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Synthesis and Basic Properties of Tetra-*tert*-butyltetrabenzo-5,10,15-triazaporphyrin

Yu. B. Ivanova[a], Yu. I. Churakhina[a], A. S. Semeikin[b], and N. Zh. Mamardashvili[a]

[a] *Institute of Solution Chemistry, Russian Academy of Sciences, ul. Akademicheskaya 1, Ivanovo, 153045 Russia*
e-mail: ybi@isc-ras.ru

[b] *Ivanovo State University of Chemical Technology, Ivanovo, Russia*

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Abstract—$2^2,7^2,12^2,17^2$-Tetra-*tert*-butyltetrabenzo-5,10,15-triazaporphyrine was synthesized, and its basic properties were studied by spectrophotometric titration. It was found that in the system ethanol–sulfuric acid nitrogen atoms in the tetrapyrrole macroring undergo protonation in three steps. The corresponding ionization constants and concentration ranges for mono-, di-, and tricationic forms of the examined compound were determined.

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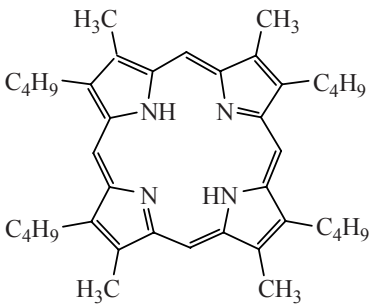
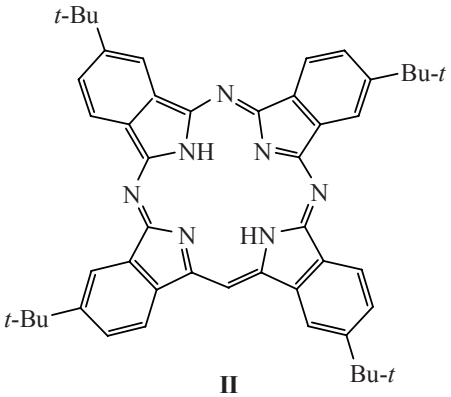
Development of new efficient procedures for detection of chemical compounds in various media with the aid of molecular sensors constitutes an important problem in modern chemistry. The main parameters determining the efficiency of any chemosensor are physicochemical properties of a compound (source of analytical signal), which indicate recognition of one or another substrate [1, 2]. Tetrapyrrole derivatives may be used to transform primary analytical signals into optical response. For example, porphyrins can be used to detect anions in solution. Protonated forms of tetrapyrrole compounds are capable of forming complexes with acid anions through hydrogen bonds.

We previously studied the possibility of using protonated porphyrins as receptors for halide ions (Hlg^-) [3]. The results of direct titration of singly (H_3P^+) and doubly protonated species (H_4P^{2+}) of 3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin (**I**, H_2P) with halide salt solutions revealed formation of stable complexes $H_3P^+ \cdot Hlg^-$ and $H_4P^{2+} \cdot 2\,Hlg^-$ in acetonitrile, and their stability constants were determined at 298 K. Fluorescence of porphyrin molecules in a solution containing halide ions was effectively quenched in keeping with the internal and external heavy atom effects. Analysis of the dependences of the fluorescence intensity and lifetime on the concentration of iodide ions in solution showed that H_4P^{2+} may be used as fluorescent receptor for halide ions [4].

In the present work we synthesized $2^2,7^2,12^2,17^2$-tetra-*tert*-butyltetrabenzo-5,10,15-triazaporphyrine (**II**)



I



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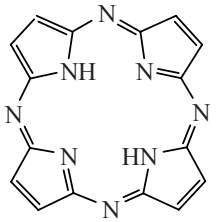


III

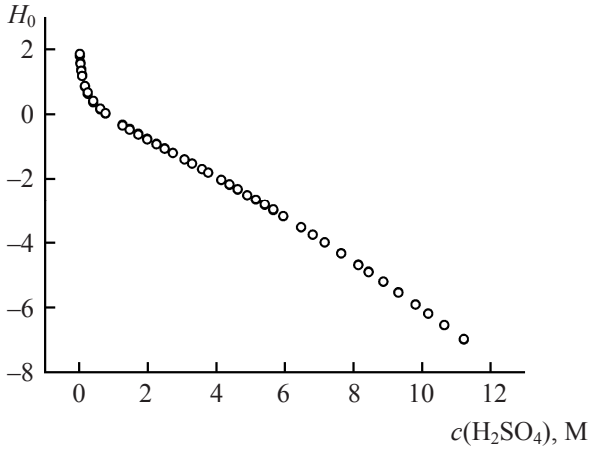


Fig. 1. Plot of the Hammett acidity function H_0 vs. sulfuric acid concentration $c(H_2SO_4)$ (M) in the system ethanol–sulfuric acid for diphenylamine derivatives [5].

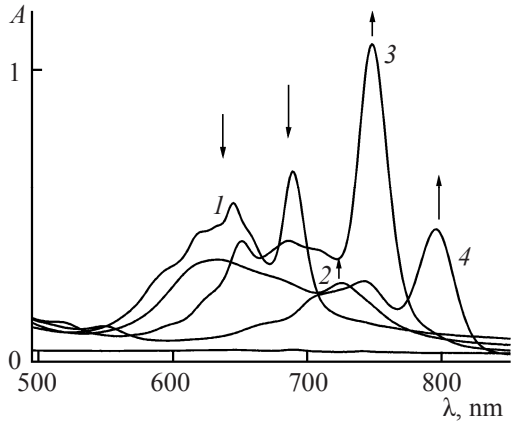


Fig. 2. Electronic absorption spectra of (*1*) neutral H_2BP and its (*2*) singly (H_3BP^+), (*3*) doubly (H_4BP^{2+}), and (*4*) triply protonated species (H_5BP^{3+}) in the system ethanol–sulfuric acid; $c_{porph} = 1.5 \times 10^{-5}$, $c(H_2SO_4) = 0.0$–3.85 M.

and examined its basic properties. We found that in the system ethanol–sulfuric acid the tetrapyrrole macroring in **II** is protonated at nitrogen atoms in three steps. We estimated the corresponding ionization constants and concentrations ranges for singly, doubly, and triply protonated species.

Porphyrin **II** magnesium complex was obtained by heating a mixture of 4-*tert*-butylphthalonitrile, metallic magnesium, and methyl iodide in anhydrous diethyl ether in the presence of iodine. The complex was converted into free base **II** (H_2BP) by treatment with trifluoroacetic acid. Compound **II** was purified by column chromatography on aluminum oxide of activity grade III according to Brockmann (eluent chloroform). The electronic absorption and mass spectra of porphyrin **II**, as well as its elemental composition, were fully consistent with the assumed structure.

Solvent nature is an important factor affecting the basicity of compounds. Ethanol was selected as a medium, taking into account its inertness with respect to porphyrin **II** and amphoteric properties (it is both weak acid and weak base). The system ethanol–sulfuric acid with the acid concentration ranging from 0.01 do 11.22 M was studied in detail [5, 6]. More than 15 ionization constants were found [Eq. (1)] for different diphenylamine derivatives, and the pK_{HL^+} values covered the range from –6.21 (4,4'-dinitrodiphenylamine) to +1.36 (for 4-methoxydiphenylamine).

$$pK_{HL^+} = H_0 + \log (c_{HL^+}/c_L). \quad (1)$$

Figure 1 shows the plot of the Hammett acidity function H_0 that characterizes proton-donor power of a medium versus sulfuric acid concentration in the system $EtOH–H_2SO_4$, which is described by Eq. (2):

$$H_0 = \frac{2.0482 + 0.7776c(H_2SO_4)}{1 + 8.7975c(H_2SO_4) - 0.2413c_2(H_2SO_4)}. \quad (2)$$

Here, $c(H_2SO_4)$ is the concentration of sulfuric acid (M). The $\log [c(H_3BR^+)/c(H_2BR)]$ dependence on H_0 is a straight line with a slope equal to unity.

Porphyrin H_2BP in acid medium gives rise to three kinds of species differing by the position and intensity of absorption maxima in the electronic spectra (Fig. 2). Theoretically, acid–base interactions could involve two pyrrole nitrogen atoms and one to three *meso*-nitrogen atoms in molecule **II**. Spectrophotometric titration of H_2BP in ethanol–sulfuric acid showed that protonation of the tetrapyrrole macroring was accompanied by successive (as the concentration of sulfuric acid rises) appearance of three families of spectral curves, each being characterized by its own set of isosbestic points (Figs. 3–5). In the range of sulfuric acid concentration from 0.01 to 1.80 M we observed one jump on the titration curve (Fig. 6), indicating formation of singly protonated triazaporphyrin species according to equilibrium (3).

$$H_2BP + H^+ \underset{}{\overset{k_{b1}}{\rightleftharpoons}} H_3BP^+. \quad (3)$$

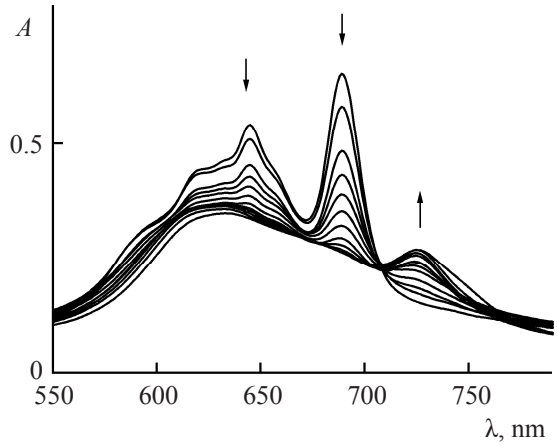


Fig. 3. Variation of the electronic absorption spectra of the system H_2BP–C_2H_5OH–H_2SO_4; $c_{porph} = 1.5 \times 10^{-5}$, $c(H_2SO_4)$ = 0.01–1.80 M.

This is consistent with published data for *meso*-tetrazaporphyrin **III**. As shown in [7], compound **III** is protonated at one of the four *meso*-nitrogen atoms (K_{b1} = 0.74). The site of protonation of molecule **II** (i.e., *meso*-nitrogen atom) follows from the character of variation of the spectral pattern in going from H_2BP to H_3BP^+ (Fig. 2). As the concentration of sulfuric acid increases to 1.8 M, the two-band absorption spectrum of H_2BP is transformed into one-band spectrum; the intensity of the remaining absorption band decreases, and it becomes strongly broadened (Fig. 3).

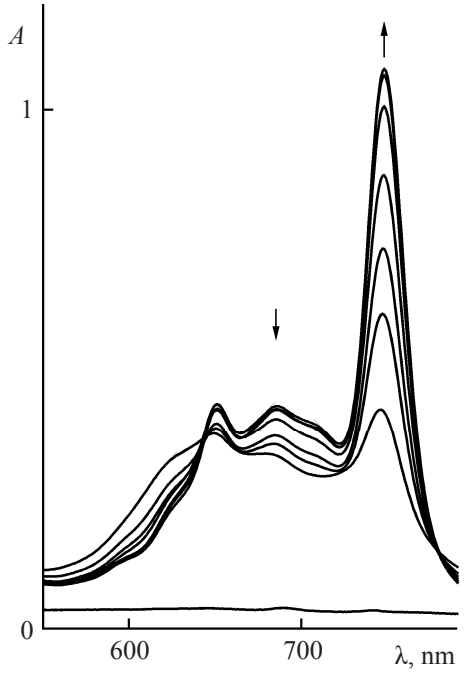


Fig. 4. Variation of the electronic absorption spectra of the system H_2BP–C_2H_5OH–H_2SO_4; $c_{porph} = 1.5 \times 10^{-5}$, $c(H_2SO_4)$ = 1.81–3.30 M.

According to published data [8], the observed variation in the spectral pattern results from rupture of π-conjugation in the tetrapyrrole chromophore due to protonation of the *meso*-nitrogen atom which is forced

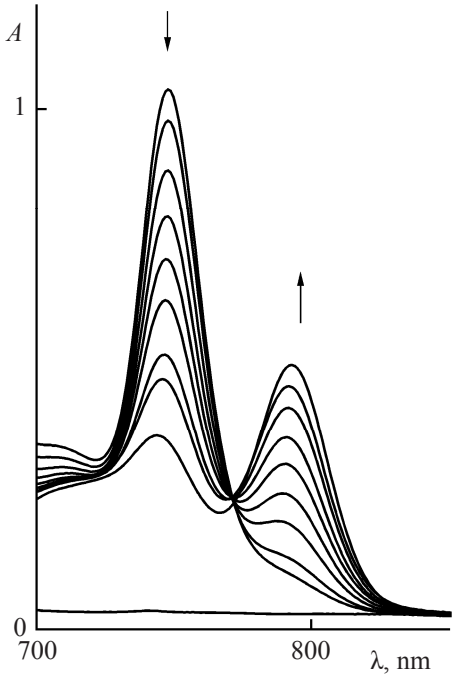


Fig. 5. Variation of the electronic absorption spectra of the system H_2BP–C_2H_5OH–H_2SO_4; $c_{porph} = 1.5 \times 10^{-5}$, $c(H_2SO_4)$ = 3.31–3.82 M.

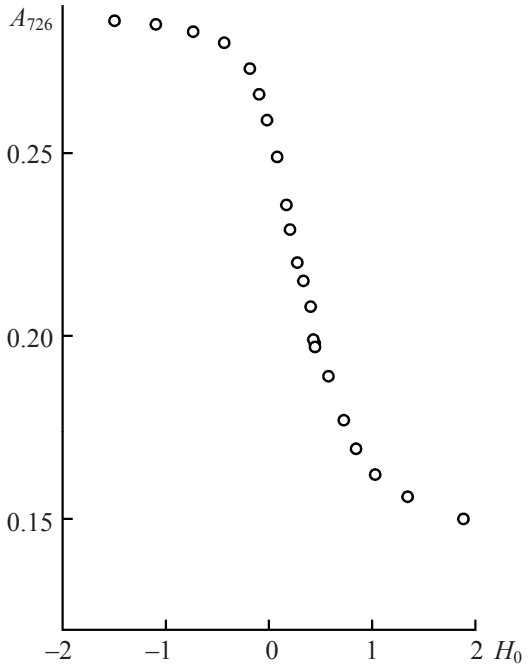
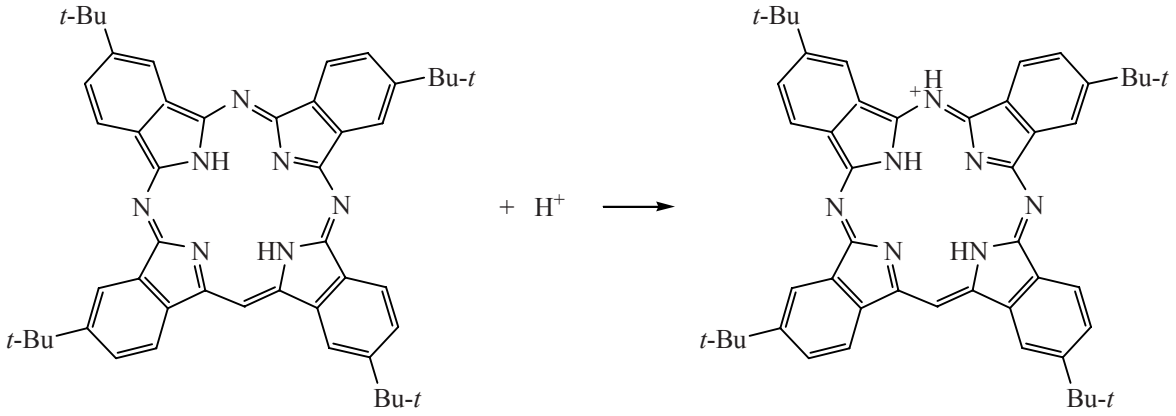


Fig. 6. Spectrophotometric titration of H_2BP ($c_{porph} = 1.5 \times 10^{-5}$ M) with sulfuric acid [$c(H_2SO_4)$ = 0.01–1.80 M] in ethanol; λ = 726 nm, 298 K.

Scheme 1.



out from conjugation. Thus the first step of protonation of H_2BP may be represented by Scheme 1.

Further raising the acid concentration in the system $H_2BP–C_2H_5OH–H_2SO_4$ gives rise to a family of absorption curves with one isosbestic point (Fig. 7). The titration curve has one jump in the sulfuric acid concentration range from 1.81 to 3.30 M (Fig. 8), and the corresponding acid–base interaction is described by equilibrium (4).

$$H_3BP^+ + H^+ \overset{k_{b2}}{\rightleftharpoons} H_4BP^{2+}. \quad (4)$$

The broad low-intense absorption band at λ 725 nm is transformed into a strong band with its maximum at λ 748 nm (Fig. 4). In keeping with the data of [9], this pattern is typical of protonation of pyrrole nitrogen atom (Scheme 2). Analogous results were obtained for protonation of H_4BP^{2+} in the sulfuric acid concentration range from 3.31 to 3.82 M [Fig. 5, 9; equilibrium (5); Scheme 3].

$$H_4BP^+ + H^+ \overset{k_{b3}}{\rightleftharpoons} H_5BP^{3+}. \quad (5)$$

We can conclude that, like tetramethyltetrabutylporphyrin **I** [2], triazaporphyrin **II** in the system $C_2H_5OH–H_2SO_4$ containing 1.81 to 3.82 mol l^{-1} of sulfuric acid undergoes successive protonation at one *meso*-nitrogen atoms and two pyrrole nitrogen atoms. On the basis of variations in the spectral patterns of the $H_2BP–C_2H_5OH–H_2SO_4$ systems (Figs. 3–5) we cal-

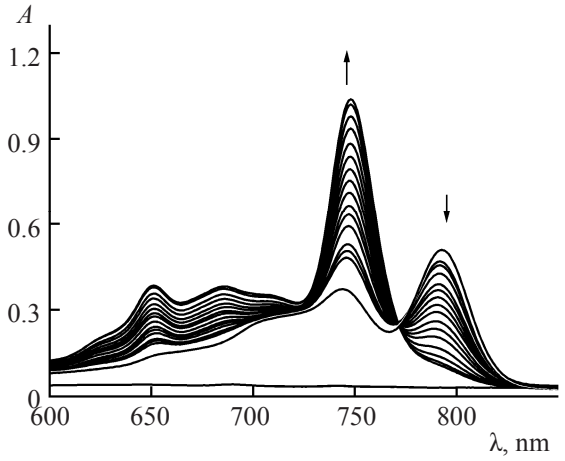


Fig. 7. Variation of the electronic absorption spectra of the system $H_2BP–C_2H_5OH–H_2SO_4$; $c_{porph} = 1.5 \times 10^{-5}$, $c(H_2SO_4)$ = 1.81–3.82 M.

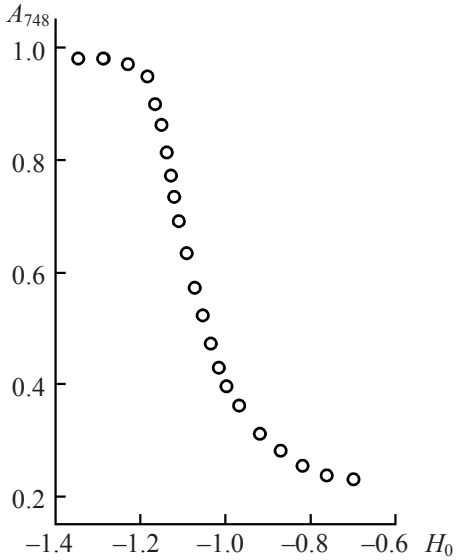
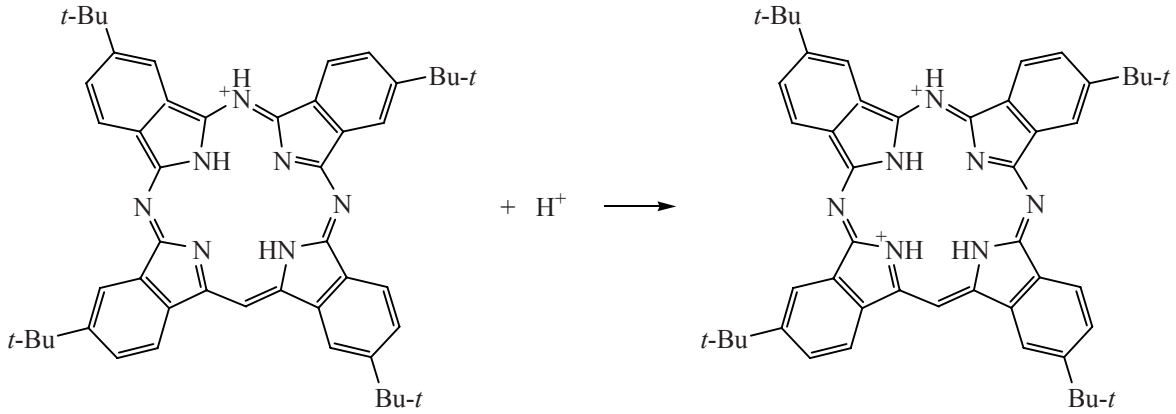
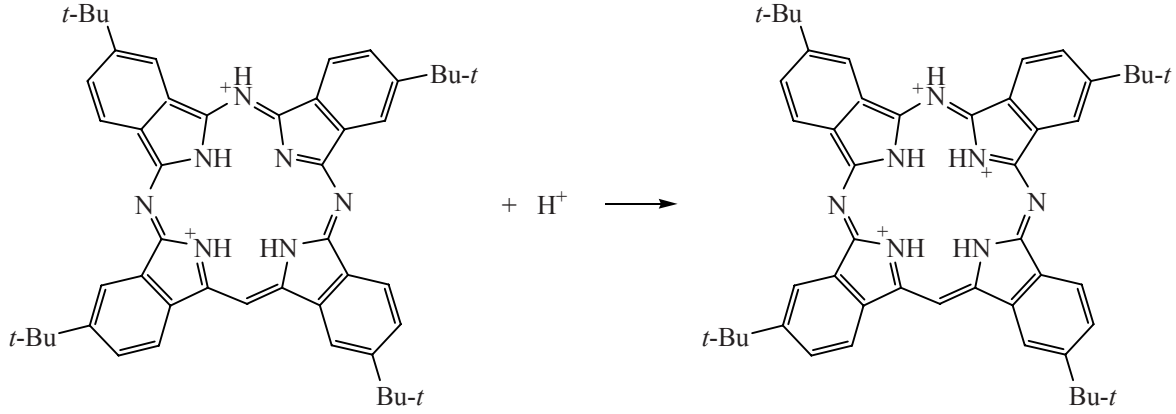


Fig. 8. Spectrophotometric titration of H_2BP (c_{porph} = 1.5 × 10^{-5} M) with sulfuric acid [$c(H_2SO_4)$ = 1.81–3.30 M] in ethanol; λ = 748 nm, 298 K.

Scheme 2.



Scheme 3.



culated the equilibrium constants for the formation of protonated species H_3BP^+, H_4BP^{2+}, and H_5BPH^{3+} using Eqs. (6)–(8).

$$pK_{b1} = H_0 + \log [c(H_3BP^+)/c(H_2BP)]; \quad (6)$$

$$pK_{b2} = H_0 + \log [c(H_4BP^{2+})/c(H_3BP^+)]; \quad (7)$$

$$pK_{b3} = H_0 + \log [c(H_5BPH^{3+})/c(H_4BP^{2+})]. \quad (8)$$

The calculated constants [$c_{\mathbf{II}} \approx 1.5 \times 10^{-5}$ M, $c(H_2SO_4)$ = 0.01–3.82 M] are given below:

Porphyrin	**I**	**II**	**III**
K_{b1}	–	1.86	0.74
K_{b2}	398	0.08	–
K_{b3}	64.52	0.045	–

It is seen that the constant for formation of monocation H_3BP^+ (protonation at the *meso*-nitrogen atom) is higher by a factor of ~20 than the constant for formation of dication H_4BP^{2+} (protonation at the pyrrole nitrogen atom) and that protonation of the second pyrrole nitrogen atom is approximately twice as difficult as proton addition to the first pyrrole nitrogen atom. This is very consistent with published data [10]. Each protonation step is characterized by a strong response in the visible region of the electronic absorption spectrum, which provides the possibility for controlling properties of the tetrapyrrole chromophore by varying the acidity of the medium. Our results show that $2^2,7^2,12^2,17^2$-tetra-*tert*-butyltetrabenzo-5,10,15-triazaporphyrine (**II**) may be regarded as basis structure for the design of pH-switchable molecular device for detection of anions in solution.

EXPERIMENTAL

The electron-impact (70 eV) mass spectrum was obtained on an MKh-1310 instrument (ion source temperature 150–200°C). Spectrophotometric titration of triazaporphyrin **II** with sulfuric acid in ethanol was performed on a Varian Cary 100 spectrophotometer. The experimental procedure and procedure for data processing were described in [4]. The error in the determination of the protonation constants was ±(3–5)%.

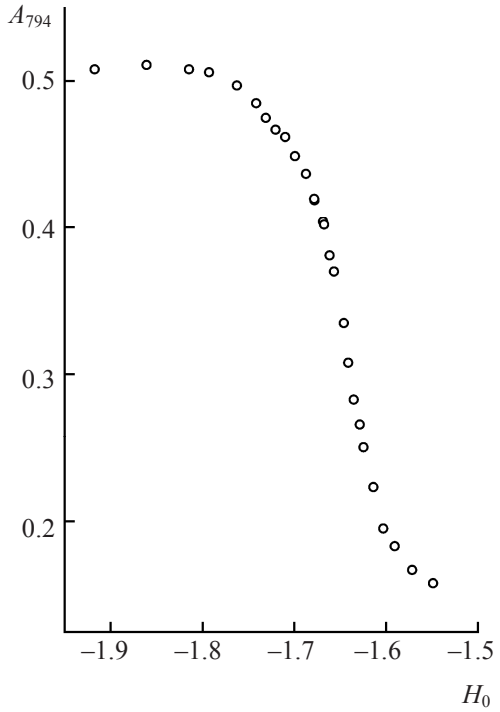


Fig. 9. Spectrophotometric titration of H_2BP (c_{porph} = 1.5 × 10^{-5} M) with sulfuric acid [$c(H_2SO_4)$ = 3.31–3.82 M] in ethanol; λ = 794 nm, 298 K.

2^2,7^2,12^2,17^2-Tetra-*tert*-butyltetrabenzo-5,10,15-triazaporphyrin (II). A small crystal of iodine and 0.25 ml of methyl iodide were added to a suspension of 0.1 g of magnesium in 30 ml of anhydrous diethyl ether, and the mixture was heated under reflux until complete dissolution of magnesium. A solution of 1.0 g of 4-*tert*-butylphthalonitrile in 30 ml of anhydrous diethyl ether was added, the mixture was heated for 0.5 h under reflux, the solvent was distilled off to dryness, and 20 ml of anhydrous quinoline was added to the residue. The mixture was heated for 1 h under reflux, cooled, and diluted with 50 ml of dilute hydrochloric acid (1 : 5 by volume). The precipitate was filtered off, washed with water, and dried in air at 70°C. The product was dissolved in chloroform and subjected to column chromatography on aluminum oxide of activity grade III according to Brockmann using chloroform as eluent. The first blue fraction contained magnesium complex of triazoporphyrin **II**, and the second fraction contained magnesium complex of tetra-*tert*-butylphthalocyanine. The second fraction was evaporated to a minimal volume and subjected to repeated chromatography on silica gel, the first fraction being collected. The solvent was distilled off under reduced pressure, the residue was dissolved in 5 ml of trifluoroacetic acid, and the solution was heated for 5 min under reflux. It was then cooled and diluted with 50 ml of water. The precipitate was filtered off, washed with water, and dried in air at 70°C. The product was dissolved in chloroform and subjected to chromatography on aluminum oxide of activity grade III according to Brockmann usinf chloroform as eluent. The eluate was evaporated to a minimal volume, and porphyrin **II** was precipitated by adding 50 ml of methanol. Yield 129 mg (12%). Electronic absorption spectrum (ethanol), λ_{max}, nm (log ε): 689.1 (4.24), 645.2 (4.17). Mass spectrum: *m*/*z* 736.81 (I_{rel} 67%) $[M]^+$. Found, %: C 79.72; H 6.92; N 13.25. $C_{49}H_{51}N_7$. Calculated, %: C 79.75; H 6.96; N 13.29.

ACKNOWLEDGMENTS

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REFERENCES

1. Ogoshi, H., Mizutani, T., Hayashi, T., and Kuroda, Y., *The Porphyrin Handbook*, Kadish, K.M., Smith, K.M., and Guilard, R., Eds., San Diego: Academic, 2000, vol. 6, p. 280.
2. Sanders, J.K.M., *The Porphyrin Handbook*, Kadish, K.M., Smith, K.M., and Guilard, R., Eds., San Diego: Academic, 2000, vol. 3, p. 47.
3. Kruk, N.N., Starukhin, A.S., Mamardashvili, N.Zh., Sheinin, V.B., and Ivanova, Yu.B., *Zh. Prikl. Spektrosk*., 2007, vol. 74, no. 6, p. 750.
4. Ivanova, Yu.B., Churakhina, Yu.I., and Mamardashvili, N.Zh., Abstracts of Papers, *VII Shkola-konferentsiya molodykh uchenykh stran CHG po khimii porfirinov i rodstvennykh soedinenii* (VIIth School–Conf. of Young Scientists from UIS Countries on the Chemistry of Porphyrins and Related Compounds), Odessa, September 7–10, 2007, p. 86.
5. Dolman, D. and Stewart, R., *Can. J. Chem*., 1967, vol. 45, no. 9, p. 903.
6. Gordon, A.J. and Ford, R.A., *The Chemist's Companion*, New York: Wiley, 1972.
7. Berezin, B.D., Stuzhin, P.A., and Khelevina, O.G., *Khim. Geterotsikl. Soedin*., 1986, no. 12, p. 1677.
8. Dzilin'ski, K.,Vrublevskii, A.I., Sinyakov, G.N., and Gurinovich, G.P., *J. Appl. Spectrosc*., 1980, vol. 33, no. 1, p. 114.
9. Stone, A. and Fleischer, E.S., *J. Am. Chem. Soc*., 1968, vol. 90, no. 11, p. 2735.
10. 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, p. 520.