IR AND ELECTRONIC ABSORPTION SPECTRA AND STRUCTURES OF 3-HYDROXY-4-PHENYLAZOQUINOLINE AND 4-HYDROXY-3-PHENYLAZOISOQUINOLINE DERIVATIVES

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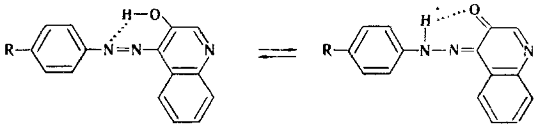
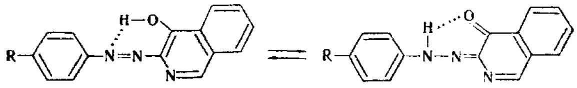
It was shown by an analysis of the IR and electronic absorption spectra that 3-hydroxy-4-azophenylquinoline derivatives exist primarily in the azo form in organic solvents, whereas 4-hydroxy-3-phenylazoisoquinoline derivatives exist primarily in the quinone-hydrazone form. The introduction of electron-acceptor groups into the para position of the phenyl ring of 3-hydroxy-4-azophenylquinoline shifts the tautomeric equilibrium to favor the formation of the quinonehydrazone form. It is shown that the band at 550 nm in electronic spectrum of this compound is related to the $n \rightarrow \pi^*$ transition of the unshared pairs of electrons of the nitrogen atoms of the azo groups.

The recently synthesized [1] 3-hydroxy-4-phenylazoquinoline (I), 4-hydroxy-3-phenylazoquinoline (II) and their derivatives have not been studied. It should be expected that these compounds may exist in azo (Ia and IIa) and quinonehydrazone (Ib and IIb) forms. It seems of interest to obtain data on the structures of I and II by means of electronic and IR spectroscopy and to compare the results with the data for adequately studied o-hydroxyazonaphthalenes [2].



Ia Ib



IIa IIb

Electronic Spectra

Because of the π-isoelectronic character of I and II with respect to the corresponding o-phenylazonaphthols, the electronic spectra of the latter and the compounds under investigation in this paper should be similar to one another. In fact, it is seen from Table 1 that the maxima of the long-wave absorption bands of derivatives of I, just as in the case of its OCH_3-fastened form, are observed at 425-432 nm. It is known [3, 4] that a band at 420 nm is also observed in the absorption spectra of 1-phenylazo-2-naphthol and its O-methyl form, which are analogs of I, in hexane and chloroform solutions. The presence of the azo form (21%) in a chloroform solution of 1-phenylazo-2-naphthol was confirmed by PMR spectroscopy [5].

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TABLE 1. Electronic Spectra of Derivatives of I and II

Compound	R	Solvent	λ_{max}, nm (lg ε)		
I	H	$CHCl_3$	550 (3,40)	422 (3,89)	325 (3,93)
		Alcohol	545 (3,13)	420 (3,91)	328 (4,02)
		CCl_4	545 (3,19)	428 (3,85)	315 (3,90)
		H_2O	520 (3,70)	425 (3,80)	
I	SO_3H	0,5 N H_2SO_4	550 (3,03)	422 (3,89)	
I	Br	0,1 N H_2SO_4	550 (2,75)	422 (3,69)	
		CCl_4	550 (3,01)	435 (3,77)	330 (3,61)
		$CHCl_3$	555 (3,39)	432 (4,08)	342 (4,01)
		Alcohol	550 Shoulder	425 (4,02)	342 (3,97)
I	OCH_3	Alcohol	570 Shoulder	427 (4,02)	338 (3,79)
		$CHCl_3$	575 Shoulder	428 (3,97)	335 (3,78)
		CCl_4	550 Shoulder	433 (4,07)	320 (4,11)
I	NO_2	$CHCl_3$	550 Shoulder	495 (4,01)	320 (4,05)
I	CH_3	Alcohol	550 (3,16)	420 (4,04)	355 (4,04)
		CCl_4	480 (4,33)	428 (4,03)	
II	H	Alcohol	478 (4,35)	285 (4,00)	257 (3,96)
		$CHCl_3$	483 (4,24)		
II	Br	$CHCl_3$	485 (4,51)	290 (4,03)	
		Alcohol	480 (4,37)	280 (3,98)	
		CCl_4	485 (4,30)	295 (3,98)	
		H_2O	485 (4,23)	277 (2,87)	260 (3,90)
II	SO_3H	Alcohol	490 (4,33)	280 (3,79)	265 (3,81)
		50% alcohol	490 (4,22)	280 (3,79)	265 (3,81)

A weak band is observed at 540 nm in the spectrum of I. Inasmuch as this band is of low intensity and vanishes in the spectra of acid solutions, it should be ascribed to the n → π* transition of the unshared pairs of electrons of the nitrogen atoms of the azo group. Absorption bands are not observed at 480 nm in the spectrum of I, although weak bands are possibly overlapped.

Thus, according to the absorption spectra, I exists primarily in the azo form. At the same time, 1-phenylazo-2-naphthol exists primarily in the quinonehydrazone form under the same conditions.

The introduction of substituents such as CH_3, Br, OCH_3, and SO_3H into the para position of the phenyl ring of I does not lead to substantial changes in the intensity of the band of the azo form. This attests to the relative stability of the azo form of I. However, the introduction of a nitro group, which has strong-electron-acceptor properties, into this position leads to the appearance of a very intense band in the spectrum at 490 nm, which characterizes a shift in the equilibrium to favor the quinonehydrazone form.

The absorption spectra of II and its derivatives in various solvents contain a band at 480-490 nm (Table 1), which, in analogy with the absorption band in the same region in the spectra of 2-phenylazo-1-naphthol, characterizes the quinonehydrazone form.

Substantial changes are not observed in the spectra of CCl_4, $CHCl_3$, and ethanol solutions of I and II; this constitutes evidence for the weak effect of these solvents on the tautomeric equilibrium.

IR Spectra

It follows from the IR spectra in the crystalline state and in dilute $CHCl_3$ solutions that the valence vibrations of the NH and OH bonds appear as diffuse low-intensity bands at 2500-3500 cm^{-1} with the approximate position of the maxima at ~3000 cm^{-1}. Consequently, like the corresponding azonaphthols [6], the investigated compounds form strong intramolecular hydrogen bonds. This is in agreement with the PMR data, according to which the chemical shift of the hydroxyl proton in the spectra of $CDCl_3$ solutions of II and 2-hydroxy-1-phenylazonaphthalene is 16.0 and 16.1 ppm, respectively. At the same time, $\delta = 3.59$ ppm in the spectrum of 4-hydroxy-1-azophenylnaphthalene, which does not form intramolecular hydrogen bonds [7].

The quinonehydrazone form of azonaphthols is characterized by an absorption band of $\nu_{C=O}$ stretching vibrations at 1650-1675 cm^{-1} and a set of intense bands at 1200-1300 cm^{-1}, which are related to ring vibrations. A band of medium intensity at 1650-1655 cm^{-1}, which can be assigned to $\nu_{C=O}$ vibrations, and a number of bands at 1200-1300 cm^{-1} are observed in the spectra of derivatives of II (R = H).

A weak absorption band is observed at 1520-1650 cm^{-1} in the IR spectra of I (R = H), and the band at 1385-1396 cm^{-1}, according to the literature data [9], can be assigned to the stretching vibrations of the

N=N bond. This is confirmed by the disappearance of this band when a nitro group is introduced into the para position of the phenyl ring of I.

Thus the IR spectral data are in agreement with the conclusions regarding the structures of I and II drawn from the electronic spectra.

EXPERIMENTAL

The electronic spectra were recorded with an SF-4A spectrophotometer. The IR spectra of KBr pellets, mineral-oil suspensions, and chloroform solutions of the compounds were recorded with a UR-20 spectrometer. The PMR spectra of $CDCl_3$ solutions were recorded with a BS-487B spectrometer (80 MHz) with hexamethyldisiloxane as the internal standard.

LITERATURE CITED

1. L. D. Smirnov, N. A. Andronova, V. P. Lezina, and K. M. Dyumaev, Izv. Akad. Nauk SSSR, Ser. Khim., 2382 (1970).
2. N. Ya. Bershtein and O. F. Ginzburg, Usp. Khim., 16, 177 (1972).
3. A. Buraway, A. G. Salem, and A. R. Thompson, J. Chem. Soc., 4793 (1952).
4. A. Buraway and J. Markowisch, Ann., 503, 180 (1933).
5. A. H. Berrie, P. Hampson, S. W. Longwerth, and A. Mathias, J. Chem. Soc., B, 1308 (1968).
6. D. N. Shigorin, I. Ya. Pavlenishvili, and V. I. Kakachashvili, Zh. Fiz. Khim., 40, 3006 (1966).
7. F. D. Saeva, J. Org. Chem., 36, 3842 (1971).
8. L. Bellamy, Infrared Spectra of Complex Molecules, Methuen (1958).
9. Yu. M. Dedkov and A. V. Kotov, Zh. Prirodn. Soedin., 14, 431 (1971).