ACID – BASE PROPERTIES OF 2,2'-DIQUINOLYL AND ITS ANALOGS

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The acid–base properties of 10 derivatives of 2,2'-diquinolyl, as well as quinoline and 5,6-benzoquinoline, were studied by spectrophotometry. It was established that the protonation constants of the systems correlate with the regularities due to the I and M effects of the substituents.

The results of a study of the acid–base equilibria of some bonded heterocyclic systems representing a group of complexing agents of the 2,2'-diquinolyl series are presented in the present paper. The study of the protolytic equilibria of heterocyclic systems seems necessary, first, in connection with the absence of protonation constants of III-XII (Table 1) in the literature and, second, for the establishment of the regularities in the change in the pK values of the bases of this series as a function of various factors.

The equilibrium constants of the ionization processes were determined in 60 wt.% ethanol, since the investigated compounds are only slightly soluble in water. We obtained the pK values of quinoline and 5,6-benzoquinoline at the same solvent concentrations. A bufferless spectrophotometric method [1] was used for the investigation with a hydrochloric acid solution with a precisely established concentration as the oxonium ion donor. The equation

$$\mathrm{B} + \mathrm{H}^{+} \rightleftarrows \mathrm{BH}^{+} \quad \sigma \quad \lg \sigma = \mathrm{p}K,$$

$$\frac{(\mathrm{BH}^{+})}{(\mathrm{B})\,(\mathrm{H}^{+})} = \sigma.$$

was used for the calculation of the protonation constants (σ) and the pK_1 values of the bases. Since the measurements were made at ionic strength $I < 10^{-4}$, it may be assumed that the constants are the thermodynamic values.

Typical absorption spectra of protonated (BH^+) and deprotonated (B) particles are presented in Fig. 1. Intense absorption of both forms is observed at 270-290 nm, and hypsochromic and bathochromic shifts are characteristic for λ_{max} of BH^+. When the solution is acidified, the long-wave maximum of the absorption band of BH^+ is shifted without an appreciable change in intensity. The bathochromic shift of λ_{max} of the BH^+ particle relative to B reaches 60 nm. The presence in the spectra of one or two isobestic points makes it possible to assume two-component character of the investigated systems; this is also confirmed by the results of a study of the dependence of the optical characteristics of solutions of the bases on the acidity of the medium. The typical dependences of the optical density on the hydrochloric acid concentration ($-\log C_{HCl} = pH$) is presented in Fig. 2, from which it is seen that there are only two B and BH^+ particles at pH 0-6, despite the presence of several possible protonation centers.

It is known that the basic properties of quinoline are due to the free pair of π electrons of the nitrogen atom, which are situated in the orthogonal plane and do not participate in aromatization of the ring. By comparing the pK_1 values of quinoline I and 5,6-benzoquinoline II it can be concluded that annelation in the 5,6 position of benzene practically does not change the basic properties of the ring heteroatom (Table 1). A decrease in the basic properties and a corresponding increase in the acid properties are observed on passing to bonded systems (for example, III and IV). It is possible that this phenomenon is due to the effect of the second nitrogen atom, which displays –I and –M effects, as well as to the three-dimensional structure of the molecules. These data contradict the conclusions drawn on the basis of computational methods [2], according to which the distribution of the π-electron densities in the structure is such that the quinoline rings behave in an isolated manner from one another, and the substituents in one ring do not affect the chemical properties of the second ring.

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TABLE 1. Principal Properties of I-XII

No.	Compound	λ_{an}, nm	σ	pK_1
I	Quinoline	330	$(2,41 \pm 0,03) \cdot 10^3$	3,38
II	5,6-Benzoquinoline	370	$(2,28 \pm 0,04) \cdot 10^3$	3,36
III	2,2'-Diquinolyl	375	$(1,56 \pm 0,02) \cdot 10^2$	2,19
IV	5,6-Benzo-2,2'-diquinolyl	390	$(1,92 \pm 0,03) \cdot 10^2$	2,28
V	4-Anilino-2,2'-diquinolyl	360—395	$(3,20 \pm 0,1) \cdot 10^4$	4,50
VI	4-1-Naphthyl)amino-2,2'-diquinolyl	360—395	$(1,64 \pm 0,1) \cdot 10^4$	4,21
VII	2-(4-Phenyl-1-quinolyl)-5,6-benzoquinoline	400	$(0,99 \pm 0,02) \cdot 10^2$	1,99
VIII	2-(2-Quinolyl)-5,6-benzocinchoninic acid N,N'-diethylamide	390	$(2,76 \pm 0,02) \cdot 10^1$	1,42
IX	2-(4-Phenyl-1-quinolyl)-5,6-benzocinchoninic acid N,N'-diethylamide	400	$(1,20 \pm 0,02) \cdot 10^1$	1,08
X	2-(2-Quinolyl)-5,6-benzocinchoninic acid anilide	400	$(3,79 \pm 0,03) \cdot 10^1$	1,58
XI	Isoamyl 2-(2-quinolyl)-5,6-benzocinchoninate	410	$(1,75 \pm 0,04) \cdot 10^1$	1,24
XII	Isoamyl 2-(4-phenyl-2-quinolyl)cinchoninate	395	$(1.23 \pm 0,04) \cdot 10^1$	1,09

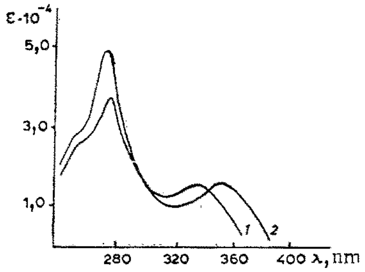

Fig. 1

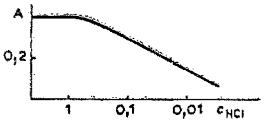

Fig. 2

Fig. 1. Absorption curves of benzoquinoline VII: 1) B form; 2) BH form (VII concentration $1 \cdot 10^{-5}$ mole/liter).

Fig. 2. Dependence of the optical density of an ethanol solution of IX on the hydrochloric acid concentration in 60% ethanol (IX concentration $1 \cdot 10^{-5}$ mole/liter).

Upon comparison of the effect of structural changes on the acid—base properties of the systems it is seen that the introduction of an NH—Ar group in the 4 position of the quinoline ring (V, VI) leads to an appreciable increase in the pK_1 value. Since the nitrogen atom in aromatic amines has weaker basic properties, the proton adds to the nitrogen atom of the heterocyclic ring. This is confirmed to a certain degree by the decrease in the basic properties of the nitrogen atom on comparison of the pK values of aniline (4.58) and diphenylamine (0.9) in water. The electron-donor ability of the NH—Ar groups of IV-VI is due to the ability of the unshared pair of electrons to participate in conjugation with the 10π-electron system of the quinoline ring via a conjugation mechanism and an inductive mechanism [3]. In evaluating the effect of the phenyl group, it may be noted that it does not lead to an appreciable change in the pK_1 values of the investigated systems (VII, IX, and XII). The introduction in the 4 position of the quinoline ring of $-\mathrm{C}\Big\langle^{O}_{R}$ groups, which have an electron-acceptor effect (—M effect), gives rise to a considerable increase in the pK_1 value to 1.24 in the case of ester XI. A similar pattern is observed when C_6H_5-and $-\mathrm{C}\Big\langle^{O}_{N(C_2H_5)_2}$ substituents are present in different rings. It is possible that electrons are shifted from the ring to the substituent as a result of conjugation of the heteroaromatic ring and the carbonyl group, and this also gives rise to a decrease in the basic properties. One should also take into account the fact that the dihedral angle between the rings increases when bulky substituents are introduced, and this undoubtedly affects the degree of conjugation of the system as a whole.

Thus the number of rings, the character of the substituents, the number of substituents, and steric effects have a considerable effect on the acid—base properties of quinoline structures.

EXPERIMENTAL

The investigated compounds were obtained by the methods in [4, 5]. The quinoline was distilled and stored in a nitrogen atmosphere. The spectrophotometric measurements were made with an SF-4A spectrophotometer.

Twice-distilled water was used. The hydrochloric acid concentration was established by means of 4-aminopyridine [8]. The ethanol was purified by the method in [6], and the concentrations of the alcohol solutions were established with a pycnometer. The general method for the investigation was as follows. The necessary concentrations of the solvent and the investigated compounds were created in a volumetric flask. The absorption spectra of the protonated and deprotonated particle were recorded, and the analytical wavelength (λ_{an}) was determined [7]. The optical densities at λ_{an} were determined for solutions containing various amounts of hydrochloric acid. The molar absorption coefficients for the particles were determined from the Bouguer–Lambert–Beer law, and the σ and pK values were calculated from the formula presented above. The data were treated statistically by the usual method [9] with fixed reliability $\alpha = 0.95$ for no less than seven experiments.

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MASS SPECTROMETRIC STUDY OF 2-AZAFLUORENES

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The fragmentation of 2-azafluorene and its methyl- and phenyl-substituted derivatives was studied. It is shown that ejection of an RCN fragment ($R = CH_3$, C_6H_5) by the molecular ions leads to a more intense peak if R is in the 3 position of the azafluorene ring. It was established that, in contrast to the dissociative ionization of fluorene, all of the ions of which are formed from the $(M - H)^+$ fragment, the fragmentation of 2-azafluorene and its derivative also takes place from the molecular ion. Randomization of the deuterium atoms attached to C_9 with the remaining hydrogen atoms was observed.

The mass spectral behavior of many classes of nitrogen-containing heterocyclic compounds is currently being studied quite adequately [1, 2]. However, the dissociative ionization of 2-azafluorenes has not been previously examined in the literature, although the fragmentation of fluorene, the hydrocarbon analog of the compounds studied in the present research, has been subjected to a quite detailed study [3, 4].

The present paper is devoted to the establishment of the fundamental regularities in the fragmention of 2-azafluorenes under the influence of electron impact, to the study of the dependence of their dissociative ionization on the position and character of the substituents in the pyridine and benzene rings of the molecules of these substances, and to an examination of the problem of exchange of hydrogen and deuterium atoms in the molecular ion of 9,9-D_2-2-azafluorene.

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