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RESEARCH OF NAPHTHYRIDINES

IX.† ACID–BASE TRANSFORMATIONS OF BENZO[b]-1,8-NAPHTHYRID-10-ONES

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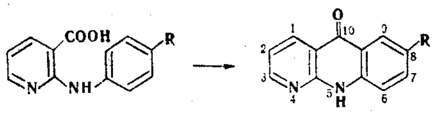
UDC 547.836.3.541.124.7:543.422.6

It is shown by means of the UV spectra that a singly charged ion due to protonation at the $N_{(4)}$ atom develops when benzo[b]-1,8-naphthyrid-10-ones are dissolved in dilute mineral acids. The oxygen of the carbonyl group is also protonated in 96% sulfuric acid. Salts of the phenoxide type are formed in the reaction of these compounds with aqueous sodium hydroxide solutions. The pK_a values of benzo[b]-1,8-naphthyrid-10-ones determined spectrophotometrically in a sulfuric acid–water system range from −4.69 to −5.69, depending on the substituent in the 8 position, and correlate with the Hammett σ_p constants.

It is known that 9-acridone displays weak basic properties and gives a cation of the acridinium type when it is dissolved in sulfuric acid. In this case the proton adds to the oxygen atom of the carbonyl group [2]. In order to study the previously uninvestigated acid–base transformations of benzo[b]-1,8-naphthyrid-10-ones and to compare their properties with those of 9-acridone we accomplished the synthesis of several compounds of this series (Ia–e) by cyclization of 2-anilinonicotinic acids in polyphosphoric acid (PPA) or sulfuric acid.



I a R=H; b R=CH_3; c R=CH_3O; d R=Cl; e R=Br

Like 9-acridone [2, 3], benzonaphthyridones Ia–e exist in the oxo rather than hydroxy form, as evidenced by the data from the IR spectra of solutions in CCl_4, which contain a ν_{NH} band at 3440 cm^{-1} and a ν_{CO} band at 1640 cm^{-1} but no hydroxyl group band.‡ Maxima are observed in the UV spectra of benzonaphthyridones Ia–e (see the spectra of Ia in Figs. 1 and 2) at 235, 256, 385, and 400 nm, and they are very similar to the spectrum

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† See [1] for communication VIII.

‡ The bands were assigned in accordance with [3].

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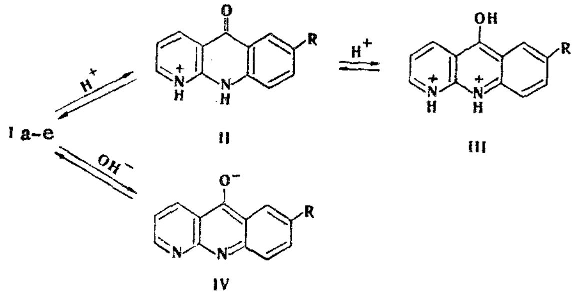
TABLE 1. Correlation Parameters of the Logarithms of the Indicator Ratios with the H_0 and pK_a Values of Benzo[b]-1,8-naphthyrid-10-ones in a Sulfuric Acid–Water System

Compound	R	λ_{max}, nm†	lg ε	$-H_0$ interval	$-a$	$-b$	$-pK_a$	r	S
I a	H	336	4,38	6,48—4,90	5,30	1,014	5,22±0,01	0,999	0,025
I b	CH_3	344	4,36	5,92—4,56	4,94	1,026	4,81±0,01	0,999	0,021
I c	OCH_3	350	4,35	5,92—4,40	4,74	1,010	4,69±0,02	0,997	0,040
I d	Cl	344	4,37	7,12—5,28	5,79	1,020	5,68±0,02	0,999	0,028
I e	Br	348	4,38	7,12—5,28	5,79	1,019	5,69±0,02	0,998	0,039

† The data for solutions of Ia–e in 96% sulfuric acid are presented.

of 9-acridone [2] and differ from the latter only with respect to a small bathochromic shift; this also indicates their identical structures. Maxima at 232, 252, 365, and 385 nm are observed in the spectrum of naphthyridone Ia in hexane, and the spectrum is shifted hypsochromically as compared with the spectrum of an ethanol solution. This provides evidence that the absorption of Ia–e in the UV region is due to $\pi-\pi^*$ electron transitions. The spectra of solutions of naphthyridone Ia in hydrochloric acid in a base-to-acid ratio of 1 : 1 and of solutions of the same compound in 0.1 N HCl are identical. As compared with the spectrum of an ethanol solution of Ia, they contain an inflection at 290 nm, the maximum at 385 nm is absent, and the curves of these spectra undergo a bathochromic shift. The spectra of naphthyridone Ia in 30% sulfuric acid and dilute hydrochloric acid are entirely similar. Some of the differences in the intensities and positions of their bands are probably associated with the effect of the medium.

The changes in the character of the spectra on passing from ethanol solutions of naphthyridone Ia to solutions in dilute mineral acids are evidently associated with protonation of $N_{(4)}$ and the formation of cation II.



Since the pK of pyridine is considerably higher than the pK of 9-acridone [4], protonation of $N_{(4)}$ should precede protonation of the carbonyl group.

Beginning with 60% sulfuric acid concentration, a band with a maximum at 336 nm, the intensity of which increases as the acidity of the medium increases and reaches its maximum value in 85% sulfuric acid, appears in the spectrum of naphthyridone Ia. A bathochromic shift of the long-wave maximum to 425 nm is also observed. When the acidity of the medium is increased further, the character of the spectrum does not change. The spectra of solutions of 9-acridone in concentrated acids also contain a band at 340 nm [2], and they are entirely similar to the spectrum of naphthyridone Ia in 96% sulfuric acid. This provides a basis for the conclusion that the product of the reaction of concentrated sulfuric acid with Ia is similar in structure to the product of protonation of 9-acridone and is a doubly charged ion (III) in which the second proton is attached to the oxygen atom of the carbonyl group. It is clear from the above that the acid–base transformations of Ia–e at media acidities ranging from −4.46 to −8.14 H_0 units are determined by the equilibrium II $\rightleftharpoons$ III. The pK_a values (Table 1) were calculated from the equation $pK_a = H_0 + \log([III]/[II])$. They range from −4.69 to −5.69 units on the H_0 scale [5] and are four to five logarithmic units lower than the pK_a of 9-acridone [4].

The lower basicities of ions II as compared with acridone are due to the electron-acceptor properties of the protonated pyridine ring. The pK values of benzo[b]-1,8-naphthyrid-10-ones depend on the effect of the substituent in the benzene ring and correlate with the Hammett σ_p constants ($r = 0.996$, $\rho = -2.84$, pK_a^0 calc. = -5.24, and $S = 0.037$). The correlation with σ_p but not with σ_p^+ provides evidence for considerable charges delocalization due to interaction with the π-electron system of the pyridine ring and conjugation with the hydroxyl group attached to $C_{(10)}$.

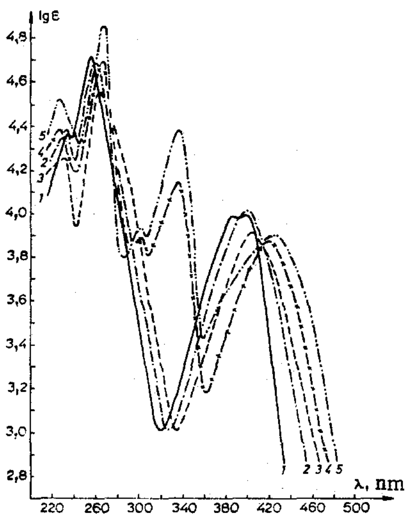


Fig. 1

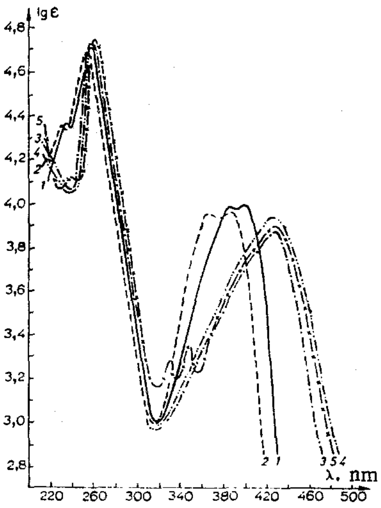


Fig. 2

Fig. 1. UV spectra of Ia: 1) in ethanol; 2) in 0.1 M HCl; 3-5) in, respectively, 30, 70, and 96% sulfuric acid.

Fig. 2. UV spectra of Ia: 1) in ethanol; 2) in hexane; 3 and 4) in 0.1 N and 1 N NaOH, respectively; 5) 10-aminobenzo[b]-1,8-naphthyridine in 0.1 N ethanolic NaOH.

Compounds Ia-e also display acidic properties and are soluble in concentrated sodium hydroxide solutions. In analogy with the acridolate ion [2], the benzo[b]-1,8-naphthyrid-10-olate structure (ion IV) should be assigned to the product of the reaction of Ia with alkali.

In connection with the fact that the effects of a negatively charged oxygen atom and an amino group on the UV spectrum are similar [2], for proof of the structure of the IV ion we obtained the spectra of 10-aminobenzo[b]-1,8-naphthyridine V [6] and Ia in sodium hydroxide solutions with various concentrations (Fig. 2). The curves presented in Fig. 2 show the similarity in the spectra of alkaline solutions of Ia and V and the difference from them of the spectrum of Ia in ethanol; this confirms the structure assigned to ion IV.

EXPERIMENTAL

The IR spectra of carbon tetrachloride solutions of the compounds were recorded with a UR-20 spectrometer. The UV spectra were obtained with a spectroMOM-202 spectrophotometer. The ionization constants in a sulfuric acid–water system were determined spectrophotometrically with the same apparatus for $2 \cdot 10^{-5}$ M solutions at 20 ± 1°. The analytical wavelength corresponded to the maximum at 336-350 nm. The parameters of the dependence of the logarithm of the indicator ratios on the H_0 values were calculated by the method of least squares. The pK_a values were calculated from seven points at a fixed reliability of 0.98.

8-Methoxybenzo[b]-1,8-naphthyrid-10-one (Ic). A 0.01-mole sample of 2-(p-anisidino)nicotinic acid was heated in 10 g of polyphosphoric acid (PPA) at 160°C for 5 h, after which the mixture was cooled, diluted with water, and neutralized with 10% sodium hydroxide solution. The resulting precipitate was crystallized from ethanol to give 0.97 g (43%) of a product with mp 280-282°C. Found: C 69.05; H 4.50; N 12.41%. $C_{13}H_{10}N_2O$. Calculated: C 69.02; H 4.47; N 12.38%. A similar procedure was used to obtain Ia,b,d, the compositions and structures of which were confirmed by the results of elementary analysis, the IR spectra, and comparison of their melting points with the melting points of previously obtained samples [7-9].

8-Bromobenzo[b]-1,8-naphthyrid-10-one (Ie). This compound, with mp 342-345°C (dioxane), was obtained in 52% yield by cyclization of 2-(p-bromoanilino)nicotinic acid in concentrated sulfuric acid at 150°C. Found: C 52.42; H 2.61; N 10.13%. $C_{12}H_7BrN_2O$. Calculated: C 52.39; H 2.58; N 10.15%.

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BENZO[*f*]-3-AZA- AND -10-AZAFLUOROANTHENES

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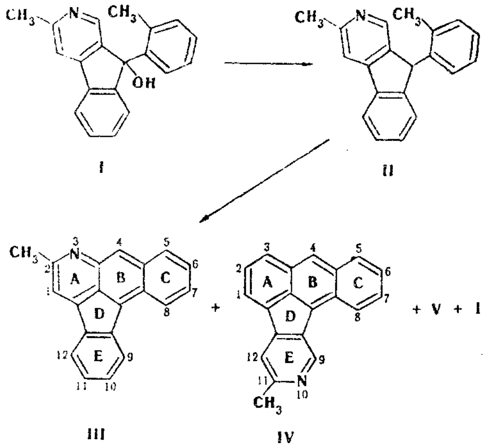
Reduction of 3-methyl-9-(o-tolyl)-2-azafluoren-9-ol (I) with tin in hydrochloric acid gave 3-methyl-9-(o-tolyl)-2-azafluorene, dehydrocyclization of which on a K-16 catalyst at 520-500°C gave a complex mixture, from which four substances – 2-methylbenzo[*f*]-3-azafluoranthene, 11-methylbenzo[*f*]-10-azafluoranthene, benzo[*f*]-3-azafluoroanthene (II), and I – were isolated and identified by means of the IR, UV, and PMR, and mass spectra. It is shown that the dehydrocyclization proceeds through the hydrogen atoms of the methyl group of the tolyl substituent and takes place at the 8-C or 1-C atom of the azafluorene system. The formation of products II and I constitutes evidence that the reaction is accompanied by partial demethylation or oxidation.

3-Methyl-9-(o-tolyl)-2-azafluoren-9-ol (I), which we described in [1], was used as the starting compound for the synthesis of benzo[*f*]-3-aza- and -10-azafluoranthene systems. Reduction of this alcohol with tin in hydrochloric acid gave 3-methyl-9-(o-tolyl)-2-azafluorene (II), which was subjected to dehydrocyclization in a K-16 catalyst at 520-550°C. Four crystalline compounds were isolated from the resulting complex mixture of substances by chromatography.



In all cases involving the formation of a benzoazafluoranthene structure (III-V) dehydrocyclization proceeds through the hydrogen atoms of the methyl group of the o-tolyl substituent of azafluorene II. Dehydrocyclization in the α position of the pyridine ring leads to the formation of 2-methylbenzo[*f*]-3-azafluoranthene

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