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Investigation of Acidic and Coordination Properties of Octabromo-Substituted Porphyrins in the System of 1,8-Diazabicyclo[5,4,0]unde-7-ene–Acetonitrile

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Abstract—Acidity and metal ion coordination are described for three porphyrin derivatives, different in their macrocycle conformation and electronic substitution effects due to bromine substitution in pyrrole rings and trifluorometyl or phenyl groups in *meso*-positions. Combination of these facts allows modulating both steric and electronic effects on the macrocycle π-conjugated system. The role of electronic substitution effects in the macrocycle deprotonation and metal ion complex formation is found dominating with comparable resonance and inductive contributions, whereas non-planar conformation of reactive species contributes to the reaction rates to a lesser extent. The interaction of two single-electron ($a_{1u}e_g$) and ($a_{2u}e_g$) configurations is studied as a function of non-planar distortions of the molecular structure for the three tetrapyrrole compounds. The additive influence of disturbing factors on the configuration interaction of single-electron ($a_{1u}e_g$) and ($a_{2u}e_g$) configurations in the tetrapyrrole macrocycle is demonstrated.

Keywords: porphyrins, acid-base equilibria, substitution effects, molecular orbitals conformation

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INTRODUCTION

Chemical design of macrocyclic compounds with prescribed physical and chemical characteristics aimed to create unique optical, electrochromic, semiconducting, and magnetic materials, as well as information storage devices is a priority direction for the development of modern science. The structure and properties of porphyrin ligands and their metal complexes makes it possible to develop such materials through fine-tuning of their properties both by widely varying the complexing agent nature and by modifying the peripheral part of the molecules [1–3]. In this connection, it seems a very urgent task to study the influence of electronic and steric effects of the porphyrin macrocycle substituents as a tool for directed changes in coordination and acid-base properties of porphyrins.

Porphyrins and their metal complexes can perfectly bind neutral organic molecules [4–9]. The interest to ionic forms of porphyrins is primarily caused by a wide range of opportunities to use them as electrode-active components for the creation of cation- and anion-selective materials [10–19]. In addition, they are useful models to investigate the interrelation of characteristics of the non-planar structure and spatial distortions in the macrocycle with the acid-base properties of porphyrins [20–23].

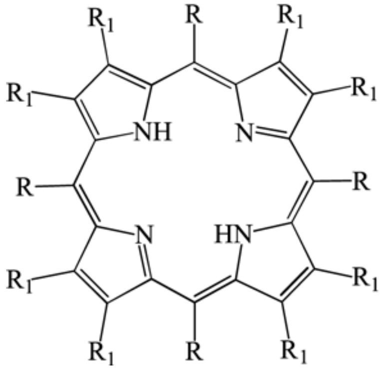
Porphyrins (H_2P) can be regarded as typical amphoteric compounds with both basic (N-bases) and very weak acidic (NH-acids) properties. Depending on the acidity of the medium, it is possible to obtain both singly- and doubly-charged ions that are in equilibrium with each other and with the neutral form [1].

In the first approximation (without participation of the solvent and stabilization of the resulting particles with counter-ions), the processes of acid-base interacttions of porphyrins can be represented by the following equilibria:

$$H_4P^{2+} \xrightleftharpoons[H^+]{K_1} H_3P^+ \xrightleftharpoons[H^+]{K_2} H_2P \xrightleftharpoons[H^+]{K_3} HP^- \xrightleftharpoons[H^+]{K_4} P^{2-}.$$

It is fundamental that porphyrins are chemically stable in the ground state, as well as in the cationic and anionic form. Stabilization of ionic forms of porphyrins in solutions is caused by a number of electronic, solvation, and steric factors [24]. The first group of factors is characterized by changes in electron density of the macrocycle in the process of protonation or deprotonation, including active participation of electrons of β- and *meso*-substituents of H_2P molecule. The solvation factors result from stabilization of ionic forms of porphyrins in the solution by molecules of the solvent (Solv), as well as associative bonds with M^+ or X^- counter-ions. The steric factors of stabilization include the ability of the ionic particle to distortion (if required for structural reasons).

This paper presents the results of spectrophotometric studies of acidic properties and formation of zinc complexes *of meso*-substituted β-bromo-derivatives of porphine, containing substituents of different nature in *meso*-positions of the macrocycle: 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(trifluoromethyl) porphyrin (**1**) and 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenyl porphyrin (**2**) as compared to the previously studied 5,10,15,20-tetrakis-(trifluoromethyl)porphyrin (**3**) [25].



1–3

R_1 = Br; R = CF_3 (**1**), R_1 = Br; R = Ph (**2**), R_1 = H; R = CF_3 (**3**).

EXPERIMENTAL

The porphyrins under investigation: 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(trifluoromethyl)porphyrin (**1**); 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (**2**); and 5,10,15,20-tetra(trifluoromethyl)porphine (**3**), were synthesized by the known methods [26, 27].

Porphyrin 1 was purified at the chromatographic column (silicagel–cyclohexane) and recrystallized from the mixture of CH_2Cl_2–MeOH. Found, %: C 23.69; H 0.17; N 4.63. $C_{24}H_2N_4Br_8F_{12}$. Calculated, %: C 23.72; H 0.16; N 4.61. Spectral characteristics of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(trifluoromethyl)porphyrin were in conformance with work [26]. ^1H NMR spectrum (500 MHz, $CDCl_3$, TMS), –1.63 s (2H, NH); EAS ($CHCl_3$), λ, nm (log ε): 433 (4.87); 636 (4.09).

We obtained **2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin (2)** as a result of bromination reaction of *meso*-tetraphenylporphyrinate of copper(II) with further acid dimetallization according to methodology [27]. Purification of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenyl porphyrin was carried out by chromatography on aluminium oxide of II and III activity degree. The developing agent composition was chloroform–benzene. Individuality of compounds was verified by TLC on Silufol plates. Electronic absorption spectra (EAS) did not differ from EAS described in literature. EAS (toluene), λ, nm (log ε): 470 (5.25); 622 (4.10); 738 (3.85). ^1H NMR spectrum (500 MHz, $CDCl_3$, TMS), 8.21 m (8H, phenyl *o*-H), 7.79 m (12H, phenyl *m-*, *p*-H), –1.65 br.s (2H, H). Found, %: C 42.35; H 1.90; N 4.40; Br 51.32. $C_{44}H_{22}N_4Br_8$. Calculated, %: C 42.42; H 1.78; N 4.49; Br 51.30.

Porphyrin (3) was purified by the column chromatography method on silica gel with the use of binary solvent with hexane–benzene ratio of 10 : 1 as an eluent. The compound was recrystallized from the mixture of methylene chloride and methanol. Found, %: C 49.53; H 1.64; N 9.33. $C_{24}H_{10}N_4F_{12}$. Calculated, %: C 49.50; H 1.73; N 9.62. Spectral characteristics of 5,10,15,20-tetrakis(trifluoromethyl)porphine corresponded to [25, 28]. ^1H NMR spectrum (500 MHz, $CDCl_3$, TMS), δ, ppm: 9.60 s (8H, β-H), –2.08 s (2H, NH); EAS (CH_2Cl_2), λ, nm (log ε): 403 (5.08), 510 (3.97), 545 (3.97), 593 (3.67), and 649 (4.00).

The solvent applied in the process of titration was dipolar aprotic solvent of high-purity acetonitrile

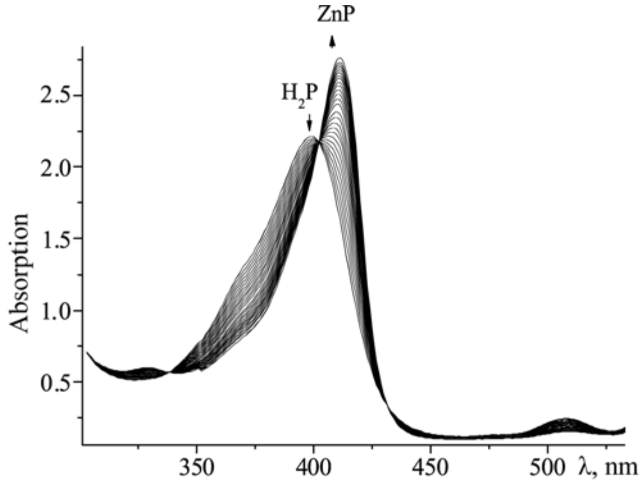


Fig. 1. Changes in EAS in reaction of $H_2(CF_3)_4P$ coordination by zinc acetate in acetonitrile at $T = 298$ K [$c_{porph}=1.31\times10^{-5}$ mol/L; $c(ZnAc_2) = 1.14\times10^{-2}$ mol/L].

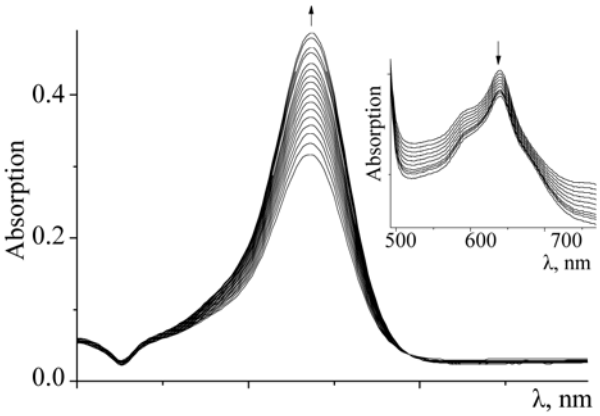


Fig. 2. Changes in EAS in reaction of porphyrin **2** coordination by zinc acetate in acetonitrile at $T = 298$ K [$c_{porph} = 3.54\times10^{-6}$ mol/L; $c(ZnAc_2) = 4.5\times10^{-3}$ mol/L].

(water content less than 0.03%), wherein the source objects were in the molecular form.

The deprotonating agent applied to study acidic properties of porphyrins was 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), for which the constant of ionization of the conjugate acid in acetonitrile was equal to $pK_a = 13.2$ [29]. The chemical agent was used without further purification.

Spectrophotometric titration of porphyrin solutions in acetonitrile with DBU solution was performed using Shimadzu UV-1800 spectrophotometer. The methodology applied in the experiment and processing of the experimental data is presented in detail in works [30, 31]. The error margin in determination of acid ionization constants did not exceed 3–5%. Electronic absorption spectra were recorded on Shimadzu UV-1800 spectrophotometer. H^1 NMR spectra were recorded on Bruker-500 spectrometer with operating frequency of 500 MHz in $CDCl_3$ (internal standard—TMS).

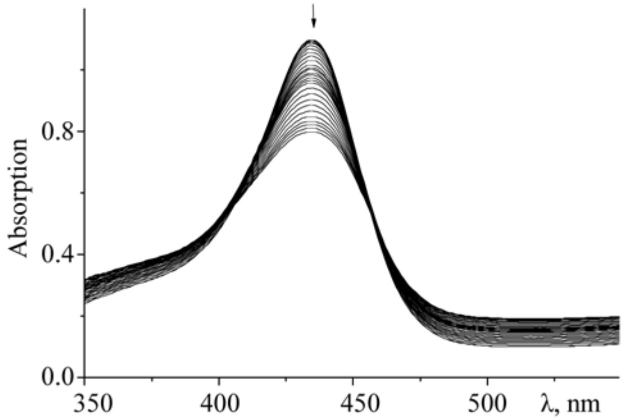


Fig. 3. Changes in EAS in reaction of porphyrin **1** coordination by zinc acetate in acetonitrile at $T = 323$ K [$c_{porph} = 2.77\times10^{-5}$ mol/L; $c(ZnAc_2) = 4.5\times10^{-3}$ mol/L].

Studies of complex-formation reactions between porphyrins and zinc acetates were carried out based on the spectrophotometric method in thermostatically controlled cells on glass joints. Temperature fluctuations in the course of the experiment did not exceed ±0.1 K. In all cases, clear isosbestic points were observed in electronic absorption spectra (EAS) of the reacting systems (Figs. 1–3). The reaction of formation of metalporphyrins [Eq. (1)] is of the first kinetic order with respect to ligand [1].

$$H_2P + [MX_2(Solv)_{n-2}] \rightarrow MP + 2HX + (n-2)Solv, \quad (1)$$

where H_2P is a porphyrin, M is a metal central cation, X is an acid ligand–salt anion, Solv is a ligand-solvent molecule, and n is a coordination number of metal cation.

Kinetic experiments were performed under conditions of a hundredfold excess of $Zn(OAc)_2$ salt with respect to porphyrin, which made it possible to calculate effective constants (k_{eff}) of the complex-formation reaction rate according to Eq. (2).

$$k_{eff} = (1/t)\ln[(A_0 - A_\infty)/(A - A_\infty). \quad (2)$$

Here, A_0, A, and A_∞ are optical densities of the solution at the initial moment, at the time of t, and at the end of the reaction, respectively.

The reaction rate constants of n+1 order were calculated according to Eq. (3).

$$k_{n+1} = k_{\mathrm{eff}}/c^{n}_{[\mathrm{M(OAc)2}]}, \quad (3)$$

where n is an order of reaction (2) with respect to salt, which equals to 1 for $Zn(OAc)_2$ in acetonitrile [32].

The activation energy (E_a) for the temperature range under study was calculated based on the Arrhenius equation as follows:

$$k = Ae^{-E_{\mathrm{a}}/RT}$$

or

$$E_{\mathrm{a}} = 19.1[(T_1T_2)/(T_2 - T_1)]\log(k_2/k_1), \quad (4)$$

whereas entropy of the transition state formation process ($\Delta S^{\neq}$) was calculated based on the equation below:

$$\Delta S^{\neq} = 19.1\log k_v + E_{\mathrm{a}}/T - 253. \quad (5)$$

RESULTS AND DISCUSSION

Spectral characteristics of the examined porphyrins (Table 1), as well as the data of X-ray spectroscopy and computer modelling suggest a distorted *“sad”*-type structure of β-bromo-substituted porphyrins (**1** and **2**) and an almost planar structure of 5,10,15,20-tetrakis(trifluoromethyl)-porphyrin (**1**) with a certain degree of corrugation [25, 28, 33, 34]. The presence of strong electron-acceptor substituents in *meso*-positions of the macrocycle contributes to a hypsochromic shift of bands in electronic absorption spectra. According to the four-orbital model by Simpson–Platt–Gouterman [35, 36], the hypsochromic shift in electronic absorption spectra is caused by a decrease in energy of the upper occupied molecular orbitals due to the higher electron density at methine atoms of carbon.

Table 1. Spectral characteristics in acetonitrile, acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene and indicators of acidity constants for porphyrins **1**–**3**

H_2P	λ, nm	log $K_{1,2}$
H_2P (**1**)	435 (5.0), 639 (4.1)	–6.78
H_2P (**2**)	470 (5.25), 568 (3.95), 622 (4.10), 738 (3.85)	–10.77
H_2P (**3**)	400 (5.23), 509 (4.14), 544 (4.13), 591 (3.84), 647 (4.11)	–9.69
P^{2-} (**1**)	483(4.6)	
P^{2-} (**2**)	497 (5.30), 774 (4.80)	
P^{2-} (**3**)	431 (4.96), 598 (4.00), 717 (3.89)	

Thus, as compared to trifluoromethyl porphyrin [413 (5.02), 512 (3.56), 546 (3.12), 592, and 646 (2.96)], the electronic absorption spectrum of compound **3** in the Soret area is shifted by ~13 nm into the short-wave part of the spectrum. It is obvious that introduction of eight bulk substituents (bromine atoms) into the pyrrole fragments of porphyrin **3**, as in the case of tetraphenylporphin, causes deformation of the molecule plane. In electronic absorption spectra, it manifests itself as a substantial bathochromic shift of absorption bands: ~50 nm for the derivative of trifluoromethyl porphyrin and somewhat lower for bromo-substituted derivative of **3**.

The acidic properties of porphyrins **1**–**3** were studied using the spectrophotometric titration method in the system of acetonitrile–1,8-diazabicyclo[5.4.0]-undec-7-ene (**1**) at T = 298 K.

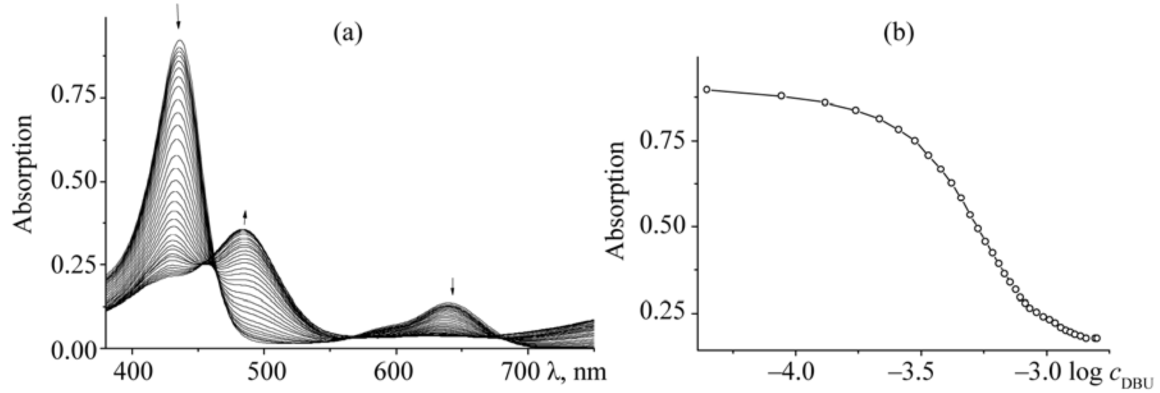


Fig. 4. (a) Changes in EAS in titration of compound **1** (c_{porph}=1.16×10^{-5} mol/L) by solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (c_{DBU} = 0–1.4×10^{-3} mol/L) in acetonitrile at T = 298 K and (b) titration curve.

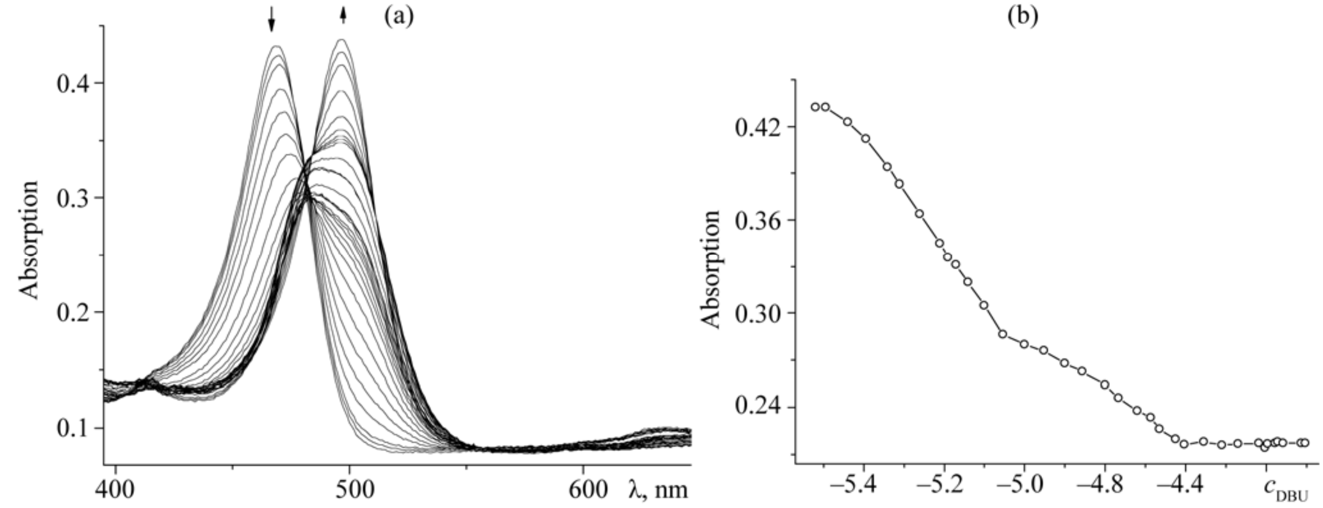


Fig. 5. (a) Changes in EAS of compound **2** ($c_{porph} = 0.24\times10^{-5}$ mol/L) in system of acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene ($0–5\times10^{-5}$ mol/L) at $T = 298$ K and (b) titration curve.

In the process of titration, in the absorption spectra of compounds **1**–**3** it was possible to observe the formation of two families of spectral curves, with its own system of isobestic points, corresponding to each of the two (Figs. 4–6 demonstrate typical examples for porphyrins **1**, **2)**. With increasing concentration of the titrant (c_{DBU}), the electronic spectrum of absorption of the molecular form of porphyrins **1**–**3** (H_2P) gradually transformed into the electronic spectrum of the final form of P^2 dianion (Table 1).

Considering the processes of stepwise deprotonation in the equilibrium system and the material balance Eq. (6), it is possible to determine the distribution of concentrations of the molecular and deprotonated forms of H_2P and H_2P^{2-} in the titration processes (Figs. 7–9).

$$c_a = c(H_2P) + c(HP^-) + c(P^{2-}). \qquad (6)$$

As can be seen from Figs. 7–9, at indicated concentrations of the titrant almost all porphyrin molecules exist in a doubly deprotonated form. The calculation methods are described in detail in work [37].

The total constant of the first- and second-stage acid ionization for porphyrins **1**–**3** was calculated according to Eq. (7).

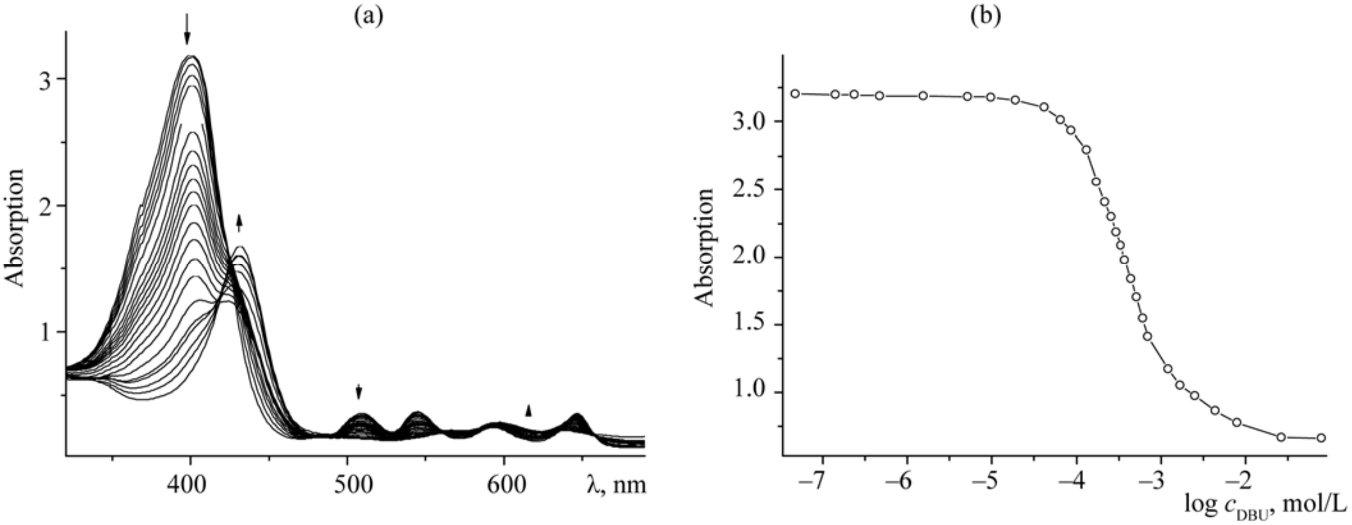


Fig. 6. (a) Changes in EAS of compound **3** ($c_{porph} = 1.89\times10^{-5}$ mol/L) in system of acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene ($0–7.9\times10^{-3}$ mol/L) at $T = 298$ K and (b) titration curve.

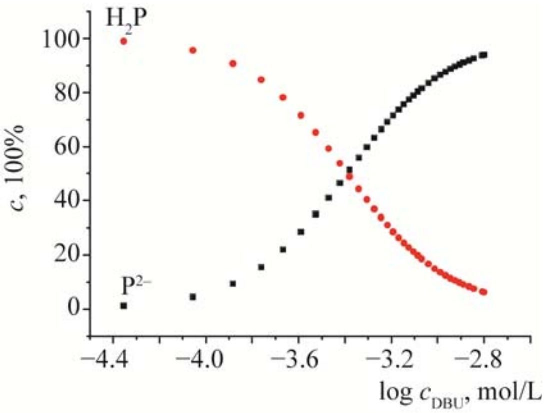


Fig. 7. Distribution of concentrations of molecular and doubly deprotonated forms for compound **1**.

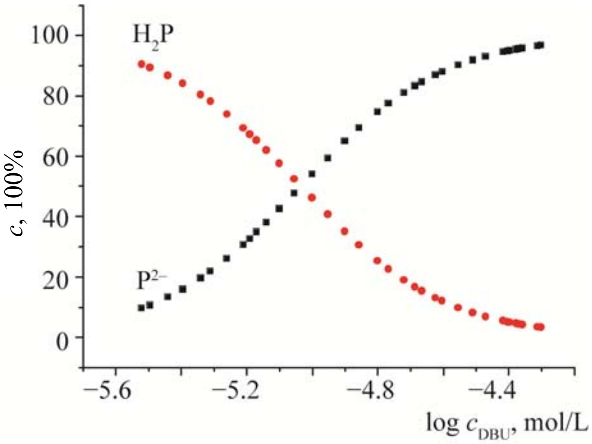


Fig. 8. Distribution of concentrations of molecular and doubly deprotonated forms for compound **2**.

$$\log K_{1,2} = \log Ind + 2\log c_{DBU}, \quad (7)$$

where $K_{1,2}$ is a total constant of the compound acidity at the first and second stages (Scheme 1); *Ind* is an indicator ratio of $[P^{2-}]/[H_2P]$ for the first and second stages; c_{DBU} is an analytical value of 1,8-diazabicyclo-[5.4.0]undec-7-ene concentration in the solution, mol/L. The resulting values of the total acidity constants for compounds **1**–**3** in the system of acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene at 298 K, as well as the electronic absorption spectra of porphyrins and their ionized forms are presented in Table 1. It should be noted that even at maximum concentrations of 1,8-diazabicyclo[5.4.0]undec-7-ene it has been impossible to obtain the anionic form of 5,10,15,20-tetraphenylporphyrin, which suggests very low acidic properties of the compound. The introduction of eight bromine atoms into β-positions of porphyrin **3** does not only result in distortion of the porphyrin macrocycle and, as a consequence, in certain isolation of π-electron systems of the pyrrole and pyrrolenine fragments, but also causes a reduction in electron density on the central atoms of nitrogen in the reaction center. This fact facilitates the proton separation under the influence of the deprotonating agent (1,8-diazabicyclo-[5.4.0]undec-7-ene), in which case the total constant of compound **1** acidity increases by more than three orders of magnitude as compared to compound **3**. However, substitution of the phenyl group for the trifluoromethyl group, while slightly increasing the degree of the porphyrin fragment distortion, reduces the total acidity constant of compound **2** by five orders of magnitude (Fig. 10).

It is known that the porphyrin–ligand structure that includes a system of peripheral substituents has a significant impact on the rate and energy of the complex-formation reaction. According to the reaction mechanism, presented in works [1, 38], electron-acceptor substituents, on the one hand, destabilize N–H bonds in the reaction center, thereby contributing to their stretching and separation of protons. On the other hand, they reduce electron density at tertiary nitrogen atoms, which does not contribute to strengthening of N→M bonds formed in the transition state, thus reducing the rate of metalloporphyrins formation reaction. Furthermore, introduction of a large number of β- and *meso*-substituents, having a certain volume, into the macrocycle forces the porphyrin molecule to adopt a non-planar conformation. As shown in previous studies [22, 23, 39, 40], the distortion of the porphyrin macrocycle planar structure results in a reduction in the molecule aromaticity and certain isolation of the pyrrole and pyrrolenine

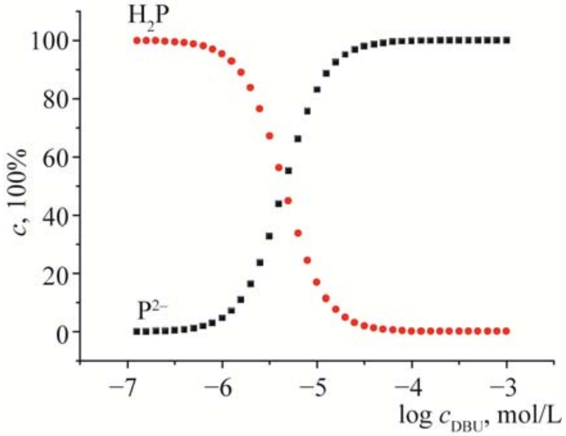


Fig. 9. Distribution of concentrations of molecular and anionic forms for compound **3**.

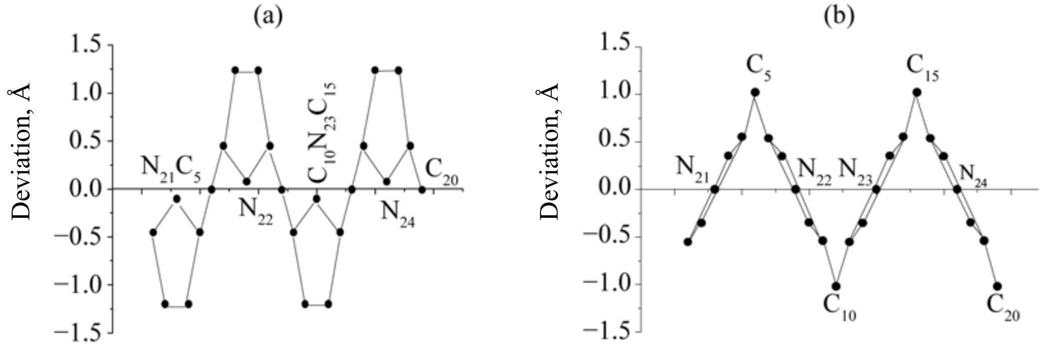


Fig. 10. Deviation of atoms from macrocycle central plane, drawn through 24 carbon atoms of porphyrin macrocycle, according to calculations based on B3LYP/6-311G. (a) 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin and (b) 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(trifluoromethyl)porphyrin.

fragments. In this case, there is an increase in both the basic [41] and acidic properties [42] of the macrocycle, which suggests that porphyrins with the distorted macrocycle structure will be readily deprotonated in the presence of strong bases and the complex-formation rate will increase in the presence of deprotonating agents. It is found that the lowest reaction rate of zinc acetate coordination corresponds to ligand **1**, which is associated with the presence of electron-acceptor substituents both in *meso-* and β-positions of the macrocycle. It is evident that the increase in the reaction rate of zinc complex formation for molecular forms of porphyrins in the transition from **1** to **2** is caused by replacement of the strong electron-acceptor group (CF_3) with the phenyl fragment, wherein the basic ionization constant also increases by more than five orders of magnitude. There is a somewhat lower increase in the complex-formation rate in the transition from **1** to **3**, which is associated with the following two opposite effects: absence of electron-acceptors (Br atoms) in β-positions of the macrocycle, on the one hand, and a flatter structure of porphyrin **3**, on the other hand.

The formation of zinc complexes of porphyrins **1–3** (Figs. 1–3) in acetonitrile in the presence of a strong organic base, namely, 1,8-diazabicyclo[5.4.0]undec-7-ene (Table 2) has been investigated and the studies have shown that the reaction rate increases by approximately 3–4 orders of magnitude in the transition from molecular to dianionic forms of ligands. At the same time, there is a decrease in energy parameters of the reaction (1). This is obviously due to the lack of energy expenditure on distortion and rupture of N–H bonds in the reaction center, as well as stronger polarization of the molecule, and as a consequence, a higher solvation degree of the porphyrins anionic forms in the transition state.

It should be noted that the values of log $K_{1,2}$ (Table 1) vary significantly depending on the substitution type. It is evident that acidity constants should correlate with the value of electron density on the macrocycle pyrrolenine rings. However, it remains undetermined in which way peripheral substituents affect it. Previous studies demonstrated that resonance and inductive effects [43] made a significant contribution into the

Table 2. Kinetic parameters of formation of porphyrins zinc complexes

Porphyrin	Solvent	$c(ZnAc_2)\times10^3$, mol/L	$c_{DBU}\times10^{-3}$, mol/L	$k_2^{298}\times10^3$, L mol^{-1} s^{-1}	E_a, kJ/mol	$\Delta S^{\#}$
H_2P (**1**)	CH_3CN	4.50	–	0.005±0.0005	123±2	58±1
H_2P (**2**)	CH_3CN	4.50	–	69±1	56±1	–88±2
H_2P (**3**)	CH_3CN	11.40	–	6.05±0.08	52±2	–175±2
P^{2-} (**1**)	CH_3CN–DBU	4.50	1.50	28.0±1	27±1	–190±2
P^{2-} (**2**)	CH_3CN–DBU	4.50	0.05	Instantaneous reaction		
P^{2-} (**3**)	CH_3CN–DBU	0.28	1.00	4006±5	24±1	–143±2

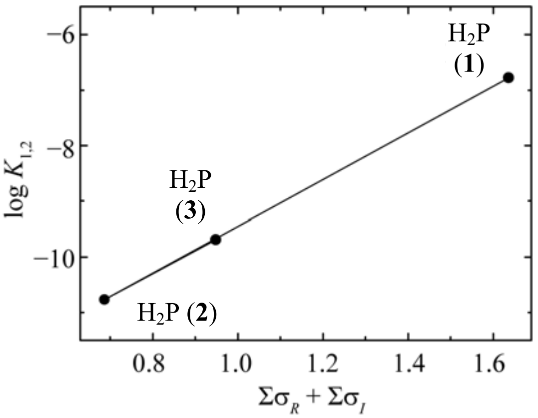


Fig. 11. Dependence of log $K_{1,2}$ on weighted total of resonance ($\Sigma\sigma_R$) and inductive ($\Sigma\sigma_I$) Hammett constants according to equation $0.59(8\sigma\beta+4\sigma^{meso})_R + 0.41(8\sigma\beta+4\sigma^{meso})_I$.

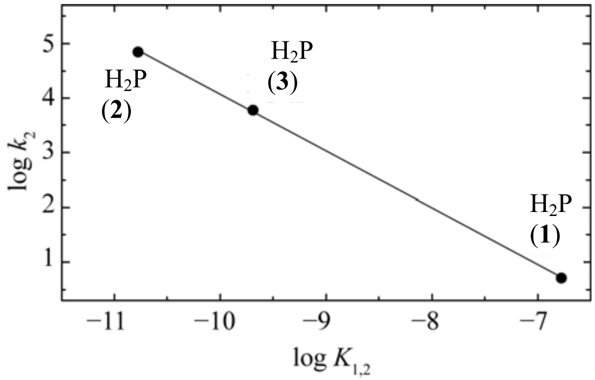


Fig. 12. Dependence of second order rate constant for complex formation of Zn^{2+} ions with free bases of porphyrins on log $K_{1,2}$ value.

formation of the macrocycle basicity constant [44, 45]. Based on general considerations, the same statement should be also true for the macrocycle acidity constants. A certain interpretation difficulty results from the fact that in this case the impact is made both by *meso*-substituents and substituents in pyrrole rings, unlike the above-mentioned works analysing only *meso*-aryl-substituted derivatives. Therefore, the total electronic effect of the substitution was calculated as a weighted total of resonance ($\Sigma\sigma_R$) and inductive ($\Sigma\sigma_I$) Hammett constants for all substituents in the macrocycle. Relative weights of the resonance and inductive contributions were calculated based on the least squares method in the assumption of a linear dependence of the acidity constant on the value of $a_1\Sigma\sigma_R + a_2\Sigma\sigma_I$ according to the free energy ratios [44, 45].

Resonance Hammett constant values (σ_R) were calculated by definition as a difference of $\sigma_p - \sigma_m$, whereas inductive Hammett constants (σ_I) were the data from work [43]. The dependence presented in Fig. 11 clearly demonstrates that there is a perfect correlation between the acidity constant logarithm and the weighted sum of $a_1\Sigma\sigma_R + a_2\Sigma\sigma_I$, where a_1 and a_2 weight coefficients are equal to 0.59 and 0.41, respectively. It is obvious that neither resonance nor inductive effects alone can ensure a satisfactory correlation with the measured values of the acidity constants. Both inductive and resonance effects have a significant impact on the acidity constant ($K_{1,2}$); moreover, a greater contribution is made by the electron density redistribution in the π-conjugated system of the macrocycle. It should be noted that the phenyl fragments and the bromine atoms contribute to the total balance in a very complicated way, since resonance Hammett constants are negative (i.e. having a resonance donating effect), while inductive Hammett constants are positive (i.e. having an inductive accepting effect).

As emphasized above, the macrocycle distortion caused by the introduction of a large number of bulk substituents has significant influence on the ligand coordination properties, slowing or increasing the complex-formation reaction rate by several orders, depending on the nature of the solvent. Furthermore, previous studies have shown that formation of non-planar conformers intensifies both the acidic and basic properties of the molecule [41, 42]. The resulting kinetic parameters of the formation of Zn^{2+} ions complexes with the studied porphyrins are consistent with this point of view (Table 2). However, the driving force of the spectral changes as well as the changes in the tetrapyrrole compounds reactivity is a result of direct and indirect electronic effects of the substituents (the latter induced by structural changes).

In order to confirm the influence of the macrocycle acidic properties on the value of the reaction rate constant k_2 corresponding to coordination of the porphyrins free bases by Zn^{2+} ions, a correlation dependence has been obtained and presented in Fig. 12. It is evident that there is a complete correlation between the two sets of values, which means that the changes in the acidity constant can fully explain the observed changes in the complex-formation constant.

It is also possible to observe an increase in the complex-formation constant for deprotonated forms of the porphyrins under study. In case of deprotonated derivatives, the activation energy value goes down as compared to the value measured in complex formation of free bases, which is accompanied by a decrease in entropy. Apparently, these manifestations are due to the lack of energy losses on the macrocycle distortion and the rupture of N–H bonds in the macrocycle core, as well as due to the non-uniform charge distribution in the macrocycle, resulting in polarization of the electron cloud of the molecule. As a result, doubly deprotonated porphyrins will be solvating more effectively in the transition state, which, in turn, facilitates coordination of the metal ion.

However, in case of free bases of porphyrins, there is a 1210-fold increase in the rate constant in the transition from porphyrin **1** to **3**, while for doubly deprotonated molecules the increase is 8.5 times lower (Table 2). Apparently, this difference can be explained by changes in the electronic structure in the formation of doubly deprotonated molecules. Thus, it is known that in molecules of tetrapyrrole compounds two singlet one-electron $^1(a_{2u}e_g)$ and $^1(a_{1u}e_g)$ configurations effectively mix in the course of configuration interaction. Using the principle of superposition states, wave functions of the two excited $S_{1,2}(Q)$ and $S_{3,4}(B)$ states can be represented as follows:

$$\psi(S_1) = A^1\psi_A - B^1\psi_B(A^2 + B^2 = 1),$$
$$\psi(S_2) = B^1\psi_A + A^1\psi_B,$$

where A and B are weights of the first and second single-electron configurations, respectively. Then, intensities of the transitions into these states can be represented as follows:

$$I(S_{1,2}) = c|\langle\psi(S_{1,2})|er|\psi(S_{1,2})\rangle|^2$$
$$= c\{A^2\Phi_{AA} - 2AB\Phi_{AB} + B^2\Phi_{BB}\},$$
$$I(S_{3,4}) = c|\langle\psi(S_{3,4})|er|\psi(S_{3,4})\rangle|^2$$
$$= c\{A^2\Phi_{AA} - 2AB\Phi_{AB} + B^2\Phi_{BB}\},$$

where

$$\Phi_{AA} = \langle^1\psi_A|er|^1\psi_A\rangle,$$
$$\Phi_{AB} = \langle^1\psi_A|er|^1\psi_B\rangle,$$
$$\Phi_{BB} = \langle^1\psi_B|er|^1\psi_B\rangle,$$

At equality of the transitions dipole moments,

$$M_{ae} = \langle^1(b_{1u}e_g)|er|^1(b_{1u}e_g)\rangle = \langle^1(a_ue_g)|er|^1(a_ue_g)\rangle$$

and assuming $\psi_A = (b_{1u}e_g)$ and $\psi_B = (a_ue_g)$, we can write down a simple ratio of the intensities of the two electron transitions, expressed in terms of weights of the two single-electron configurations as follows:

$$\frac{I(S_{1,2})}{I(S_{3,4})} = \frac{A^2 - 2AB + B^2}{A^2 + 2AB + B^2} = \frac{1 - 2AB}{1 + 2AB}.$$

Upon solving the system of algebraic equations (taking into account the normalization condition of $A^2 + B^2 = 1$), it is possible to calculate the values of A^2 and B^2. This approach was first applied to metal complexes by the authors of works [35, 46] and has recently been extended to free bases and doubly protonated forms [47]. The analysis of spectral data for porphyrin **3** based on the use of this approach gives the resulting value of $A^2 = 0.80$ for the free base and a slightly higher value of 0.84 for doubly deprotonated molecules. These estimates indicate that the electron interaction between the macrocycle and the periphery does actually change with the removal of ions from the macrocycle core and can explain the impact on the metal ions complex-formation constant in doubly deprotonated molecules.

Thus, we have studied the reactions of coordination of free bases and doubly deprotonated forms of three porphyrins with a different character of peripheral substitution by zinc acetate and have demonstrated that the reaction rate constant (1) increases by 3–4 orders of magnitude in deprotonated forms of porphyrins. Apparently, this fact is caused by the absence of energy losses on the macrocycle distortion and the rupture of N–H bonds in the macrocycle core, as well as a non-uniform distribution of the charge in the macrocycle, resulting in polarization of the electron cloud of the molecule. These findings form a theoretical basis for the creation of high-performance optical sensors for metal cations in the liquid phase.

CONCLUSIONS

The research results on acidic properties of octabromo-substituted porphyrins are presented; the impact made by the substituents electronic effects and the porphyrin macrocycle distortion effects is discussed. It is shown that substitution of the phenyl group for the trifluoromethyl group, while slightly increasing the porphyrin fragment distortion degree, reduces the total constant of acid dissociation of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(trifluoromethyl)porphyrin by four orders of magnitude as compared to 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin. At the same time, introduction of electron-donating substituents in β-positions reduces the value of $K_{a1,2}$ by approximately an order of magnitude. It is found that the reaction rate of complex formation with zinc acetate increases by 3–4 orders of magnitude in the transition from molecular to dianionic forms of porphyrins. It is evident that the reduction in the reaction activation energy is due to the absence of energy losses on the distortion and rupture of N–H bonds in the reaction center, as well as a stronger polarization of the molecule, and, as a result, a higher degree of solvation of the porphyrins anionic forms in the transition state. The obtained results on increasing the reaction rates of complex formation of the porphyrins dianionic forms (by 4–5 orders of magnitude) can lay a theoretical foundation for the creation of high-performance liquid-phase sensor materials for metal cations.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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