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Formation of Phthalocyanines Deprotonated Forms and Their Interaction with Zn Ions in the System 1,8-Diazabicyclo[5.4.0]undec-7-ene–Acetonitrile at 298 K

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Abstract—The formation of deprotonated forms of tetra(*t*-butyl)phthalocyanine ((H$_2$*t*ButPc) and octa(pentoxy)-phthalocyanine (H$_2$OAmPc) in the system acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 298 K was studied by the method of spectrophotometric titration. With increasing DBU concentration sequential formation occurs of both mono- and douby deprotonated forms. The introduction of pentoxy groups into the fused benzene rings leads to a significant decrease in the acidity of the tetrapyrrole macrocycle compared with the *tert*-butyl substitution. The interaction of douby deprotonated forms of the phthalocyanines with zinc diacetate leads to the formation of metal complexes, the chelation constant of the latter is shown to correlate with the acidity of NH-protons in the nucleus of the macrocycle. For the chelation of more acidic tetra(*t*-butyl)-phthalocyanine an equimolar concentrations of zinc diacetate is sufficient, while the less acidic octa(pentoxy)-phthalocyanine requires almost 6-fold excess.

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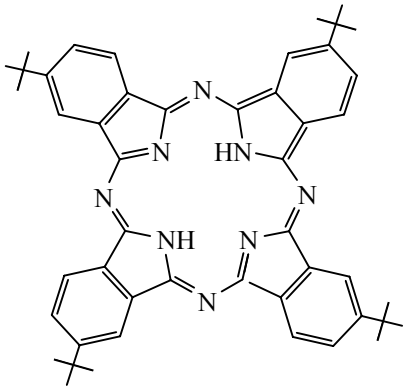
Metal complexes of tetrapyrrole compounds can be formed in an organic solution by both the molecular and ionic mechanisms [1, 2]. In the first case, tetrapyrrole compound reacts with a metal salt as a free base, while in the second case, as a deprotonated form. The type of mechanism of the complex formation is defined by the structure of the porphyrin macrocycle and/or the properties of the medium. Very different views were expressed regarding the priority of electronic effects of substituent and solvation effects of the medium [3–5].

The influence of the nature of the substituents in the pyrrole fragments on the complexation of the tetraazaporphyrin free bases with metal ions has been examined in several studies [6]. It was found that the factor determining the rate of complexation is the rupture of N–H bonds. Thus, the introduction of electron-withdrawing substituents leading to an increase in the acidity of the tetraazaporphyrin pyrrole protons results in a significant increase in the rate of complex formation. It was suggested that the increase in the rate is due to the stabilization of the douby deprotonated form of tetraazaporphyrn.

It is of considerable interest to elucidate the role of peripheral substitution in the formation of acidic properties of phthalocyanines and the complexation of the douby deprotonated forms with metal ions. With this purpose, in this paper mono- and double-deprotonated forms of tetra(*t*-butyl)phthalocyanine and octa(pentoxy)phthalocyanine were obtained, and a spectrophotometric study of complexation of Zn with the douby deprotonated forms in the system 1,8-diazabicyclo[5.4.0]undec-7-ene–ZnAc$_2$–acetonitrile at 298 K was performed.

Tetra(*tert*-butyl)phthalocyanine (**I**, H$_2$*t*ButPc) and octa(*n*-pentoxy)phthalocyanine (H$_2$OAmPc) (**II**) were synthesized by the described methods [7–9]. The structure of the compounds studied is shown in Fig. 1.

Concentrations of the studied compounds were determined spectrophotometrically using known extinction coefficients. For H_2*t*ButPc in acetonitrile: λ = 333 nm (log ε = 4.13), λ = 631 nm (log ε = 3,96), λ = 658 nm (log ε = 4.12), λ = 692 nm (log ε = 4. 14) [13]. For H_2OAmPc in acetonitrile: λ = 417 nm (log ε = 3.74), λ = 473 nm (log ε = 3,70), λ = 763 nm (log ε = 3.81). Spectrophotometric titration was carried out in the system of acetonitrile–1.8-diazabicyclo[5.4.0]-undec-7-ene at 298 K by the known method [10].



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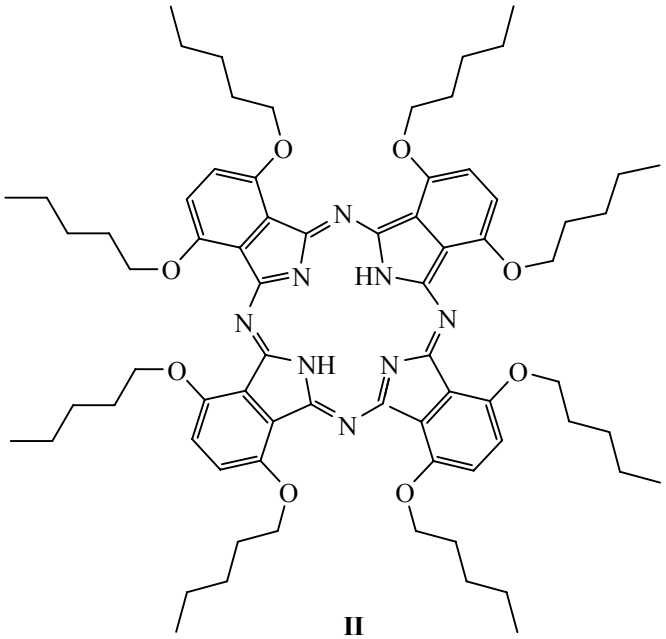

II

The chosen system contains a bipolar aprotic solvent acetonitrile of high purity (water content less than 0.03%), in which the original objects are in the molecular form, and a strong proton acceptor 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the ionization constant of its conjugated acid in acetonitrile is pK_a = 13.2 [11]. An important advantage of the deprotonating organic base DBU against the ordinary bases is its good solubility in non-aqueous organic solvents and the ability to ionize the acidic X–H bond without affecting the other groups in the molecule sensitive to the action of a base [12]. Such compounds are used widely enough in the synthesis and chemical research [13–15].

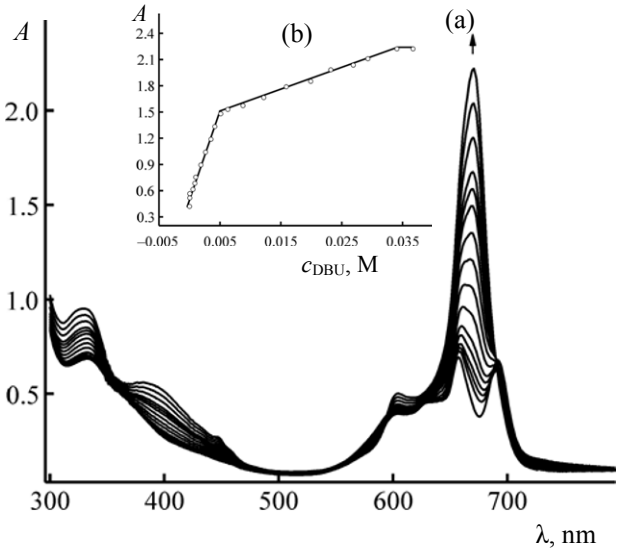

Fig. 1. (a) The absorption spectra and (b) the dependence of the optical density (A) of H_2*t*ButPc in acetonitrile at the titration with DBU (0–3.67×10^{-2} M) at 298 K. The arrow indicates the direction of spectral changes with increasing concentration of DBU. $c_{porph} = 5.25\times10^{-5}$ M, λ = 671 nm.

Figure 1 shows the absorption spectra of H_2*t*ButPc in acetonitrile measured by the spectrophotometric titration with DBU. The analysis of the spectrophotometric titration curve at the analytical wavelength 671 nm (Fig. 1a) shows that the deprotonation of the endocyclic nitrogen atoms of the tetrapyrrole macrocycle occurs in two steps. With increasing concentration of DBU ($c_{DBU} = 0 - 3.67\times10^{-2}$ M), in the electron absorption spectrum a formation was observed of two families of spectral curves, therewith, a certain family of isobestic points appeared, in line with the formation of the corresponding products.

The reactions proceeding in the solution are described by Eqs. (1), (2):

$$H_2tBuPc \overset{k_1}{\rightleftarrows} HtBuPc^- + H^+, \quad (1)$$

$$HtBuPc^- \overset{k_2}{\rightleftarrows} tBuPc^{2-} + H^+, \quad (2)$$

where H_2tButPc, HtButPc$^-$ and tButPc^{2-} denote the free base, mono-, and douby deprotonated forms of tetra(*t*-butyl)phthalocyanine, respectively.

With increasing concentration of the titrant (c_{DBU} = 0–5.01×10^{-3} M), the absorption spectrum gradually transformed into that of the mono-deprotonated form HtButPc$^-$, which is characterized by absorption bands: λ = 332 nm (log ε = 4.18), λ = 603 nm (shoulder, log ε = 3.89), λ = 669 nm (log ε = 4.45). With further increase in concentration of DBU to 3.67×10^{-2} M the transformation occurs of the mono-deprotonated form HtButPc$^-$ in the douby deprotonated form tButPc^{2-} with its characteristic absorption spectrum: λ = 328 nm (log ε = 4.25), λ = 381 nm (shoulder, log ε = 4.01), λ = 605 nm (log ε = 3.95), λ = 671 nm (log ε = 4.62). Determining the coordinates of the inflection point (and the corresponding concentration of DBU) in the titration curve (Fig. 1b), allowed us to distinguishing two DBU concentration ranges corresponding to the formation of mono- and douby deprotonated forms (1), (2). According to Eq. (3), for both processes acidic ionization constants on the first and second steps were calculated:

$$\log K_a = \log Ind + n \log c_{dbu}, \quad (3)$$

where K_a is acidity constant of the compound in the first (K_1) and second (K_2) steps; *Ind* is the indicator ratio HtButPc$^-$/H_2tButPc for the first stage and tButPc^{2-}/H_2tButPc for the second stage, c_{DBU} is analytical molar concentration of DBU in the a solution, n = 1 (number of protons bound by DBU).

The values of acidity constants of H_2tButPc in the system acetonitrile–DBU at 298 K were, respectively: K_1 = 2,05×10^{-2}, K_2 = 4.05×10^{-4}. Using the Eqs. (1), (2), (4), we can show by simple calculations [16] that at a concentration of DBU of 3.67×10^{-2} all the H_2tButPc molecules are in the deprotonated form.

$$c_0 = c(H_2tBuPc) + c(HtBuPc^-) + CP\ (tBuPc^{2-}). \quad (4)$$

Similar experiments on spectrophotometric titration were performed with H_2OAmPc (Fig. 2). With increasing concentration of the titrant (c_{DBU} = 0–4.03×10^{-2} M) the electron absorption spectrum gradually transformed into the spectrum of the mono-deprotonated form (HOAmPc$^-$): λ = 414 nm (log ε = 3.89), λ = 740 nm (log ε = 3.83) and with further increase in DBU concentration, in the range of 4.03×10^{-3}–7.83×10^{-2} M, the formation of douby deprotonated form OAmPc^{2-} was observed with the parameters: λ = 415 nm (log ε = 4.00), λ = 665 nm (shoulder, log ε = 3.83), λ = 730 nm (log ε = 4.25).

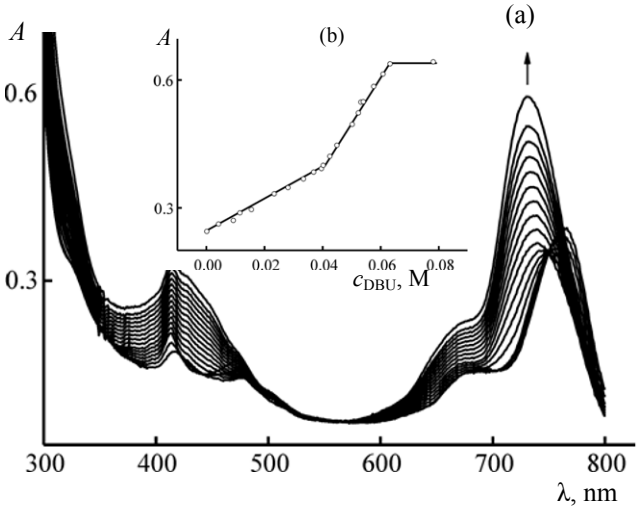

Fig. 2. (a) The absorption spectra and (b) the dependence of the optical density (A) of the H_2OAmPc in acetonitrile at the titration with DBU (0–7.83×10^{-2} M) at 298 K. The arrow indicates the direction of spectral changes with increasing concentration of DBU. c_{porph} = 5.96×10^{-5} M, λ = 730 nm.

By determining the coordinates of the inflection point (and the corresponding DBU concentration) on the titration curve (Fig. 2b) we were able to distinguish two areas in the electron absorption spectrum of the reaction system related to the first and second deprotonation steps. According to Eq. (3), for both processes the ionization constants of the acid in the first and second steps were consistently calculated. The values of the acidity constants in the system acetonitrile–H_2OAmPc–DBU at 298 K were as follows: K_1 = 4.37×10^{-2}, K_2 = 8.94×10^{-4}.

In order to study the complexation of deprotonated macrocyclic ligands with metal ions, we performed the direct titration of the douby deprotonated forms **I** and **II** with zinc diacetate (Figs. 3, 4).

With increasing concentration of titrant $ZnAc_2$ to 6.78×10^{-5} M the electron absorption spectrum of douby deprotonated form tButPc^{2-} transformed to the absorption spectrum of zinc complex ZntButPc with

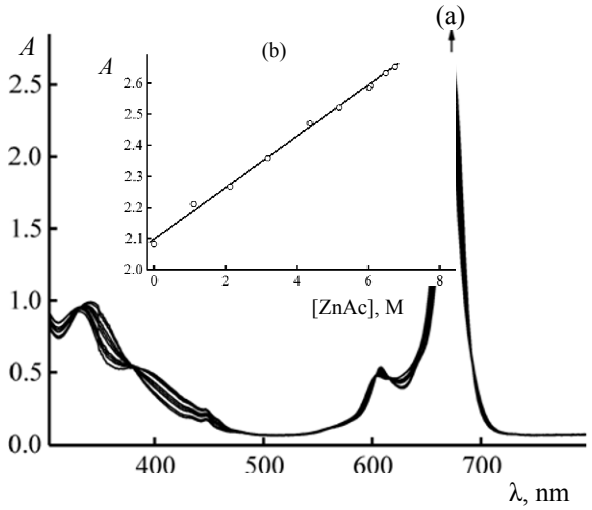

Fig. 3. (a) The absorption spectra and (b) titration curve of douby deprotonated form *t*ButPc^{2-} in the acetonitrile–DBU–Zn(OAc$_2$) [Zn(OAc$_2$) = 0–6.78×10^{-5} M] at 298 K. c_{porph} = 5.25×10^{-5} M, λ = 674 nm. The arrow indicates the direction of spectral changes with increasing concentration of the titrant.

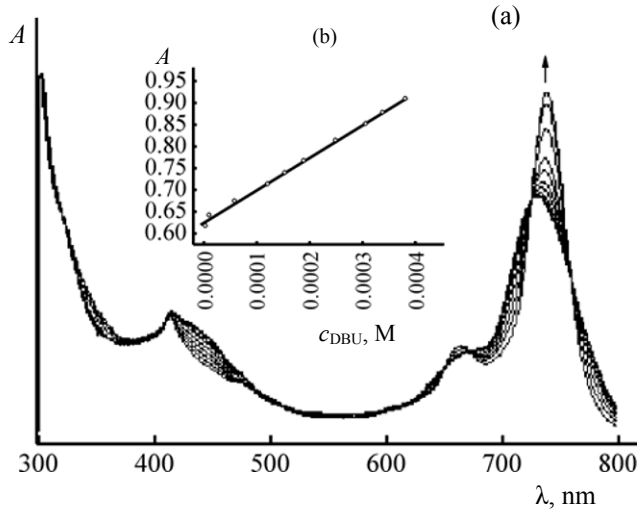

Fig. 4. (a) The absorption spectra and (b) titration curve of douby deprotonated form *n*AmPc^{2-} in the acetonitrile–DBU–Zn(OAc$_2$) [Zn(OAc$_2$) = 3.36×10^{-4} M] at 298 K. c_{porph} = 5.96×10^{-5} M, λ = 739 nm. The arrow indicates the direction of spectral changes with increasing concentration of the titrant.

the following parameters of the spectrum: λ = 346 nm (log ε = 4.30), λ = 447 nm (shoulder, log ε = 3.44), λ = 608 nm (log ε = 4.03), λ = 641 nm (shoulder, log ε 4.00), λ = 675 nm (log ε = 4.73). The resulting absorption spectrum is in good agreement with literature data on the absorption spectrum of Zn*t*ButPc in benzene [9, 17], which confirms the conclusion about the formation of zinc complex as a result of the titration of the douby deprotonated form *t*ButPc^{2-} with zinc diacetate.

Similarly, as a result of the titration of the douby deprotonated form OAmPc^{2-} with zinc diacetate zinc complex ZnOAmPc formed with a characteristic absorption spectrum: λ = 412 nm (log ε = 3,99), λ = 665 nm (log ε = 3.64), λ = 739 nm (log ε = 4.18). The resulting absorption spectrum corresponds to the absorption spectrum of ZnOAmPc synthesized in the usual way. It should be noted that in both cases, the formation of axially arranged DBU molecules as the ligands in the zinc complexes was not observed [18].

In conclusion, let us consider the relationship between the molecular structure of a compound and the efficiency of formation of metal complex at the titration of its douby deprotonated form. As we have shown above, the introduction of different substituents in the fused benzene rings of phthalocyanine molecules leads to significant changes in the acidity of the pyrrole NH protons. The tetra-*tert*-butylphthalocyanine molecule **I** is more acidic than octa(*n*-pentoxy)phthalocyanine (**II**), which results in substantially lower (more than twofold) values of the constants K_1 and K_2. As a result, the complete chelation of zinc ions by the douby deprotonated form *t*ButPc^{2-} is achieved at the slightly higher $ZnAc_2$ concentration than the concentration of phthalocyanine (i.e., at almost equimolar ratio), and in the case of douby deprotonated form OAmPc^{2-} only at the 6-fold excess of $ZnAc_2$ (Fig. 4). Thus, we conclude that the constant of formation of Zn complexes in the reaction of $ZnAc_2$ with the douby deprotonated phthalocyanines increases significantly with increasing acidity of the pyrrole NH protons.

The studies of acid and complexing properties of tetra(*tert*-butyl)- and octa(*n*-pentoxy)phthalocyanines in the system acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-ene at 298 K showed the possible advantage of chelation of metal ions by the douby deprotonated form over the complex formation with the neutral ligand in the development of new methods for porphyrins. A significant decrease in the concentration range (1:6) as compared with conventional (1:10, 1:100) [1, 4, 5], and instant proceeding of the reaction appear to be most promising for designing the synthesis of new molecules with specific functional properties.

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REFERENCES

1. Berezin, B.D., *Koordinatsionnye soedineniya porfirinov i ftalotsianinov* (Coordination Compounds of Porphyrins and Phthalocyanines), Moscow: Nauka, 1978, p. 280.
2. Mironov, A.F., *Sorosovsk. Obrazovat. Zh*., 1998, no. 7, p. 10.
3. Rumyantsva, S.V., Stuzhin, P.A., Khelevina, O.G., Metel'kova, S.S., and Berezin, B.D., *Izv. Vuzov, Ser. Khim. i Khim. Tekhnol*., 1986, vol. 29, no. 5. p. 19.
4. Stuzhin, P.A., Khelevina, O.G., and Berezin, B.D., *Zh. Fiz. Khim*., 1987, vol. 61, no. 1, p. 82.
5. Berezin, B.D., Khelevina, O.G., and Stuzhin, P.A., *Zh. Fiz. Khim*., 1985, vol. 59, no. 9, p. 2181.
6. Stuzhin, P.A. and Khelevina, O.G., *Usp. Khim. Porfirinov, SPb: NII himii SPbGU*, 1997, vol. 1, p. 151.
7. Cook, M.J., Dunn, A.J., Howe, S.D., and Thomson, A.J., *J. Chem. Soc., Perkin Trans. 1,* 1988, p. 2453.
8. Donzello, M.P., Ercolani, C., Gaberkorn, A.A., Kudrik, E.V., Meneghetti, M., Marcolongo, G., Rizzoli, C., and Stuzhin, P.A., *Chem. Eur. J*., 2003, vol. 9, no. 17, p. 4009.
9. Mihalenko, S.A., Barkanova, S.V., Lebedev, O.A., and Luk'yanets, E.A., *Zh. Obshch. Khim*., 1971, vol. 41, no. 12, p. 2735.
10. Ivanova, Yu.B., Churakhina, Yu.I., and Mamardashvili, N.Zh., *Zh. Obshch. Khim*., 2008, vol. 78, no. 4, p. 691.
11. Kaljurand, A., Kütt, L., Sooväli, T., Rodima, V., Mäemets, I., Leito, I., and Koppel, A., *J. Org. Chem*., 2005, vol. 70, p. 1019.
12. Pozharskii, A.F., *Usp. Khim*., 1998, vol. 67, no. 1, p. 3.
13. Alder, R.W., Bowman, P.S., Steele, W.R.S., and Winterman, D.R., *J. Chem. Soc. Chem. Commun*., 1968, p. 723.
14. Lau, Y.K., Saluya, P.P.S., Kebarle, P., and Alder, R.W., *J. Am. Chem. Soc*., 1978, vol. 100, p. 7328.
15. Staab, H.A., Saupe, T., and Krieger, C., *Angew. Chem. Int. Ed. Engl*., 1983, vol. 22, p. 731.
16. Bernshtein, I.Ya. And Kaminskii, Yu.L., *Spektrofotometricheskii analiz v organicheskoi khimii* (Spectro photometric Analysis in Organic Chemistry), Leningrad: Khimiya, 1986, p. 202.
17. Dent, C.E. and Linstead, R.P., *J. Chem. Soc.,* 1934, p. 1027.
18. Lebedeva, N.Sh., Pavlycheva, N.A., and V'yugin, A.I., *Zh. Org. Khim*., 2004, vol. 40, p. 1776.