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Structure and Physicochemical Properties of Substituted Porphyrins

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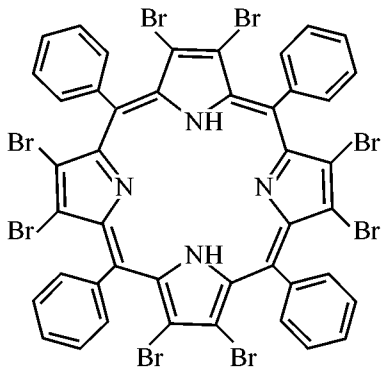
Abstract—Reactions of substituted porphyrins: 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphine, 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphine, and dodecaphenylporphine with organic bases (pyridine, piperidine, dimethylformamide, dimethyl sulfoxide) and acetic acid were studied by spectrophotometry. Acid–base interaction between porphyrins and organic bases and formation of ionic species in toluene solution containing an organic base were revealed for the first time. The effect of electronic and structural factors on the acid–base interactions of porphyrin ligands with organic bases is discussed. The stability constants were calculated for complexes of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphine with organic bases, and electronic absorption spectra of substituted porphyrins in basic organic solvents were recorded.

Specific chemical behavior of substituted porphyrins results mainly from the presence of a complex conjugation system, strong π,π-overlap throughout the macroring [1, 2], and macrocyclic effect, i.e., steric shielding of π-reaction centers by groups of atoms and spatial distortion of the macroring [3, 4]. Porphyrins with unusual structures, i.e., those formed by exhaustive substitution, attract a particular interest. Among numerous specific physicochemical properties of porphyrins, the most important are acid–base properties of the central coordination entity H_2N_4, which depend very strongly on the porphyrin structure [2–7].

This work continues our previous studies [8–10] on the effect of structural features of substituted porphyrins on their behavior in reactions with organic bases.



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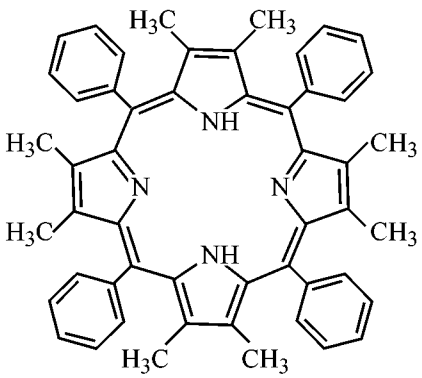

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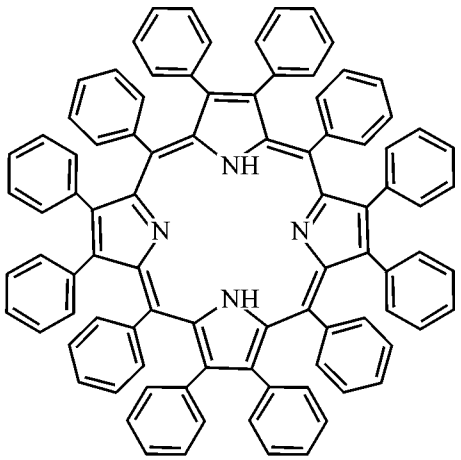

III

The subjects for study were 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphine (**I**), 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphine (**II**), dodecaphenylporphine (**III**), and 5,10,15,20-tetraphenylporphine (**IV**). As coordinating organic solvents (L) we used compounds having completed nonbonding φ_N-orbitals and possessing σ-donor properties: pyridine (py), piperidine (pip), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).

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Table 1. Positions (λ_{max}, nm) and intensities ($\log\varepsilon$) of absorption bands *I*–*V* in the electronic spectra of substituted tetraphenylporphines **I**–**III**

Porpyrin no.	Solvent	*I*	*II*	*III*	*IV*	*V*
I	Toluene	738 (3.85)	622 (4.10)	568 (3.95)	470 (5.25)	367 (4.41)
	Piperidine	775 (4.38)	–	–	504 (5.08)	388 (4.44)
	Pyridine	760 (3.89)	646 (4.08)	–	477 (5.10)	371 (4.38)
	DMF	734 (3.63)	627 (3.44)	–	473 (4.81)	393 (4.10)
	DMSO	794 (3.94)	677 (4.12)	–	486 (5.06)	373 (4.35)
II	Toluene	690 (3.53)	621 (3.67)	586 (3.86)	543 (4.05)	445 (5.17)
	Piperidine	695 (3.65)	662 sh	588 (3.93)	544 (4.10)	447 (5.13)
	Pyridine	695 (3.78)	625 (3.89)	587 (3.99)	544 (4.07)	448 (5.15)
	DMF	704 sh	648 (3.86)	590 (3.81)	538 (3.84)	452 (4.82)
	DMSO	689 (4.29)	–	–	–	461 (4.65)
						364 (4.14)
III	Toluene	725 (4.09)	609 (3.83)	555 (3.84)	464 (4.96)	–
	Piperidine	728 (3.78)	626 (4.03)	563 (3.98)	470 (5.11)	379 (4.45)
	Pyridine	742 (3.86)	637 (4.03)	566 (3.89)	477 (5.05)	379 (4.43)
	DMF	750 (3.97)	653 (4.15)	–	481 (5.11)	377 (4.58)
	DMSO	728 (4.21)	–	–	494 (4.96)	424 (4.19)

Solutions of porphyrins **I**–**III** in toluene are characterized by red shift of the Soret band (*B*), while their long-wave absorption bands (*Q*) become weaker and more diffuse as compared to tetraphenylporphine (**IV**) [10]. Two factors are assumed to be responsible for the observed pattern; these are change of the macroring conformation and electronic effect of substituents [11, 12]. The electronic spectra of porphyrins **I**–**III** in toluene and acetic acid strongly differ from those recorded in organic bases in the position and intensity of absorption bands (Table 1).

As follows from the data of [5–7, 11, 12], introduction of substituents into the pyrrolic β-positions of tetraphenylporphine leads to loss of planar structure of the molecule. The degree of distortion of the macroring depends on the substituent nature. The highest occupied molecular orbital of porphyrin (a_{2u} and a_{1u}) is localized on the pyrrolic and *meso*-carbon atoms, respectively [1, 2]. The presence of substituents in these positions is considered [11] to induce perturbations which give rise to numerous configurational interactions. It is presumed that Q_y and Q_x transitions

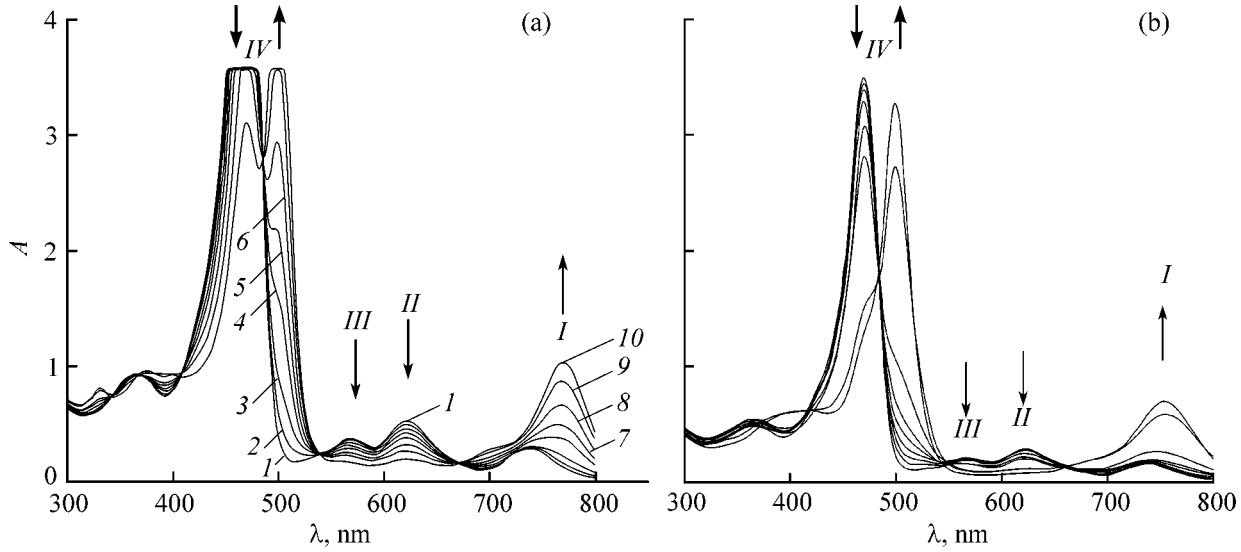

Fig. 1. Variation of the electronic absorption spectra of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphine (**I**) in toluene on addition of (a) piperidine and (b) acetic acid. $c_{H_2P} = 4.23\times10^{-5}$ M; c_{pip}, M: (*1*) 0, (*2*) 0.008, (*3*) 0.016, (*4*) 0.025, (*5*) 0.033, (*6*) 0.041, (*7*) 0.058, (*8*) 0.083, (*9*) 0.125, and (*10*) 0.166; c_{AcOH} = 0.001–0.1 M.

in poprhyrin **I** overlap to produce a strong band with λ_{max} 626 nm ($\log\varepsilon$ 4.12) in methylene chloride solution. We have found that an analogous ratio of absorption bands of porphyrin **I** is observed in toluene. In addition, substitution of the β-pyrrolic positions by groups possessing different electronic properties (CH_3, C_6H_5, Br) results in π-electron density redistribution over the conjugation system and nitrogen atoms of the coordination entity and hence changes the acid–base properties of porphyrins.

The electronic spectra of porphyrins **I**–**III** in piperidine and DMSO show increased intensity of the long-wave absorption band (Table 1) and disappearance of bands *II* and *III*. This pattern indicates that the symmetry of the macroring changes from D_{2h} to D_{4h} as a result of acid–base interaction with the solvent [3, 13]. An analogous interaction was observed for phthalocyanines and tetraazaporphines [3, 14]. As concerns porphyrins *per se*, such interaction with organic bases was observed for the first time. Titration of porphyrin **I** in toluene with piperidine gives rise to a strong absorption maximum at λ 775 nm (Fig. 1). Four isobestic points in the spectra are clearly observed at different piperidine concentrations; this indicates that only two absorbing species are present in solution: HP^- anion and neutral H_2P molecule. On the basis of the data obtained for different solvents at various concentrations we presumed the existence of the following equilibrium:

$$H_2P + L \rightleftarrows HP^-\cdots HL^+ \rightleftarrows HP^- + HL^+,$$
$$L = \text{pip, py, DMSO, DMF,} \quad (1)$$

$$K_{eq} = [HP^-][HL^+]/[H_2P]. \quad (2)$$

The concentration of ionic species in solution was determined by spectrophotometry using the formula for a mixture of two colored substances:

$$c_{HP^-} = c_{H_2P}\frac{A_{eq} - A_\infty}{A_0 - A_\infty}. \quad (3)$$

Here, c_{HP^-} is the concentration of porphyrin monoanion; c_{H_2P} is the initial porphyrin concentration; A_0 is the initial optical density; A_{eq} is the optical density of the equilibrium mixture; and A_∞ is the optical density of the equilibrium mixture with the maximal concentration of organic base L. According to Eq. (1), proton is transferred from the porphyrin ligand H_2P to a stronger base (in our case, to piperidine).

The number of organic base molecules participating in the acid–base interaction with porphyrin **I** was determined graphically as the slope of the log dependence $\log c_L$–$\log[(A_0 - A_{eq})/(A_{eq} - A_\infty)]$ (for piperidine, n = 1.2; Fig. 2). Presumably, one NH proton is transferred to piperidine molecule according to Eq. (1) to give monoanion, whereas formation of the ion pair $[P^{2-}\cdot(LH^+)_2]$ on titration with piperidine cannot be detected spectrally. Such a behavior of porphyrin **I** is likely to result from several factors: effect of the halogen atoms, spatial deformation of the macroring, and basicity of the organic base L. Bromine atoms exhibit a positive mesomeric effect and negative inductive effect. Replacement of hydrogen atoms in the β-pyrrolic positions by bromine reduces the energy of the lower unoccupied molecular orbital, thus favoring transfer of the nitrogen *n*-electrons to the macroring. As a result, the polarity of the N–H bond increases, and its acidity sharply rises. According to the X-ray diffraction data and the results of quantum-chemical calculations [7, 11], the presence of bromine atoms and phenyl groups in the *meso*-positions leads to distorion of the planar structure of the macroring. This means that protons of the coordination entity are differently accessible and that synchronous interaction of piperidine with both protons is sterically hindered.

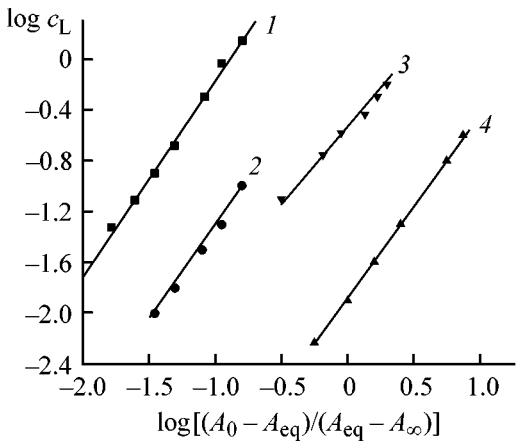

Fig. 2. Determination of the number of organic base molecules (*n*) added to 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphine (**II**) in toluene: (*1*) piperidine, n = 1.2; (*2*) DMF, n = 1.1; (*3*) pyridine, n = 1.1; (*4*) DMSO, n = 1.1.

During titration of a solution of porphyrin **I** with less basic solvents than piperidine, namely, with DMSO and DMF we observed a two-band spectrum (Table 1), which is likely to correspond to the ion pair $[HP^-\cdot HL^+]$ [Eq. (1)] [13, 14]. The stability constants K_s (Table 2) calculated by Eqs. (2) and (3) change in parallel with the basicities of the organic solvent L. The K_s value for piperidine (pK_a 11.12) is larger than the corresponding value for pyridine

Table 2. Stability constants and thermodynamic parameters of acid–base interaction of porphyrin **I** with organic bases

Base	K_s				ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}
	298 K	308 K	318 K	328 K		
Piperidine	6.3 ± 0.4	4.2 ± 0.3	2.6 ± 0.2	1.8 ± 0.2	–35 ± 0.7	–102 ± 3
Pyridine	(2.5 ± 0.1) × 10^{-2}	(2.0 ± 0.1) × 10^{-2}	(1.6 ± 0.1) × 10^{-2}	(1.3 ± 0.1) × 10^{-2}	–18 ± 1.1	–90 ± 4
DMF	0.87 ± 0.05	0.76 ± 0.05	0.67 ± 0.04	0.59 ± 0.04	–11 ± 0.5	–36 ± 2
DMSO	2.87 ± 0.17	2.32 ± 0.15	1.87 ± 0.16	1.50 ± 0.13	–17 ± 1.6	–49 ± 4

(pK_a 5.17) by two orders of magnitude. The lack of a distinct correlation between ΔH, ΔS, and K_s for reaction (1) indicates different solvation mechanisms of sterically hindered porphyrins in organic solvents with different structures and basicities.

Despite the weaker basicity of bromo-substituted porphyrin **I** relative to tetraphenylporphine (**IV**) [11], titration of **I** with acetic acid (Fig. 1b) results in displacement of the absorption spectrum toward longer wavelengths with simultaneous reduction in the intensity of bands *I* and *II*. The only possible reason is protonation of porphyrin **I** [2, 13].

$$H_2P + CH_3COOH \rightleftarrows H_3P^+ + CH_3COO^-. \quad (4)$$

For the sake of comparison, we also examined the electronic absorption spectra of porphyrins **II** and **III** under similar conditions. A molecule of **III** contains 12 phenyl rings; the macroring is strongly distorted (it adopts a *saddle* conformation) [5, 12], and basic properties of **III** increase. The electronic absorption spectrum of porphyrin **III** in toluene (Table 1, Fig. 3) corresponds to monoprotonated species H_3P^+, and such salt can be isolated. The salt is stable both in the crystalline state and in solution in chloroform or toluene. On addition of acetic acid (c = 1–10 M) to a solution of **III** in toluene the intensity of band *I* (λ_{max} 730 nm) increases, which suggests formation of dication [H_4P^{2+}] (Fig. 3a, curve *13*). However, we failed to isolate the salt from solution [15]. An anal-

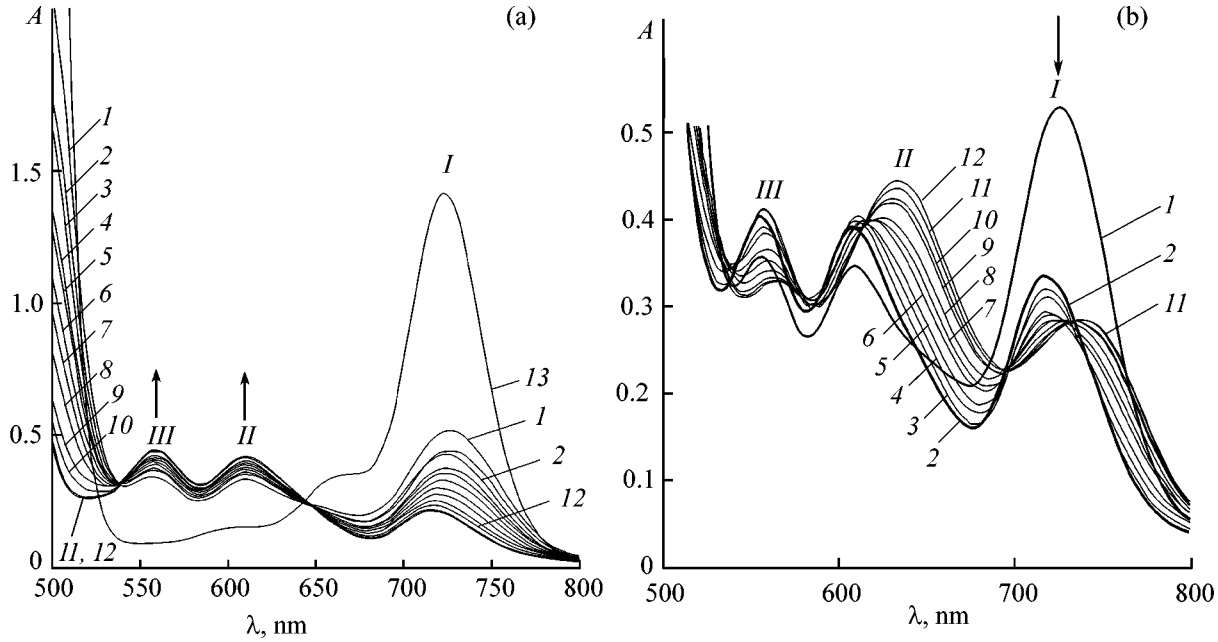

Fig. 3. (a) Variation of the electronic absorption spectrum of protonated dodecaphenylporphine (**III**) in toluene on addition of piperidine, $c_{H_3P^+} = 4.20 \times 10^{-5}$ M, c_{pip}, M: (*1*) 0, (*2*) 0.0015, (*3*) 0.0032, (*4*) 0.0047, (*5*) 0.0063, (*6*) 0.0079, (*7*) 0.011, (*8*) 0.015, (*9*) 0.019, (*10*) 0.039, (*11*) 0.079, and (*12*) 0.11; (*13*) absorption spectrum in the presence of acetic acid, c_{AcOH} = 10.5 M; (b) variation of the electronic absorption spectrum of dodecaphenylporphine (**III**) in toluene on addition of pyridine: (*1*) $c_{H_2P^+} = 4.20 \times 10^{-5}$; (*2–11*) c_{py} = 2.0–9.8 M.

ogous spectral pattern was observed for porphyrin **II** (Fig. 4).

The titration of monoprotonated porphyrin **III** in toluene with organic bases leads to decrease in the intensity of band *I* (λ_{max} 725 nm), and bands *II* and *III* also change their position and intensity (Table 1). The absorption curves obtained on addition of piperidine to a solution containing H_3P^+ species are shown in Fig. 3a (*2–12*); here, the Soret band shifts red. Basic solvents L abstract a proton from the weaker donor of electron pair, protonated porphyrin **III**, according to Eq. (5):

$$H_3P^+ + L \rightleftarrows H_2P + HL^+. \quad (5)$$

Here, H_3P^+ is protonated porphyrin **III**, and L is pyridine, piperidine, DMF, or DMSO.

$$K_{eq} = [H_2P][HL^+]/[H_3P^+]. \quad (6)$$

The equilibrium constants [Eq. (6)] are as follows: $K_{eq}(288) = 183 \pm 5.5$ (c_{pip} = 0.0015–0.15 M) and 11 ± 0.8 (c_{py} = 0.02–2.0 M). As the concentration of pyridine rises from 2.9 to 9.8 M, band *II* increases in intensity and shifts to the long-wave region (λ_{max} 637 nm; Fig. 3b). A similar pattern is typical of titration of porphyrin **III** with DMF and DMSO. We believe that the above spectral changes result from formation of acid–base ion pair $[HP^- \cdot HL^+]$ according to Eq. (1). Such interaction of **III** with organic bases implies strong polarization of the N–H bonds due to both spatial distortion of the macroring [5, 12] and π-electron-acceptor effect of the phenyl rings.

It should be noted that, in contrast to bromo-substituted analog **I** (Table 1), we observed no interaction between porphyrin **III** and more basic piperidine (pK_a 11.12). The absorption spectrum did not change on raising the piperidine concentration above 0.11 M. Presumably, conformational transformations of piperidine in solution [16] hamper its interaction with protons of the coordination entity in sterically hindered porphyrins **II** and **III**.

The influence of organic base L on the electronic absorption spectra of octamethyl-substituted porphyrin **II** (Table 1) may be explained by solvatochromic properties of the spatially distorted macroring. No such effect was observed for unsubstituted tetraphenylporphine (**IV**) [10]. On the other hand, compound **II** is more basic than its brominated analog, as follows from its ability to react with acetic acid (Figs. 1a, 4).

Thus we were the first to reveal acid–base interaction between porphyrins and organic bases and formation of porphyrin anions in toluene solution containing an organic base. The ionization of the N–H bond in porphyrins **I** and **III** in DMF is also indicated by almost instantaneous complex formation with a manganese salt [17] due to reduced activation energy [2].

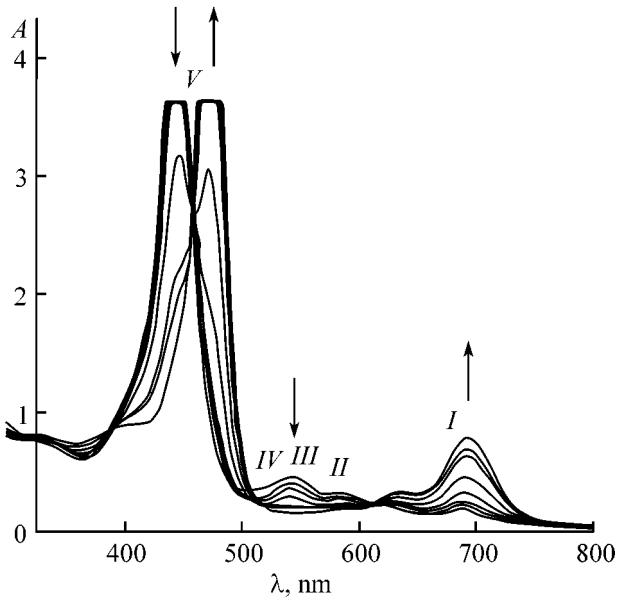

Fig. 4. Variation of the electronic absorption spectrum of 2,3,7,8,12,13,17,18-octamethyl-5,10,15,20-tetraphenylporphine (**II**) in toluene on addition of acetic acid; $c_{H_2P} = 5.25 \times 10^{-5}$ M, $c_{AcOH} = 1 \times 10^{-4}$ to 2×10^{-2} M.

EXPERIMENTAL

Porphyrins **II** and **III** were synthesized by condensation of 3,4-disubstituted pyrroles with benzaldehyde and were purified by the procedure described in [12, 18]. Porphyrin **I** was obtained according to [11]. The compounds were identified by the IR and electronic absorption spectra [5, 6, 12]. The solvents were dried and purified by standard methods [19]; the concentration of water therein was checked by Fischer titration. Acid–base interactions of porphyrins were studied as follows. A set of 10–12 solutions with the same concentration of H_2P (10^{-5} M) and increasing concentration of organic base L or acetic acid was prepared, and their electronic absorption spectra were recorded using leak-proof quartz cells (Hitachi U-2000 spectrophotometer equipped with a temperature-controlled unit). The spectra were recorded in the range where differences in the absorption patterns were the strongest (Figs. 1–4).

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