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Acid–Base Properties of Sterically Strained Tetraethyltetramethylporphyrin Derivatives

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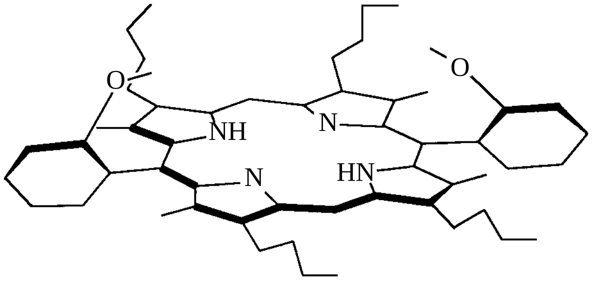
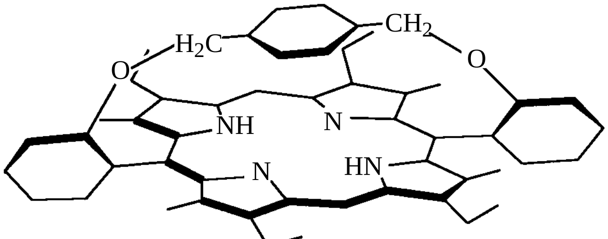
Abstract—Acid dissociation constants in acetonitrile were determined for cationic forms of sterically strained tetraethyltetramethylporphyrin derivatives. These compounds are more basic than their unstrained analog because of deformations of the porphyrin macroring, that increase the electron density on tertiary nitrogen atoms of the reaction center and make them more accessible for reaction.

Sterically strained porphyrins (paled, girded, picked-fence, capped, etc.) are widely known as chemical models of porphyrin–protein complexes [1, 2]. Screening of the reaction center of the macrocyclic ligand by bulky substituents, combined with violation of the planarity of the porphyrin nucleus predetermine peculiar coordination properties of these compounds [3–5].

In the present work we compared the acid–base properties of 5,15-bis(*o*-methoxyphenyl)-2,8,12,18-tetrabutyl-3,7,13,17-tetrametylporphyrin (**I**) and its benzene- (compound **II**) and dimethoxybenzene-capped derivatives (compound **III**) with those of tetra-(*m*-butoxyphenyl)porphyrin (**IV**) and its dimeric analog **V**.



I



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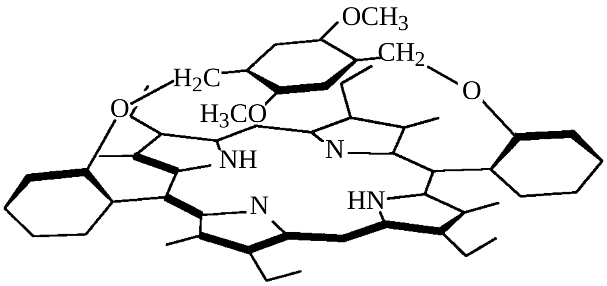

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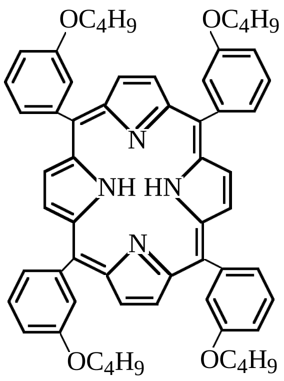

IV

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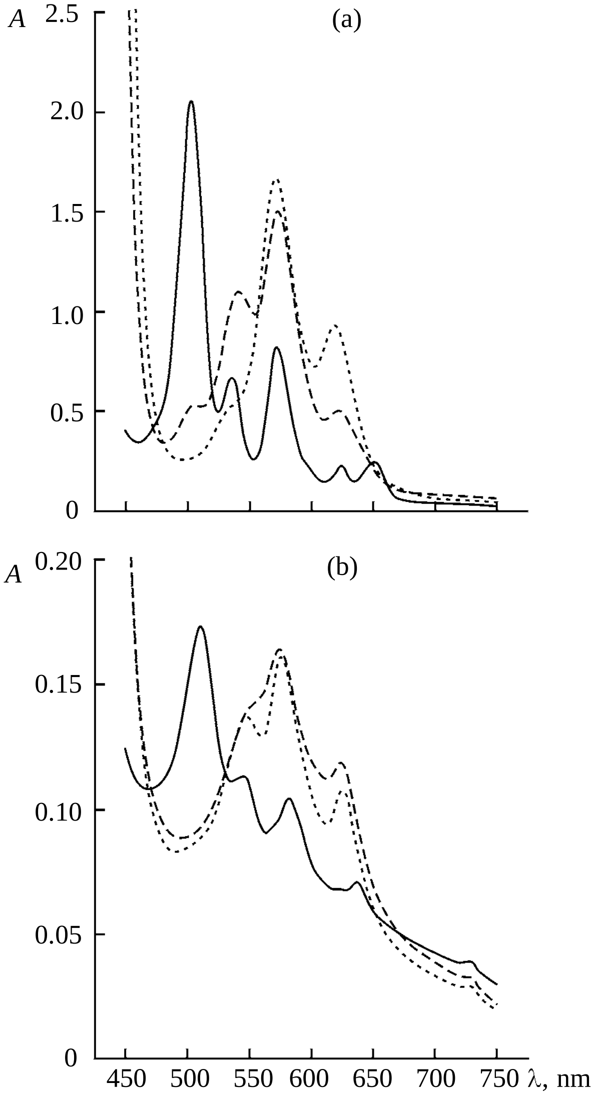


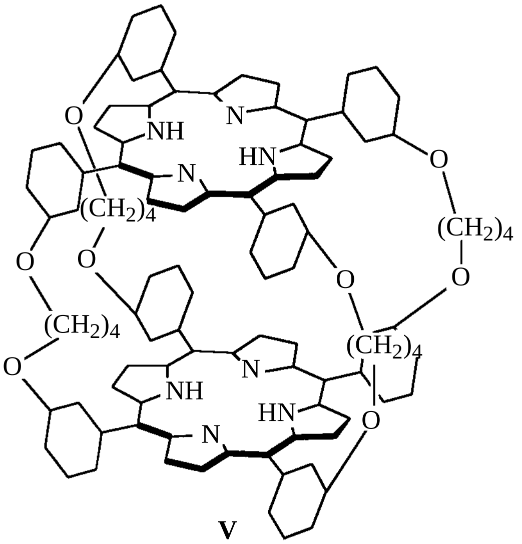
Fig. 1. Changes in the electronic absorption spectra on addition of perchloric acid in acetonitrile. (a) Porphyrin **I** and (b) capped porphyrin **III**.

Porphyrins are rather weak diacid bases, and in acid media they undergo step protonation by tertiary nitrogen atoms [6] to give mono- and dicationic forms according to equilibria (1) and (2).

$$H_3P^+ \xrightleftharpoons{K_3} H_2P + H^+, \tag{1}$$

$$H_4P^{2+} \xrightleftharpoons{K_4} H_3P^+ + H^+. \tag{2}$$

Therewith, the electronic absorption spectra radically change, consecutively passing from four- to three- and two-band. A typical example is shown in Fig. 1.



V

By spectrophotometric titration with perchloric acid in acetonitrile with potentiometric acidity control we measured thermodynamic acid dissociation constants for cationic forms of compounds **I**–**III**. The resulting values are listed in the table. Figure 2 depicts the titration curves of porphyrins **I** and **III**. The number of protons added was determined by inflection points in the titration curves.

In order of increasing basicity the porphyrins studied can be arranged in the following orders: in terms of pK_3: **II** < **I** < **III** < **IV** < **V**; and in terms of pK_4: **I** < **II** < **III** < **IV** < **V**.

Porphyrin **I** is a weaker base than compound **IV**. The difference in their equilibrium constants both by the first and second steps is about two orders of magnitude. Likewise, tetraphenylporphyrin is a stronger base than porphyrin [7, 8]. This is probably associated with the electronic effects of substituted phenyl groups.

In neutral porphyrins, *meso*-phenyl groups are almost perpendicular to the mean plane of the porphyrin nucleus. The electronic effect of these groups is restricted to the –*I* effect that decreases the electron density on tertiary nitrogen atoms, thus rendering the porphyrins less basic. Protonation of the porphyrins substantially violates planarity of the tetrapyrrole macroring, and the latter acquires a puckered conformation which allows conjugation of *meso*-phenyl substituents with the macroring [9]. Thus, the basicity increase in going from compound **I** to compound **IV** is explained by the +*C* effect of *meso*-phenyl substituents in protonated porphyrins.

According to [10, 11], violation of the planarity of the porphyrin macroring results in a slight aromaticity decrease, isolation of the π-electron clouds of pyrrole

Constants, enthalpies, entropies, and Gibbs energies of acid dissociation of protonated forms of porphyrins **I**–**III** in acetonitrile

Comp. no.	pK_i	pK			ΔH, kJ/mol	ΔG^0, kJ/mol	ΔS, J mol^{-1} K^{-1}
		298 K	308 K	318 K			
I	pK_3	7.15 ± 0.10	6.23 ± 0.20	5.23 ± 0.10	174 ± 18	41 ± 5	450 ± 50
	pK_4	8.27 ± 0.10	7.98 ± 0.20	7.43 ± 0.10	78 ± 8	47 ± 5	97 ± 10
II	pK_3	6.75 ± 0.06	6.25 ± 0.05	5.85 ± 0.10	82 ± 8	39 ± 4	147 ± 15
	pK_4	9.68 ± 0.06	8.18 ± 0.05	6.75 ± 0.10	280 ± 30	55 ± 6	740 ± 70
III	pK_3	9.16 ± 0.10	8.25 ± 0.12	7.45 ± 0.20	151 ± 15	52 ± 5	33 ± 3
	pK_4	10.19 ± 0.10	9.45 ± 0.12	8.75 ± 0.20	131 ± 13	58 ± 6	25 ± 3

fragments, and increase in the electron density on tertiaty nitrogen atoms. The puckered, dome-shaped structure of the macrorings in dimer **V**, which arises as a result of strained conformations of bridging groups, is responsible for a much stronger basicity of the dimer (pK_3 12.65 ± 0.25, pK_4 13.77 ± 0.27) compared with monomer **IV** (pK_3 9.21 ± 0.18, pK_4 10.48 ± 0.21).

Molecular mechanics, as well as semiempirical calculations by the MOPAC program (PM3 force field) show that capped porphyrins **II** and **III** in the neutral and protonated forms have uniformly distorted porphyrin macrorings, with C^5 and C^{15} displaced to the benzene “cap,” and C^{10} and C^{20}, in the opposite direction. The increase in pK_4 in going from porphyrin **I** to its capped analog **II** is probably associated with the distortion of the porphyrin nucleus.

Further transfer from compound **II** to compound **III** is accompanied by additional stabilization of the H_3P^+ form. This may be explained by the possibility of hydrogen bonding between the methoxyl oxygen atom of the cap with a proton localized in the reaction center of the porphyrin. The hydrogen bonding turns the cap benzene fragment so that it arranges at a angle of ~75° with respect to the mean plane of the porphyrin nucleus. The screening *para*-phenylene residue in the neutral and protonated forms of porphyrin **II** arranges almost parallel to the mean plane of the aromatic macroring.

It should be noted that the bridging groups of porphyrins **II** and **III** fix *meso*-benzene residues perpendicular the mean plane of the porphyrin nucleus both in the neutral and protonated forms. Therefore, the *meso*-phenyl fragments are no longer able to exhibit +*C* effect, and compounds **II** and **III** are less basic than compound **IV**.

In going from compound **I** to compound **II**, the pK_3 value decreases, whereas pK_4 increases. At the same time, compound **III** is more basic than compound **I**, both in the mono- and diporotonated forms, and the pK_3 values differ from each other as much as pK_4, i.e. two orders of magnitude. This result is likely to be explained by the structural difference of the diprotonated forms of porphyrins **II** and **III**. In compound **III**, the screening dimethoxyphenylene fragment locates at 75° to the mean plane of the porphyrin macroring and creates no impediments to solvation of the reaction center (Fig. 3). The benzene cap in compound **II** locates very close and parallel to the porphyrin nucleus. The distance between these two fragments is ~300 pm, which compares with the size of the π-electron cloud. Obviously, such structure unfavors effective solvation of the diprotonated form of porphyrin **II** and decreases its basicity.

As judged from the Δ*S* values, solvation strongly affects the acid–base properties of porphyrins **I**–**III** in acetonitrile. Their protonation invariably produces negative entropy changes, implying that the systems are highly ordered, probably, owing to additional solvation of these large, readily polarizable molecules.

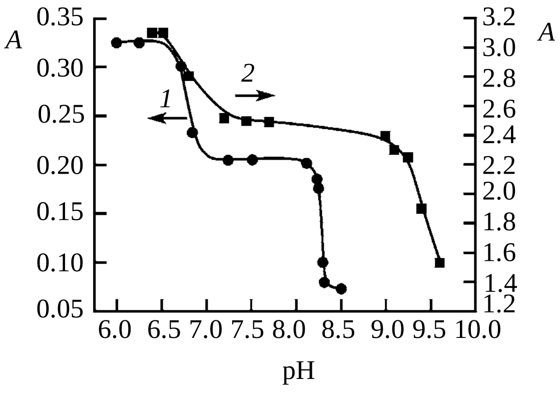


Fig. 2. Titration curves with perchloric acid in acetonitrile. (*1*) Porphyrin **I** and (*2*) porphyrin **III**.

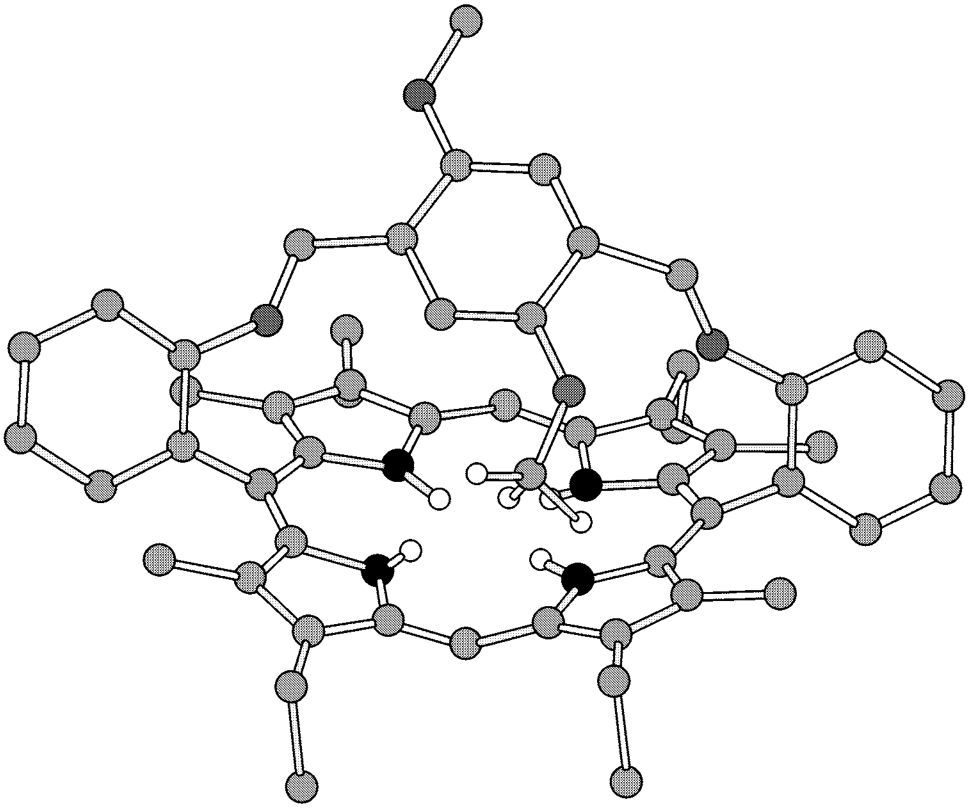


Fig. 3. Structure of a protonated form of capped porphyrin **III**, as given by molecular mechanics calculations (shown are hydrogen atoms in the vicinity of the reaction center).

Mono- and diprotonation of porphyrins **I**–**III** is accompanied by negative enthalpy changes. The ΔH values vary in a complicated fashion with porphyrin structure and protonation degree, on account of the different degrees of solvation of the neutral and protonated forms.

EXPERIMENTAL

5,15-Di(*o*-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin (**I**), capped porphyrins **II** and **III**, tetra(*m*-butoxyphenyl)porphyrin (**IV**), and dimer **V** were prepared as described in [12–15] and purified by repeated column chromatography on Brockmann activity grade III alumina (eluent chlro-form–benzene). The electronic absorption spectra of porphyrins **I**–**V**, measured on a Specord M-400 spectrophotometer, are consistent with published data.

Acetonitrile was purified by the procedure in [16], and its water content, as determined by Fischer titration, was no more than 0.2 wt%. The titrant was perchloric acid with a concetration of 0.001–0.1 M. The porphyrin concentrations in acetonitrile were 10^{-4}–10^{-6} M.

The acid dissociation constants were determined by spectrophotometric titration on an SF-18 instrument with potentiometric control of the pH of the medium, in a temperature-controlled cell by the procedure in [17]. The temperature varied no more than ±0.1 K.

The acid dissociation constants were calculated by Eq. (3).

$$\mathrm{p}K = \mathrm{pH} + \log[(A_0 - A)/(A - A_\infty)]. \qquad (3)$$

Here A_0 is the initial optical density of the porphyrin solution, A is the optical density in the course of titration, and A_∞ is the optical density at the end of titration.

REFERENCES

1. *Porfiriny: struktura, svoistva, sintez* (Porphyrins: Structure, Properties, Synthesis), Enikolopyan, N.S., Ed., Moscow: Nauka, 1987.
2. Collman, J.P., *Acc. Chem. Res.*, 1977, vol. 10, no. 1, p. 265.

3. Golubchikov, O.A., Pukhovskaya, S.G., and Vakhonin, A.V., *Koord. Khim.*, 1993, vol. 19, no. 3, p. 240.
4. Golubchikov, O.A., Lomova, T.N., Kuvshinova, E.M., Korovina, S.G., Klyueva, M.E., Zhilina, Z.I., and Berezin, B.D., *Zh. Fiz. Khim.*, 1989, vol. 63, no. 2, p. 346.
5. Pukhovskaya, S.G., Guseva, L.Zh., Mamardashvili, N.Zh., Kuvshinova, E.M., Semeikin, A.S., and Golubchikov, O.A., *Koord. Khim.*, 1998, vol. 24, no. 11, p. 857.
6. Gurinovich, G.P., Sevchenko, A.N., and Solov'ev, K.N., *Spektroskopiya khlorofilla i rodstvennykh soedinenii* (Spectroscopy of Chlorophyll and Related Compounds), Minsk: Nauka i Tekhnika, 1968.
7. Malkova, O.V., Andrianov, V.G., and Berezin, B.D., *Zh. Org. Khim.*, 1990, vol. 26, no. 11, p. 2440.
8. Ushakova, L.V., *Cand. Sci. (Chem.) Dissertation*, Ivanovo, 1989.
9. Sheinin, V.B., Andrianov, V.G., and Berezin, B.D., *Zh. Org. Khim.*, 1984, vol. 20, no. 10, p. 2224.
10. Golubchikov, O.A., Pukhovskaya, S.G., and Pukhovskii, Yu.P., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1998, vol. 41, no. 5, p. 113.
11. Korovina, S.G., Sheinin, V.B., and Golubchikov, O.A., Abstracts of Papers, *III Vsesoyuznaya konferentsiay po khimii i biokhimii makrotsiklicheskikh soedinenii* (III All-Union Conf. on Chemistry and Biochemistry of Macrocyclic Compounds), Ivanovo, 1988, p. 170.
12. Semeikin, A.S., *Doctoral (Chem.) Dissertation*, Ivanovo, 1995.
13. Mamardashvili, N.Zh., Semeikin, A.S., and Golubchikov, O.A., *Zh. Org. Khim.*, 1993, vol. 29, no. 12, p. 2445.
14. Mamardashvili, N.Zh., Semeikin, A.S., and Golubchikov, O.A., *Zh. Org. Khim.*, 1993, vol. 29, no. 3, p. 391.
15. Golubchikov, O.A., Korovina, S.G., Kuvshinova, E.M., Semeikin, A.S., Shul'ga, A.M., and Perfil'ev, V.A., *Zh. Org. Khim.*, 1988, vol. 24, no. 11, p. 2378.
16. Hofmanova, A. and Angelis, K., *Chem. Listy*, 1978, vol. 72, p. 306.
17. Malkova, O.V., Andrianov, V.G., and Berezin, B.D., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1986, vol. 29, no. 11, p. 37.