STRUCTURE OF 2-METHOXY-3-HYDROXY-6-PHENYLAZOPYRIDINE

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Electronic and IR spectroscopy were used to observe that 2-methoxy-3-hydroxy-6-phenylazopyridine exists in azo and hydrazo forms. The tautomeric equilibrium is shifted to favor the formation of the hydrazo form on passing from aprotic to protic solvents. The ratios of the tautomers in various solvents were estimated. The stabilities of both forms were determined by the MO method.

It is known that p-hydroxyazo aromatic compounds can exist in azo and hydrazo forms [1, 2]. The azo form is characterized by an absorption band at 360-400 nm in the electronic spectra of solutions of p-hydroxyazo compounds, while the hydrazo form is characterized by a band at 440-480 nm.

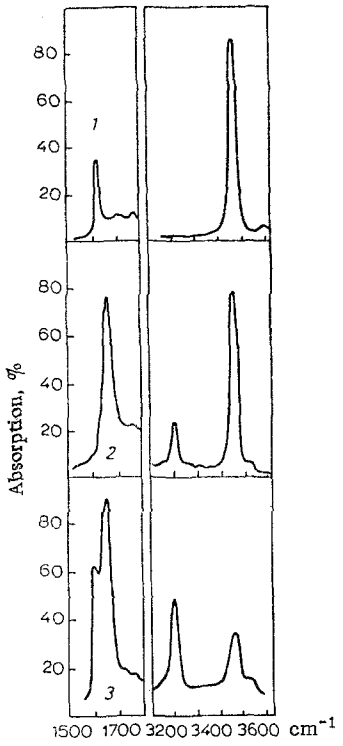
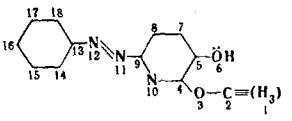
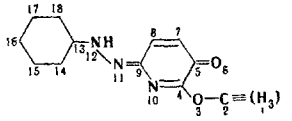


Fig. 1. IR spectra: 1) 2-methoxy-3-hydroxypyridine in CCl_4; 2) 2-methoxy-3-hydroxy-6-phenylazopyridine in CCl_4; 3) 2-methoxy-3-hydroxy-6-phenylazopyridine in $CHCl_3$.

One should expect that 2-methoxy-3-hydroxy-6-phenylazopyridine, like p-hydroxyazo aromatic compounds, also exists in two tautomeric forms, I and II.



I



II

The presence of a nitrogen atom in the ring should affect the position of the tautomeric equilibrium. If the concentration of tautomers in solution is sufficiently high, both the electronic and IR spectra can be used successfully for the study of the azo and hydrazo forms. For this end, we studied I in the crystalline state and in solutions by electronic and IR spectroscopy.

IR Spectra

It follows from an examination of the IR spectra of I (Table 1) that the absorption bands of this compound are observed in the region of the stretching vibrations of the OH, NH, C=O, and C=N groups (Fig. 1). The positions of the absorption maxima and the ratio of the intensities of the observed bands (3540-3560, 3280-3293, and 1654 cm^{-1}) do not change on successive dilution of solutions of I in carbon tetrachloride and chloroform, and no new bands appear. The

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TABLE 1. Frequencies (ν), Half Widths ($\Delta\nu_{1/2}$), and Integral Intensities (I) of the Absorption Bands of 2-Methoxy-3-hydroxy-6-phenylazopyridine and 2-Methoxy-3-hydroxy-pyridine in Solutions and in the Crystalline State

Comp.	Solvent	ν, cm^{-1}			$\Delta\nu_{1/2}$, cm^{-1}			$I \cdot 10^{-4}$, liter/mole·cm^2		
		OH	NH	C=O C=N	OH	NH	C=O C=N	OH	NH	C=O C=N
I; II	CCl_4	3547	3293	1654	28		22	1,46		0,90
	$CHCl_3$	3535	3283	1650	42	28		0,71	0,90	
	Crystalline state		3235	1637—1656						
III	CCl_4	3556			25			1,81		
	$CHCl_3$	3545			37			2,10		
	Crystalline state	2500—3200								

TABLE 2. Electronic Spectra of 2-Methoxy-3-hydroxy-6-phenylazopyridine

Solvent	λ_{max}, nm (lg ε)
CCl_4	470 (3,99), 360 (4,05), 275 (3,89)
$CHCl_3$	478 (4,52), 356 (3,69), 285* (3,91), 275 (3,98)
Alcohol (95%)	472 (3,90), 370 (4,22), 280 (3,87)
Alcohol (5%)	483 (3,18), 375 (4,10), 280* (3,78), 270 (3,83)
0,001 *N* HCl	480 (3,91), 365 (4,28), 285 (3,86)
0,01 *N* HCl	480 (3,91), 365 (4,27), 277 (3,94)
0,05 *N* HCl	485 (4,03), 365 (4,24), 280 (3,83), 237 (4,06)
0,1 *N* HCl	480 (3,95), 370 (4,26), 282 (3,90)
0,45 *N* HCl	488 (4,24), 365 (4,04), 260* (3,90)
Conc. HCl	488 (4,60)
0,001 *N* NaOH	450 (4,46), 260 (3,96)
0,01 *N* NaOH	450 (4,45), 255 (3,13)
0,05 *N* NaOH	451 (4,42), 282 (3,32)
0,1 *N* NaOH	448 (4,44), 260* (3,13)
0,45 *N* NaOH	451 (4,42), 280* (3,68), 255 (3,89)

*Shoulder.

TABLE 3. Energy Characteristics of 2-Methoxy-3-hydroxy-6-phenylazopyridine

Compound form	DE_π, β units	DE_π/n, β units	E_π, β units	λ_{max}, nm	ΔE, β units
I	6,354	0,3177	1,532	365	32,844
II	4,616	0,2308	0,992	472	32,906

TABLE 4. Parameters Used for the Quantum-Chemical Calculation of Tautomeric Forms of 2-Methoxy-3-hydroxy-6-phenylazopyridine

Azo form				Hydrazo form			
atom	h_r	bond	k_{rs}	atom	h_r	bond	k_{rs}
$(H_3)_1$	−0,5	1—2	2	$(H_3)_1$	−0,5	1—2	2
O_3	1,8	2—3	0,5	O_3	1,8	2—3	0,5
C_4	0,3	3—4	0,7	C_4	0,3	3—4	0,7
C_5	0,3	5—6	0,7	C_5	0,2	4—5	0,8
O_6	2	9—11	0,5	O_6	1,2	4—10	1,2
C_9	0,2	11—12	1,4	C_9	0,1	5—6	2
N_{10}	0,5			N_{11}	0,4	7—8	1,2
N_{11}	0,4			N_{12}	1,0	9—10	0,8
C_{13}	0,1			C_{13}	0,2	9—11	1,2
						11—12	0,7
						12—13	0,4

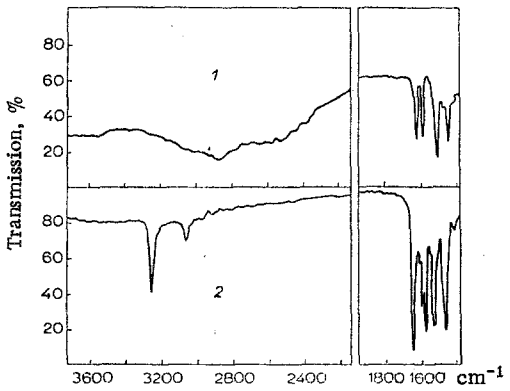

Fig. 2. IR spectra in the crystalline state: 1) 2-methoxy-3-hydroxypyridine; 2) 2-methoxy-3-hydroxy-6-phenylazopyridine.

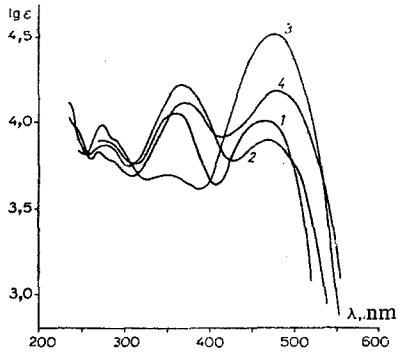

Fig. 3. Electronic absorption spectra of 2-methoxy-3-hydroxy-6-phenylazopyridine: 1) in CCl_4; 2) in 95% alcohol; 3) in $CHCl_3$; 4) in 5% alcohol.

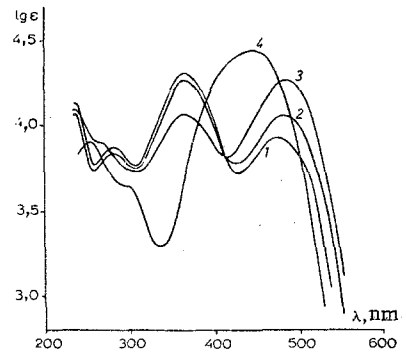

Fig. 4. Electronic absorption spectra of 2-methoxy-3-hydroxy-6-phenylazopyridine: 1) in 0.001 N HCl; 2) in 0.05 N HCl; 3) in 0.45 N HCl; 4) in 0.45 N NaOH.

bands at 3550 cm^{-1} should be assigned to the stretching vibrations of a hydroxyl group (ν_{OH}) bonded by a weak intramolecular hydrogen bond (IHB) to the methoxy group. This is proved by the presence of the same band in the spectrum of 2-methoxy-3-hydroxypyridine (III) (Fig. 1 and Table 1). The bands at 1650 cm^{-1} are related to the $\nu_{C=O}$ and $\nu_{C=N}$ stretching vibrations; this is in agreement with the position of these bands in the spectra of keto imines [3]. The band at 3296 cm^{-1} is related to the ν_{NH} stretching vibrations. The decrease in the absorption maximum of this band is probably due to the specific environment of this group. The ν_{OH} band in the IR spectra of I attests to the presence in solution of tautomeric form I. The ν_{NH}, $\nu_{C=O}$, and $\nu_{C=N}$ bands characterize hydrazo form II. The ratios of the intensities of the absorption bands that characterize the two tautomers change markedly on passing from solutions in carbon tetrachloride to solutions in chloroform (Fig. 1). Thus the intensity of the ν_{OH} band decreases markedly, while the intensities of the ν_{NH} and $\nu_{C=O}$ bands increase; this indicates a shift in the tautomeric equilibrium to favor the formation of hydrazo form II. Using the dependence of the intensity of the absorption band on the concentration, one can determine the ratio of tautomeric forms in solutions. For this, it is necessary to know the absolute intensity of the absorption bands of each of the indicated forms. The intensity of the ν_{OH} band in the spectrum of III was adopted as the absolute intensity of the absorption band of azo form I. It should be noted that the intensity of the ν_{OH} band of I should be somewhat higher than that of III because of conjugation of the pyridine ring with the azo group. The determination of the ratio of tautomeric forms is therefore by nature an approximate one. By measuring the area under the absorption curve of the hydroxyl group (A_{OH}) of solutions of I in carbon tetrachloride and chloroform and by substituting the A_{OH} values found into formula (1), we can calculate the concentration (C_I) of the azo form in solution:

$$C_I = \frac{A_{OH}}{dI_{OH}},$$

where I_{OH} is the integral intensity of the ν_{OH} band of III, and d is the layer thickness.

As a result, it is found that the ratio of tautomeric forms (C_I/C_{II}) in solution in carbon tetrachloride is 1.411, compared with 0.563 in chloroform. Consequently, the tautomeric equilibrium is shifted markedly to favor the formation of hydrazo form II on passing from solutions of I in carbon tetrachloride to solutions in chloroform.

One narrow band (3235 cm^{-1}) and a very intense band at 1637-1656 cm^{-1} are observed in the IR spectra of crystalline I in the region of absorption of NH and OH groups. However, a diffuse band at 2500-3200 cm^{-1} and two narrow intense bands at 1611 and 1583 cm^{-1} are observed in the spectrum of III in the region of absorption of an OH group (Fig. 2). Consequently the spectra of I and III differ markedly. The narrow band at 3235 cm^{-1} is characteristic in a number of cases for the secondary amine group in the crystalline state. The intense band at 1637-1656 cm^{-1} in the spectrum can most likely be assigned to $\nu_{C=O}$ of the hydrazo form. Consequently, I probably exists in the hydrazo form in the crystalline state.

Electronic Spectra

It is apparent from an examination of the electronic spectra of I in various media and solvents that the compound is characterized by absorption maxima at 480 and 365 nm, which are related to the hydrazo and azo forms, respectively (Figs. 3 and 4 and Table 2). The ratios of the intensities of the bands that characterize tautomers I and II change in analogy with the ratios of the intensities of the absorption bands of these forms in the IR spectra on passing from solutions in carbon tetrachloride to solutions in chloroform. Thus bands of both forms with about the same intensity are observed in the spectrum of a solution of the compound in carbon tetrachloride. The intensity of the absorption band of the azo form decreases sharply on passing to solutions in chloroform, while the intensity of the hydrazo form increases. This attests to a shift in the tautomeric equilibrium to favor the formation of the hydrazo form. In alcohol solutions, the equilibrium is shifted to favor the formation of form I. The absence of model compounds makes it impossible to quantitatively determine the tautomer ratio in solution. The absorption bands in the short-wave region correspond to the electronic spectra of III (λ_{max} 280 nm, log ε 3.76) [4].

In acidic media the tautomeric equilibrium depends on the pH of the medium. Thus the intensity of the absorption band of the hydrazo form (λ_{max} 480 nm) increases as the acidity of the medium increases, while the intensity of the azo band (λ_{max} 365 nm) decreases. An isosbestic point that characterizes the presence of both tautomeric forms is observed in the spectra of solutions of I in hydrochloric acid. An increase in the intensity of the absorption band of the hydrazo form (λ_{max} 488 nm, log ε 4.60) is initially observed in solution in concentrated hydrochloric acid. The absorption spectrum of I in alkaline media is characterized by absorption bands that are related to the anionic form of this compound (λ_{max} 450 nm). The absorption bands in the short-wave region correspond to the spectrum of the anionic form of III at pH 12 (λ_{max} 242 nm, log ε 3.95; λ_{max} 296 nm, log ε 3.83) [4]. A yellow precipitate that turns red in air precipitates immediately on protonation of an orange solution of I in chloroform. The precipitate turns red in air because of decomposition of the hydrochloride of I.

Quantum-Chemical Calculation

It is of interest to estimate the relative stabilities of the isoelectronic tautomeric forms and to obtain data on the distribution of the π-electron density in them. For this purpose, we calculated the π-electron energies (E_π), the delocalization energies (DE_π), the π-electron densities on the atoms (q_r), and the bond orders (p_{rs}) by the Hückel MO method.

It is apparent from Table 3 that the overall π-electron energies of the tautomers are close in magnitude. The DE_π and DE_π/n values are larger for the azo form than for the hydrazo form. Consequently, the azo form is energetically more favorable. The differences in the energies of the upper occupied and lower vacant MO correlate with the long-wave bands in the electronic spectra of both tautomers.

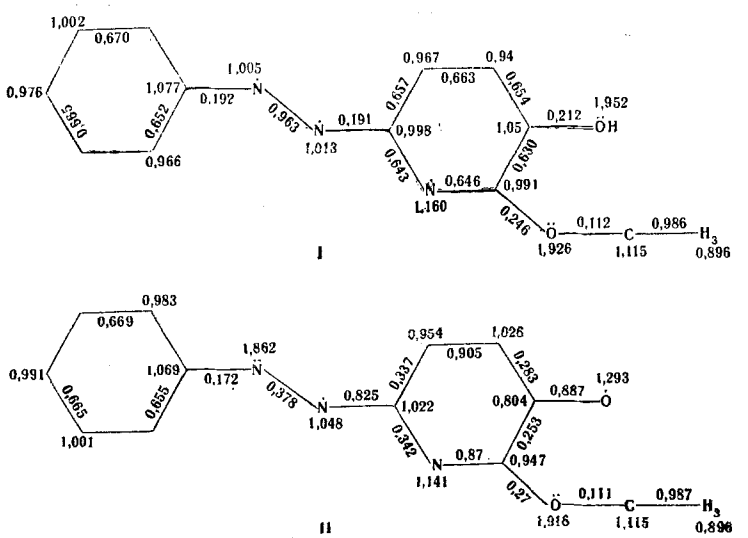

Fig. 5. Molecular diagrams of 2-methoxy-3-hydroxy-6-phenylazopyridine: I) azo form; II) hydrazo form.

It follows from an examination of the molecular diagram (Fig. 5) of the azo form that the order of the N=N bond is 0.963; i.e., it approaches p_{rs} of the double bond. This is in agreement with the x-ray structural data on the length of this bond in azobenzene (1.23 Å [5]). The orders of the exocyclic C–N and C–O bonds, which range from 0.191 to 0.246, attest to the multiplicities of these bonds (about 20%). The decrease in the π-electron density on the exocyclic oxygen atoms is evidence for their interaction. The orders of the bonds of the benzene and pyridine rings are close to one another; this explains their high degree of aromatic character.

It is seen from an examination of the molecular diagram of the hydrazo form that the orders of the exocyclic C=O and C=N bonds in the para position and of the cyclic C–C and C–N bonds in the pyridine ring correspond to a quinoid structure of the bonds. In fact, the orders of the conjugated exocyclic and cyclic C=N, C=O, and C=C bonds are close to double (0.825-0.905), while the p_{rs} values of the bonds adjacent to the carbonyl and imine groups are 0.253-0.342. The $p_{C=O}$ and $p_{C=N}$ values of the exocyclic bonds correlate with the frequencies of the stretching vibrations of these bonds in the IR spectra. Since the order of the N–N bond (0.378) is twice the $p_{C=N}$ value (0.172), one can conclude that conjugation of the amine nitrogen is realized predominantly with the quinoid system.

EXPERIMENTAL

Compound I was synthesized via the method in [6] in 91% yield and had mp 135-136°. The IR spectra of solutions and crystals of I were recorded with a UR-20 spectrophotometer (Table 1 and Figs. 1 and 2). The integral intensities were measured by the Bourgin method, and the accuracy in the determination of the frequencies in the region of a NaCl prism was ± 2 cm^{-1}, compared with ± 5 cm^{-1} in the region of an LiF prism. The electronic spectra were obtained with an SF-4A spectrophotometer (Table 2 and Figs. 3 and 4). The calculations were made by the Hückel method with the parameters presented in Table 4.

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