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QUASI-TAUTOMERISM OF 5-HYDROXY-5-PHENYL-5H-PYRIDO[2,3-b]CHROMENES IN SULFURIC ACID

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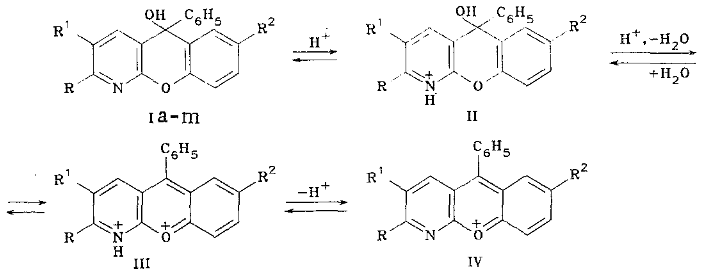
The existence of a quasi-tautomeric equilibrium in solutions of 5-hydroxy-5-phenyl-5H-pyrido[2,3-b]chromenes in sulfuric acid, which was confirmed by a linear dependence of the logarithms of the indicator ratios on acidity function $H_R - H_0$ with a slope close to unity, was established. The pK values of this equilibrium correlate with the σ_p^0 and σ_R^0 substituent constants.

The synthesis and ionization constants of 5-hydroxy-5-phenyl-5H-pyrido[2,3-b]chromene derivatives were described in [1, 2]. It was assumed that upon protonation these compounds undergo stepwise ionization with the successive formation of singly charged ion II and doubly charged pyridinium-chromenylium ion III.



However, a quantitative study of the equilibrium between the protonated forms showed that, although a linear relationship between the logarithms of the indicator ratios and acidity function H_R [3] is observed, the slopes of this relationship differ significantly from unity and range from 0.55 to 0.65. This fact compelled us to reexamine the concept of the investigated equilibrium and to advance the assumption of the existence of the three-component

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TABLE 1. Parameters of the Correlation of the Logarithms of the Indicator Ratios with $H_R - H_0$ and the pK Values of 5-Hydroxy-5-phenyl-5H-pyrido[2,3-b]chromenes

Compound	R	R^1	R^2	λ_{max}, nm (lg ε)[a]	$-a$[b]	$-b$[b]	$-pK$	r	s
Ia	H	H	H	367 (4,53)	4,20	0,95	4,44±0,05	0,998	0,032
Ib	H	H	CH_3	380 (4,51)	3,84	1,01	3,80±0,01	0,999	0,018
Ic	H	H	Br	381 (4,54)	5,84	1,06	5,52±0,04	0,999	0,018
Id	H	H	Cl	381 (4,54)	5,87	1,06	5,53±0,04	0,999	0,007
Ie	H	H	F	372 (4,51)	5,52	1,03	5,35±0,06	0,997	0,039
If	CH_3	H	H	374 (4,51)	4,04	1,17	3,47±0,03	0,987	0,022
Ig	CH_3	H	CH_3	384 (4,54)	3,26	1,06	3,08±0,03	0,997	0,013
Ih	CH_3	H	Br	392 (4,56)	5,08	1,09	4,68±0,09	0,992	0,064
Ii	CH_3	H	Cl	387 (4,59)	4,95	1,05	4,70±0,07	0,993	0,057
Ij	CH_3	H	F	377 (4,53)	4,83	1,07	4,50±0,08	0,996	0,048
Ik	CH_3	CH_3	H	382 (4,51)	3,44	1,03	3,34±0,04	0,984	0,026
Il	CH_3	Br	H	391 (4,41)	3,49	1,12	3,10±0,02	0,998	0,012
Im	CH_3	Cl	H	387 (4,43)	3,45	1,11	3,11±0,02	0,999	0,007

[a] For solutions in 96% sulfuric acid. [b] Coefficients of the equation $\log([IV]/[II]) = a + b(H_R - H_0)$.

TABLE 2. Parameters of the Correlation of the pK Values with the σ Constants of the Substituents

Series	Compound	Set of σ constants[a]	r	$-\rho$	$-pK^0_{calc}$	s
1	Ia-e	σ_p^0	0,993	4,26	4,46	0,08
2	If-j	σ_p^0	0,988	4,12	3,63	0,09
3	If,k-m	σ_R^0	0,952	2,03	3,49	0,05

[a] In the correlation of the pK values of the compounds of series 1 with the σ_p and σ_m constants [8] the coefficients of the correlation were 0.942 and 0.982, respectively, whereas they were 0.929 and 0.973 in the case of series 2.

equilibrium II $\rightleftarrows$ III $\rightleftarrows$ IV [4], which is similar to the quasi-tautomeric equilibrium of aminotriarylcarbinols [5, 6], for compounds of the Ia-m type (Table 1) in concentrated solutions of sulfuric acid (30-96%). Ions III are short-lived: At the instant that they are formed they are immediately converted to ions IV and, as a consequence of this, are present in solution in small amounts, i.e., the observed transformation reduces to the II $\rightleftarrows$ IV equilibrium.

To confirm this assumption we recorded the UV spectrum of a model compound, viz., 9-hydroxy-9-phenylxanthene, in 65% sulfuric acid, in which it exists in the form of the 9-phenylxanthylium cation, since the acidity of the medium exceeds its ionization constant (0.35 [7]) by many orders of magnitude. This spectrum (λ_{max} 260, 374, and 450 nm) is similar, on the whole, to the spectrum of 2-methyl-5-hydroxy-5-phenyl-5H-pyrido[2,3-b]chromene [4] in 65% sulfuric acid (λ_{max} 254, 376, and 480 nm) and differs only with respect to lower absorption intensity at 275-320 nm (minimum) and higher absorption intensity at 450 nm. This indicates the great similarity in the corresponding chromophore systems. In addition, in [4] it was shown that a linear relationship with a slope close to unity is observed between the logarithms of the indicator ratios [log([IV]/[II])] and acidity function $H_R - H_0$ [5] for 5-aryl-3-methyl-5-hydroxy-5H-pyrido[2,3-b]chromenes; this constitutes evidence for the existence of the quasi-tautomeric equilibrium II $\rightleftarrows$ IV.

In the light of this, from the data in [1, 2] we calculated the pK values of the quasi-tautomeric equilibrium for Ia-m (Table 1). It is apparent from Table 1 that the slopes of the dependence of the logarithms of the indicator ratios on the acidity of the medium expressed by acidity function $H_R - H_0$ are close to unity. This constitutes evidence that a quasi-tautomeric equilibrium is observed in the case of Ia-m. The pK values depend on the substituents in both the benzene and pyridine rings of the heterocyclic system and correlate with the σ_p^0 [8] and σ_R^0 constants [9] of the substituents, respectively (Table 2).

In the compounds of reaction series 1 and 2 the substituents, as a consequence of their spatial proximity, affect primarily the stabilities of ions IV, and these series are characterized by high reaction constants. Their absolute values are higher by a factor of two than in the case of the ρ series of compounds that contain substituents in the phenyl ring [4]. This should be explained by the fact that in series 1 and 2 the substituents are located directly in the pyridochromene system throughout which the positive charge is concentrated and interact more actively with it. In series 3 the substituents evidently have approximately the same effect on the stabilities of both ions II and IV, and in this case the ρ value is lower by a factor of two than in series 1 and 2.

EXPERIMENTAL

The previously found optical densities at the corresponding acidities of the medium [1, 2] were used to calculate the logarithms of the indicator ratios [log([IV]/[II])]. Verification of the observance of a linear dependence of log([IV]/[II]) on the acidity of the medium expressed in terms of acidity function $H_R - H_0$ was carried out by the method of least squares. The pK values of the quasi-tautomeric equilibrium were calculated from the equation pK = $(H_R - H_0)$ + log ([IV]/[II]) [4] from seven points at a predesignated reliability of 0.98.

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THREE-DIMENSIONAL STRUCTURE OF 2-DIMETHYLAMINO-1,3-DIOXACYCLANES

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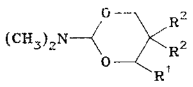
It was established by ^{1}H NMR spectroscopy that a chair conformation with an equatorial orientation of the dimethylamino group is the preferred conformation for methyl and 5,5-spiro derivatives of 2-dimethylamino-1,3-dioxanes.

It is known [1-5] that most substituted 1,3-dioxanes are chair conformers. Alkyl groups in the α position relative to the heteroatom ensure the preferableness of a conformation with an equatorial orientation of the substituents, whereas alkoxy groups ensure the preferableness of a conformation with an axial orientation of the substituents. At the same time, the literature does not contain information regarding the three-dimensional structure of nitrogen analogs of 2-alkoxy-1,3-dioxanes.

We have synthesized a number of 2-dimethylamino-1,3-dioxanes (I-IV):



I–III

IV

I R^1=R^2=H; II R^1=CH_3, R^2=H; III R^1=H, R^2=CH_3

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