and recrystallized. Compound VIIa was obtained in 60% yield and had mp 255-256°C (dec., from ethanol—ethyl acetate). UV spectrum (in CH_3CN): λ_{max} 295, 365, 620 nm; log ε 3.79, 3.08, 4.85. Compound VIIb was obtained in 68% yield and had mp 260°C (dec., from CH_3CN). UV spectrum (in CH_3CN): λ_{max} 310, 355, 455, 675 nm; log ε 3.75, 3.75, 3.58, 5.04.

2-(2,4,5-Trimethyl-1,3-dithiol-2-yl)methylidene-4,5-dimethyl-1,3-dithiole (X, $C_{12}H_{16}S_4$). A 0.5-g sample of IIb was dissolved by heating in 5 ml of perchloric acid, and the solution was refluxed for 10 min, cooled, and poured over a mixture of ice and water. The aqueous mixture was extracted with ether, and the ether layer was washed with water, dried, and evaporated. The residue was recrystallized from hexane (~5 ml) to give 0.15 g (58%) of colorless crystals with mp 91-92°C. PMR spectrum: 1.8 (s, 6H), 1.85 (s, 6H), 1.93 (s, 3H), 5.18 (s, 1H); (in CF_3COOH): 2.78 (s, 6H), 3.32 (s, 3H).

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PORPHYRAZINES AS MULTICENTER BASES

A. S. Akopov and N. Yu. Borovkov

UDC 547.979.733

A critical analysis is made of the existing work on the acid-base properties of porphyrazines.

In [1], the acid-base properties of porphyrazine (tetraazaporphine, H_2TAP) were studied. A series of assertions of the authors as well as an examination of the results of the investigation of the acid-base equilibria of H_2TAP, provoke a reply. It is known that if the special technique of photoexcitation [2] is not used, a spectrophotometric method [3] can serve to determine the equilibrium constant K_a (K_{BH^+}) or K_b of molecules in the ground state. On the other hand, the idea itself of singly protonated phthalocyanines, developed in the work of Berezin (see the literature in [4]), is a simplication of the acid-base behavior of phthalocyanines, assuming only one meso atom of nitrogen participates in the protonation, although there are four such atoms having unshared electron pairs in phthalocyanine molecules, MPc (Pc is the $C_{32}H_{16}N_8$ fragment). This simplification came about because they only studied the acid-base properties in concentrated H_2SO_4 [4] without first studying the behavior in mediums of lower acidity.

The spectrophotometric method is compared in [1] with the thermodynamic method, by which is understood the study of the equilibria of H_2Pc and MPc in concentrated H_2SO_4 under isothermal conditions [4]. The inadequacy of using this lies in the fact that the dissolu-

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tion of phthalocyanines in concentrated H_2SO_4 over a large amount of the solid phase, leads to the formation of a supersaturated solution (it is known that MPc crystals swell in concentrated H_2SO_4) and to a marked influence of the intermolecular association of the protonated species on the equilibrium constant of the dissolution since the concentration of MPc in solution is significant, up to 0.1 M. Under these conditions, the metal-free compound, H_2Pc, also partially decomposes. Calculation using the data in [4] on the half-life of the decomposition of H_2Pc shows that in 17 M H_2SO_4, 18% of the added pigment undergoes decomposition in the first 20 minutes.

In Eq. (1), on the basis of which equilibrium constants for the dissolution of phthalocyananines in sulfuric acid (pK_{MPc}) were calculated [4, p. 71], there are a number of factors not taken into consideration: the solubility of the initial form of the pigment and its solubility at subsequent stages of protonation, the effect of a significant amount of organic base on the acidity function of the medium, and the different solubility of the protonated forms and their solvated states.

$$pK_{MPc} = pS + pK_{H_2SO_4} - H_0. \qquad (1)$$

The constancy of pK_{MPc} is not evidence of the one-step protonation of the meso nitrogen atoms in phthalocyanine and its MPc complexes as asserted in monograph [4]. It is caused by the linear dependence of the index of solubility, pS, on the acidity function of the medium, H_0, with the sequential protonation of the four meso atoms. We have succeeded in following this in aqueous H_2SO_4 for the third and fourth protonation of MPc complexes. The linear dependence is lacking for H_2Pc because H_2Pc is destroyed during the experiment. The combination of all these reasons leads to a weak dependence of pK_{MPc} on the nature of the metal atom. It changes over a rather narrow range of from 0.9 to 2.7 [4, p. 81]. Despite this, the author of [4] drew a conclusion about the size and direction of the σ- and π-effects of coordination in MPc complexes and arranged them in order of their basicities. This order was later contradicted by the results of spectrophotometry [5-11]. For example, according to [4], ZnPc is the least basic in a series of MPa complexes of divalent metals. Hence it was concluded that the σ-effect of coordination in MPc has the direction M ← N (inward). The spectrophotometric results show [5-17, 19, 20] that ZnPc is, on the contrary, one of the strongest bases in the series of phthalocyanines, while quantum chemical calculations [21] and photoelectron spectroscopic data for ZnPc [22] agree in a similar conclusion. Consequently, the method used by the author of [4] to investigate the acid-base properties of metallophthalocyanines cannot be called thermodynamic, and the conclusion of a one-step protonation of the meso nitrogen atoms of H_2Pc and MPc at any acidity of the medium does not correspond to reality. The latter is clearly seen in the data from [5-9] where it is shown that all four meso atoms in the phthalocyanines can be protonated as the acidity of the medium is increased. The investigation of the electrical conductivity of phthalocyanines in chlorsulfonic and 100% sulfuric acids [18, 23] confirm this point of view. Equation (1) actually defines, not pK_{MPc}, but the combined equilibrium constant for dissolution without taking account of the phenomena discussed above.

The weak dependence of the pK_{MPc} constants of the phthalocyanines on the nature of the metal atom also results from the leveling effect of the medium (concentrated H_2SO_4) on the protonated forms of MPc molecules, which, in the $(MPcH_3)_{solv}{}^{3+}$ state act as very weak bases.

Let us follow the arguments of the authors of [1] concerning the acid–base properties of tetraazaporphine. At high acidity of the medium, H_2TAP forms several species in a CH_3-$COOH/H_2SO_4$ system [1] with maxima at 613 (primary species), 625 (species II), 571 (III), and 643 (IV) (species numeration ours). For species II, pK_{BH^+} was determined to be −0.15 ± 0.03. The authors attribute to this species an ion–ion associate structure, $N(meso)H^{\delta+}...OSO_3H^{\delta-}$. Species III is identified with a structure in which the meso atoms of nitrogen form an N...HX type associate, and it is the inner ring N atoms that undergo protonation to form the same ion–ion associate, $2(NH^{\delta+}...OSO_3H^{\delta-})$ with $pK_{BH^+} = -(4...5)$. Species IV, with $\lambda_{max} = 643$ nm and $pK_{BH^+} = -7$, corresponds, in our opinion of the authors of [1], to the single protonation of a meso atom, H_2TAPH^+, with the remaining three meso atoms being bound in weak associates with molecules of proton donors, N...HX. It follows from the authors' analysis that, as the acidity of the medium is increased, a meso nitrogen atom is first protonated (species II), then the bond of the N(meso) atom to the proton is weakened (species III), and then strengthened again on going to species IV. In our view, there are no actual grounds for such conclusions.

TABLE 1. pK_{BH^+} Values of Tetra-tert-butylporphyrazines in a CH_3COOH/H_2SO_4 Medium at 25 ± 0.1°C

Compound λ_{anal} (cm^{-1})	pK_1	pK_2	pK_3	pK_4
H_2TAP'	0*1*2	−9±2*3	−14±1*3	−15*3
λ anal	15 750	15 245	14 705	—
CuTAP'	2,90±0,14*1	−2,40±0,15	−5,70±0,25	−15±1
λ_{anal}	16 560	16 180	15 875	15 750 ... 15 625

*Determined in an antipyrene (or urea): CH_3COOH/H_2SO_4 medium.

*2The pK_{BH^+} value is the average for one meso atom and two inner ring atoms of nitrogen.

*3An estimated value found from the nature of the absorption spectrum.

TABLE 2. Change in the Acid Dissociation Constant, pK_{BH^+}, as a Function of the Structure of the Porphyrazines*

Porphyrazine	Medium	pK_1	pK_2	pK_3	pK_4
H_2Pc' [9]	$CH_3COOH—H_2SO_4$	0,86±0,12	−1,58±0,09	−4,60±0,12	−7,05±0,08
CuPc'	$CH_3COOH—H_2SO_4$	2,10±0,25	−0,33±0,04	−3,03±0,12	−6,23±0,10
H_2TPyP [24]	$H_2SO_4—H_2O$	−8,20±0,03	≪ −12	—	—
CuTPyP	$H_2SO_4—H_2O$	−6,81±0,08	≪ −12	—	—
H_2TrP'	$CH_3COOH—H_2SO_4$	2,80±0,14	−0,76±0,20	−4,62±0,17	<−15
CuTrP'	$CH_3COOH—H_2SO_4$	2,92±0,14	0,32±0,17	−3,16±0,10	<−15

*Determined spectrophotometrically at 25 ± 0.1°C.

For the purpose of analyzing the acid–base properties of the porphyrazines, we will first consider their copper complexes (Tables 1 and 2), in which the acid–base equilibria are not complicated by the phenomena of inner ring protonation. The pK_{BH^+} values that we have determined for the tetra-tert-butylporphyrazinate, CuTAP'* (the apostrophe designates tert-butyl substitution) and the tetra-tert-butyltetrabenzotriazaporphinate, CuTrP', showed that as the acidity of the medium increases, stepwise protonation of all the meso nitrogen atoms takes place. Only for the complex of tetra-2,3-pyridineporphyrazine, CuTPyP (Table 2), in solutions up to 100% H_2SO_4, is the protonation of one meso atom [24] observed.

Although the metal-free compounds have smaller basicities than the copper complexes, they too are protonated, depending on the acidity of the medium, at all of the center (meso) nitrogens (see, for example, H_2Pc', H_2TrP', and H_2TAP' in Tables 1 and 2). For H_2TAP', it was not possible by the spectrophotometric method to determine separately the equilibrium constants of the protonation of the inner, ring nitrogens and the first two steps of protonation of the meso nitrogen atoms. From the nature of the electronic absorption spectrum of H_2TAP', we have estimated the combined equilibrium constants for the species $(H_4TAP'H_2)^{4+}$ to be $pK_{BH^+} = -9 \pm 2$. The three-center protonation of the meso atoms in a molecule of H_2TAP' is observed in high concentrations of oleum or chlorsulfonic acid, with $pK_{BH^+} = -14 \pm 1$ and an absorption maximum of the $(H_4TAP'H_3)^{5+}$ species at 14,705 cm^{-1} (680 nm) (Table 1).

Not having tert-butyl substituents on the periphery of the molecule, H_2TAP has a lower basicity than H_2TAP'. However, as we saw above, there are no grounds for considering that its "acid form can be limited, like that of phthalocyanine, to a one-step protonation" [1]. It should be emphasized here that quantum chemical calculation by the INDO method has shown [25] agreement with the experimental changes in the electronic absorption spectra with increasing acidity of the medium and the four-center protonation of the meso nitrogen atoms. In our opinion, tetraazaporphine species II is $(H_2TAPH^+)_{solv}$, singly protonated at a meso atom. The degree to which the N(meso)H^+ group in it interacts with the counter ion is not known at this stage of the investigation. This could be ion–ion pair contact or ion–ion association, differing in the extent of charge separation under the influence of the solvent, $NH^+ \cdot HSO_4^- \rightleftarrows NH^{\delta+} \ldots HSO_4^{\delta-}$.

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*Samples of CuTAP' and H_2TAP' were kindly made available by V. N. Kopranenkov, for which we are sincerely grateful.

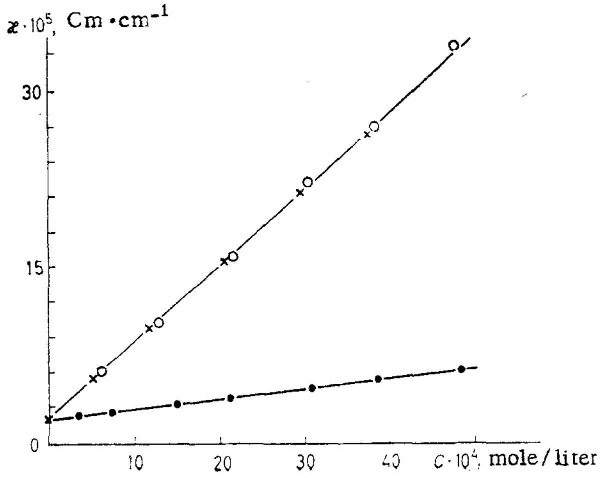

Fig. 1. Change in the specified electrical conductivity of HCOOK (×), pyridine (o), and tetra-4-tert-butylphthalocyanate zinc (•) in anhydrous formic acid as a function of its concentration in solution.

We agree with the authors of [1] in the conclusion that species III with λ_{max} = 571 nm, correspond to the inner ring protonation of nitrogen atoms, converting the porphyrazine to $(H_4TAPH)_{solv}{}^{3+}$. However, it in no way follows from the experiments of the authors of [1] that the $NH^+ \ldots HSO_4{}^- \rightleftarrows N \ldots H_2SO_4$ equilibrium at the meso atoms is shifted to the right. Consequently, a further increase in the acidity of the medium does not lead to the one-center protonation of the meso nitrogen atoms, but to the two-center protonation, and species IV will correspond to the $(H_2TAPH_2)_{solv}{}^{2+}$ state, otherwise we would find the same spectrum as for species II, with λ_{max} 625, and not 643 nm. It was shown in [9] that the extent of the charge separation between a protonated meso atom and a counter ion (the extent of protonation, in the terminology of [4]), influences primarily the intensity of the absorption band in the spectrum, not its location. This confirms the results of a cooperative study of the acid-base properties of complexes of tetra-2,3-pyridineporphyrazine [24].

Similar deficiencies characterize [26] on the determination of the acid-base properties of tetracyclohexenetetraazaporphine (H_2CycP) in a CH_3COOH/H_2SO_4 medium. The sequential appearance of new absorption maxima in the electronic spectrum of this compound as the acidity of the medium increased (625, primary species, 642, 685, 667, and 691 nm) is ascribed by the authors of [26] to the formation of the following species:

	H_2CycP	$H_2CycP \cdot\cdot H^+ \cdots A^-$	$H_4CycP^{2+} \cdot\cdot 2A^-$	H_2CycPH^+	$H_2CycPH_2{}^{2+}$
pK_{BH^+}	—	1.81	0.80	−7.21	−9.32

It follows from the material presented that the hypersochromic shift from 685 to 667 nm in the spectra of the tetracyclohexeneporphyrazine derivatives is due to the protonation of inner ring, not meso, nitrogen atoms. Consequently, the pK_{BH^+} values obtained in [26] belong, in all probability, to the species $(H_2CycPH)_{solv}{}^+$, $(H_2CycPH_2)_{solv}{}^{2+}$, $(H_4CycPH_2)_{solv}{}^{4+}$, and $(H_2CycPH_3)_{solv}{}^{3+}$, i.e., under these conditions, H_2CycP forms not two, but three species protonated at the meso atoms. The reference of the authors of [26] to the phenomenon of contrapolarization on the protonation of a second meso atom and the possibility thereby of a hypsochromic shift in the absorption spectrum previously predicted by Berezin [4], have not only received no experimental confirmation so far, but have been refuted by the works of other investigators [8, 13, 15].

The question of how much this or that protonated state is solvated cannot be answered on just the basis of spectrophotometry as the authors of [1, 26] have tried to do. Some information about this was obtained by us in a study of the electrical conductivity of solutions of phthalocyanines in 100% H_2SO_4 [27]. The divalent metal complexes, MPc and H_2Pc turned out under these conditions to have only three centers of protonation contributing to the increase in the electrical conductivity of the solution. Taking account of the results of a review of the electronic absorption spectra [6-11], we came to the conclusion that in the structure of the protonated species, three meso nitrogen atoms form loose, $NH^+ \cdot solv \cdot HSO_4^-$ ion pairs and the fourth meso atom forms a $NH^+ \cdot HSO_4^-$ contact ion pair which does not contribute to the electrical conductivity of the solution. The mobility of the compounds studied can be neglected in anhydrous H_2SO_4 in view of the peculiar mechanism of electrical conduction in the solvent [28].

We have observed that zinc 4-tetra-tert-butylphthalocyanate (ZnPC') is, according to the spectrophotometric data, doubly protonated in formic acid. Figure 1 shows the change in the electrical conductivity of pyridine, ZnPc', and potassium formate in anhydrous HCOOH as a function of the solute concentration. It is clear from Fig. 1 that in formic acid, pyridine is singly protonated to form the solvated cation $C_5H_5NH^+ \cdot solv$. In the HCOOH medium, ZnPc' has a smaller electrical conductivity than does pyridine. However, the virtual equality of the ratio of the slopes of the lines (Fig. 1) and the ratio of the cross-section of the molecules, d, which influences their mobility in solution, is evidence that ZnPc' in formic acid has only one meso atom protonated to form the solvated group $NH^+ \cdot solv \cdot HCOO^-$, which gives the molecule the ability to carry charge transport in solution.

$$\frac{\mathrm{tg}\,\alpha(\mathrm{Py})}{\mathrm{tg}\,\alpha(\mathrm{ZnPc'})} = \frac{6.53 \cdot 10^{-2}}{9.31 \cdot 10^{-3}} = 7.0; \quad \frac{d(\mathrm{ZnPc'})}{d(\mathrm{Py})} = \frac{20}{2.81} = 7.1. \tag{2}$$

The second meso atom forms a contact ion-pair, $NH^+ \cdot HCOO^-$, which, along with the other two meso atoms included in H-associates, N...HOOCH, does not contribute to the electrical conductivity of the solution.

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MASS SPECTROMETRY AND STRUCTURES OF IONS OF HETEROCYCLIC COMPOUNDS ACTIVATED BY COLLISION.

2.* 2-METHYLNITROINDOLIZINES

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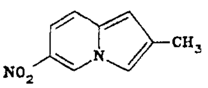
UDC 543.51:547.759.3

The principal pathways of the fragmentation of 2-methylnitroindolizines were investigated. The fragmentation and structures of the isomeric $[M - OH]^+$ and $[M - NO]^+$ ions formed in the fragmentation of these compounds were studied by the method of dissociative activation by collision (DAC). It was established that the stable $[M - OH]^+$ ions formed in the fragmentation of the 1- and 3-nitro isomers as a result of the "ortho effect" have different structures and that their DAC spectra can be used to determine the position of the nitro group in the molecule.

The mass spectra of 2-methyl-6-nitroindolizine and 2-methyl-8-nitroindolizine have been previously studied [2, 3]; however, only a brief communication [4] has been devoted to the fragmentation of the isomeric 1- and 3-nitro derivatives. It is known that, in addition to the common pathways of fragmentation of heterocyclic nitro compounds, there are specific fragmentation pathways that are determined by the position of the nitro group [5]. One such pathway is the formation of $[M - OH]^+$ ions in those cases in which a substituent that contains hydrogen atoms is located in the ortho position relative to the nitro group [5, 6]. In this connection it seems of interest to study the fragmentation of isomeric 2-methylnitroindolizines with nitro groups in different positions and to establish the structures of the principal fragment ions from the spectra of the products of their metastable fragmentation and dissociation activated by collision (DAC).

The following nitro derivatives of 2-methylindolizine were investigated:



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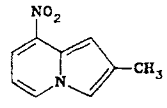

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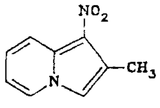

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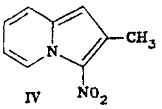

IV

Under the influence of electron impact these compounds form stable molecular ions $M^{+\cdot}$, the peaks of which have the maximum intensity in the mass spectra (Table 1), but their contribution to the total ion current depends on the position of the substituents in the molecule (Table 2). From the data obtained from the spectra of the metastable fragmentation of $M^{+\cdot}$ and the elementary composition of the ions determined from the high-resolution mass spectra (Table 3) one can isolate the following principal pathways of fragmentation of the molecular ions: a) splitting out of a nitro group; b) splitting out of a nitroso group; c) detachment of a hydroxyl radical. The latter process is observed only for isomers with an ortho orientation of the substituents and determines their lower stability with respect to electron impact (Table 2).

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*See [1] for Communication 1.

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