TAUTOMERISM OF PHENYLAZO DERIVATIVES OF 3-HYDROXYPYRIDINE AND THEIR N-OXIDES

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Azophenol–quinone hydrazone tautomerism was detected for phenylazo derivatives of 3-hydroxypyridines and their N-oxides. The absorption maxima of the phenylazo derivatives of 3-hydroxypyridine have a greater (than their N-oxides) tendency to be shifted to the longer-wavelength region.

3-Hydroxypyridine is the heterocyclic analog of phenol; this is responsible for their extremely similar physicochemical properties. In order to study the possibility of phenol quinoid tautomerism in substituted 3-hydroxypyridines, we investigated the IR and UV spectra of phenylazo derivatives of 3-hydroxypyridines and their N-oxides in various solvents. There are no data on this problem in the literature.

Up until recently, it was supposed that the possibility of quinoidization was not inherent in β-pyridols. However, in [1] it was indicated that N-alkyl-3-hydroxypyridines may exist in the pyridone form. The distinct (from phenol) peculiarity of 3-hydroxypyridine – the possibility of existing in the acid–base and oxo-hydroxy equilibrium forms – is associated with the profound effect of the nitrogen atom on the pyridine ring.

The appearance of a quinoid system of bonds should be manifested even more distinctly in phenylazo derivatives of 3-hydroxypyridines and their N-oxides, since this is associated with the gain in energy (~ 24 kcal/mole) due to quinoid conjugation in the case of azophenols [2]. In fact, we detected azophenol–quinone hydrazone tautomerism for these compounds.

According to the data of a number of authors [3, 4], the azophenol form of aromatic azo dyes has an absorption maximum at 350-400 nm, while the quinone hydrazone form has a maximum at above 440 nm. Hence it follows (see Table 1) that the absorption maxima of azo derivatives, except for IX, XV, and XIX, lie in the region characteristic for the quinone hydrazone form (455-600 nm). It is interesting that XXIV exists practically entirely in the quinone hydrazone form.

A study of the IR spectra of the synthesized compounds in the crystalline state and of solutions of them in carbon tetrachloride and chloroform showed that the phenylazo derivatives of 3-hydroxypyridines and their N-oxides exist only in the azophenol form under these conditions. The absence of absorption bands characteristic for the C=O and NH groups and the presence of one band of a free OH group at 3590-3610 cm^{-1} attest to this.

The data presented in Table 1 indicate that the regularities peculiar to the phenol azo derivatives are inherent in the investigated azo derivatives. The introduction of electron-acceptor substituents into the phenyl ring and the use of more polar solvents shift the absorption maxima of the investigated substances to the long-wave region. The greatest shift is observed for X, XX, and XXII, in which the phenylazo substituent is in the ortho position relative to the OH group. In analogy with phenols [5-7], this sort of behavior of the o-phenylazo derivatives of 3-hydroxypyridines and their N-oxides can be explained by the presence of a strong intramolecular hydrogen bond, which favors (energetically) the formation of the carbonyl form.

It was also observed that the absorption maxima of the phenylazo derivatives of 3-hydroxypyridine have a greater (than for their N-oxides) tendency to be shifted to the longer-wavelength region.

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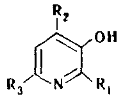
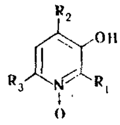
TABLE 1. Data from the UV Spectra of Phenylazo Derivatives of 3-Hydroxypyridine and Their N-Oxides*



I-X



XI-XXIV

Compound	R_1	R_2	R_3	λ_{max}, nm	
				alcohol	DMF†
I	H	H	H	280	280
II	H	H	$—N{=}N—C_6H_5$	230, 340, 435	345, 455
III	H	H	$—N{=}N—C_6H_4—NO_2$-*p*	370, 455	375, 550
IV	CH_3	H	H	280	280
V	CH_3	H	$—N{=}N—C_6H_5$	225, 280, 380, 490	355, 490
VI	CH_3	H	$—N{=}N—C_6H_5—SO_3H$-*p*	280, 360	360, 460
VII	CH_3	H	$—N{=}N—C_6H_4—NO_2$-*p*	230, 350	385, 575
VIII	H	H	CH_3	285	285
IX	$—N{=}N—C_6H_5$	H	CH_3	240, 300, 385	300, 385
X	$—N{=}N—C_6H_4—$ NO_2-*p*	H	CH_3	250, 400	300, 405, 600
XI	H	H	H	225, 240, 310	275, 315
XII	H	H	$—N{=}N—C_6H_5$	290, 410	345, 485
XIII	H	H	$—N{=}N—C_6H_4—NO_2$-*p*	290, 310	360, 550
XIV	CH_3	H	H	225, 260, 305	275
XV	CH_3	H	$—N{=}N—C_6H_5$	360	365
XVI	CH_3	H	$—N{=}N—C_6H_4—SO_3H$-*p*	245, 285, 365	360, 510
XVII	CH_3	H	$—N{=}N—C_6H_4—NO_2$-*p*	285, 365, 425	345, 505
XVIII	H	H	CH_3	255, 305	315
XIX	$—N{=}N—C_6H_5$	H	CH_3	240, 360	365
XX	$—N{=}N—C_6H_4—NO_2$-*p*	H	CH_3	240, 390	415, 540
XXI	CH_3	H	CH_3	255, 305	310
XXII	CH_3	$—N{=}N—C_6H_4—$ $—NO_2$-*p*	CH_3	290, 400	430, 595
XXIII	$C_6H_5—$	H	$—N{=}N—C_6H_5$	370, 425	295, 365, 505
XXIV	*p*-$NO_2—C_6H_4—$	H	$—N{=}N—C_6H_4—NO_2$-*p*	265, 450	515

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*The method of preparation, the structure, and the physicochemical properties of the azo derivatives of 3-hydroxypyridines and their N-oxides are described in [8, 9].

†Dimethylformamide.

EXPERIMENTAL

The IR spectra of KBr pellets (10%) and CCl_4 and $CHCl_3$ solutions ($3 \cdot 10^{-3}$ M) of the substances were recorded with a UR-20 spectrometer in KBr cuvettes at layer thicknesses of 2 and 5 cm. The absorption spectra of solutions of the azo derivatives in alcohol and DMF were measured at 20° with an SF-4 spectrophotometer (l = 1 cm, c = 10^{-4}-10^{-5} M).

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