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Effect of the Structure of the *meso*–Alkyl Substituent on the Physicochemical and Coordination Properties of the Porphyrin Ligand

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The acid-base and coordination properties for the series of meso-alkyl substituted porphyrins were studied spectrophotometrically: 5,10,15,20-tetrabutylporphyrin ($H_2(n\text{-}Bu)_4P$)*, 5,10,15,20-tetra-iso-butylporphyrin* ($H_2(i\text{-}Bu)_4P$)*, 5,10,15,20-tetrakis(tert-butyl)porphyrin* ($H_2(t\text{-}BuP)_4$)*, 5,10,15,20-tetra(trifluoromethyl)porphine* ($H_2(CF_3)_4P$)*. The electronic absorption spectra of molecular and ionized forms of meso-substituted porphyrins in acetonitrile, acid constants and basic ionization of the porphyrins were measured. It is shown that a change in the structure of the meso-substituent in the porphyrin macrocycle drastically changes the acid-base and coordination properties of the porphyrin. The analysis of complex formation of the molecular and dianionic forms of the porphyrin with zinc acetate has been made.*

Keywords: Porphyrins, acid-base properties, protonated forms, coordination properties.

Влияние структуры *мезо*–алкильного заместителя на физико–химические и координационные свойства порфиринового лиганда

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Кислотно-основные и координационные свойства семейства мезо-алкилзамещенных порфиринов были изучены спектрофотометрически: 5,10,15,20-тетрабутилпорфирин ($H_2(n\text{-}Bu)_4P$)*, 5,10,15,20-тетра-изобутилпорфирин* ($H_2(i\text{-}Bu)_4P$)*, 5,10,15,20-тетракис(трет-бутил)порфирин* ($H_2(t\text{-}Bu)_4P$)*, 5,10,15,20-тетра(трифторметил) порфин* ($H_2(CF_3)_4P$)*. Измерены электронные спектры поглощения молекулярных и ионизированных форм мезо-замещенных порфиринов в ацетонитриле, определены константы кислотной и основной ионизации порфиринов. Показано, что изменение структуры заместителя в мезо-положении макроцикла порфирина резко меняет кислотно-основные и координационные свойства порфирина. Проведен анализ комплексообразующих свойств молекулярных и дианионных форм порфириновых лигандов с ацетатом цинка.*

Ключевые слова: Порфирины, кислотно-основные свойства, протонированные формы, координационные свойства.

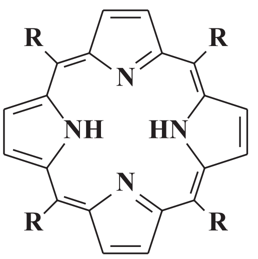
Introduction

Porphyrins are naturally occurring aromatic compounds of significant biological role. For example, heme or chlorophyll are indispensable parts of biosystems. The advantage of using porphyrin macrocycles is their conformational flexibility making them able to form multiple nonplanar conformations needed for a variety of biological functions.[1,2] Porphyrins and their metal complexes are used in catalysis,[3-5] dye-sensitized solar cells,[6-8] photodynamic therapy,[9-11] molecular sensors,[12-14] nonlinear optical elements,[15-17] and sorbents[18-19] due to their outstanding properties. Another explanation of unique porphyrin properties originates from the possibility of modification the periphery and the center of the macrocycle by introducing various substituents. A study of substitution effects allows to get closer to solving one of the fundamental problems of chemistry, namely, the relationship between structure and properties of molecules. A variety of practically useful properties of porphyrins and their analogues is also due to the peculiarities of the structure.[20-28] Porphyrins form stable coordination compounds of 1:1 composition (metal:ligand) with most metals (except alkali ones). However, a complexation proceeds as a multicenter interaction and the experimentally derived reaction mechanism has been proposed.[1] The reaction costs a lot of energy needed to overcome the potential barrier. It explains why the porphyrins being kinetically inert, able to form complexes in such conditions as solvation of NH protons and presence of solvent molecules bound in labile way within coordination sphere of metal cations. A formation of metalloporphyrins, as a rule, proceeds rather slowly, being several orders of magnitude slower than with metal ion complexation with other organic and inorganic ligands.[1,2]

Typical spectra of porphyrins and their complexes are characterized by intense absorption in the range from 400 to 500 nm (Soret band) of molar absorption coefficients reaching up to 200000 L/(mol·cm).[2] Such characteristic let us to control the process of complexation by conventional methods of chemical kinetics, for example, by spectrophotometrics.

Until recently, the influence of porphyrin structure on a metal ion complexation was expected to be negligible. One could find reasons for that, for example, a coordination of the Cu^{2+} ion by porphyrins upon varying functional substituents of porphyrin macrocycle differs in the rate constant of complex formation not larger than for two orders of magnitude.[1] However, later studies demonstrated that introduction of specific substituents may change drastically the geometric parameters of the molecule and selectively regulate desired physico-chemical properties.[24,29-31] These findings are relevant for the studies of influence of electronic and steric effects of the porphyrin macrocycle substituents on the coordination, acid-base, and spectral properties of porphyrins.

In this study, the interrelation was studied between the electronic and structural effects of the substituents at *meso*-positions of the porphyrin macrocycle on physico-chemical properties and coordinating ability of the following tetra-*meso*-alkyl substituted porphyrins: 5,10,15,20-tetrabutylporphyrin (**I**, $H_2(n\text{-Bu})_4P$), 5,10,15,20-tetra-*iso*-butylporphyrin (**II**, $H_2(i\text{-Bu})_4P$), 5,10,15,20-tetrakis(*tert*-butyl)porphyrin (**III**, $H_2(t\text{-BuP})_4$), 5,10,15,20-tetra(trifluoromethyl)porphine (**IV**, $H_2(CF_3)_4P$).



I R = $-CH_2CH_2CH_2CH_3$
II R = $-CH_2CH(CH_3)_2$
III R = $-C(CH_3)_3$
IV R = $-CF_3$

Experimental

General

Materials and Reagents

The porphyrins were synthesized and isolated by known procedures.[32-36] Spectral characteristics of porphyrins **I-IV** are in agreement with the literature.

5,10,15,20-Tetrabutylporphyrin (***I***, *$H_2(n\text{-Bu})_4P$*). UV-Vis (CH_2Cl_2) λ_{max} (lgε) nm: 417 (5.66), 520 (4.18), 555 (4.0), 600 (3.60), 659 (3.90). ^{1}H NMR ($CDCl_3$) δ_H ppm: 9.46 (s, 8H, pyr), 4.93 (t, 8H, *α*-CH_2), 2.50 (m, 8H, *β*-CH_2), 1.83 (m, 8H, *γ*-CH_2), 1.13 (t, 12H, CH_3), –2.64 (s, 2H, NH).

5,10,15,20-Tetra-iso-butylporphyrin (***II***, *$H_2(i\text{-Bu})_4P$*). UV-Vis (CH_2Cl_2) λ_{max} (lgε) nm: 417 (5.65), 519 (4.15), 553 (4.04), 598 (3.7), 658 (3.95). ^{1}H NMR δ_H ppm: –2.65 (br, s, 2H, NH), 1.19 (d, 24H, CH_3), 2.62–2.81 (m, 4H, CH), 4.86 (d, 8H, CH_2), 9.45 (s, 8H, β-H).

5,10,15,20-Tetrakis(tert-butyl)porphyrin (***III***, *$H_2(t\text{-Bu}_4)P$*). UV-Vis (CH_2Cl_2) λ_{max} (lgε) nm: 446 (5.27), 552 (3.85), 596 (3.60), 628 (3.48), 691 (3.30). ^{1}H NMR (250 MHz, $CDCl_3$, TMS) δ_H ppm: 1.52 (br s, 2H, NH), 2.01 (s, 36H, CH_3), 9.08 (s, 8H, β-H).

5,10,15,20-Tetra(trifluoromethyl)porphine (***IV***, *$H_2(CF_3)_4P$*). UV-Vis (CH_2Cl_2) λ_{max} (lgε) nm: 403 (5.08), 510 (3.97), 545 (3.97), 593 (3.67), 649 (4.00). ^{1}H NMR δ_H ppm: 9.60 (s, 8 H), –2.08 (s, 2H, NH).

Zinc acetate of analytical grade was recrystallized from aqueous acetic acid and dehydrated at 380–390 K according to.[37] Dry acetonitrile (water contaminant is not higher than 0.03 %) was used for titration experiment. The 1,8-diazabicyclo[5,4,0]undec-7-en (DBU) was used as deprotonating agent. DBU and perchloric acid $HClO_4$ were used as received without additional purification.

General Experimental Methods and Instrumentation

^{1}H NMR spectra were recorded with spectrometer Bruker-500 (Germany) using operating frequency of 500 MHz in $CDCl_3$ with TMS as the internal reference. UV-Vis spectra were recorded in the acetonitrile solutions with two-beam spectrophotometers Shimadzu UV-180 and Hitachi U-2000 utilizing a quartz cell of optical path of 1 mm and 10 mm.

Complexation was studied by spectrophotometric method utilizing thermostatic cuvettes at temperatures from 293 to 308 K. Temperature fluctuations was not higher than ±0.1 K. All studied systems demonstrated isosbestic points in the spectra in course of titration. Reactions obeyed the first order law on porphyrin, which is proved by linearity of $\lg(C^0_{H2P}/C_{H2P}) - \tau(s)$ dependence (C^0_{H2P} and C_{H2P} are the initial and current concentrations of the porphyrin, respectively). Concentration of the porphyrin during the experiment was controlled by changing the optical density of the solution.

The linearity of dependence of the optical density of the porphyrin solutions on concentration has been confirmed in previous study.[1]

Kinetic experiments were performed under conditions of ~50–100-fold excess of $Zn(OAc)_2$ over a porphyrin that allows calculating the effective rate constants (k_{eff}) of the complex formation reaction by Equation (1):

$$k_{\text{eff}} = (1/t)\ln[(A_o - A_\infty)/(A - A_\infty)] \tag{1}$$

Here A_0, A, A_∞ are the optical densities of the porphyrin solution at the initial moment, at the time t and at the end of the reaction, respectively. The optical density of the solutions was measured for each porphyrin at two wavelengths corresponding to the absorption maxima of the porphyrin and its Zn-complex. The root-mean-square error in the determination of k_{eff} does not exceed 3 %. The rate constants of $(n + 1)$ order were calculated by Equation (2):

$$k_{n+1} = k_{\text{eff}}/C^{n}_{\text{Zn(OAc)}_2}, \tag{2}$$

where n is the order of reaction (2) on zinc acetate being equal to 1.0 in acetonitrile.[38]

The activation energy (E_a) for studied temperature range was calculated according to the Arrhenius equation:

$$E_a = 19.1\cdot[(T_1\cdot T_2)/(T_2 - T_1)]\ \lg(k_{\text{eff2}}/k_{\text{eff1}}), \tag{3}$$

where k_{eff2}, k_{eff1} are the effective reaction rate constants at T_2 and T_1, respectively. The entropy of transition state formation ($\Delta S^{\neq}$) was calculated by the equation:

$$\Delta S^{\neq} = 19.1\cdot\lg k_v + E_a/T - 253 \tag{4}$$

Spectrophotometric titration of studied porphyrins with perchloric acid and 1,8-diazabicyclo[5.4.0]undec-7-ene in acetonitrile was performed by means of Shimadzu UV-1800 spectrophotometer. Experimental techniques and processing of experimental data were described previously in detail.[39,40] The error in determining the basicity constants was no higher than 3–5 %. Acetonitrile was used as a solvent for titration. The initial compounds in acetonitrile were in a molecular form that is was confirmed by the measured absorption spectra of the porphyrins.

Results and Discussion

UV-Vis Spectra and Structure of Porphyrins

Spectra of studied porphyrins (Table 1) revealed that substitution of the electron-donating alkyl groups at *meso*-positions of the macrocycle (porphyrin **I-II**) with electron-withdrawing trifluoromethyl groups (porphyrin **IV**) led to the shift of the absorption bands for about 6–10 nm into shortwave region. Such hypsochromic shift is due to decreasing in energy of HOMOs. The decrease is explained by lowering of the electron density on the carbon atoms of the methine groups. The phenomenon is in agreement with the Gouterman four-orbital model.[41]

However, the introduction of electron-donating *tert*-butyl groups (**III**) into the *meso*-position drastically changes the spectra: despite mentioned above electron-donating effect, a bathochromic shift of all the absorption bands for ~30 nm is observed (Table 1). According to the literature[33,42-45] and computer modelling data (B3LYP/6-311G) (Figure 1) all studied porphyrins have "*ruf*" type of macrocycle nonplanar deformation.

The structure of both 5,10,15,20-tetrabutylporphyrin and 5,10,15,20-tetra(trifluoromethyl)porphine remains nearly planar (maximum deviation among 24 atoms from the planarity of the macrocycle is 0.08 Å and 0.17 Å, respectively). Such structural changes are known to indirectly affect the electronic structure of the macrocycle, namely reducing its aromaticity and increasing the electron density on the central nitrogen atoms. Thus, both the base and acid properties of the molecule increase.[46-48]

Formation of the Ionized Porphyrin Species

The acid-base properties of porphyrins **I**–**IV** were studied by spectrophotometric titration at various pH values of the solution. Depending on the acidity of the medium and the type of the tetrapyrrolic molecule one can obtain both

Table 1. Wavelength, maxima and extinction coefficients of UV-Vis absorption spectra of molecular (**FB**) and ionized (monoprotonated (**MP**), doubly protonated (**DP**) and doubly deprotonated (**DD**)) forms of *meso*-substituted porphyrins in acetonitrile, indicators of acid and basic ionization of porphyrins (**I-IV**).

Porphyrin	λ(lgε) Soret	λ_4(lgε)	λ_3(lgε)	λ_2(lgε)	λ_1(lgε)	p$K_{b1,2}$	p$K_{a1,2}$
IFB	409 (4.85)	516 (3.84)	550 (3.69)	597 (3.41)	656 (3.54)	24.06	–
IMP	413 (4.83)	–	–	587 (3.64)	634 (3.63)		
IDP	415 (4.84)	–	580 (3.65)	–	627 (3.92)		
IIFB	410 (5.04)	517 (4.02)	550 (3.88)	597 (3.57)	655 (3.72)	18.41	–
IIMP	414 (5.00)	473 (3.47)	–	590 (3.77)	637 (3.80)		
IIDP	418 (5.04)	470 (3.49)	583 (3.76)	–	630 (4.03)		
IIIFB	446 (5.27)	552 (3.85)	596 (3.60)	628 (3.48)	692 (3.30)	–	–9.75
IIIDD	444 (5.24)		545 (3.50)				
IVFB	400 (5.23)	509 (4.14)	544 (4.13)	591 (3.84)	647 (4.11)	3.33	–9.69
IVMP	415 (5.24)	511 (3.74)	547 (4.01)	589 (4.08)	645 (3.80)		
IVDP	417 (5.55)	570 (4.22)	–	614 (4.13)	–		
IVDD^{-}	431 (4.96)			598 (4.00)	717 (3.89)		

single- and doubly-charged ions being in equilibrium with each other and neutral form.

$$H_3P^+ \xrightleftharpoons{K_{b1}} H_2P + H^+, \tag{5}$$

$$H_4P^{2+} \xrightleftharpoons{K_{b2}} H_3P^+ + H^+, \tag{6}$$

$$H_2P \xrightleftharpoons{K_{a1}} HP^- + H^+, \tag{7}$$

$$HP^- \xrightleftharpoons{K_{a2}} P^{2-} + H^+, \tag{8}$$

where H_2P, HP^-, P^{2-}, H_3P^+, H_4P^{2+} are the molecular, mono- and double-deprotonated and protonated forms of the porphyrins. The dissociation constants of protonated forms of porphyrins and the state of dissociation of molecular forms are traditionally designated as K_b and K_a.[48-50]

The dissociation of cationic type proceeding within acidic medium was studied in acetonitrile (AN)–perchloric acid (0.01 M solution in acetonitrile) system at 298 K. Under these conditions $HClO_4$ having high dissociation constant[49] is completely dissociated and the protonation process is due to solvated protons. Equilibria taking place in the solution are described by Equations 5 and 6. The overall constant of the first and second steps ionization for studied compounds determined with the AN–$HClO_4$ system at 298 K was calculated by Equation (9):

$$pK_b = pH + \lg Ind, \tag{9}$$

where K_b is the constant of the compound basicity, *Ind* is the indicator ratio $[H_4P^{2+}]/[H_3P^+]$, pH is the analytical value of the acidity of the solution contributed by the titrant.

The spectral features of the molecular and protonated forms, as well as the total constants of the first and second steps ionization for studied compounds in the AN–$HClO_4$ system at 298 K are presented in Table 1. Typical spectral changes during the titration are shown in Figures 2 and 3.

Substitution of trifluoromethyl groups ((I-) effect) with alkyl substituents in the *meso*-positions of the porphyrin macrocycle ((I+) effect) leads to an increase in electron density on the central nitrogen atoms and, as a result, the basicity constant ($-\lg K_{b1,2}$) increase for about 20 orders of magnitude. The porphyrins form the following series:

IV (3.33) << $\mathbf{H_2P}$ (15.35[50]) < **II** (18.41) < **I** (24.06)

The decrease in the basicity of 5,10,15,20-tetra-*iso*-butylporphyrin compared to 5,10,15,20-tetrabutylporphyrin $H_2(n\text{-Bu})_4P$ is apparently caused by steric factors providing slightly higher deformation of the macrocycle. Spectrophotometric titration of the $H_2(t\text{-Bu})_4P$ was failed to fix stable protonated forms of the compound. It is likely to be due to the extreme deformation of the macrocycle and instability

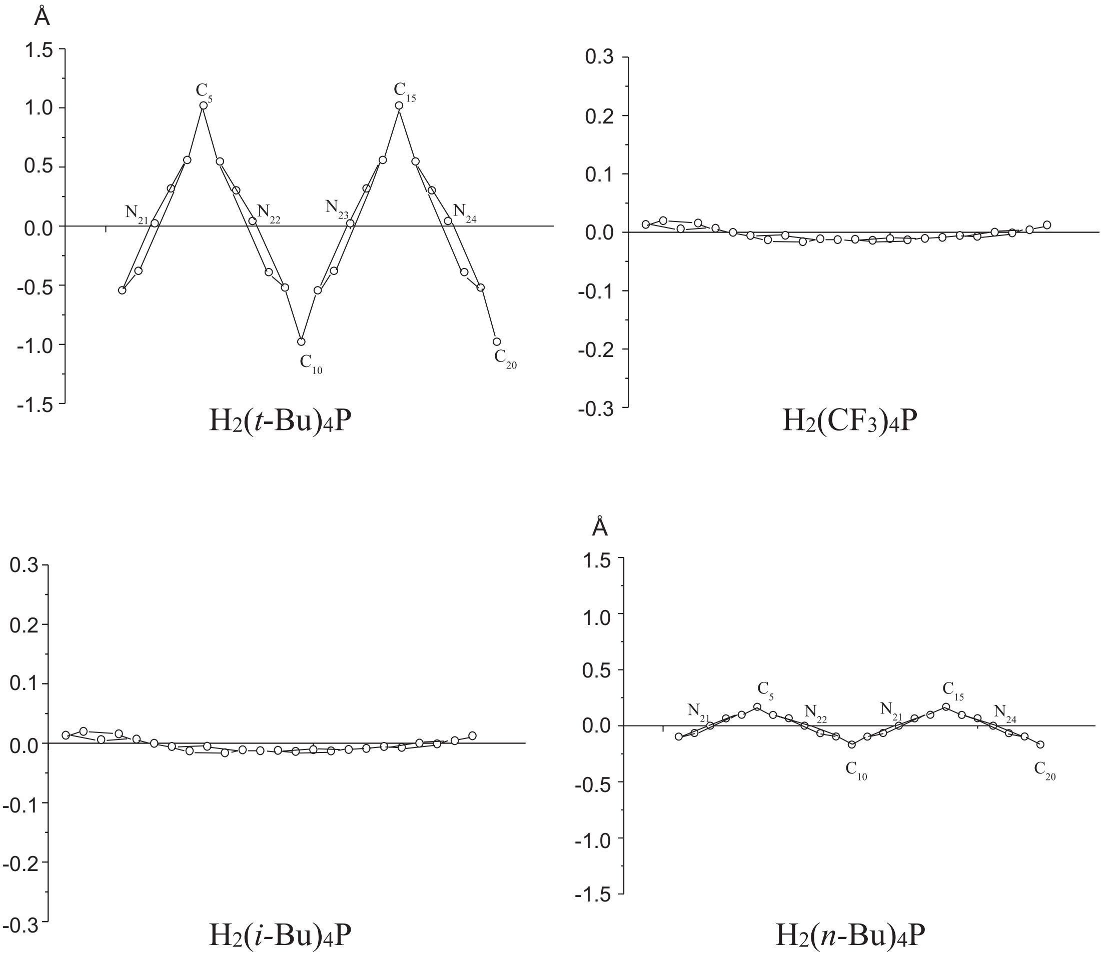
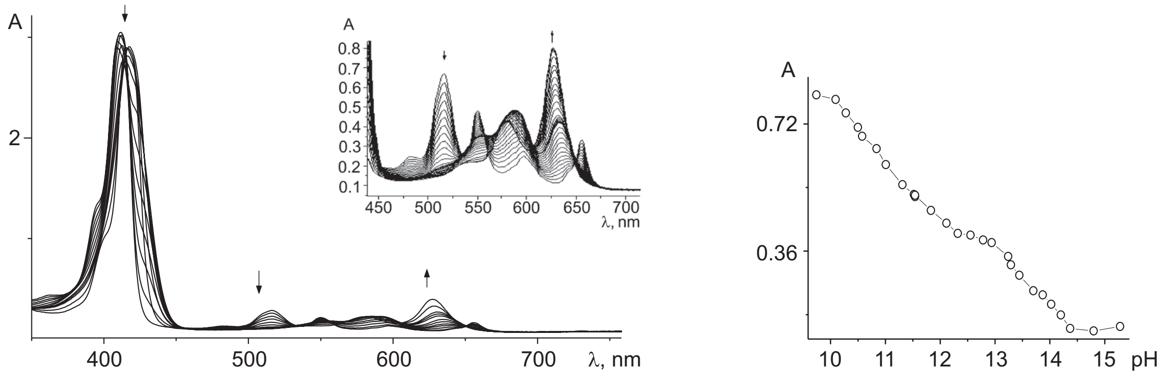
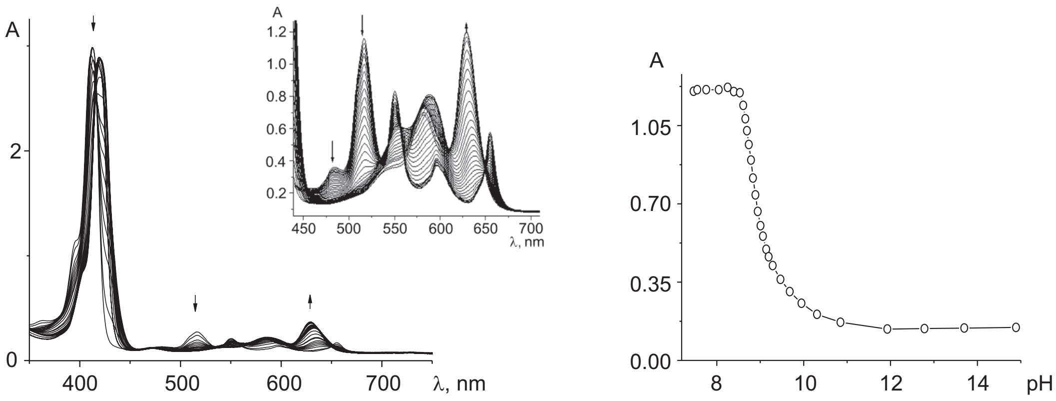


Figure 1. The deviation of the atoms from the mean planes of the macrocycle carried out through 24 atoms of the porphyrin macrocycle according to the calculations by the B3LYP/6-311G method.



(A) (B)

Figure 2. UV-Vis spectra (A) and the spectrophotometric titration curve (λ = 627 nm) (B) of compound **I** in the AN–$HClO_4$ system, ($C_{porp} = 1.71\cdot10^{-5}$ mol·L^{-1}; $C_{HClO4} = 0\div3.40\cdot10^{-5}$ mol·L^{-1}), 298 K.



(A) (B)

Figure 3. UV-Vis spectra (A) and the spectrophotometric titration curve (λ = 629 nm) (B) of compound **II** in the AN–$HClO_4$ system, ($C_{porp} = 1.4\cdot10^{-5}$ mol·L^{-1}; $C_{HClO4} = 0\div3.3\cdot10^{-5}$ mol·L^{-1}), 298 K.

of the protonated forms. However, the authors[42–43] applying more polar methanol as a solvent found protonation to occur along two opposite *meso*-carbons during the formation of the cationic form. This actually results in the formation of porphodimethene involving sp^3-hybridized carbon *meso*-atoms, which relieves the deformation stress, caused by the protonation of the central nitrogen atoms, and contributes to the stabilization of the dicationic form.

An influence of alkyl substituent structure is clear when the acidic properties of the compounds **I**–**IV** are obtained. Acid ionization constants were also obtained by spectrophotometric titration in acetonitrile–1,8-diazabicyclo[5.4.0]undec-7-en (DBU) system at 298 K. Anionic forms of the H_2(*i*-Bu)$_4$P, H_2(*n*-Bu)$_4$P were not obtained even at maximum concentrations of DBU. It indicates very low acidity of studied tetra-*meso*-alkyl substituted porphyrins. Spectrophotometric titration of the $H_2(CF_3)_4P$ and H_2(*t*-Bu)$_4$P revealed the formation of two families of spectral curves upon increase in DBU concentration, each of them have its own set of isobestic points. This fact indicates two-step deprotonation process. The coordinates of the inflection point (and corresponding C_{DBU}) determined from the titration curve (the example is shown in the Figure 4) allow distinguishing two ranges within the spectrum of the reaction system corresponding to the first and second deprotonation steps (Equations (7), (8)), *i.e.* point to the formation of mono- and dianionic types (HP^-, P^{2-}) of the $H_2(CF_3)_4P$ and H_2(*t*-Bu)$_4$P porphyrins. The values of the overall acidity constants for the $H_2(CF_3)_4P$ and H_2(*t*-Bu)$_4$P were calculated according to the Equation (10) and are presented in Table 1.

$$pK_a = \lg Ind + 2\lg C_{DBU} \qquad (10)$$

Similar values of the acidity constants for the $H_2(CF_3)_4P$ and H_2(*t*-Bu)$_4$P are due to different origin of the effects of *meso*-substituents in these two cases. From one side, the pronounced electronic influence of a strong electron-accepting group in the $H_2(CF_3)_4P$ is observed. On the other, the dominating factor for the H_2(*t*-Bu)$_4$P is the deformation of the planar structure resulting from mutual repulsion between *β*-pyrrole protons of the macrocycle and protons of the bulky *tert*-butyl group. A distortion of the macrocycle planarity leads to slightly detaching *π*-electron systems

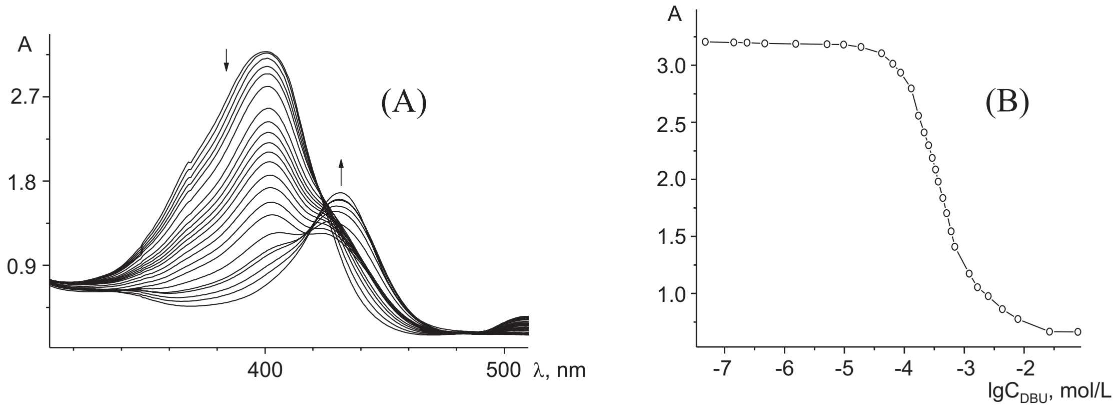


Figure 4. UV-Vis spectra (A) and the spectrophotometric titration curve (λ = 400 nm) (B) of compound **IV** in the AN–$HClO_4$ system, (C_{porp} = 1.89 10^{-5} mol·L^{-1}; C_{DBU} = 0÷7.9·10^{-3} mol·L^{-1}), 298 K.

of pyrrole and pyrrolenine fragments and, as a result, to an increasing both base and acid properties.

Interestingly, further increase of the organic base concentration (above 3.8·10^{-5} M) completely destroys the H_2(*t*-Bu)$_4$P macrocycle. In this way, the concentration range of the organic base (DBU) allowing existence of deprotonated (*t*-Bu)$_4P^{2-}$ was determined.

Kinetic Studies

The study of complexation of porphyrins with zinc acetate was carried out by a spectrophotometric method using AN and in AN+DBU systems.

The coordination of the porphyrin ligand with zinc acetate in gioven solvent proceeds according to the Equation (11):

$$H_2P+[Zn(OAc)_2(AN)_{n-2}] \rightarrow ZnP + 2HOAc + (n–2)AN \qquad (11)$$

One can study the formation of zinc complexes within the AN + H_2P + DBU system according to the “ionic mechanism” upon establishing the concentration of an organic base, at which all molecules are double-deprotonated (Figure 5). The reactions can be represented by the Equation:

$$[DBU{\cdot}2H]^{2+}P^{2-} + [Zn(OAc)_2(AN)_{n-2}] \rightarrow$$
$$\rightarrow ZnP + 2HOAc + (n–2)AN + DBU, \qquad (12)$$

where *n* is the coordination number of zinc cation.

In all the titration experiments the distinct isobestic points in the spectra have been observed. Typical spectral changes for compound **IV** are shown in Figure 6. The kinetic parameters of Zn porphyrinates formation reactions are presented in Table 2.

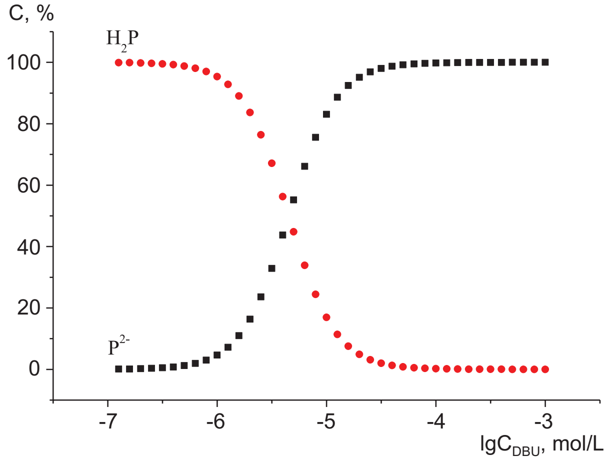


Figure 5. The distribution of the concentrations of molecular and double deprotonated forms of porphyrins during the titration of porphyrin **IV**.

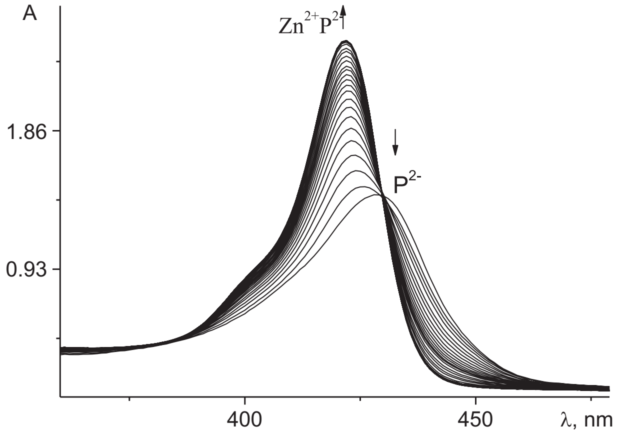


Figure 6. Changes in electronic absorption spectra during the coordination reaction of dianion **IV** with zinc acetate in the AN–DBU–$Zn(OAc)_2$ system at 298 K, $C_{Zn(OAc)_2}$ = 0.3·10^{-3} mol·L^{-1}.

Electron-accepting groups in the *meso*-positions of the macrocycle are known to reduce an electron density on the tertiary nitrogen atoms not contributing a strengthening of the N→M bonds of the transition state. As a result, it can slow down the complexation. Electron-donating substituents demonstrate the opposite effect. However, an increase in the rate constant of zinc ion complexation for three orders of magnitude, revealed for the molecular forms upon the transition from the H_2(*t*-Bu)$_4$P to $H_2(CF_3)_4P$, is likely depends not only on electronic influence of the substituent, but also on an extremely distorted structure of the H_2(*t*-Bu)$_4$P.

Table 2. Kinetic parameters of the reaction of the formation of Zn-porphyrins in acetonitrile and an AN–DBU.

Porphyrin	Solvent	$C_{Zn(OAc)_2}$, 10^3 mol·L^{-1}	k^{298}_{v}, 10^3 L·mol·s^{-1}	E_a, kJ·mol^{-1}	$\Delta S^{\neq}$, J·mol^{-1}·K^{-1}
$H_2(t\text{-Bu})_4P$	AN	4.5	4080 ± 5	46.4 ± 0.7	-85.6 ± 1.5
$(t\text{-Bu})_4P^{2-}$	AN + DBU	4.5	4620 ± 5	38.9 ± 0.5	-109.9 ± 2.0
$H_2(CF_3)_4P$	AN	11.4	6.05 ± 0.08	52 ± 2	-175 ± 2
$(CF_3)_4P^{2-}$	AN + DBU	0.30	4006 ± 5	24 ± 1	-143 ± 2

The distortion is caused by a steric effect of the bulky *tert*-butyl substituents.

The analysis of the zinc complexes formation in acetonitrile in the presence of DBU revealed that the rate of reaction (12) increases for about three orders by magnitude upon transition from molecular to dianionic forms of the compound **IV**. The process is accompanied with a 28 kJ·mol^{-1} decrease in the reaction activation energy. This fact can be explained by the lack of energy needed for the deformation and a breaking of central NH bonds, as well as by stronger polarization of the molecule. It results in the higher degree of solvation of anionic porphyrin forms in the transition state ($\Delta S^{\neq}$ decreases for about 30 J·mol^{-1}·K^{-1}).

Highly-distorted porphyrin exhibits higher basicity and acidity compared to the planar porphyrins. It means that protons in the macrocycle core are weakly bound by the nitrogen atoms and deprotonation does not significantly contribute the energy of the system. In addition, one can state that the structure of the macrocycle **III** containing nitrogen atoms exposed out of the macrocycle plane favors interaction with the metal solvatocomplex.

Conclusion

Thus, the introduction of the alkyl substituents with different electronic and steric effects into the *meso*-position of the porphyrin macrocycle changes the metal ion coordination, acid-base and spectral properties of the porphyrin ligand, as well as leads to the changes in the geometry of the molecule and promotes selective regulation of the physicochemical properties of the compound. The key fundamental problem being solved in the study contributes to the general knowledge of the processes occurring upon interaction of nitrogen-containing macrocycles and metal ions. The disclosure of the mechanism of these processes contributes to the modelling approaches needed for the successful design of complex organic compounds and development of new sensitive and selective sensors based on these compounds.

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