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# Acid–Base Properties of Octaaryltetraazaporphyrins

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**Abstract**—Stability constants were determined for acid forms of octa(4-chloromethylphenyl)-, octa(4-bromophenyl)-, and octa(4-nitrophenyl)tetraazaporphyrins, formed by acid–base interactions in $H_2SO_4$–$CH_3COOH$ mixtures. The probability of formation of each form depends not only on the electronic structure of the molecule, but also on the composition and properties of the medium.

Tetraazaporphyrins are weak many-center conjugated bases [1]. Acid–base interactions involving tetraazaporphyrins have an intricate pattern [1–5].

$$B + HA \rightleftarrows \underset{\text{acid associate}}{B\cdots HA} \rightleftarrows \underset{\text{H-associate}}{B\cdots H\cdots A} \rightleftarrows \underset{\text{ionic associate}}{BH^+\cdots A^-}$$

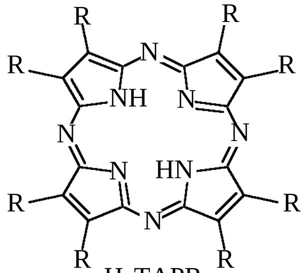
$$\rightleftarrows \underset{\text{protonated form}}{BH^+ + A^-}.$$

Here B is tetraazaporphyrin and HA is acid.

The acid forms differ from each other by the "depth" of protonation, i.e. by the degree of proton transfer from the acid molecule to the donor center. The number of donor centers involved in acid–base interactions, the character of these interactions, as well as the stability constants of the resulting acid forms depend on the structure of the tetraazaporphyrin and the properties of the proton-donor medium [2–5]. A feature of tetraazaporphyrins as many-center bases is that their donor centers all enter acid–base interactions with the medium, but to a different extent. In tetraazaporphyrins, both exocyclic (*meso*) and endocyclic nitrogen atoms can be involved in acid–base interactions. Interactions of tetraazaporphyrins with acids produce characteristic changes in the visible region of electronic absorption spectra, associated with formation of different acid–base forms [1, 6–12].

We earlier studied the base properties of tetraazaporphyrin, tetra(tetramethylene)tetraazaporphyrin, and octaphenyltetraazaporphyrin [2, 4]. It was shown that the first step of the acid–base interaction involves one of the *meso*-nitrogen atoms, and the second, endocyclic nitrogen atoms.

In the present work we used spectrophotometric titration to study the acid–base properties of octa(4-bromophenyl)-, octa(4-chloromethylphenyl)-, and octa(4-nitrophenyl)tetraazaporphyrins (**I**–**III**) in $H_2SO_4$–AcOH mixtures.



$H_2TAPR_8$

R = $C_6H_4Br$-*p* (**I**), $C_6H_4CH_2Cl$-*p* (**II**), $C_6H_4NO_2$-*p* (**III**).

In 100% AcOH, octaaryltetraazaporphyrins **I**–**III** form symmetrical acid associates $H_2TAPR_8\cdots(AcOH)_4$ [1], but the electronic absorption spectra in this solvent are almost identical to those in neutral solvents, except that the *Q* band is slightly shifted blue (~3 nm). In AcOH, the *Q* bands of the ligands are split. The $Q_x$ and $Q_y$ absorption maxima are observed at the following wavelengths, nm, respectively: $H_2TAP(C_6H_4Br\text{-}p)_8$ 662 and 598; $H_2TAP(C_6H_4CH_2Cl\text{-}p)_8$ 663 and 600; and $H_2TAP(C_6H_4NO_2\text{-}p)_8$ 663 and 595. In an AcOH–antipyrine–$H_2SO_4$ buffer solution, the absorption spectra do not change. With $H_2TAP\cdot(C_6H_4Br\text{-}p)_8$, spectral changes are observed in AcOH–$H_2SO_4$ at $H_2SO_4$ concentrations ranging from 0.149 to 11.86% ($H_0$ –0.64 to –3.02) (Fig 1a). The bands at 662 and 598 nm become weaker, the $Q_x$ and $Q_y$ components coalesce, and a single broadened band appears at $\lambda_{max}$ 756 nm. The acid form that arises exists up to $H_0$ –3.10 (12% $H_2SO_4$). The electronic absorption pattern of this form points to an ionic associate involving endocyclic nitrogen atoms $[H_4TAP(C_6H_4Br\text{-}p)_8^{2+}\cdots(HSO_4^-)_2]$. The attendant lowering of the $\pi_2^*$ orbital and its approach to $\pi_1^*$ show up in the disappearance of

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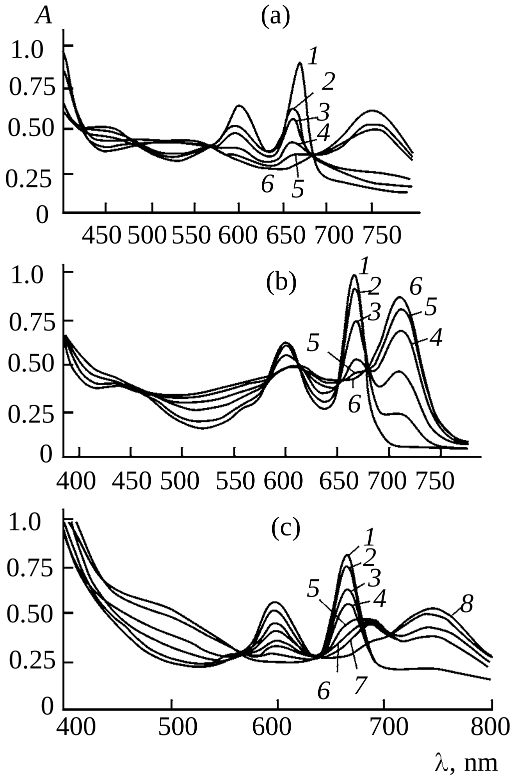

**Fig. 1.** Changes in the electronic absorption spectra. (a) $H_2TAP(C_6H_4Br\text{-}p)8$ [(*1*) benzene, (*2*) HOAc, (*3*) 0.149% $H_2SO_4$ in AcOH, (*4*) 0.525% $H_2SO_4$ in AcOH, (*5*) 1.05% $H_2SO_4$ in AcOH, and (*6*) 12% $H_2SO_4$ in AcOH], (b) $H_2TAP(C_6H_4Br\text{-}p)_8$ [(*1*) $CH_2Cl_2$, (*2*) 0.11 M $CF_3CO_2H$ in $CH_2Cl_2$, (*3*) 0.16 M $CF_3CO_2H$ in $CH_2Cl_2$ (*4*) 0.28 M $CF_3CO_2H$ in $CH_2Cl_2$, (*5*) 0.44 M $CF_3CO_2H$ in $CH_2Cl_2$, and (*6*) 3.24 M $CF_3CO_2H$ in $CH_2Cl_2$]; and (c) $H_2TAP(C_6H_4NO_2\text{-}p)_8$ [(*1*) AcOH, (*2*) 12% $H_2SO_4$ in AcOH, (*3*) 14% $H_2SO_4$ in AcOH, (*4*) 16% $H_2SO_4$ in AcOH, (*5*) 30.37% $H_2SO_4$ in AcOH, (*6*) 32.46% $H_2SO_4$ in AcOH, (*7*) 39.40% $H_2SO_4$ in AcOH, and (*8*) 46.15% $H_2SO_4$ in AcOH].

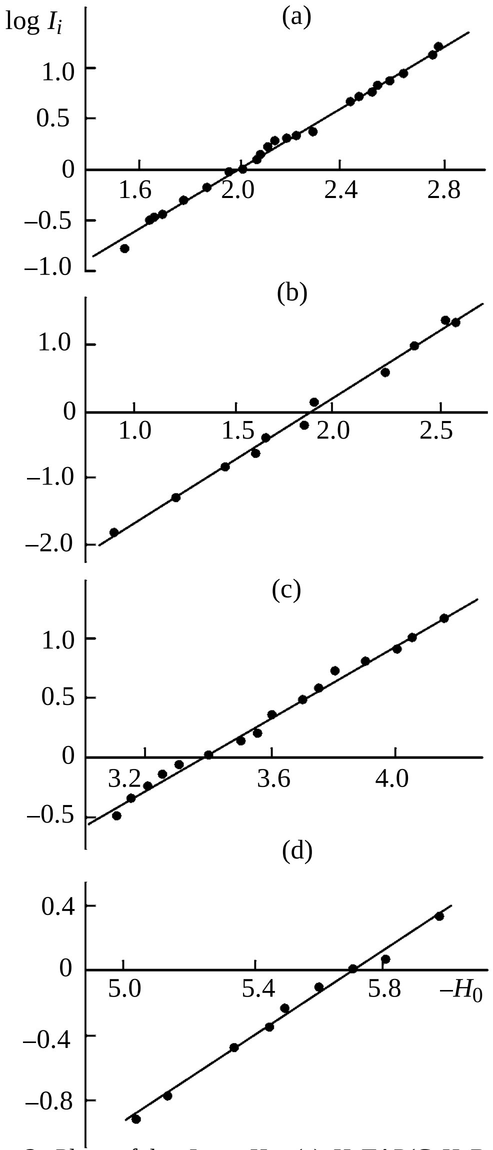

**Fig. 2.** Plots of log *I* vs. $H_0$. (a) $H_2TAP(C_6H_4Br_0\text{-}p)_8$ (λ 662 nm), (b) $H_2TAP(C_6H_4CH_2Cl\text{-}p)_8$ (λ 663 nm), (c) $H_2TAP(C_6H_4NO_2\text{-}p)_8$ (λ 664 nm), and (d) $H_2TAP \cdot (C_6H_4NO_2\text{-}p)_8$ (λ 743 nm).

splitting of the *Q* band. The involvement of two nitrogen atoms in the acid–base interaction is confirmed by spectrophotometric titration data (Fig. 2a). The number of $H_2SO_4$ molecules that take part in this stage is 1.67. The pK of the resulting acid form is –2.01 ± 0.04. As the $H_2SO_4$ concentration is increased (more than 12%), the intensity of the absorption band at $\lambda_{max}$ 756 nm decreases, and the spectrum becomes structureless, on account of association of the acid forms in the high-acidity medium.

With $H_2TAP(C_6H_4CH_2Cl\text{-}p)_8$, spectral changes are observed in AcOH–$H_2SO_4$ at $H_2SO_4$ concentrations ranging from 0.149 to 16.46% ($H_0$ –0.64 to –3.35). Like with the bromine-substituted octaphenyltetraazaporphyrin, in the electronic absorption spectrum we observe decreasing intensities and coalescence of the $Q_x$ and $Q_y$ components and appearance of a single broadened band at $\lambda_{max}$ 756 nm. The acid form that arises exists up to $H_0$ –7.07 (60% $H_2SO_4$). Presumably, this form is an ionic associate involving endocyclic nitrogen atoms $[H_4TAP(C_6H_4CH_2Cl\text{-}p)_8^{2+} \cdots (HSO_4^-)_2]$. The number of $H_2SO_4$ molecules that interact with the tetraazaporphyrin is 1.96 (Fig. 2b). The p*K* of this form is –1.85 ± 0.04. As the concentration of $H_2SO_4$ in AcOH is increased, the acid forms associate, and the spectrum becomes structureless.

Previous studies on the acid–base properties of tetraazaporphyrins in $H_2SO_4$–AcOH mixtures showed that the acid–base interaction initially one *meso*-nitrogen atom. As the acidity of the medium is increased, the monocation by a *meso*-nitrogen atom passes into a dication by endocyclic nitrogen atoms. The formation of an ionic associate by endocyclic nitrogen atoms as the first ionic form in the AcOH–$H_2SO_4$ medium proved unexpected. However, in our studies on acid–base interactions of $H_2TAP(C_6H_4Br\text{-}p)_8$ in $CF_3CO_2H$–$CH_2Cl_2$ at $CF_3CO_2H$ concentrations ranging from 0.11 to 3.24 M we found that the $Q$ band of the tetraazaporphyrin shifts red without splitting (Fig. 1b), and, therewith, the long-wave $Q_x$ component shifts by 911 $cm^{-1}$. Such spectral pattern suggests ionic association with one *meso*-nitrogen atom. The concentration stability constant of this acid form p$K$ is +0.791 ± 0.06. As the concentration of $CF_3CO_2H$ in dichloromethane was increased, association of the acid forms and macroring cleavage were observed. The above findings suggest that the $H_2TAPR_8H^+ + H^+ \rightleftarrows H_4TAPR_8^{2+}$ equilibrium in the AcOH–$H_2SO_4$ medium is almost completely shifted to a dication by endocyclic nitrogen atoms, which can be explained by features of solvation and, consequently, stabilization of protonated forms.

The spectral changes observed in the course of acid–base interactions of $H_2TAP(C_6H_4NO_2\text{-}p)_8$ in AcOH–$H_2SO_4$ (Fig. 1c) proved slightly unexpected. They begin at $H_2SO_4$ concentrations of 10.43–34.92% ($H_0$ –3.0 to –4.7) and are accompanied by decreasing intensity of the $Q_x$ and $Q_y$ components of the $Q$ band in the electronic absorption spectrum with simultaneous shifting of the $Q_x$ component red by 483 $cm^{-1}$. The electronic absorption pattern of the resulting acid form suggests protonation of a *meso*-nitrogen atom. The number of $H_2SO_4$ molecules involved in the acid–base interaction is 1. The p$K$ of the ionic associate is –3.45 ± 0.04 (Fig. 2c). Similtaneously, a single broadened band at $\lambda_{max}$ 743 nm begins to grow at an $H_2SO_4$ concentration of 16.38% ($H_0$ –3.3). The process of formation of this acid form is complete at an $H_2SO_4$ concentration of 46.15% ($H_0$ –5.7). The resulting form is stable up to an $H_2SO_4$ concentration of 79.7% ($H_0$ –9.55). The electronic absorption pattern of this form suggested an ionic associate by endocyclic nitrogen atoms, passing into the dication $H_4TAP(C_6H_4NO_2)_8^{2+}$. However, the number of $H_2SO_4$ molecules involved in the suggested dication formation proved equal to 1 (Fig. 2d). The same observations we previously reported for octaphenyltetraazaporphyrins [2]. Probably, the second proton migrates to the reaction center from a *meso*-nitrogen atom. The p$K$ of the second acid form is –5.7 ± 0.03 (Fig. 2d).

Thus, substitution in tetraazaporphyrin molecules produces not only quantitative changes, i.e. basicity increase or decrease, but also qualitative changes in the acid–base interaction pattern, i.e. changes in the structure of acid forms and their formation order. The possibility of formation of each form depends not only on the electronic structure of the molecule, but also on the composition and properties of the medium.

## EXPERIMENTAL

Octaaryltetraazaporphyrins **I**–**III** were synthesized according to [13–15]. Glacial acetic acid of chemical grade was subjected to multiple freezing and boiling with acetic anhydride, after which it was distilled (bp 118°C). Anhydrous $H_2SO_4$ was prepared from 60% oleum and 96% sulfuric acid with conductometric concentration control.

Spectrophotometric measurements were performed for solutions with a constant concentration of tetraazaporphyrins in various-acidity media on a Hitachi U-2000 spectrophotometer at 298 K. The Hammett acidity functions $H_0$ were taken from [16, 17]. The concentration ratio of equilibrium acid–base forms ($I_i = c_i/c_{i-1}$) was determined at wavelengths corresponding to their absorption maxima. The acid–base interaction constants $K$ were calculated by the Hammett equation $pK = nH_0 + \log I_i$ [$H_0$ is the Hammett acidity function, $I_i = c_i/c_{i-1}$ is the concentration ratio of the $i$th and ($i$ – 1)th equilibrium forms (indicator ratio), $K$ is the stability constant of the $i$th form, and $n$ is the number of donor centers involved in the acid–base interaction at the given stage]. The p$K$ values were calculated by the least-squares procedure for 15–20 experimental points.

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