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Study of Acidity and Coordination Properties of 2,3,7,8,12,13,17,18-Octabromo-5,10,15,20-tetraphenylporphyrin in the System of 1,8-Diazabicyclo[5.4.0]undec-7-ene–Acetonitrile

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Abstract—Spectrophotometric titration method was used to study the acidic properties of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin in the presence of a deprotonated agent, 1,8-diazabicyclo[5.4.0] undec-7-ene, in acetonitrile. The spectral characteristics of the ionized forms and combined ionization constant for the first and second stages were revealed. The reaction of complex formation between the dianionic forms of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin and zinc acetate was studied.

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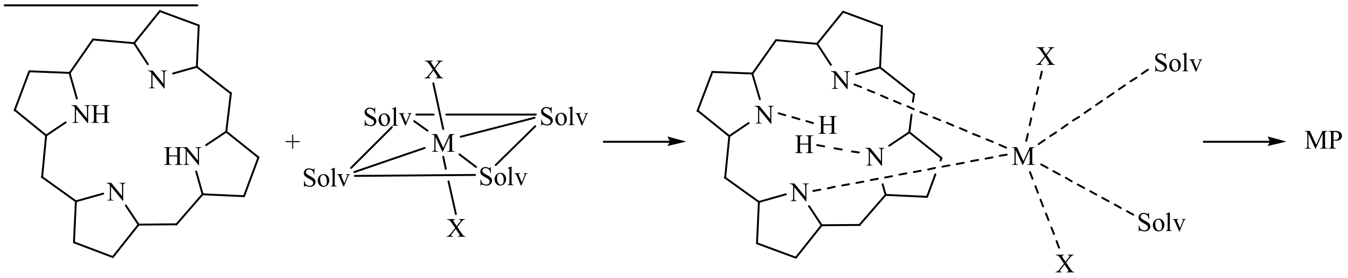
Porphyrins form stable coordination compounds of the 1:1 composition with most metals of the periodic system (except for alkaline metals). The coordination with bivalent transition metal ions is particularly favorable. Numerous studies of coordination properties of porphyrins as well as studies of metalloporphyrins were summarized in monographs [1–4]. The accumulated experimental data led to the identification of common regularities in the formation of metalloporphyrins and to the suggestion of the reaction mechanism of the complex formation [1] in the nonaqueous media in one step in a bimolecular reaction.



According to the proposed mechanism the transition state is reached through the reorganization and partial destruction of the coordination sphere of the metal solvatocomplex followed by the formation of coordination bonds between the metal cation and the tertiary nitrogen atoms of the porphyrin, which is results in the elongation and polarization of N–H bonds of the ligand. It is assumed that in the salts of octahedral structure $[M(Solv)_4X_2]$ (Solv ligands are the solvent molecules, X are acido ligands, M is the metal cation), including the majority of the studied salts, the leaving ligands are two solvent molecules. Their removal provides the metal–porphyrin contact and the formation of coordination bonds.

The main contribution to the activation energy originates from the partial destruction and deformation of the coordination sphere of the salt solvatocomplex:

the removal of two ligands (Solv) from the metal cation and elongation of the remaining bonds (M–Solv, M–X). In the transition state the porphyrin N–H bonds are elongated, which also, of course, affects the process energy. [1, 5].

Electronic effects of the peripheral substituents also affect the energy course of the complexation reaction, although to a lesser extent. On the one hand, the electron-acceptors destabilize N–H bonds, thus contributing to their elongtion and cleavage of a proton, and on the other hand, they reduce the electron density on the tertiary nitrogen atoms. The electron-releasing groups exhibit the opposite effect. In addition, the introduction of a large number of β - and *meso*-substituents of a certain size to the macrocycle forces the porphyrin molecule to take the conformation most favorable by energy, even by destroying the planar structure of the macrocycle [6–9]. As shown in previous studies [9–10], the deterioration of the planar structure of the porphyrin macrocycle reduces the molecule aromaticity and results in a certain isolation of some pyrrole and pyrrolenine fragments, thus increasing both basic [10] and acidic [11] properties of the porphyrin molecule. This suggests that the porphyrins with a deformed structure of macrocycle readily deprotonate in the presence of strong bases, and the reaction rate of the metalloporphyrin formation raises.

Some organic bases, called "proton harpoons" possess the unique ability to ionize weak acids, including free porphyrins, at the N–H bonds, while they do not affect other labile groups. Their important advantage compared with alkali is their solubility in organic solvents, which makes them suitable as deprotonating agent in non-aqueous media.

In this paper, we investigated the ionization and the formation of zinc complex with 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin **I** in the presence of deprotonating agent 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU). The ionization constant of its conjugated acid pK_a = 13.2 [12]. The acidic properties of the porphyrin **I** were studied by spectrophotometric titration in the system of acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene at 298 K.

The process of deprotonation of the endocyclic nitrogen atoms of the tetrapyrrole macrocycle of compound **I** occurs in two steps, according to Eqs. (1) and (2):

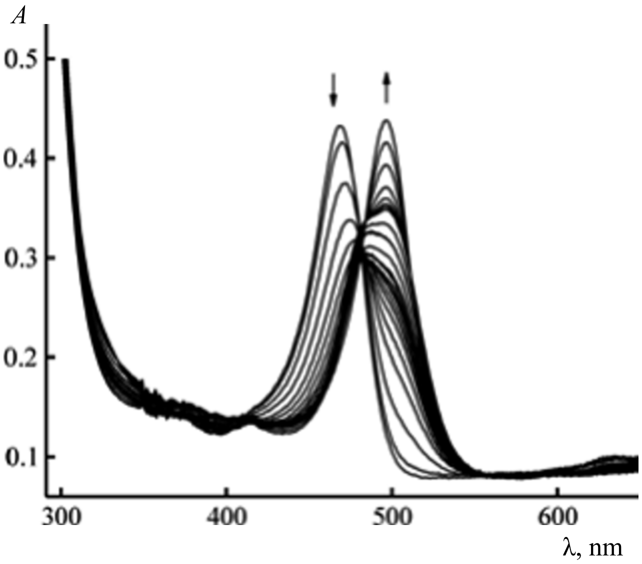
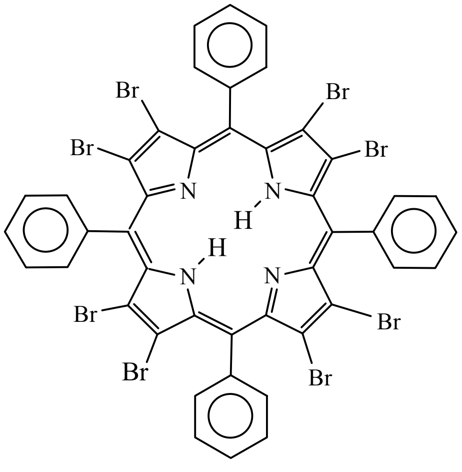


Fig. 1. Changes in EAS of compound **I** (c_I = 2.11×10^{-6} M) in acetonitrile at the titration by DBU (0 to 4.14×10^{-6} M) at 298 K.



I

$$H_2P \rightleftarrows HP^- + H^+, \quad (1)$$

$$HP^- \rightleftarrows P^{2-} + H^+. \quad (2)$$

Here H_2P, HP^-, and P^{2-} are, respectively, neutral and deprotonated forms of the porphyrin **I**.

At the deprotonation, in the absorption spectra two families of spectral curves form, each having its own system of isobestic points (Figure 1). With increasing concentration of titrant (c_{DBU}) from 0 to 4.14×10^{-6} M the electron absorption spectrum of molecular form [H_2P; λ_{max}, nm (log ε): 470 (5.25), 568 (3.95), 622 (4.10), 738 (3.85)] transforms gradually into the spectrum of the final form of dianion {P^{2-}; λ_{max}, nm (log ε): 497 (5.30), 774 (4.80)].

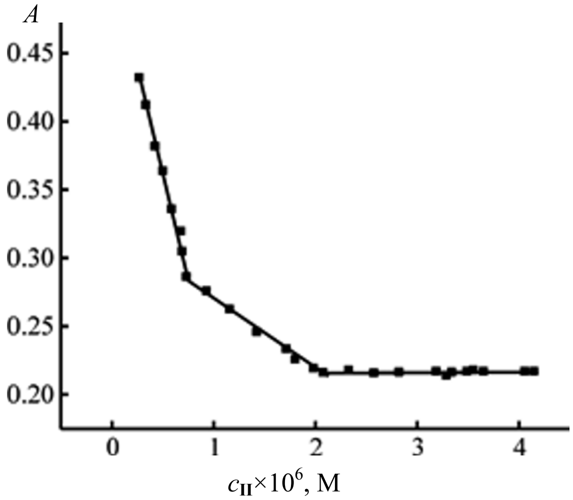


Fig. 2. Titration curve of the compound **I** (c_I = 2.11×10^{-6} M) at the titration by DBU in acetonitrile at 298 K, λ = 468 nm.

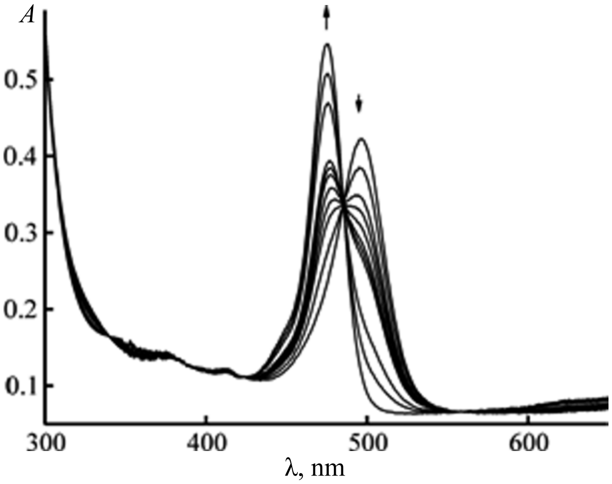


Fig. 3. Changes in EAS of compound **I** dianion ($c_{I^{2-}}$= 2.11×10^{-6} M) at the titration with ZnAc$_2$ (0–2.48×10^{-6} M) at 298 K in the system of $\mathbf{I}^{2-}$–CH$_3$CN–DBU.

The determination of the coordinates of the inflection (and the corresponding concentration of DBU) on the titration curve (Fig. 2) allowed us to distinguish two areas in the electron absorption spectra of the reaction system that are likely to belong to the first and second steps of deprotonation, namely, to the formation of mono- and dianionic forms (HP^- and P^{2-}) of compound **I**.

Combined acid ionization constant for the first and second steps was calculated according to Eq. (3).

$$\log k_a = \log Ind + n\log c_{II}, \qquad (3)$$

where k_a is the combined acidity constant of the compound, Ind is the indicator ratio $[P^{2-} + HP^-]/[H^2P]$, c_{DBU} is the analytical value of DBU concentration in solution, M.

Calculation of current concentrations of deprotonated and molecular forms with accounting for the material balance equation showed that at the DBU concentration of about 3.5×10^{-6} compound **I** almost completely is in the double deprotonated form.

$$c_0 = c(H_2TPPBr_8) + c(TPPBr_8^{2-}). \qquad (4)$$

The index of total acidity constant of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin in the acetonitrile–DBU system at 298 K is pK_a = 10.77.

The comparison of the acidity constant of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin with the previously published data for 2,3,12,13-tetrabromo-5,10,15,20-tetraphenylporphyrin (pK_a = 5.29) [13] shows that the introduction of four bromine atoms to the macrocycle leads to an increase in the acidity of the compound by about 5 orders of magnitude. Apparently, this is due to the overall effect associated with an increase in the number of electron-withdrawing groups and the deformation of the porphyrin macrocycle. It is known from the literature that 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin has a strongly deformed structure, and the mean deviation of the atoms from the plane of the macrocycle (δ) averaged over 24 carbon atoms is ≈ 75 pm [14, 15], which agrees with the X-ray diffraction data (for β-carbon atoms δ_{max} ≈ 126 pm) [16]. The computer modeling suggests much smaller deformation of the macrocycle of 2,3,12,13-tetrabrom-5,10,15,20-tetraphenylporphyrin (for β-carbon δ_{max} ≈ 46 pm) [17].

To study the complex formation between the macrcocyclic deprotonated ligands and metal ions, we performed spectrophotometric titration of the twice deprotonated form of compound **I** by zinc acetate at 298 K.

At adding to the system the zinc salt solution [c(ZnAc$_2$) = 2.48×10^{-6} M] in acetonitrile in the presence of DBU the coordination occurs almost instantly reaching equilibrium between the coordinated form and the free ligand (Fig. 3). Upon increase in the concentration of ZnAc$_2$ the electron spectrum of dianionic form is transformed into the spectrum of zinc complex ZnL (L is twice deprotonated 2,3,7,8,12,-

13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin) with the parameters λ_{max} (log ε): 475 (5.41), 676 (4.68) (Fig. 3), which slightly ($\Delta\lambda_{max}$ ~ 3 nm) differ from the published data [18] obtained with DMF as a solvent. In benzene solution the EAS of ZnL is shifted to shorter wavelength region: λ_{max} (log ε): 470 (5.25), 605 (4.10), 659 (4.08) in agreement with the data of [15]. Obviously, the formation of the zinc complex is accompanied by addition of extra ligand DBU (extracoordination), which is a stronger electron donor than DMF.

EXPERIMENTAL

Purification of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetraphenylporphyrin was performed by chromatography on silica gel and alumina of II and III grade of activity, eluent chloroform-benzene. Individuality of the compound was checked by TLC on Silufol plates. The electron absorption spectra did not differ from those described in the literature [19, 20].

Spectrophotometric titration by DBU in acetonitrile was performed using a Varian Cary 100 spectrophotometer. The experimental procedure, preparation of compounds and reagents, and processing the experimental data were similar to the described methods [21, 22]. The error in determining the constants was ±3–5%.

The deprotonating reagent, 1,8-diazabicyclo[5.4.0]-undec-7-ene of extra pure grade was used without further purification. Solvents (benzene, chloroform, acetonitrile) were purified by standard methods [23, 24]. Zinc acetate of analytical grade was purified by recrystallization from aqueous acetic acid and dehydrated at 380–390 K [25].

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