FACTORS THAT AFFECT THE TAUTOMERIC EQUILIBRIUM OF HYDROXYAZOPYRIDINE DERIVATIVES*

B. E. Zaitsev, G. V. Sheban, L. D. Smirnov, and K. M. Dyumaev

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The ratio of azo and quinonehydrazone forms of 3-hydroxy-6-phenylazopyridine derivatives was determined by IR and electronic spectroscopy. The formation of two crystalline modifications of 2-methoxy-3-hydroxy-6-phenylazopyridine is explained by crystallization of the molecules either in the form of dimers of predominantly the quinonehydrazone form or in the form of polyassociates of the azo form, which are formed by a strong hydrogen bond.

2-Methoxy-3-hydroxy-6-phenylazopyridine (I) exists in organic solvents in azo and quinonehydrazone forms [2]. It is interesting to ascertain the factors that affect the tautomeric equilibrium of 3-hydroxy-6-phenylazopyridine derivatives (I). With this end in mind, we investigated the derivatives of I in the gaseous and crystalline states and in various solvents by IR and electronic spectroscopy.

In conformity with the Bronsted [3] and Kabachnik [4] concepts, the tautomerism of these compounds can be considered from the point of view of an acid—base equilibrium. Compound I is characterized by two "basic" groups (the azo group and the pyridine nitrogen atom) and one "acidic" OH group. However, the ratio of the pK_a values of the basic and acidic groups is insufficient for the formation of a zwitterion or a quinonehydrazone tautomer. This is confirmed by the fact that 3-hydroxypyridine exists primarily in the phenol form in inert solvents [5, 6]. The form of the existence of I is demonstrated unambiguously by the IR absorption spectra in the gas phase. It is seen from Table 1 that a doublet band of stretching vibrations of a free OH group at 3612/3635 cm^{-1} is observed in the spectrum, and bands of the stretching vibrations of carbonyl and amine groups are absent. Consequently, in the absence of intermolecular interaction, in the gaseous state (at 140°C) I exists in the azo form. This conclusion is confirmed by a comparison of the atomization energies (ΔH) and the total bond energies (E_b) of the azo and quinonehydrazone forms of 3-hydroxy-6-phenylazopyridine, 2,3-dihydroxy-6-phenylazopyridine, and 2-phenyl-3-hydroxy-6-phenylazopyridine calculated by the quantum-chemical self-consistent-field (SCF) method (Table 2).

As the concentration increases and the temperature is reduced, I, which has acid—base properties, should associate strongly; this shows up in the tautomeric equilibrium. In order to exclude the effect of the solvent on association, we recorded the IR spectra of $\sim 4 \cdot 10^{-2}$ M solutions in hexane (Table 1). Under these conditions, ν_{OH}, ν_{NH}, and $\nu_{C=O+C=N}$ bands, which characterize both tautomers, are observed in the IR spectra of I. The decrease in the frequency of the band by 50-90 cm^{-1} as compared with ν_{OH} in the IR spectra of I in the gaseous state and its independence on the degree of dilution attests

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TABLE 1. Frequencies of the Stretching Vibrations of the OH, NH, and CO Groups of 2-Methoxy-3-hydroxy-6-phenylazopyridine

Solvent	$\nu_{C=O+C=N}$, cm^{-1}	ν_{OH}, cm^{-1}	ν_{NH}, cm^{-1}	$\varepsilon_{OH}/\varepsilon_{NH}$
		3612 3635 [a]		
Hexane	1661	3562	3286	5,0
CCl_4	1662 1653	3547	3295	3,6
Benzene	1664 1648	3520 3550	3295	2,5
Toluene	1663	3510 3550	3287	1,9
Xylene	1665	3552 3512	3295	1,8
Dimethylnaphthalene	1666	3550 3513	3290	1,0
Chlorobenzene	1665 1649	3533	3289	1,2
Fluorobenzene	1662 1642	3540	3281	1,2
Trichlorobenzene	1654 1646	3541	3288 3244	1,0
	1638 b strong			
	1639c weak	2900÷ 3600		
$CHCl_3$	1662 1636	3545	3286	0,8

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a) The IR spectrum of the gas phase was recorded. b) The IR spectrum of the compound in the crystalline state (mp 135°C) was recorded. c) The IR spectrum of the compound in the crystalline state (mp 150°) was recorded.

TABLE 2. Calculated π-Bond ($E_{\pi b}$), σ-Bond ($E_{\sigma b}$), Total-Bond ($E_b = E_{\pi b} + E_{\sigma b}$) Energies and Atomization Energies (ΔH) of the Azo (A) and Quinohydrazone (QH) Forms of 2-Substituted 3-Hydroxy-6-phenylazopyridines

R	Form	$E_{\pi b}$	$E_{\sigma b}$	E_b	ΔH	$\Delta H_A - \Delta H_{QH}$
H	A	25,224	55,533	80,769	120,706	0,977
	QH	24,396	55,632	80,027	119,729	
OH	A	25,935	59,542	85,477	125,417	0,835
	QH	25,227	59,652	84,879	124,582	
C_6H_5	A	35,227	81,551	117,442	175,131	0,877
	QH	35,118	81,685	116,802	174,254	

to tying up of the OH group in an intramolecular hydrogen bond (IHB) with the methoxy group. The observed position of the ν_{NH} band, which characterizes the quinonehydrazone form, is strongly depressed as compared with the expected value. In fact, the amino group in the quinonehydrazone form is in conjugation with the phenyl group and the quinonehydrazone group. This sort of environment of the amino group is to a great degree similar to its environment in diphenylamine, which absorbs at 3433 cm^{-1} in CCl_4 solution [6]. The decrease in the ν_{NH} frequency of the quinonehydrazone tautomer can be explained by self-association. Inasmuch as the ratio of the ν_{NH} and ν_{OH} intensities does not change as the concentration changes and the appearance of new bands is not observed, while the ν_{NH} band is sharp, it can be assumed that the associates have a dimeric structure of the A or B type.

TABLE 3. Characteristics of the Long-Wave Absorption Bands [λ_{max}, nm (ε)] and Concentrations of the Quinonehydrazone Tautomers (C_{QH}%) of 2-Substituted 3-Hydroxy-6-phenylazopyridines

R		Cl		I		C_6H_5		$CH_2C_6H_5$		CH_3		OCH_3	
Solvent	C_{QH}	λ, nm (ε)	C_{QH}	λ, nm (ε)	C_{QH}	λ, nm (ε)	C_{QH}	λ, nm(ε)	C_{QH}	λ, nm (ε)	C_{QH}	λ, nm (ε)	C_{QH}
Dioxane	A	340 (14200)	18,1	350 (20500)	7,4	355 (24400)	7,2	357 (22300)	5,5	347 (13300)	6,0	365 (11500)	22,6
	QH	451 (1700)		480 (1100)		456 (1400)		463 (1200)		460 (800)		468 (5200)	
Acetonitrile	A	347 (10800)	37,7	350 (13400)	36,2	355 (23000)	12,4	355 (22200)	6,0	350 (13000)	7,6	360 (6900)	54,0
	QH	447 (3500)		497 (5400)		450 (2400)		465 (1300)		453 (1000)		465 (12300)	
Benzene	A	340 (12800)	26,0	345 (14200)	36,2	350 (19500)	25,8	340 (17800)	24,5	340 (8200)	41,7	360 (7300)	51,0
	QH	476 (2400)		449 (4900)		499 (5100)		482 (5200)		476 (5500)		465 (11600)	
Toluene	A	339 (11700)	32,3	345 (14400)	35,2	350 (19300)	26,6	340 (15700)	33,3	340 (8100)	42,7	360 (7100)	52,4
	QH	474 (3000)		496 (4800)		498 (5200)		475 (7100)		475 (5700)		464 (12000)	
CCl_4	A	340 (13800)	19,9	343 (17600)	21,1	340 (18900)	28,0	340 (12000)	51,0	330 (6100)	56,2	350 (8800)	41,1
	QH	464 (1800)		490 (2900)		499 (5500)		480 (10500)		474 (7500)		464 (9400)	
$CHCl_3$	A	345 (12700)	26,4	345 (15400)	30,8	350 (19800)	24,7	345 (16000)	31,9	345 (9500)	36,4	345 (2900)	79,5
	QH	480 (2400)		502 (4200)		502 (4800)		487 (6800)		480 (4300)		457 (18400)	
Chlorobenzene	A	340 (11600)	33,1	345 (13900)	37,4	350 (17400)	33,7			340 (6500)	53,8	360 (4800)	64.7
	QH	480 (3000)		501 (5100)		502 (6600)				479 (7100)		471 (15400)	

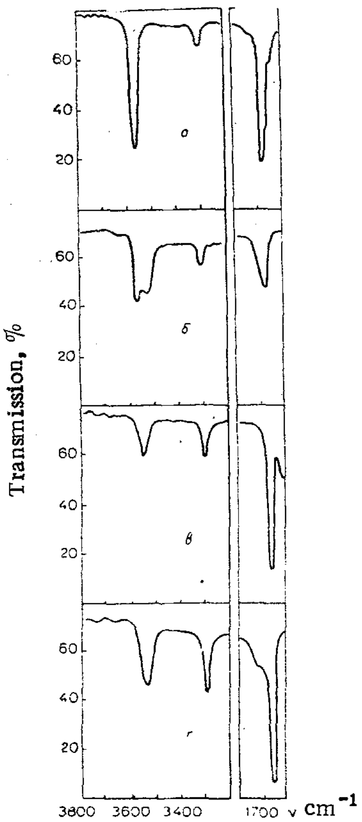


Fig. 1. IR spectra of 2-methoxy-3-hydroxy-6-phenylazopyridine in solutions: a) in CCl_4; b) in toluene; c) in chlorobenzene; d) in o-dichlorobenzene.

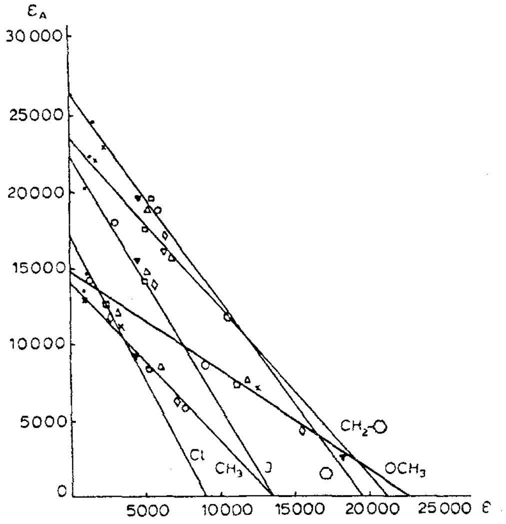
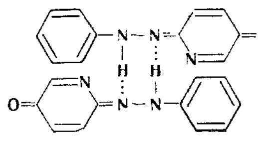
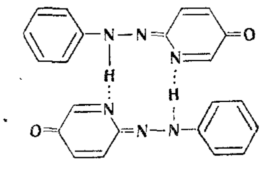


Fig. 2. Dependence of the extinction coefficients of the azo form (ε_A) on the extinction coefficients of the quinonehydrazone form (ε_{OH}) in the electronic spectra of the 2-substituted-3-hydroxy-6-phenylazopyridines: •) dioxane; ×) acetonitrile; □) benzene; Δ) toluene; ○) CCl_4; ▾) $CHCl_3$; ◇)chlorobenzene (R = Cl, CH_3, I, C_6H_5, $CH_2C_6H_5$, OCH_3).



A



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The assumption regarding association is in agreement with the position of the ν_{NH} band (3330-3370 cm^{-1}) in the IR spectra of solutions of 4-arylazo-1-naphthols in CCl_4 and $CHCl_3$ [7]. Morgan [7] ascribes this band to the stretching vibration of the NH bond, but he does not explain its low value. As compared with the expected frequency (ν_{NH} 3433 cm^{-1}) it is reduced by 60-100 cm^{-1}, and it should therefore be assigned to the vibrations of an associated NH bond.

The concentration of the dimers should depend upon the nature of the solvent. It is apparent from the ratio of the intensities of the absorption bands in the IR spectra ($\varepsilon_{OH}/\varepsilon_{NH}$) that the concentration of the quinonehydrazone form of I increases in the following order of solvents: hexane, CCl_4, benzene, chlorobenzene, and $CHCl_3$ (Table 1, Fig. 1).

A similar regularity is also observed in the spectra of 3-hydroxy-6-phenylazopyridine derivatives (Table 3).

The observed effect of the solvents should be explained by dissociation of the OH group of the p-hydroxyazo compounds in the above-presented series of solvents. In fact, the CCl_4 molecule, in contrast to hexane, has unshared pairs of electrons that are to a certain degree proton acceptors. It is also known that the OH group forms a stronger H bond with aromatic molecules than with CCl_4 molecules [8].

The type of substituent in the 2 position of the pyridine ring has a substantial effect on the tautomeric equilibrium (Tables 3 and 4). The explanation of this effect requires additional investigations.

A similar effect of solvents on the ratio of the azo and quinonehydrazone forms was detected by PMR spectroscopy for p-hydroxyazobenzenes [9].

Compound I crystallizes in two modifications (Ia and Ib) with mp 135 and 150°, respectively. Modification Ia is considerably more soluble in organic solvents. The IR spectra of these modifications in the regions of absorption of OH and NH groups differ markedly. One narrow band at 3244 cm^{-1}, which can be assigned to the stretching vibrations of the NH group of the quinonehydrazone form tied up in a hydrogen bond in dimers of the A type, is observed in the spectrum of the crystal phase of Ia in the region of the absorption of OH and NH groups. This is confirmed by the presence of a very intense $\nu_{C=O+C=N}$ band of the quinonehydrazone tautomer in the spectrum. Consequently, modification Ia is formed by crystallization of molecules of I primarily in the form of dimers. A broad band characteristic for intermolecular hydrogen bonds of the $OH\cdots N\!<$ and OH...N=N type appears in the IR spectra of the crystalline phase of modification of Ib. A band of medium intensity is observed in the $\nu_{C=O+C=N}$ region, and this is evidence for a certain percentage of the quinonehydrazone form in this modification. Consequently, modification Ib crystallizes primarily in the form of hydroxyazo tautomers linked by intermolecular hydrogen bonds.

The shift in the tautomeric equilibrium to favor the formation of the quinonehydrazone form in 3-hydroxy-6-phenylazopyridine derivatives is much greater than in the corresponding p-hydroxyazobenzene derivatives. Thus absorption bands that characterize the quinonehydrazone form cannot be observed for the latter in the electronic spectra of solutions in various solvents. This difference in the position of the tautomeric equilibrium is due to the effect of the ring-nitrogen atom, which has a strong inductive effect on the hydroxyl group; this promotes dissociation of the OH group with subsequent conversion of the molecule to the quinonehydrazone form.

A linear relationship between the extinction coefficients of the maxima of the absorption bands of the azo (ε_A) and quinonehydrazone (ε_{QH}) forms (Fig. 2), which is expressed by the following equation, is observed as a result of an examination of the electronic spectra of the investigated compounds:

$$\varepsilon_A = K\varepsilon_{QH} + \varepsilon_A^0. \tag{1}$$

Under the assumption that the linear relationship between ε_A and ε_{QH} is retained on extrapolation of the lines to intersection with the coordinate axes, the concentrations of the tautomers in solution can be determined. When this is done, the intersection of the lines with the coordinate axes gives the ε_A^o and ε_{QH}^o values for 100% concentrations of the azo and quinonehydrazone forms, respectively. When the indicated dependence is used, the concentrations of the tautomers in solution are determined (Table 3). It follows from Table 3 that the conclusions regarding the tautomeric equilibrium of the investigated compounds in solution that were drawn from an analysis of the IR spectra are in agreement with the results of electronic spectroscopy. Thus the concentrations of quinonehydrazone tautomers (C_{QH}) of 3-hydroxy-6-phenylazopyridine derivatives in dioxane do not exceed 23%; as indicated above, this attests to cleavage of dimer A by the solvent with subsequent conversion of the monomer of the quinonehydrazone form to the azo form tied up in intermolecular hydrogen bonds with the solvent molecules.

Correlation of the slopes of the lines (K) with the Hammett σ constants was accomplished from the linear dependence of ε_A on ε_{QH} for each substituent [10].

The calculated [by the Pariser—Parr—Pople (PPP) method] characteristics of the long-wave absorption bands of the azo and quinonehydrazone forms of the investigated compounds are in good agreement with the experimental data (Tables 3 and 5). The band at 350 nm, which characterizes the azo tautomer, is due to excitation of the $2p_z$ electrons of the entire π-conjugated system with a small amount of participation of charge transfer of the unshared electron pair of the oxygen atom (λ_{max} 370 nm, $f \cong 1.074$). The

TABLE 4. Frequencies of the Stretching Vibrations of the C=O, C=N, OH, and NH Bonds in the IR Absorption Spectra of 2-Substituted 3-Hydroxy-6-phenylazopyridines

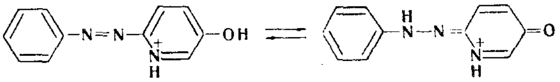
R	CCl₄			CHCl₃		
	ν_{OH}	ν_{NH}	$\nu_{C=O+C=N}$	ν_{OH}	ν_{NH}	$\nu_{C=O+C=N}$
$CH_2C_6H_5$	3521 3595 m			3522 3594 m		
OCH_3	3547	3295	1662 1653	3545	3286	1662
I	3472 3590 w	3265	1632	3473 3612 w	3255	1630
Cl	3530 3590	3270	1640	3530 3612	3260	1635
C_6H_5	3550 3590	3268 w				
p-$C_6H_4CH_3$	3548 3595		1630	3540— 3590 w		1630
p-$C_6H_4OCH_3$	3550 3590 w	3270 3452 w	1635 w	3549 3590	3270 3452 w	1635 w
p C_6H_4Cl	3552 3590 w	3268 3442 w	1630 w	3550 3590 w	3260 w	1632 w
Br	3548 3590 w					

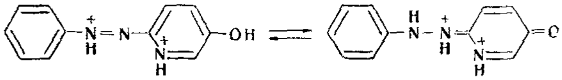
TABLE 5. Calculated Wavelengths (λ, nm) and Oscillator Forces (*f*) of the Long-Wave Absorption Bands of the Azo (A) and Quinonehydrazone (QH) Forms of 2-Substituted 3-Hydroxy-6-phenylazopyridines

R	Form	λ, nm(*f*)			
H	A	364 (1,293)	232 (0,179)	227 (0,204)	
	QH	485 (0,886)	304 (0,224)	265 (0,456)	
OH	A	387 (1,074)	271 (0,189)	239 (0,201)	228 (0,165)
	QH	488 (0,870)	283 (0,660)		
C_6H_5	A	372 (1,382)	297 (0,315)	267 (0,191)	246 (0,272)
	QH	486 (1,118)	335 (0,133)	286 (0,255)	281 (0,415)

transition is polarized parallel to the long axis of the molecule. The band that characterizes the quinonehydrazone form (λ_{max} 486 nm, $f \cong 0.886$) pertains to 30% transition with charged transfer of the $2p_z$ electrons of the bridged-nitrogen atom in the quinoid ring of the molecule. The transition is polarized parallel to the long axis of the molecule. The long-wave absorption bands were assigned on the basis of an analysis of the type of MO between which the transition occurs, the magnitudes of the coefficients of expansion of the MO and AO, and the redistribution of the electron density during the electron transition.

In [2] it was shown by electronic spectroscopy that in acidic media the percentage of the azo form initially increases as the pH decreases, after which the concentration of the quinonehydrazone form increases sharply as the pH is lowered further. On the basis of the reasoning above, it might be assumed that in moderately acidic media dimer A decomposes, and the monomer is converted to the azo form. As the acidity is increased further, the molecule undergoes monoprotonation and diprotonation at the ring-nitrogen atom and at the azo group. As a result, the following equilibrium of the mono- and diprotonated molecules may be realized.





The acidity of the OH group of the mono- and diprotonated molecule increases sharply, and the equilibrium is shifted to favor the formation of the quinonehydrazone form.

Thus, it has been shown by IR and electronic spectroscopy that the ratio of the azo and quinonehydrazone tautomers of 3-hydroxy-6-phenylazopyridine derivatives is determined by the aggregate state of the compound, the electron-donor, and electron-acceptor properties of the organic solvent, and the acidity of the medium.

EXPERIMENTAL

The investigated compounds were obtained by previously described methods [11]. The IR spectra were recorded with a UR-20 spectrometer. The IR spectra in the gas phase were recorded with a UR-10 spectrometer. The accuracy in the measurement of the frequencies in the range of an NaCl prism was ±2 cm^{-1}, while the accuracy in the range of an LiF prism was ±4 cm^{-1}. The electronic spectra were recorded with SF-4A and SF-14 spectrophotometers. The calculations by the PPP method within the "approximation of a variable β" were made from programs composed by G.I. Kagan [12]. The interaction of 25 singly excited confugurations were taken into account in the calculations. The internuclear distances were optimized with respect to the atomization energies (ΔH) from a program that realizes the Dewar algorithm with the use of an M-220 computer.

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