectra and their positions and relative intensities.

Up until now, little study has been devoted to the structure of dihydroxypyridines. The UV spectra of all of the dihydroxypyridines in acid and aqueous alcoholic solutions are presented in [1]. It was demonstrated by means of UV spectroscopy that 2,4-dihydroxypyridine exists as 4-hydroxy-2-pyridone in 50% aqueous ethanol [2]. The tautomerism of 2,4-dihydroxypyridine has also been studied by the semiempirical method of molecular orbitals [3]. The structure of 2,6-dihydroxypyridine was investigated in [4] by means of UV and IR spectroscopy. The structures of the cations and anions of dihydroxypyridines remain virtually uninvestigated.

The present paper is devoted to an investigation of the structures of 2,3- and 2,5-dihydroxypyridines and their cations and anions by UV and IR spectroscopy and by the method of molecular orbitals (MO).

According to [4], 2,3-dihydroxypyridine (I) may exist in forms Ia, b in neutral media, in form Ic in acid media, and in forms Id-f in alkaline media.


Ia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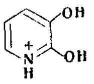
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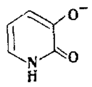
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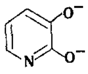
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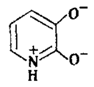
If

According to the well-known principle of "fixed configurations" [5], N-methyl-3-hydroxy-2-pyridone (II) is the model of the pyridone form. It is seen from Table 1 that the UV spectra of I and II in dimethyl sulfoxide and ethanol are identical. This is evidence in favor of form Ia for I in neutral media. This conclusion is confirmed by IR spectroscopy. In fact, absorption bands at 1660-1675 cm^{-1}, which are characteristic for the valence vibrations of the C=O group in 2-pyridone, are observed in the IR spectra of I and II in dimethyl sulfoxide and in the crystalline state (in KBr), and the integral intensities of these bands are approximately equal to the intensities of the band of the C=O group in 2-pyridone (Table 2).

The identical character of the UV spectra of 2,3-dihydroxypyridine and 2-methoxy-3-hydroxypyridine and of the spectra of I and II in acid media and the absence of the characteristic absorption band of a carbonyl group in the IR spectra of I and II under these conditions attest to the existence of form Ic in this medium.

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TABLE 1. UV Spectroscopic Data

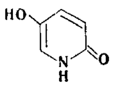
Compound	Medium	λ_{max}, nm	log ε
2,3-Dihydroxypyridine	Dimethyl sulfoxide	300	4.22
	Ethanol	240, 300	3.47, 3.87
	Aqueous [1]	240, 300	3.47, 3.87
	0.1 N HCl [1]	234, 297	3.54, 3.81
	1 N HCl	290	4.25
	Strongly acid [4]	222, 290	3,45, 3.92
	0.1 N NaOH	252, 310	3.81, 3.96
	1 N NaOH	253, 310	4.21, 4.40
N-Methyl-3-hydroxy-2-pyridone	Dimethyl sulfoxide	320	4.31
	Ethanol	300	3.80
	0.1 N HCl	235, 298	3.55, 3.84
	1 N HCl	290	4.44
	0.1 N NaOH	256, 310	3.82, 4.00
	1 N NaOH	259, 310	4.30, 4.35
2-Methoxy-3-hydroxypyridine	Aqueous [4]	221, 280	3.76, 3.76
	Acid [4]	229, 292	3.60, 3.92
2,5-Dihydroxypyridine	Dimethyl sulfoxide	336	4.07
	Ethanol	230, 330	4.06, 3.84
	0.1 N HCl [1]	229, 313	3.81, 3.64
	0.1 N NaOH	230, 290, 347	4.63, 4.40, 3.84

In acid media, the long-wave $\pi \to \pi^*$ absorption band of I experiences a hypsochromic shift due to protonation of the oxygen in the 2 position. In alkaline media, on the other hand, this band experiences a bathochromic shift. One of the reasons for the bathochromic shift is ionization of the hydroxyl group in the 3 position. This is in agreement with the pK values of 9.00 for I [4] and 8.72 for 3-hydroxypyridine [6].

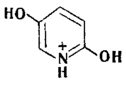
The identical character of the UV spectra of I and II and the absence of an absorption band of a C=O group in alkali media in their IR spectra are evidence for the existence of form If rather then Id and Ie in this medium.

Thus 2,3-dihydroxypyridine exists in forms Ia, Ic, and If, respectively, in neutral, acid, and alkaline media.

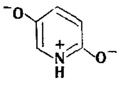
Similarly, one should expect the existence of forms IIIa, IIIc, and IIIf in neutral, acid, and alkaline media, respectively, for 2,5-dihydroxypyridine (III).



III a



III c



III f

In fact, within the limits of experimental error, the integral intensity of the carbonyl group absorption band of III observed in the IR spectrum of a solution in dimethyl sulfoxide and in the crystalline state (KBr) is equal to the integral intensity of the band of the C = O group in 2-pyridone and 2,3-dihydroxypyridine. The absorption band of the C=O group vanishes in the IR spectra of III in acid and alkaline media.

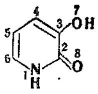
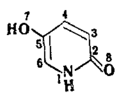
The long-wave $\pi \to \pi^*$ absorption band in the UV spectrum of III undergoes a hypsochromic shift in acid media and a bathochromic shift in alkaline media, as in the case of 2,3-dihydroxypyridine. Three absorption maxima instead of the usual two for 2-pyridone derivatives are observed in the electronic absorption spectrum of III in alkaline media.

As in the case of 2,3-dihydroxypyridine, it follows from a comparison of the acidity constants of III (pK 8.51 [6]), 2-pyridone, and 3-hydroxypyridine that the β-hydroxyl group undergoes ionization in alkaline media.

TABLE 2. IR Spectroscopic Data

Compound	Solvent	Concn., mole/liter	$\nu_{C=O}$, cm^{-1}	$\Delta\nu_{1/2}^{a}$, cm^{-1}	Integral intensity, liter/mole · cm^2
2,3-Dihydroxypyridine	Dimethyl sulfoxide	0,0454	1660	25,0	54000
	KBr	0,0480	1670	35,5	50000
	1 *N* HCl	0,091	—	—	—
	1 *N* NaOH	0,091	—	—	—
N-Methyl-3-hydroxy-2-pyridine	Dimethyl sulfoxide	0,0454	1660	28,0	57000
	KBr	0,0480	1660—1665	31,0	48000
	1 *N* HCl	0,091	—	—	—
	1 *N* NaOH	0,091	—	—	—
2-Pyridone	Dimethyl sulfoxide	0,0454	1675—1657	28,0	60000
	KBr	0,0480	1665	32,2	50000
2,5-Dihydroxypyridine	Dimethyl sulfoxide	0,0454	1675	26,4	55000
	KBr	0,0480	1665	38,2	50000
	0,1 *N* HCl	0,091	—	—	—
	0,1 *N* NaOH	0,091	—	—	—

TABLE 3. Energy and Electronic Characteristics of Forms Ia and IIIa of 2,3- and 2,5-Dihydroxypyridines in the Ground State

Compound and its form	Energy level No. n	E_n, eV	π→π* transition	ΔE, eV	λ, nm	f	Atom No., r	Q_r	$\psi_5=\sum_r a_r f_r$
	1	−15,733	5→6	4,261	291	0,380	1	+0,388	−0,281
	2	−14,210	5→7	4,871	254	0,269	2	+0,166	−0,116
	3	−12,314	5→8	6,170	201	0,348	3	+0,010	−0,405
	4	−11,110	4→6	6,922	179	0,292	4	−0,064	−0,340
	5	−8,749	4→7	7,166	173	0,493	5	−0,049	+0,335
	6	−1,484	4→8	7,424	167	0,445	6	−0,049	+0,412
Ia	7	−0,528	3→6	8,578	144	0,038	7	+0,143	+0,337
	8	+1,889	3→7	9,152	135	0,059	8	−0,543	+0,480
			3→8	10,426	119	0,030			
	1	−15,661	5→6	3,915	317	0,227	1	+0,386	+0,359
	2	−14,412	5→7	5,217	238	0,320	2	+0,172	+0,087
	3	−12,082	5→8	6,218	199	0,843	3	0,015	+0,336
	4	−11,197	4→6	6,750	184	0,148	4	+0,008	+0,058
	5	−8,798	4→7	7,312	170	0,212	5	−0,030	−0,402
	6	−1,720	4→8	7,359	163	0,273	6	−0,095	−0,449
IIIa	7	−0,313	3→6	8,294	149	0,215	7	+0,116	+0,312
	8	+1,854	3→7	9,347	133	0,009	8	−0,543	−0,514
			3→8	10,087	123	0,077			

Thus an analysis of the UV and IR spectra and the ionization constants of III is evidence in favor of the existence of forms IIIa, IIIc, and IIIf in neutral, acid, and alkaline media, respectively.

The results of calculation by the PPP method of the energy levels (E_n), energies (ΔE), wavelengths (λ), and forces of the oscillators (*f*) of the singlet–singlet transitions, as well as the distribution of π-electron charges and coefficients (a_r) of the upper occupied MO ($\psi_5 = \sum_r a_r f_r$), for forms Ia and IIIa of 2,3- and 2,5-dihydroxypyridines are presented in Table 3.

For Ia and IIIa the calculation predicts the appearance in the region above 220 nm of two absorption bands due to singlet transition of the molecules to the first (5 → 6) and second (5 → 7) excited states, and the oscillator force of the first long-wave π band in Ia is greater than the oscillator force of the second band, while the opposite is true in IIIa. It is apparent from a comparison of the calculated values with the experimental data from UV spectroscopy for 2,3- and 2,5-dihydroxypyridines in neutral media (Table 1) that the calculations satisfactorily predict the number of π → π* absorption bands in the accessible region of the UV spectrum and their positions and relative intensities.

From an analysis of the a_r coefficients of the upper occupied MO (ψ_5) it can be concluded that the 5 → 6 and 5 → 7 transitions are most probably due to the transition of a π electron of the carbonyl-group oxygen.

The uneven distribution of the effective π-electron charges in Ia, IIIa, and II is apparently due to the effects of conjugation of the cyclic nitrogen atom of the pyrrole type and of the exocyclic oxygen atom of the phenol type and to the inductive effect of the oxygen atom of the carbonyl group. The maximum positive π-electron charge in Ia and IIIa is concentrated on the nitrogen atom, while the negative charge is concentrated on the carbonyl oxygen.

EXPERIMENTAL

The UV spectra were measured with an SF-4A spectrophotometer (Table 1). The IR spectra of KBr pellets and solutions were recorded with a UR-10 spectrophotometer at 400-4000 cm^{-1} (Table 2). The integral intensities of the IR absorption bands of the carbonyl group were calculated by the method in [7]. The neutral molecules of 2,3- and 2,5-dihydroxypyridines were calculated via the MO LCAO method within the Pariser–Parr–Pople method [8, 9] from a program kindly provided by Kruglyak and co-workers [10]. The so-called variable β approximation [11], according to which the bond integrals ($\beta_{\mu\nu}^{\text{frame}}$) are changed in each iteration in accordance with the adopted dependence on the bond order values being calculated, was introduced into the variant of the PPP program in order to refine the values of the $\beta_{\mu\nu}^{\text{frame}}$ integrals calculated for different interatomic distances. The Nishimoto and Foster system of parameters was used in the calculations. The orbital ionization potentials (I_μ) and the orbital affinity (A_μ) for the atoms were taken from Hinze and Jaffe. The two-center electron-repulsion integrals were estimated from the Matago-Nishimoto formula. Nine singly excited configurations were taken into account in the calculation of the electron transitions. The bond lengths and angles were assumed to be the same as in 2-pyridone [11] in the selection of the molecular geometry for the pyridone forms but were assumed to be the same as in pyridine [11] for the hydroxy form, with an average C–O bond length of 1.35 Å.

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