ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 4, pp. 673–677. © Pleiades Publishing, Ltd., 2008.
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Synthesis and Basic Properties of Bisporphyrinocalix[4]arene

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Received April 9, 2007

Abstract—A bisporphyrinocalix[4]arene was prepared, and its basicity was examined spectrophotometrically. The protonation of tetrapyrrole fragments of the porphyrinocalixarene conjugate in the ethanol–sulfuric acid system occurs in two steps and is described by the Hammett equation. The ionization constants and the concentration intervals of the formation of the mono- and dicationic forms of the bisporphyrinocalixarene were determined.

DOI: 10.1134/S1070363208040269

The design of molecular receptors for a definite type of substrates is an important problem of the modern chemistry [1–3]. Porphyrins show much promise for this purpose. Selective functionalization of their tetrapyrrole macroring allows creation of spatially preorganized structures in which the required reaction centers can be arranged in a definite steric orientation relative to each other. The presence of a delocalized π-electron system allows the use of tetrapyrrole chromophores as a source of a signal responding to the occurring processes [4, 5].

Protonated porphyrins can be used as molecular receptors for anions. We examined previously [6, 7] the complexing ability of octaalkylporphyrin (H_2P, **I**) toward halide ions (X = Cl^-, Br^-, I^-) in systems (1)–(3) at 298 K:

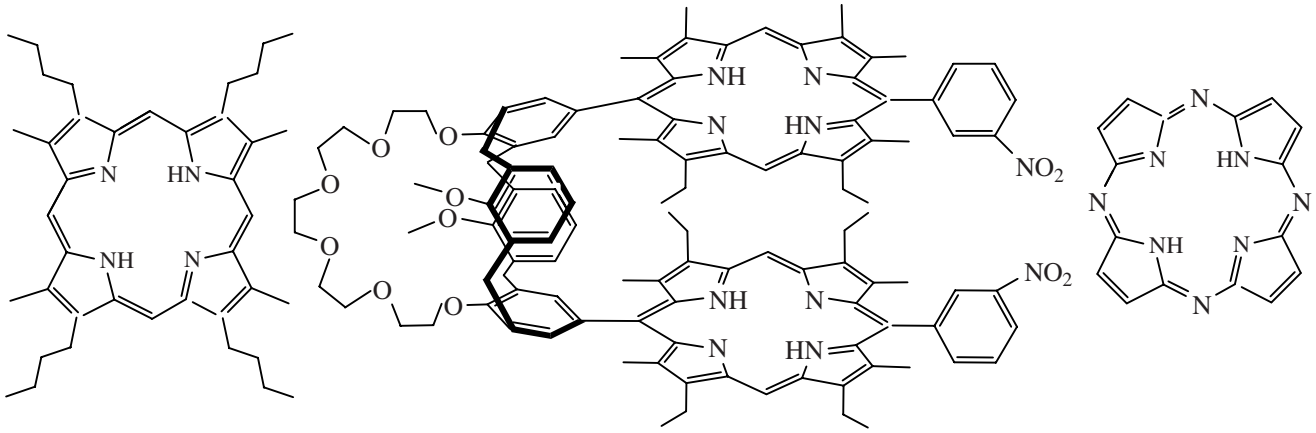
$$H_2P–HClO_4–(C_2H_5)_4NCl–CH_3CN, \quad (1)$$

$$H_2P–HClO_4–(C_2H_5)_4NBr–CH_3CN, \quad (2)$$

$$H_2P–HClO_4–NaI–CH_3CN. \quad (3)$$

We found that the stability of the complexes $(H_3P^+)X^-$ and $(H_4P)^{2+}(X^-)_2$ in acetonitrile increases with a decrease in the radius of the halogen anion (the stability of chloride associates is approximately 100 times higher than that of the bromide and iodide associates). Low binding constants for the bromide and iodide ions are due to larger volume and lower ionic potential of these ions, compared to chloride ion.

It should be noted that, although the results obtained suggest that porphyrins may be suitable as

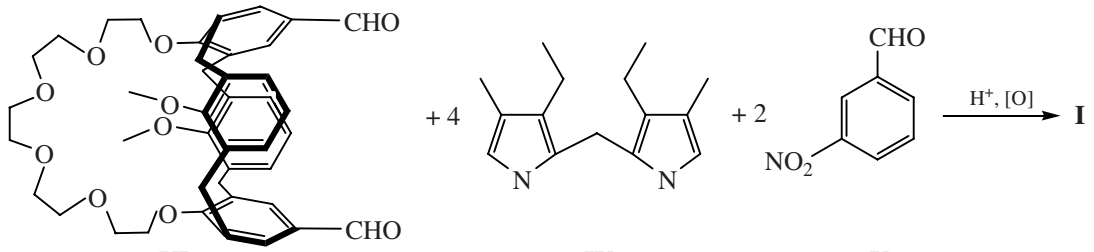


II **I** **III**

receptors for halide ions, the effect of electronic and structural factors on the basicity of porphirins is still poorly understood.

In this study we examined by spectrophotometrictitration the basicity of bis(3,7,13,17-tetramethyl-2,8,12,18-tetraethylporphyrino)calix[4]arene **I** and its monomeric analog, 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin **II**. We found that porphyrins **I** and **II** in the ethanol–sulfuric acid system are protonated in two steps. The process is reasonably well described by the Hammett equation. We determined the ionization constants and the concentration intervals of the formation of the mono- and dicationic forms of the tetrapyrrole bases.

Bisporphyrinocalixarene **I** was prepared by condensation of dipyrrolylmethane **IV** with aldehydes **V** and **VI** in dichloromethane in the presence of trifluoroacetic acid, followed by oxidation of the condensation product with tetrachloro-1,2-benzoquinone:



VI **IV** **V**

The mass spectrum of **I** contains a strong peak of the molecular ion. The electronic absorption spectrum of **I** is characterized by significantly broadened Soret band and decreased molar extinction coefficients, compared to **II**. The hypsochromic shift (by ~5 nm) of the Soret band of **I** compared to **II** also counts in favor of the FTF structure when the π-electron systems of the tetrapyrrole chromophores in the dimer significantly interact with each other. The ^{1}H NMR spectrum of **I** contains signals from protons of the calixarene and porphyrin fragments. The presence of well-defined signals of the methylene protons (two symmetrical doublets at δ ~3.00 and 4.31 ppm) indicates that the calixarene fragment in **I** occurs in the *crown* conformation. It should also be noted that the signals of all the porphyrin fragments in **I** are shifted upfield relative to the corresponding signals of monomeric porphyrin **II**.

As our studies are aimed at design of selective molecular receptors for anions, we performed spectrophotometric titration of **I** and related model compound with the aim to examine how the chemical modification of the tetrapyrrole macroring affects its basicity (the basicity determines the complexing ability of porphyrins toward anions).

One of the most important factors affecting the strength of a base is the nature of the solvent used. The choice of ethanol as a medium is governed in our case by the fact that it is inert toward porphyrin and exhibits the properties of a weak acid and a weak base simultaneously. The ethanol–sulfuric acid system was well studied in the range of acid concentrations from 0.01 to 11.22 M [8]. More than 15 ionization constants [Eq. (4)] were obtained for various diphenylamine derivatives. The corresponding pK^+_{HL} values cover the range from –6.21 (for 4,4'-dinitrodiphenylamine) to +1.36 (for 4-methoxydiphenylamine):

$$pK^+_{HL} = H_0 + \log (C^+_{HL}/C_L). \quad (4)$$

The dependence of the Hammett constant (H_0, acidity function characterizing the proton-donor power of a medium) on the sulfuric acid concentration in the ethanol–sulfuric acid system is described by Eq. (5):

$$H_0 = \frac{2.0482 + 0.7776C(H_2SO_4)}{1 + 8.7975C(H_2SO_4) - 0.2413C^2(H_2SO_4)}, \quad (5)$$

where $C(H_2SO_4)$ is the sulfuric acid concentration, M. The dependence of $\log (C^+_{HL}/C_L)$ on H_0 is a straight line with a slope close to unity.

Among tetrapyrrole compounds, only tetraazaporphine **III** was studied in the ethanol–sulfuric acid system. According to Dolman and Stewart [9], ionization of **III** occurs at one of the four *meso*-N atoms, pK_{bH^+} –0.11. The results of our studies are well con-

sistent with the published data: The dependence of log $[C(H_3P^+)/C(H_2P)]$ on H_0 is a straight line with the slope $\alpha = 0.9994$, i.e., compound **III** can be considered as a Hammett base [8, 10]. The curve of spectrophotometric titration of **III** with sulfuric acid in ethanol has only one step (Fig. 1), i.e., the ionization occurs in one step with pK_{BH^+} –0.13.

A study of the ionization of bisporphyrinocalixarene **I** in the ethanol–sulfuric acid system showed that the corresponding titration curve has two steps (Fig. 2). Spectral changes in the **I**–C_2H_5OH–H_2SO_4 system occur with successive formation of two families of curves, with a set of isobestic points corresponding to each transition (Fig. 3).

By determining the coordinates of the inflection point (i.e., the corresponding sulfuric acid concentration) in the titration curve (Fig. 2), we can distinguish in the electronic absorption spectrum of the reaction system two regions corresponding to the first and second ionization steps, i.e., to the formation of the mono- and diprotonated forms of bisporphyrinocalixarene **I**. The protonation constants for the first and second steps were calculated successively for both processes using Eqs. (6) and (7). The corresponding basicity constants in the ethanol–sulfuric acid system at 298 K are given below:

$$pK_{H_3P^+} = H_0 + \log [C(H_3P^+)/C(H_2P)], \quad (6)$$

$$pK_{H_4P^{2+}} = H_0 + \log [C(H_4P^{2+})/C(H_4P^+)]. \quad (7)$$

Ionization of monomeric porphyrin **II** in the ethanol–sulfuric acid system, as well as the ionization of bisporphyrin **I**, occurs in steps. The spectrophotometric titration curve consists of two portions (Fig. 4). The spectral changes in the **II**–C_2H_5OH–H_2SO_4 system (Fig. 5) allow calculation of the protonation constants for the first and second steps. For **I**, pK_{b1} 2.03, pK_{b2} 2.66; for **II**, pK_{b1} 1.81, pK_{b2} 2.60; and for **III**, pK_{b1} –0.13. The error of determining the constants is ±3–5%.

A decrease in the basicity of dimer **I** compared to monomer **II** may be due to the *meso*-aryl substitution of the tetrapyrrole macroring. The aryl substituents in dimer **I** are arranged perpendicularly to the tetrapyrrole macroring. Hence, the conjugation of the benzene and porphyrin fragments in this case can be neglected. The induction effect of the aryl groups is negative, and their introduction leads to a decrease in the electron density on the tertiary nitrogen atoms of the porphyrin and, as a consequence, to a decrease in the basicity of

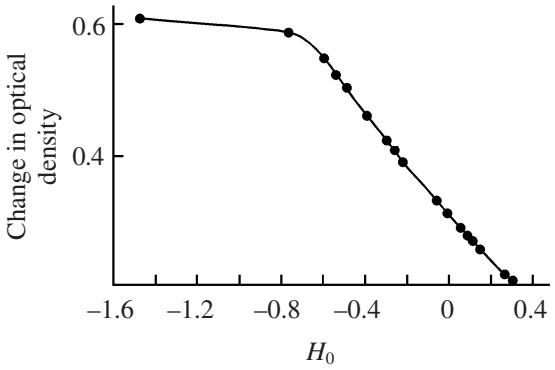


Fig. 1. Spectrophotometric titration curve of **III** (C 0.75 × 10^{-5} M) with sulfuric acid (C 0.4–3.5 M) at λ = 512 nm (absorption increases in the course of titration) in ethanol at 298 K.

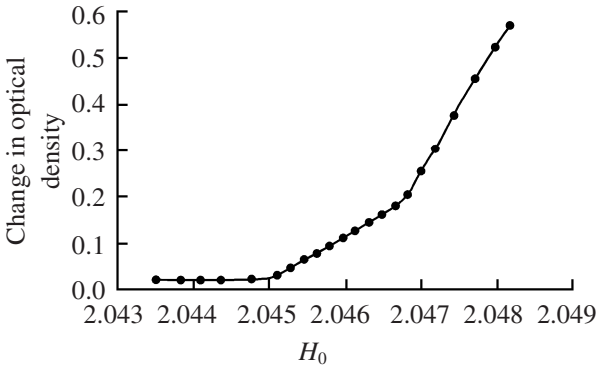


Fig. 2. Spectrophotometric titration curve of **I** (C 1.5 × 10^{-5} M) with sulfuric acid (C 1 × 10^{-5}– 3 × 10^{-4} M) at λ = 496 nm (absorption decreases in the course of titration) in ethanol at 298 K.

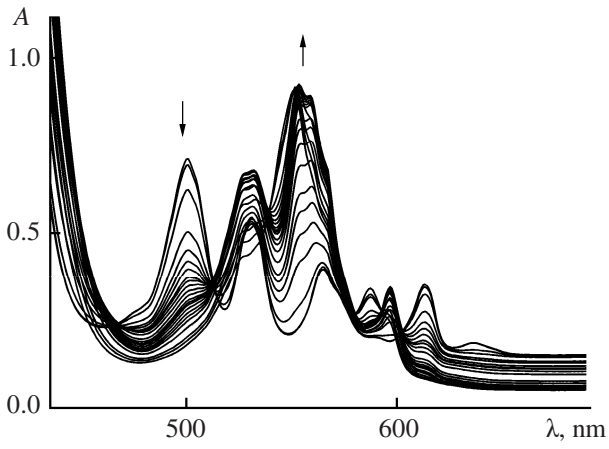


Fig. 3. Evolution of the electronic absorption spectrum of **I** (C 1.5 × 10^{-5} M) in the ethanol–sulfuric acid system (C 1 × 10^{-5} to 3 × 10^{-4} M) at 298 K.

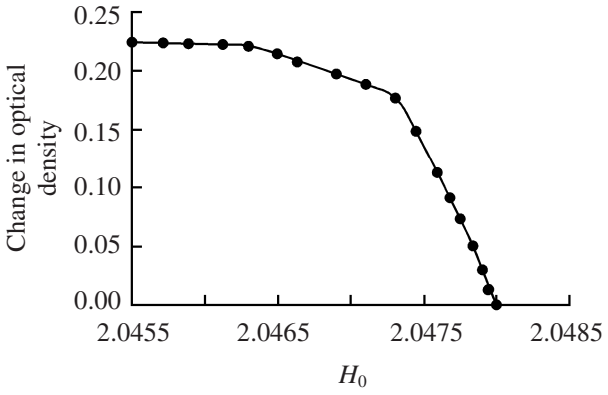


Fig. 4. Spectrophotometric titration curve of **II** (C 1.2×10^{-5} M) with sulfuric acid (C 1×10^{-5}–1.6×10^{-4} M) at λ = 555 nm (absorption increases in the course of titration) in ethanol at 298 K.

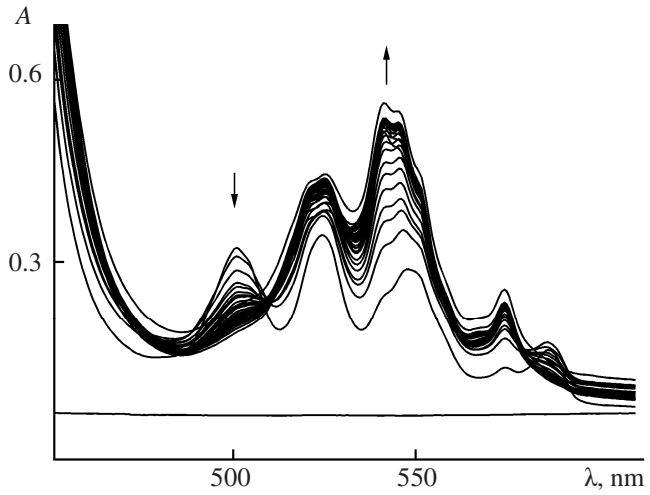


Fig. 5. Evolution of the electronic absorption spectrum of **II** (C 1.2×10^{-5} M) in the ethanol–sulfuric acid system (C 1×10^{-5} to 1.6×10^{-4} M) at 298 K.

the tetrapyrrole macroring. A decrease in $\Delta pK_{1,2}$ in dimer **I** compared to monomer **II** may be due to association of the monocationic form with the acid anion (the counterion is "clamped" between two positively charged macrorings). Enhancement of the specific interactions of the protonated forms of the porphyrins with solution components is accompanied by leveling of the protonation steps. Importance of this phenomenon is determined by high sensitivity of porphyrins to low-energy actions, which provides conditions for the control of processes involving porphyrins.

EXPERIMENTAL

Porphyrin **II** and tetraazaporphine **III** were prepared according to [11]. Spectrophotometric studies of equilibria (8) and (9) in system (10) were performed with a Cary 100 device (Varian).

$$H_2P + H^+ \overset{k_{b1}}{\rightleftharpoons} H_3P^+, \quad (8)$$

$$H_3P^+ + H^+ \overset{k_{b2}}{\rightleftharpoons} H_4P^{2+}, \quad (9)$$

$$H_2P–C_2H_5OH–H_2SO_4. \quad (10)$$

A quartz cell was charged with 50 ml of a ~1.5×10^{-5} M solution of appropriate porphyrin ligand. A 0.01 M solution of sulfuric acid in ethanol was used as titrant. Each change in the acidity was accompanied by a change in the absorption spectrum. The titrant concentration was chosen so that the total change in the solution volume by the end of titration did not exceed 1%. The solution dilution was taken into account by formula (11). Ethanol was purified and dried according to [9].

$$A_c = A_c^0/(1 + \Sigma V/V_0), \quad (11)$$

where A_c is the current optical density after adding the titrant; A_c^0, initial value of the current optical density before adding the titrant; ΣV, total volume of the titrant added; and V_0, initial volume of the ligand solution in the cell.

5,17-Bis[*meso*-(3-nitrophenyl)tetramethyltetraethylporphyrino]-25,27-dimethoxy-26,28-crown[6]calix[4]arene (I). Diformylcalix[4]arene **III** (0.27 g), 4,4'-dimethyl-3,3'-diethyldipyrrolylmethane (**IV**) (0.36 g), and 3-nitrobenzaldehyde (**V**) (0.11 g) were dissolved in 100 ml of dichloromethane. After adding a solution of 68.4 mg of trifluoroacetic acid in 10 ml of dichloro-methane, the mixture was stirred in a CO_2 atmosphere for 1 h and oxidized with a solution of 1.46 g of tetra- chloro-1,2-benzoquinone in 20 ml of dichlorometh- ane. The contents were stirred for 0.5 h, the solvent was evaporated to a volume of 30 ml, and the residue was washed with 10% ammonia. The organic layer was chromatographed on alumina, eluent

methylene chloride–hexane, 1 : 1. Yield of the target product 51.6 mg (5%), R_f 0.53 (Al_2O_3, eluent CH_2Cl_2–C_6H_{14}, 1 : 2). Electronic absorption spectrum (ethanol), λ_{max}, nm (log ε): 403.3 (4.91), 505.6 (4.03), 541.5 (3.60), 572.1 (3.73), 629.4 (3.21). ^{1}H NMR spectrum, δ, ppm: 10.08 s (4H, *ms*-H), 7.92–7.82 m (4H, $Ar_{ortho,\ porph}$ + 4H, $Ar_{calixarene}$), 7.63–7.41 m (2H, $Ar_{meta,\ porph}$ + 4H, $Ar_{calixarene}$), 7.26 d (2H, $Ar_{para,porph}$), 7.01 t (2H, $Ar_{para,\ calixarene}$), 4.40 s (6H, OCH_3), 4.31 d (4H, $ArCH_2Ar$), 3.85 q (8H, CH_2CH_3), 3.79 m (8H, CH_2CH_3), 3.70 s (4H, OCH_2CH_2O), 3.64 m (16H, OCH_2CH_2O), 3.00 d (4H, $ArCH_2Ar$), 2.05 s (12H, CH_3), 2.14 s (12H, CH_3), 1.05 t (12H, CH_2CH_3), 0.91 t (12H, CH_2CH_3), –2.81 s (4H, NH). Mass spectrum, *m/e* (I_{rel}, %): 1940.01 (81), M^+. Found, %: C 75.39; H 7.42; N 7.16. $C_{122}H_{145}N_{10}O_{12}$. Calculated, %: C 75.43; H 7.47; N 7.21.

3,7,13,17-Tetramethyl-2,8,12,18-tetrabutylporphyrin II. R_f 0.71 (Al_2O_3, eluent CH_2Cl_2–C_6H_{14}, 1 : 2). Electronic absorption spectrum (ethanol), λ_{max}, nm (log ε): 408.1 (5.09), 507.6 (4.27), 542.7 (3.78), 572.9 (3.61), 629.7 (3.34). ^{1}H NMR spectrum, δ, ppm: 9.87 s (4H, *ms*-H), 3.85 t (8H, $CH_2CH_2CH_2CH_3$), 3.41 quintet (8H, $CH_2CH_2CH_2CH_3$), 2.15 s (12H, CH_3), 1.61 m (8H, $CH_2CH_2CH_2CH_3$), 0.91 t (12H, $CH_2CH_2CH_2CH_3$), –3.01 s (2H, NH).

ACKNOWLEDGMENTS

The study was financially supported by the Russian Foundation for Basic Research (project nos. 05-03-32 055-a and 06-03-81 001-Bel-a) and Program no. 7 of the Division of Chemistry and Materials Science, Russian Academy of Sciences "Chemistry and Physical Chemistry of Supramolecular Systems and Clusters."

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