ISSN 1070-3632, Russian Journal of General Chemistry, 2015, Vol. 85, No. 3, pp. 640–647. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © Yu.B. Ivanova, N.Zh. Mamardashvili, A.V. Glazunov, A.S. Semeikin, 2015, published in Zhurnal Obshchei Khimii, 2015, Vol. 85, No. 3, pp. 478–485.

Synthesis and Spectrophotometric Study of Acidic and Complexing Properties of 5,15-Bis(4'-methoxyphenyl)-10,20-bis(4''-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyn in Acetonitrile

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

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

[b] *Ivanovo State University of Chemical Technology, pr. Sheremetevskii 7, Ivanovo, 153000 Russia*

Received October 6, 2014

Abstract—5,15-Bis(4'-methoxyphenyl)-10,20-bis(4''-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyne was synthesized and studied spectrophotometrically in the systems 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile, $Zn(OAc)_2$–acetonitrile, 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile. The orders of acidity and kinetic activity were obtained for methoxyphenyl alkyl derivatives of porphyrins in these systems.

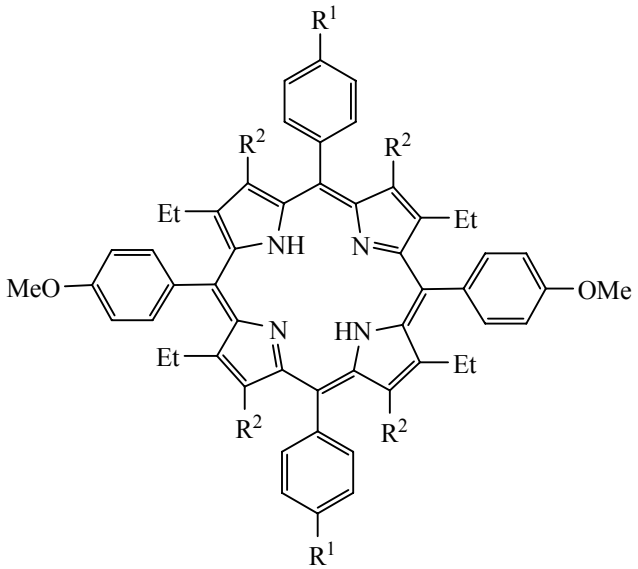
Keywords: porphyrins, acid-base properties, substituent electronic effects, structure

DOI: 10.1134/S1070363215030196

Structural diversity of complex tetrapyrrole compounds originates from the necessity of synthesis of compounds with predetermined properties [1, 2]. The introduction of various substituents into the porphyrin molecule substantially affects the physicochemical properties of the macrocycle by changing the geometry of the molecule, its acid-base properties and complexing ability [3–7]. Variation of the number and type of the substituents in porphyrin allows the regulation of the required physicochemical properties of the molecule, in particular, its electronic and steric effects.

Earlier, we have obtained the results of the spectrophotometric investigation of acidic and complexing properties of methoxyphenyl alkyl derivatives of porphyn **I, II** containing substituents of different nature [8, 9]. In continuation of these studies, in the present work we present the results of synthesis and spectrophotometric study of the acidic and complexing properties of 5,15-bis(4'-methoxyphenyl)-10,20-bis(4''-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyn (**III**) in the systems 1,8-diazabicyclo[5.4.0]-undec-7-ene–acetonitrile, $Zn(OAc)_2$–acetonitrile, 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile at 298–318 K (Scheme 1).

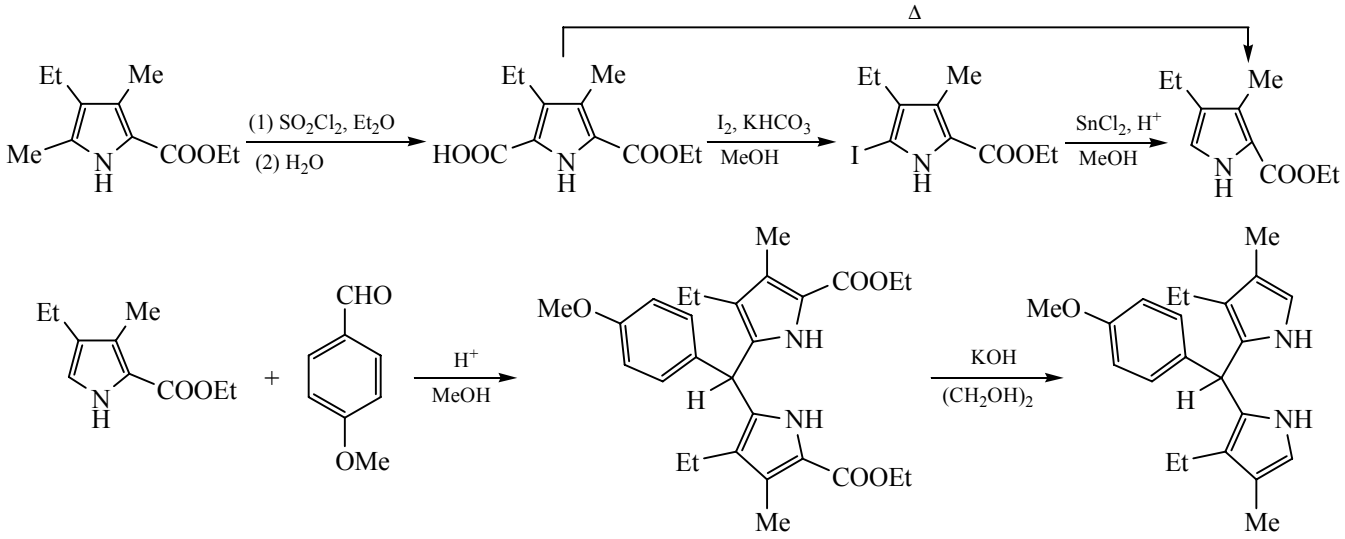
Scheme 1.



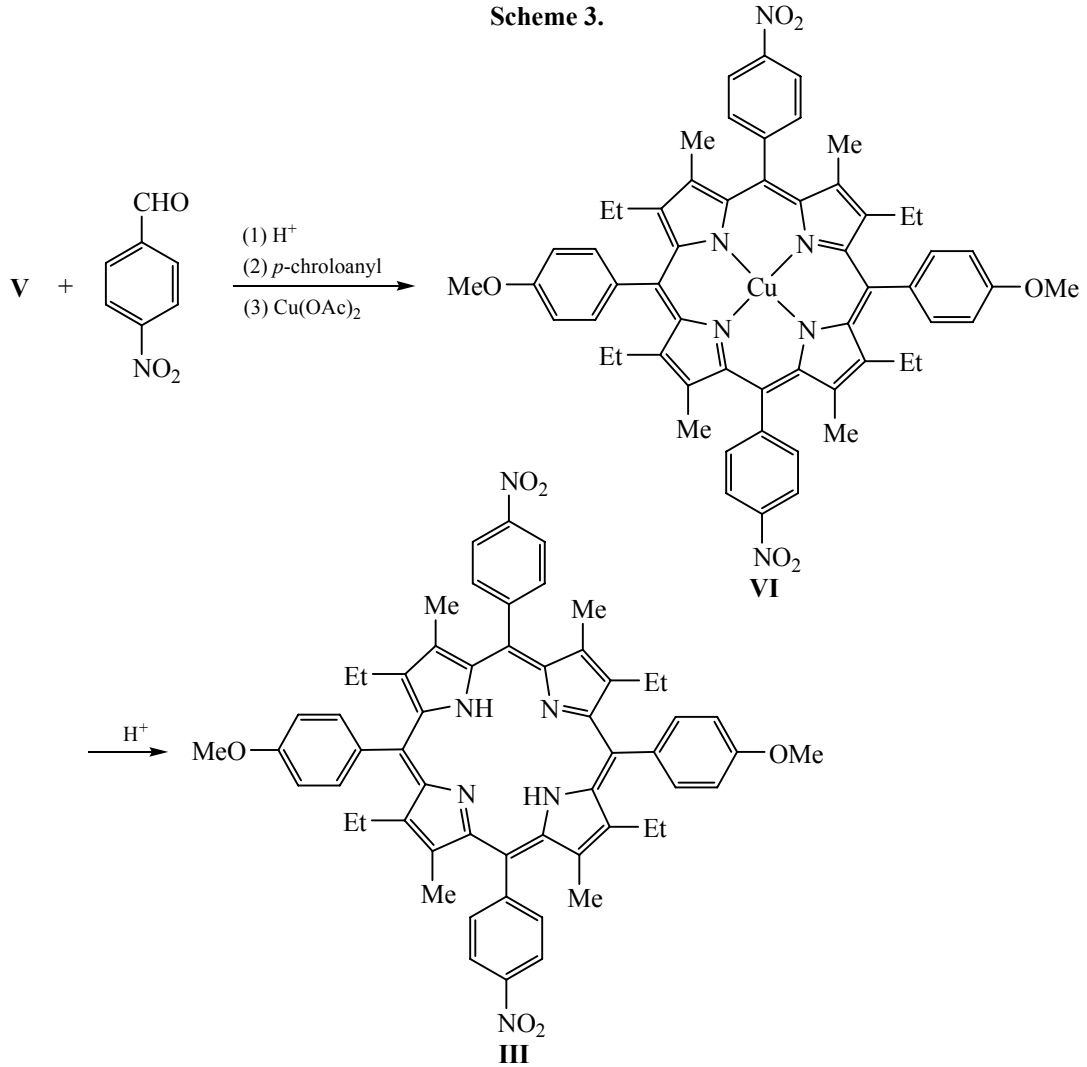
I–III

R^1 = H, R^2 = Me (**I**); R^1 = OMe, R^2 = Et (**II**); R^1 = NO_2, R^2 = Me (**III**).

Scheme 2.



Scheme 3.



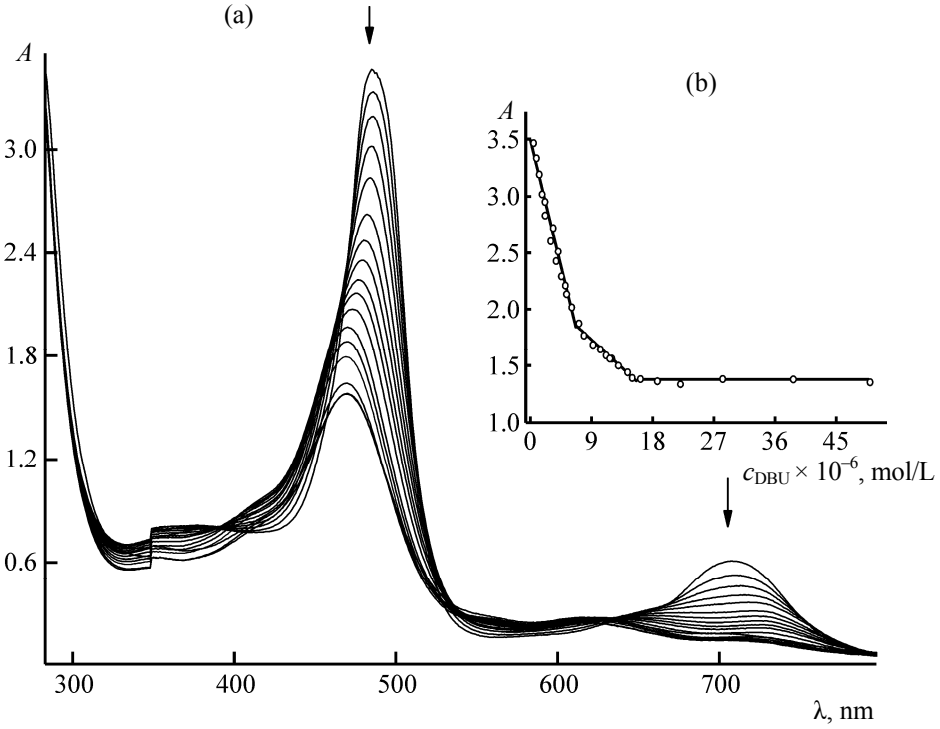


Fig. 1. Variations in electron absorption spectra (a) and spectrophotometric titration curve (λ = 485 nm) (b) of compound **III** in the system 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile, (c_{porph} = 1.01 × 10^{-5} mol/L; c_{DBU} 0–5.01 × 10^{-5} mol/L), 298 K.

The spatially distorted porphyrin of the ABAB type I was synthesized in total yield of 7.4% (with respect to dipyrrolylmethane **IV**) by condensation of 5,5'-unsubstituted dipyrrolylmethane **V** with 4-nitrobenzaldehyde in the presence of HBr with subsequent oxidation of the intermediate porphyrinogene with *p*-chroloanyl in THF, its transformation into the copper complex **VII** by the action of copper(II) acetate **VI** and final demetalation (Schemes 2, 3).

The results of spectrophotometric investigation of compound **III** in the system 1,8-diazabicyclo[5.4.0]-undec-7-ene–acetonitrile are shown in Fig. 1. The analysis of the spectra showed that with the increase of the 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) concentration the appearance of two sets of spectral curves was observed in the electronic absorption spectrum, each being characterized by its own set of isosbestic points, which is indicative of a two-step process of deprotonation. The parameters of the spectra of molecular (without DBU) and the finally formed doubly deprotonated forms (DBU concentration of 5 × 10^{-5} mol/L) for compound **III** in system (1) are presented in Table 1.

Similar reactions for the porphyrin ligands in system (1) with DBU as a proton acceptor were performed earlier [8–12].

The two-step character of the curve of spectrophotometric titration (Fig. 1) is indicative of elimination of two protons upon the reaction of the ligand with the DBU molecule [Eq. (1)]:

$$H_2P \overset{k}{\rightleftarrows} P^{2-} + 2H^+, \quad (1)$$

where H_2P and P^{2-} are the free base and the doubly deprotonated forms of porphyrin **III** respectively.

The combined constant of the two-step acid ionization was calculated by Eq. (2). Its value for compound **III** in the system DBU–CH_3CN at 298 K was log k_a = –10.32 with the error of ±3–5%.

$$\log k_a = \log Ind + n\log c_{DBU}, \quad (2)$$

where k_a is the combined constant of acidity; *Ind* is the indicator ratio P^{2-}/H_2P; c_{DBU} is the analytical value of the DBU concentration in solution in mol/L, n = 2 is the number of protons bound by DBU.

Taking into account reaction (1) and the equation of material balance (3) we find that for the DBU

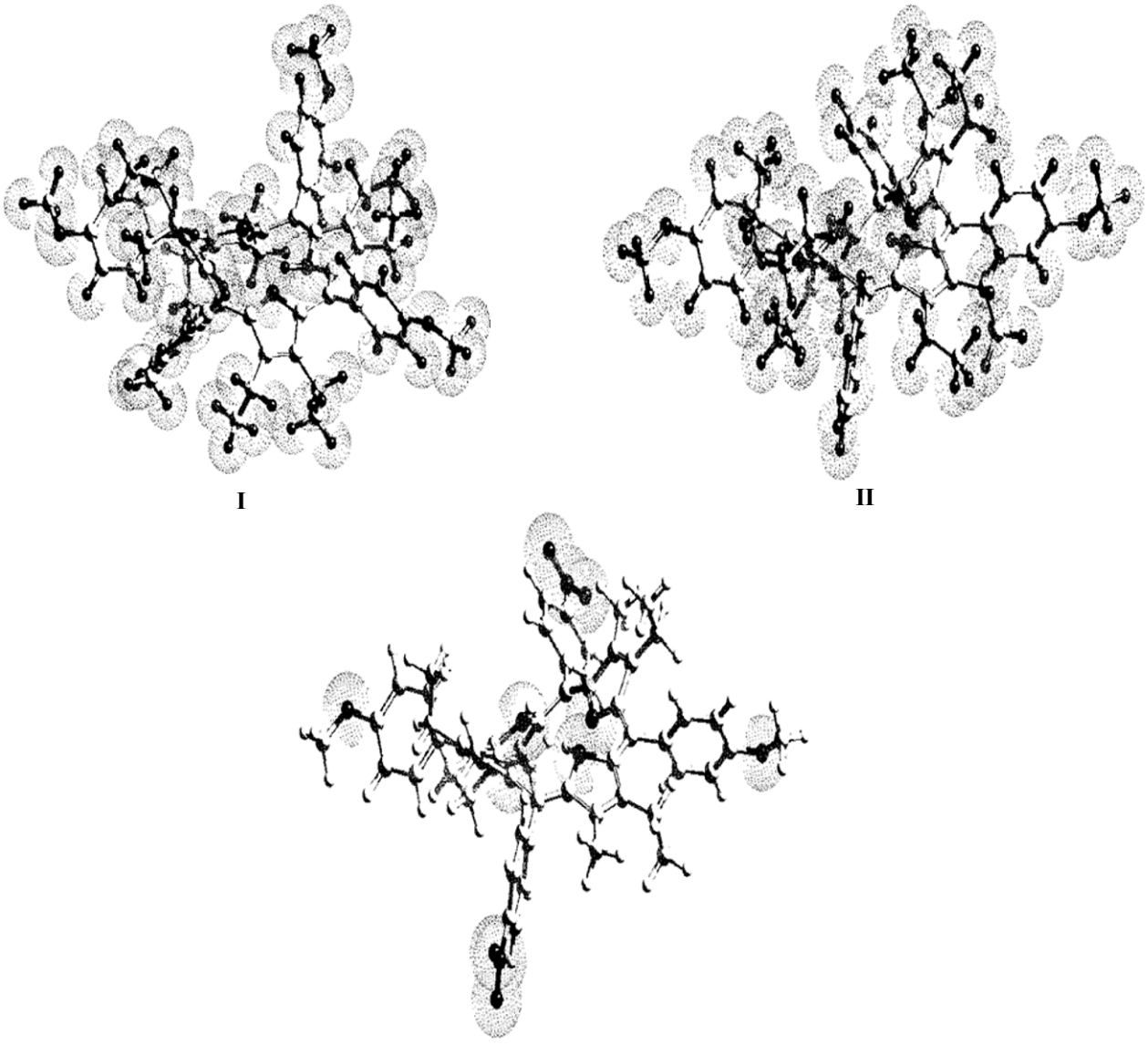


Fig. 2. Optimized geometry of zinc complexes of compounds **I–III** (program POLYGRAF, Ver. 3.1).

concentration of ~2.6 × 10^{-5} mol/L practically all molecules of **III** exist in the doubly deprotonated form. The procedures of calculations are described in [13].

$$c_0 = c(H_2P) + c(P^{2-}). \quad (3)$$

The earlier obtained results of spectrophotometric titration of compounds **I** (log k_a = –10.41) and **II** (log k_a = –11.04) in the system 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile [8, 9] allowed to obtain the following order of acidity for the processes of deprotonation of these ligands in the above system: **III** > **I** > **II**.

The results of calculation of the geometry of compounds **I–III** by PM3 method (program HyperChem) (Fig. 2) showed that the nitrophenyl groups in

Table 1. Parameters of electron absorption spectra of the molecular and the doubly deprotonated forms of 5,15-bis(4'-methoxyphenyl)-10,20-bis(4"-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyn and its zinc complex in the systems 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile (λ_1), $Zn(OAc)_2$–acetonitrile (λ_2), 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile (λ_3)

Forms of compound **III**	λ_1(log ε)	λ_2(log ε)	λ_3(log ε)
H_2P	385 sh (4.84)	485 (5.54)	708 (4.82)
P^{2-}	–	470 (5.19)	616 (4.48)
$Zn^{2+}P^{2-}$, ZnP	–	474 (5.11)	620 (4.49)

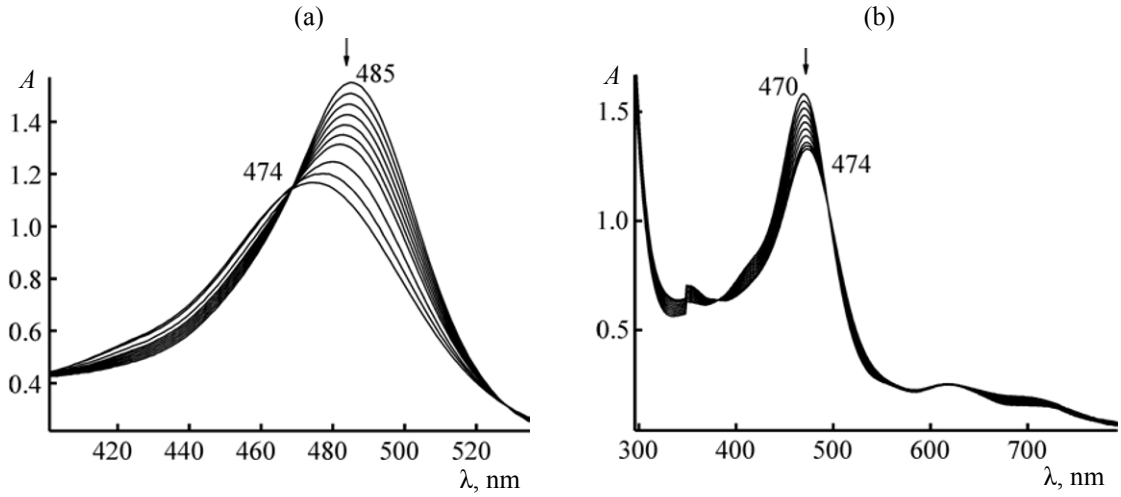


Fig. 3. Variations of electron absorption spectra in the reaction of compound **III** with zinc acetate in MeCN, 298 K: (a) in the absence of DBU, [c_{porph} = 4.46 × 10^{-6} mol/L, $c(ZnAc_2)$ = 2.28 × 10^{-3} mol/L]; (b) in the presence of DBU [c_{porph} = 1.02 × 10^{-5} mol/L, $c(ZnAc_2)$ = 4.71 × 10^{-4} mol/L, c_{DBU} = 3 × 10^{-5} mol/L].

the phenyl fragments, as well as the methoxyphenyl groups in the *meso*-position are turned with respect to the macrocycle plane at the angle of 70°–85°. The presence of twelve peripheral substituents leads to distortion of the macrocycle. The dependence of the degree of the macrocycle distortion on the acidic properties of the porphyrin macrocycle was noted in [9]. Compounds **I** and **II** contain, respectively, two and four electron-donor methoxy groups, which is manifested in more basic properties of these ligands. Mutual effect of the nitro and methoxy groups in the structure of porphyrin **III** leads to easier acidic dissociation of this compound than of compounds **I, II**.

The kinetics of the formation of zinc complexes of compound **III** was studied spectrophotometrically in the systems $Zn(OAc)_2$–acetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile. The formation of complexes can be represented by Eqs. (4), (5):

$$H_2P + [MX_2(Solv)_{n-2}] \rightarrow MP + 2HX + (n–2)Solv, \quad (4)$$

$$P^{2-} + [MX_2(Solv)_{n-2}] \rightarrow MP + 2X^- + (n–2)Solv. \quad (5)$$

Here, H_2P is the molecule of porphyrin, X is the acidoligand, Solv is the solvent molecule, n is coordination number of the metal cation. Changes in the electronic spectra during the reaction of coordination of compound **III** with zinc acetate in systems $Zn(OAc)_2$–acetonitrile and 1,8-diazabicyclo-[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile at 298 K are shown in Fig. 3.

The calculation of kinetic parameters, of the reaction order with respect to the salt and porphyrin was performed by routine procedures [8, 11, 12]. The experiment was repeated at least thrice at three temperatures. The kinetic parameters for the reaction of formation of zinc complexes of porphyrins **I–III** in the systems $Zn(OAc)_2$–acetonitrile and 1,8-diazabi-

Table 2. Kinetic parameters of the reaction of coordination of porphyrins with zinc acetate in the systems $Zn(OAc)_2$–acetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile

Porphyrin	$[Zn(OAc)_2]$, mol/L	$K_v \times 10^{-2}$, L mol^{-1} s^{-1}	ΔE, kJ/mol	$\Delta S^{\neq}$, J mol^{-1} K^{-1}
III [$Zn(OAc)_2$–CH_3CN]	2.28 × 10^{-3}	55	13.6	–222
III [$Zn(OAc)_2$–CH_3CN–DBU]	4.71 × 10^{-4}	1200	6.4	–185
I [$Zn(OAc)_2$–CH_3CN] [9]	3.13 × 10^{-3}	59	17	–206
I [$Zn(OAc)_2$–CH_3CN–DBU] [9]	1.06 × 10^{-4}	1560	10	–167
II [$Zn(OAc)_2$–CH_3CN] [8]	5.60 × 10^{-3}	53	22	–191
II [$Zn(OAc)_2$–CH_3CN–DBU] [8]	4.71 × 10^{-4}	1819	12	–157

cyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile are presented in Table 2.

The donor-acceptor effect of the substituents in compounds **I–III** is manifested upon complexation in the system 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile as shown by Eq. (5). The rate of formation of the zinc complexes of porphyrins **I–III** in system 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile decreases in the order **II** > **I** > **III**. Therewith, the rate of complexation of ligands **I–III** in the system 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile is 21–34 times higher than in the system $Zn(OAc)_2$–acetonitrile with molecular forms of porphyrins. The energies of activation $E^{\neq}$ of complexation of ligands **I–III** in the system 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile are 1.72–2.15 times lower than in the system $Zn(OAc)_2$–acetonitrile, which is usually ascribed to the absence of energy expenses for deformation and rupture of the N−H bonds at the reaction center. However, complexation of ligands **I–III** in the system $Zn(OAc)_2$–acetonitrile occurs with approximately equal rates (Table 2) and virtually does not depend on the electronic and steric effects of the substituents. Therefore, the change of the mechanism of complexation results not only in the increase of the rate of complexation but also favors manifestation of the effect of peripheral substituents on the reactivity of the ligand molecule. More negative values of $\Delta S^{\neq}$ in the system $Zn(OAc)_2$–acetonitrile as compared to the system 1,8-diazabicyclo[5.4.0]undec-7-ene–$Zn(OAc)_2$–acetonitrile are consistent with lower rates of formation of zinc complexes of the studied ligands in the former system.

The results of spectrophotometric and kinetic studies allowed ranking the order of acidity and kinetic activity for methoxyphenyl alkyl derivatives of porphyrins in the systems with different pH values of the reaction medium. The increase in the pH value was found to enhance the manifestation of the donor-acceptor effects of the peripheral substituents and to increase the rate of formation of the zinc complexes for the series of methoxyphenyl alkyl derivatives of porphyrin. The obtained results allow determining and regulating the rates of the processes of complexation of tetrapyrrole macrocycles by varying pH of the medium, which should be useful for the synthesis of complex tetrapyrrole structures and also for investigation of catalysis of slow chemical reactions.

EXPERIMENTAL

Electron absorption spectra were registered on a Shimadzu UV1800, Hitachi U2000 and Cary 100 Varian spectrophotometers. ^{1}H NMR spectra were recorded on a Bruker 500 spectrometer (internal reference TMS). Spectrophotometric titration with DBU in acetonitrile was carried out on a Cary 100 Varian spectrophotometer. Kinetic experiments and treatment of the experimental data were performed by the known protocols [14, 15]. Acetonitrile of high degree of purification (<0.03% of water) was used. As deprotonating agent, DBU was used, whose pK_a value in acetonitrile is 13.2. Zinc acetate of "pure for analysis" grade was purified by crystallization from aqueous acetic acid and dried at 380–390 K [16].

5,15-Bis(4'-methoxyphenyl)-10,20-bis(4''-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrin. To the solution of 50.0 g (0.256 mol) of 2-carbethoxy-4-ethyl-3,5-dimethylpyrrole [17] in 500 mL of dry ether at cooling (<20°C) 68.5 mL (0.84 mol) of sulfuryl chloride was gradually added. The mixture was kept overnight at room temperature, ether was removed, 400 mL of acetone and 100 mL of water was added, and the mixture was refluxed for 20 min. To the obtained solution the solution of 150 g (1.102 mol) of sodium acetate trihydrate in 200 mL of water was added, the mixture was refluxed for 2 h, acetone was removed, the reaction mixture was cooled, filtered, the precipitate was washed with water, then mixed with the mixture of 100 mL of ether and 200 mL of water, and the solution of 70.0 g of Na_2CO_3 in 200 mL of water was gradually added. The ethere layer was separated, water layer was extracted with 50 mL of ether and acidified with diluted HCl (1 : 5 v/v) to pH = 6. The precipitated product was filtered off, washed with water, and dried in air at 70°C. Yield 41.2 g (71.5%). mp 210–211°C. ^{1}H NMR ($CDCl_3$), δ, ppm: 9.40 br.s (1H, NH), 4.31 q (2H, *J* 7.2 Hz, CH_2O, Et), 2.74 q (2H, ^1J 7.6 Hz, CH_2, Et), 2.23 s (3H, CH_3), 1.32 t (3H, *J* 7.2 Hz, CH_3, OEt), 1.07 t (3H, ^1J 7.6 Hz, CH_3, Et).

2-Iodo-5-carbethoxy-3-ethyl-4-methylpyrrole. To the solution of 9.0 g (0.04 mol) of 2-carboxy-5-carbethoxy-3-ethyl-4-methylpyrrole in 100 mL of methanol, the solution of 12.0 g (0.12 mol) of $KHCO_3$ in 100 mL of water was added, the mixture was heated to 60°C, and the solution of 10.5 g (0.041 mol) of iodine and 17.2 g (0.1 mol of KI in 100 mL of water was gradually added. The mixture was stirred for

30 min, cooled, the precipitate was filtered off, washed with water, and dried in air at room temperature. Yield 10.6 g (86.3%). ^{1}H NMR spectrum ($CDCl_3$) δ, ppm: 9.91 br.s (1H, NH), 4.27 q (2H, *J* 7.2 Hz, CH_2, OEt), 2.32 q (2H, ^1J 7.6 Hz, CH_2, Et), 2.25 s (3H, CH_3), 1.29 t (3H, *J* 7.2 Hz, CH_3, OEt), 0.99 t (3H, ^1J 7.6 Hz, CH_3, Et).

2-Carbethoxy-3-methyl-4-ethylpyrrole. *a*. 8.0 g (35.5 mmol) of 5-carboxy-2-carbethoxy-3-methyl-4-ethylpyrrole was heated on an oil bath at 230°C for 2 h until evolution of CO_2 ceased, then pyrrole was distilled off in a vacuum of a water-jet pump. Yield 2.9 g (45.1%).

b. A mixture of 15.0 g (48.8 mmol) of 2-iodo-3-ethyl-4-methyl-5-carbethoxypyrrole, 12.5 g (55.4 mmol) of tin(II) dichloride dihydrate, 0.7 g (4.2 mmol) KI, and 20 mL of conc. HCl in 150 mL of ethanol was refluxed for 1 h, poured in water, extracted with ether, the extract was washed with water, ether was removed, the residue was distilled in a vacuum of a water-jet pump. Yield 4.3 g (48.6%). mp 24–25°C. ^{1}H NMR spectrum (CCl_4), δ, ppm: 9.14 br.s (1H, NH), 6.53 d (1H, *J* 3.6 Hz, 5-H), 4.17 q (2H, ^1J 7.1 Hz, CH_2, OEt), 2.27 q (2H, ^2J 7.5 Hz, CH_2, Et), 2.23 s (3H, CH_3); 1.27 t (3H, ^1J 7.1 Hz, CH_3, OEt), 1.08 t (3H, ^2J 7.5 Hz, CH_3, Et).

***ms*-(4''-Methoxyphenyl)-5,5'-dicarbethoxy-4,4'-dimethyl-3,3'-diethylpyrrole (IV).** The mixture of 3.0 g (16.6 mmol) of 2-carbethoxy-3-methyl-4-ethylpyrrole and 1.0 mL (8.3 mmol) of anisaldehyde was dissolved in 50 mL of methanol, heated to reflux, 5.0 mL of conc. HCl was added, the reaction mixture was refluxed for 4 h, cooled, and kept overnight in a refrigerator. The precipitate was filtered off, washed with methanol, and dried in air at room temperature. Yield 3.6 g (90.2%). ^{1}H NMR spectrum (CCl_4), δ, ppm: 9.73 br.s (2H, NH), 6.67 d (2H, *J* 8.1 Hz, 2",6"-H), 6.43 d (2H, *J* 8.1 Hz, 3",5"-H), 5.33 s (1H, *ms*-H), 3.88 q (4H, ^1J 7.1 Hz, CH_2, OEt), 3.57 s (3H, OCH_3), 2.27 q (4H, ^2J 7.5 Hz, CH_2, Et), 2.10 s (6H, CH_3), 1.07 t (6H, ^1J 7.1 Hz, CH_3, OEt), 0.88 t (6H, ^2J 7.5 Hz, CH_3, Et).

Copper complex of 5,15-bis(4'-methoxyphenyl)-10,20-bis(4''-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyn (VI). The mixture of 1.0 g (2.36 mmol) of *ms*-(4''-methoxyphenyl)-5,5'-dicarbethoxy-4,4'-dimethyl-3,3'-diethyldipyrrolylmethane (**IV**) and a solution of 1.0 g (17.8 mmol) of KOH in 6 mL of water was heated at 180°C for 4 h in a sealed tube, the tube was cooled, opened, the precipitate of *ms*-(4'-methoxyphenyl)-4,4'-dimethyl-3,3'-diethyldipyrropylmethane (**V**) was filtered off.

Compound **V** was dissolved in 20 mL of methanol, 0.36 g (2.36 mmol) of 4-nitrobenzaldehyde was added, 0.5 mL of HBr was added at stirring in inert atmosphere, and the mixture was stirred at room temperature for 2 h. The precipitate of porphyrinogene was filtered off, dissolved in 20 mL of THF, was added 0.87 g (3.54 mmol) of *p*-chloroanyl and 0.5 g (2.5 mmol) of copper(II) acetate hydrate, 0.6 mL (4.28 mmol) of triethylamine, the mixture was refluxed for 0.5 h, and the solvent was removed to dryness. The residue was dissolved in methylene chloride and chromatographed on Al_2O_3 (Brockmann activity grade III) eluting the first red zone of the copper complex with methylene chloride. The eluate was evaporated, the complex was sedimented with methanol, filtered off, washed with methanol, and dried in air at 70°C. Yield 0.31 g (26.8%); R_f (silufol) = 0.14 (benzene–hexane, 1 : 1); UV spectrum (chloroform), λ_{max}, nm (log ε): 578 (4.20); 435 (5.00).

5,15-Bis(4'-methoxyphenyl)-10,20-bis(4''-nitrophenyl)-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyn (III). Solution of 0.1 g (0.1 mmol) of copper complex **VI**, 1.0 mL (10.9 mmol) of $POCl_3$ and 1 drop of conc. HCl in 50 mL of CH_2Cl_2 was refluxed for 0.5 h, cooled, washed with 5% HCl, 5% ammonia and water, the solution of porphyrin in CH_2Cl_2 was dried with Na_2SO_4 and chromatographed on a short column with Al_2O_3 (Brockmann activity grade III) eluting the first green zone of porphyrin with CH_2Cl_2. The eluate was evaporated, the porphyrin sedimented with methanol, filtered off, washed with methanol, and dried in air at 70°C. Yield 0.067 g (72.0 %); R_f (silufol): 0.69 (benzene–methanol, 10 : 1). UV spectrum (chloroform), λ_{max}, nm (log ε): 700 (4.01); 605 (4.00); 554 (4.06); 456 (5.28). ^{1}H NMR ($CDCl_3$), δ, ppm: 8.63 d (4H, *J* 7.5 Hz, 2",6"-H), 8.49 d (4H, ^1J 8.1 Hz, 2',6'-H), 8.18 d (4H, *J* 7.5 Hz, 3",5"-H), 7.28 d (4H, ^1J 8.1 Hz, 3',5'-H), 2.47 br.s (8H, CH_2, Et), 1.81 br.s (12H, CH_3); 0.50 br.s (12H, CH_3, Et).

ACKNOWLEDGMENTS

This work was performed with the financial support from Russian Scientific Foundation (agreement no. 14-23-00204).

REFERENCES

1. *Porfiriny: struktura, svoistva, sintez* (Porphyrins: Structure, Properties, Synthesis), Enikolopyan, N.S., Ed., Moscow: Nauka, 1985.

2. *Porfiriny: spektroskopiya, elektrokhimiya, primenenie* (Porphyrins: Spectroscopy, Electrochemistry, Application), Enikolopyan, N.S., Ed., Moscow: Nauka, 1987.
3. *Uspekhi khimii porfirinov* (Progress of Chemistry of Porphyrins), Golubchikov, O.A., Ed., St. Petersburg: NII Khimii SPbSU, 1997, vol. 1.
4. Jentzen, W., Simpson, M.C., Hobbs, J.D., Song, X., Ema, T., Nelson, N.Y., Medforth, C.J., Smith, K.M., and Veyrat, M., *J. Am. Chem. Soc.,* 1995, vol. 117, p. 11085. DOI: 10.1021/ja00150a008.
5. Gentemann, S., Medforth, C.J.,Forsyth, T.P., Nurco, D.J., Smith, K.M., Fajer, J., and Holten, D., *J. Am. Chem. Soc*., 1994, vol. 116, p. 7363. DOI: 10.1021/ja00095a046.
6. Regev, A., Galili, T., Medforth, C.J., Smith, K.M., Barkigia, K.M., Fajer, J., and Levanon, H., *J. Phys. Chem., 199*4, vol. 98, p. 2520. DOI: 10.1021/j100061a005.
7. Pukhovskaya, S.G., Guseva, L.Zh., Semeikin, A.S., and Golubchikov, O.A., *Jinet. Catal.,* 2007, vol. 48, no. 2, p. 190. DOI: 10.1134/S0023158407020024.
8. Ivanova, Yu.B., Mamardashvili, N.Zh., Glazunov, A.V., Semeikin, A.S., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 7, p. 1404. DOI: 10.1134/S1070363214070287.
9. Ivanova, Yu.B., Glazunov, A.V., Semeikin, A.S., and Mamardashvili, N.Zh., *Proc. VIII Mezhd. konf. "Kinetika i mekhanizm kristallizatsii. Kristallizatsiya kak forma samoorganizatsii veshchestva"* (VIII Int. Conf. "Kinetics and Mechanism of Crystallization. Crystallization As a Form of Self-Organization of Matter"), Ivanovo, 2014, p. 197.
10. Ivanova, Yu.B., Nam Dao The, Glazunov, A.V., Semeykin, A.S., Pukhovskaya, S.G., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 1, p. 108. DOI:10.1134/S1070363214010162.
11. Ivanova, Yu.B., Chizhova, N.V., Pukhovskaya, S.G., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 5, p. 939. DOI: 10.1134/S1070363214050260.
12. Ivanova, Yu.B., Nam Dao The, Chizhova, N.V., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2014, vol. 84, no. 6, p. 1030. DOI:10.1134/S1070363214060255.
13. Bernshtein, I.Ya., *Spektrofotometricheskii analiz v organicheskoi khimii* (Spectrophotometry Analysus in Organic Chemistry), Leningrad: Khimiya, 1986, p. 202.
14. Ivanova, Yu.B., Sheinin, V.B., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2007, vol. 77, no. 8, p. 1458. DOI: 10.1134/S1070363207080270.
15. Ivanova, Yu.B., Churakina, Yu.I., and Mamardashvili, N.Zh., *Russ. J. Gen. Chem*., 2008, vol. 78, no. 4, p. 673. DOI: 10.1134/S1070363208040269.
16. Karyakin, Yu.V., Angelov, I.I., *Chistye khimicheskie reaktivy* (Pure Chemicals Reactives), Moscow: Khimiya, 1974, p. 407.
17. Berezin, M.B., Semeikin, A.S., V'yugin, A.I., and Krestov, G.A., *Russ. Chem. Bull*., 1993, vol. 42, no. 3, p. 449.