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Synthesis and Spectrophotometry Study of the Acid-Base Properties of Nitro-Substituted 5-Phenyl-β-Octaalkylporphines

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Abstract—10,15-Dinitro-5-phenyl-2,3,7,8,12,13,17,18-octamethylporphine, 10,15,20-trinitro-5-phenyl-2,3,7,8,12,13,17,18-octamethylporphine, and 10,15,20-trinitro-5-(4-nitrophenyl)-2,3,7,8,12,13,17,18-octamethylporphine were synthesized and identified by electronic absorption, IR, and ^{1}H NMR spectroscopy. The acid–base properties of the synthesized compounds were studied by spectrophotometric titration in $HClO_4$–acetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile systems at 298 K. Parameters of the electronic absorption spectra and concentration ranges of existence of the mono- and diprotonated, as well as mono- and dideprotonated forms of the corresponding ligands and the acid and base dissociation constants of the latter were determined. Comparative analysis of the effect of nitro groups on the reactivity of the synthesized compounds was performed.

Keywords: porphyrins, acid–base properties, 5-aryl-*meso*-nitro-β-octamethylporphyrin, 1,8-diazabicyclo[5.4.0]-undec-7-ene

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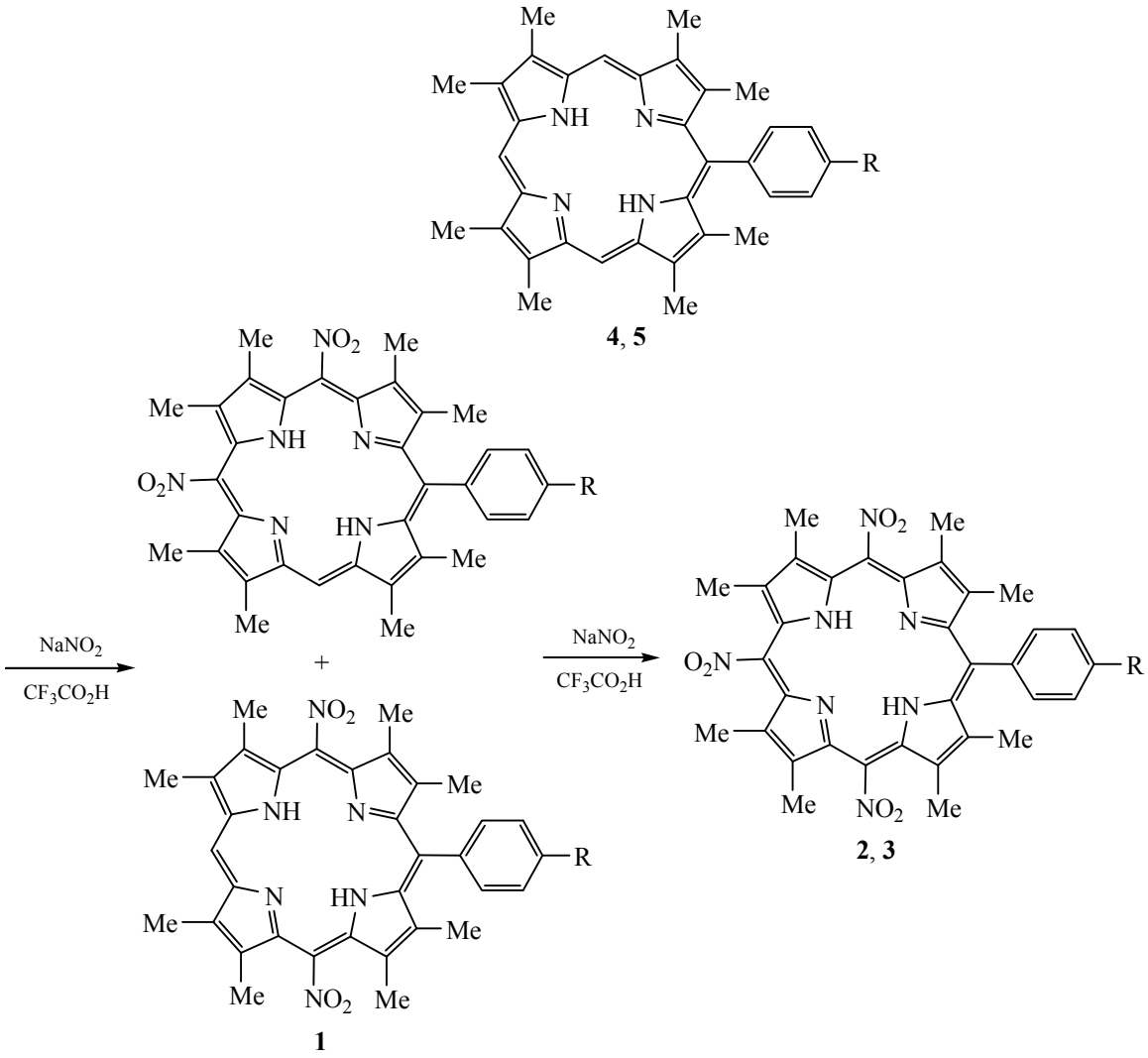
Tetrapyrrole pigments : porphyrins : play an exceptionally important role in animal, plant, and bacteria lives. These brightly colored compounds comprise a macroring including four pyrrole units. Metal complexes of pophyrins fulfil key functions in photosynthesis and the maintenance of human and animal life, which explains the enduring interest in the structure and synthesis of known and novel, peripherally modified, porphyrin ligands with desired properties [1–20]. However, targeted application of novel tetrapyrrole compounds and their metal complexes in practice is complicated by insufficient knowledge of the interrelationship between the structure of porphyrins and their complexing power with respect to metals [21, 22]. On the one hand, acceptor or donor substitution in the porphyrin macroring not infrequently leads to its deformation due to electronic effects of the substituents, and this affects the coordination and acid–base properties of the porphyrins [21]. On the other hand, the activity of the ligands in such systems is primarily dependent on the structure of the acid–base complexes that form in solutions, because the ionizing ability of such complexes depends on the degree of electron transfer from the acid to base (solvent). Systematic research in this field would allow building up the knowledge of the reactivity of systems containing porphyrins and their molecular fragments having a high chemical affinity to ions and molecules.

In the present work we synthesized 10,15-dinitro-5-phenyl-2,3,7,8,12,-13,17,18-octamethylporphine **1**, 10,15,20-trinitro-5-phenyl-2,3,7,8,12,-13,17,18-octamethylporphine **2**, and 10,15,20-trinitro-5-(4-nitrophenyl)-2,3,7,8,12,13,17,18-octamethylporphine **3** and performed a spectrophotometric study of their acid–base properties in acetonitrile.

Highly strained, electron-deficient 5-aryl-*meso*-nitro-β-octamethylporphyrines **1**–**3** were synthesized by the nitration of 5-aryl-β-octamethylporphyrins with sodium nitrite in trifluoroacetic acid as described in [23, 24]. It was found that the reaction involved a fast mononitration stage and proceeds further to give a dinitro-substituted product **1**; therewith, the second stage occurred in a nonselective fashion. Two hardly separable 10,15(20)-dinitro-substituted isomers formed in roughly equal amounts. With a large excess of sodium nitrite

Scheme 1.



R = H (**1, 2, 4**), NO_2 (**3, 5**).

and much longer reaction time, trinitroporphyrins **2** and **3** were obtained (Scheme 1).

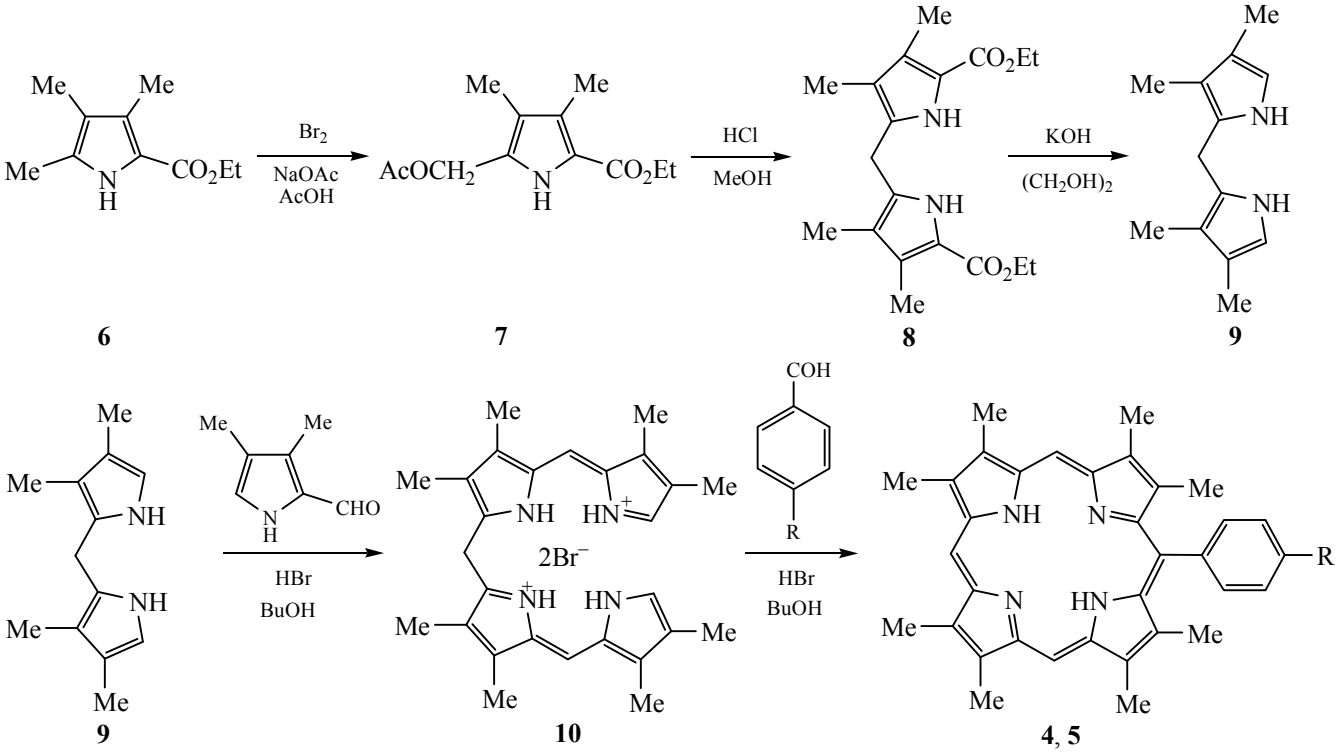
The starting 5-aryl-β-octamethylporphyrins **4** and **5** were synthesized from 2-ethoxycarbonyl-3,4,5-trimethylpyrrole **6** via intermediate dipyrrolylmethanes (**8** and **9**) and biladiene **10** by analogy with what is described in [25]. 5,5'-Diethoxycarbonyl-3,3',4,4'-tetramethyldipyrrolylmethane **8** was prepared by the radical bromination of pyrrole **6** followed by the nucleophilic substitution of bromine by the acetoxy group. The resulting acetoxymethylpyrrole **7** was subjected to self-coupling by the procedure in [26] (Scheme 2).

In its turn, 2-ethoxycharbonyl-3,4,5-trimethylpyrrole **6** was prepared by the reductive coupling of 3-methylpentane-2,4-dione with hydroxyiminomalonic ester as described in [27] (Scheme 3). We used this procedure bearing in mind that the synthesis involving nitrosoacetoacetic ester (Knorr procedure [28] gives fairly much by-product 3-acetyl-2-ethoxycarbonyl-3,4-dimethylpyrrole which can only be removed by multiple recrystallization.

The resulting ligands **1**–**3** were purified by column chromatography on alumina (Brockmann activity grade III) with dichloromethane as eluent.

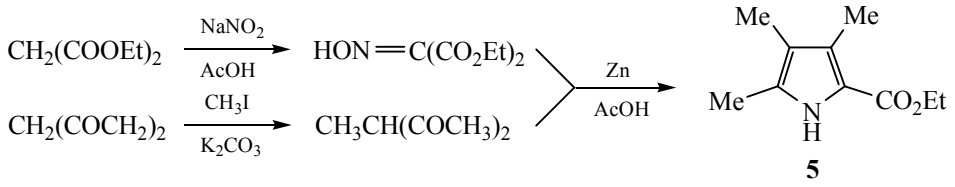
The acid–base properties of ligands **1**–**3** were studied by spectrophotometry in the systems $HClO_4$–acetonitrile (1) and 1,8-diazabicyclo[5.4.0]undec-7-ene–acetonitrile (2) at 298 K. Porphyrins (H_2P) exhibit

Scheme 2.



R = H (**4**), NO_2 (**5**).

Scheme 3.



amphoteric properties in organic solvents, and in the presence of acids and bases they can undergo protonation or deprotonation involving endocyclic nitrogen atoms.

$$H_4P^{2+} \overset{k_{b1}}{\rightleftarrows} H_3P^+ + H^+, \quad (1)$$

$$H_3P^+ \overset{k_{b2}}{\rightleftarrows} H_2P + H^+, \quad (2)$$

$$H_2P \overset{k_{a1}}{\rightleftarrows} HP^- + H^+, \quad (3)$$

$$HP^- \overset{k_{a2}}{\rightleftarrows} P^{2-} + H^+. \quad (4)$$

Here H_2P, HP^-, P^{2-}, H_3P^+, and H_4P^{2+} are the molecular, mono- and dideprotonated, as well as mono- and diprotonated forms of the porphyrin ligand.

In systems (1) and (2), porphyrin ligands **1**–**3** are both protonated and deprotonated [equilibria (1)–(4)]. Figures 1–6 show the electronic absorption (EA) spectra of ligands **1**–**3** in acetonitrile under titration with 0.01 M acetonitrile solutions of $HClO_4$ and 1,8-diazabicyclo[5.4.0]undec-7-ene. As the $HClO_4$ concentration in system (1) increased, two groups of signals, each with its specific set of isosbestic points, formed in the EA spectra. The spectrophotometric titration curves constructed using the rexperimental data (Figs. 1–3) provided further evidence for the step nature of the reactions of porphyrins **1** and **2** with $HClO_4$, gives us grounds to suggest that the pyrrolenine (=N–) nitrogen atoms in the porphyrin macrorings are protonated following reactions (1) and (2). The titration curve of compound **3** was smooth, monotonic, and contained no step, even though the EA spectrum showed two sets of isosbestic points (Fig. 3), implying a step protonation process. Two-step and

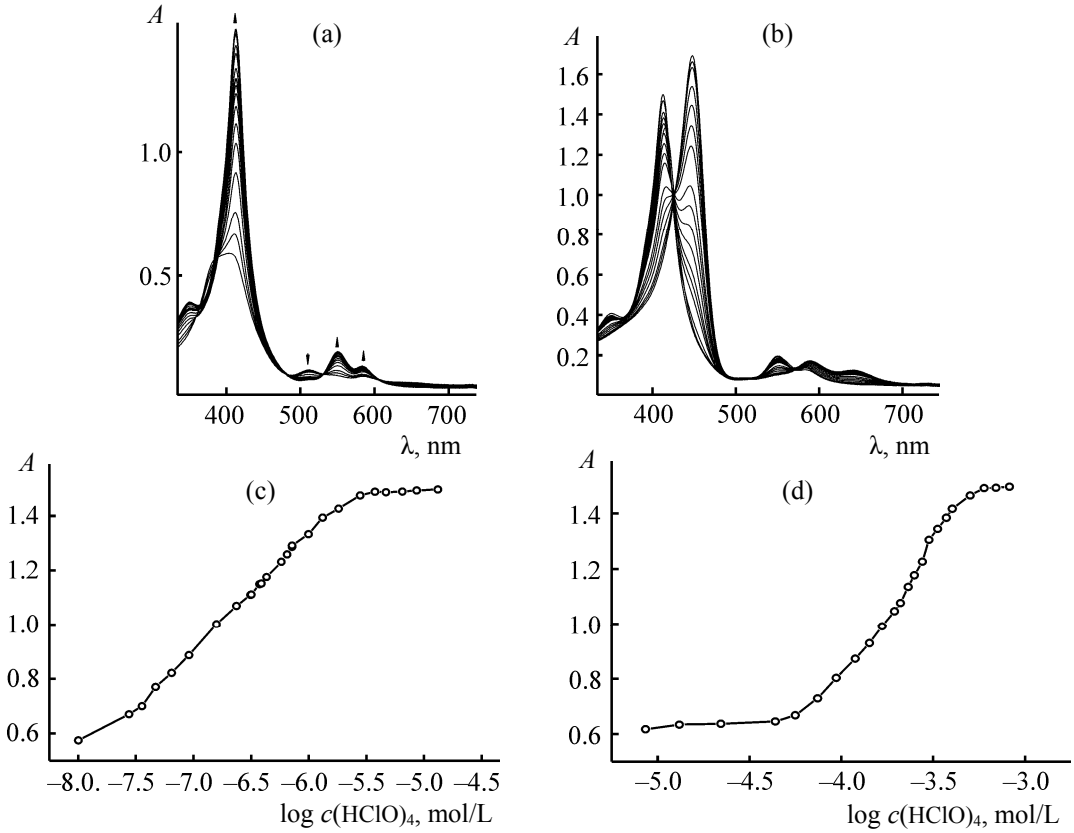


Fig. 1. (a, b) Changes in the EA spectra and (c, d) spectrophotometric titration curves of 2,3,7,8,12,13,17,18-octamethyl-10,15-dinitro-5-phenylporphine **1** at the (a, c) first and (b, d) second steps in system (1) at 298 K ($[H_2P] = 4.80\times10^{-5}$ M, $[HClO_4] = 0–8.23\times10^{-4}$ M).

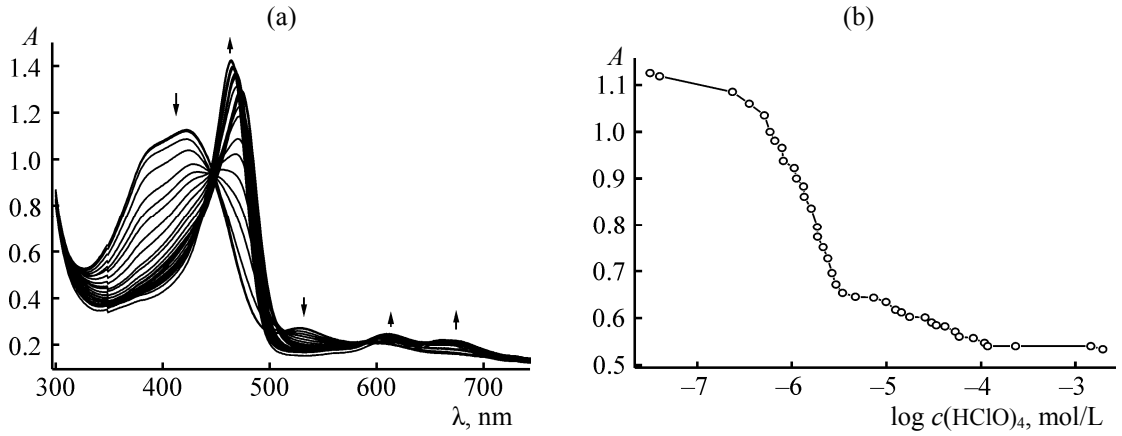


Fig. 2. (a) Changes in the EA spectrum and (b) spectrophotometric titration curve of 2,3,7,8,12,13,17,18-octamethyl-15,20-trinitro-5-phenylporphine **2** in system (1) at 298 K ($[H_2P] = 1.08\times10^{-5}$ M, $[HClO_4] = 0–1.95\times10^{-3}$ M).

monotonic and smooth spectrophotometric titration curves together with two sets of isosbestic points, too, suggest a two-step protonation process with the very difference that in the latter case the mono- and deprotonation, as well as deprotonation rates are likely to be close to each other [29]. In system (2), too, porphyrin ligands **1**–**3** undergo deprotonation by both reaction (3) and reaction (4). Figures 4–6 show the EA spectra of compounds **1**–**3** in acetonitrile under titration with a 0.01 M acetonitrile solution of 1,8-diazabicyclo[5.4.0]undec-7-ene. In these spectra, as the concentration of 1,8-diazabicyclo[5.4.0]undec-7-

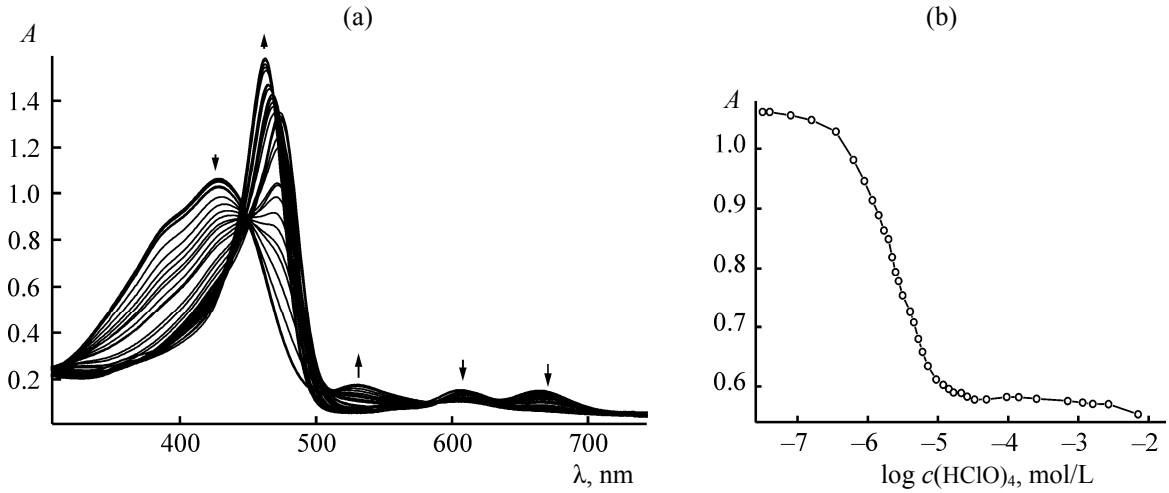


Fig. 3. (a) Changes in the EA spectrum and (b) spectrophotometric titration curve of 2,3,7,8,12,13,17,18-octamethyl-10,15,20-trinitro-5-(4-nitrophenyl)porphine **3** in system (1) at 298 K ($[H_2P] = 6.70\times10^{-5}$ M, $[HClO_4] = 0–7.24\times10^{-3}$ M).

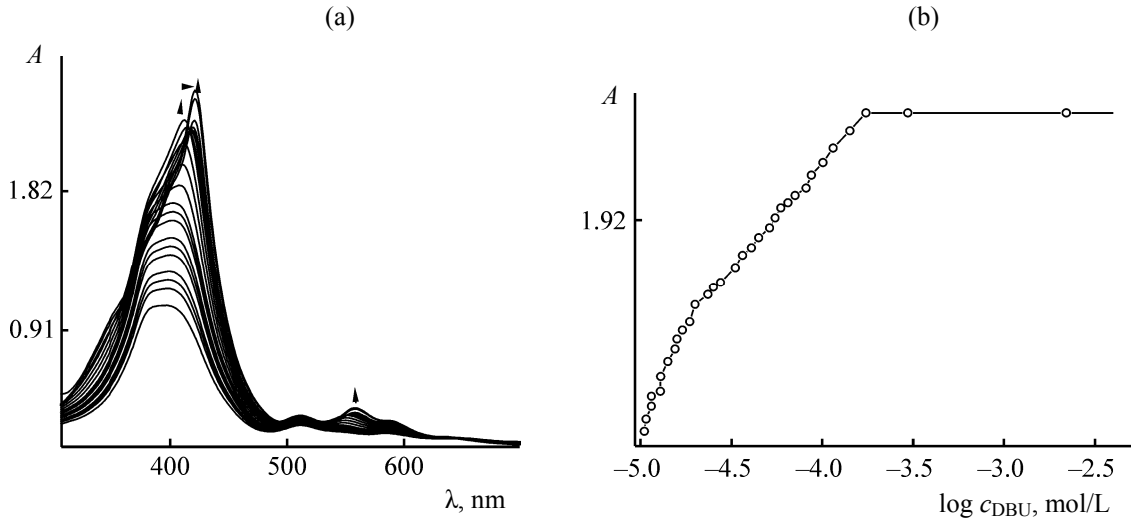


Fig. 4. (a) Changes in the EA spectrum and (b) spectrophotometric titration curve of 2,3,7,8,12,13,17,18-octamethyl-10,15-dinitro-5-phenylporphine **1** in system (2) at 298 K ($[H_2P] = 8.68\times10^{-5}$ M, [DBU] = 0–2.21×10^{-3} M).

ene was increased, we also observed the formation of two groups of signals, each containing its specific set of isosbestic points.

In the case of compound **1**, the spectrophotometric titration curve constructed with the experimental data (Fig. 4) had a step, thereby providing evidence showing that the reaction of the porphyrins with 1,8-diazabicyclo[5.4.0]undec-7-ene occurred in two steps [reactions (3) and (4)]. The titration curves for compounds **2** and **3** in system (2), like that for the protonation of compound **3** in system (1), contained no steps, which, too, suggested close step deprotonation constants.

The table lists the parameters of the EA spectra for equilibria (1)–(4) in systems (1) and (2), as well as the corresponding protonation and deprotonation constants. The basicity and acidity constants for processes (1)–(4) were calculated by Eq. (5).

$$\log K = \log (Ind) + n\log c_{an}. \quad (5)$$

Here K is the equilibrium constants for the first and second steps; *Ind*, indicator $[H_2P]/[H_3P^+]$ ratio for the first step and $[H_3P^+]/[H_4P^{2+}]$ ratio for the second step (or [HP–]/$[H_2P]$ and $[P^2–]/[HP–]$); c_{an}, analytical concentration of the titrant in the solution; n, number of protons involved in the process ($pK = –\log K$). The The constants were measured accurate to within 3–5%.

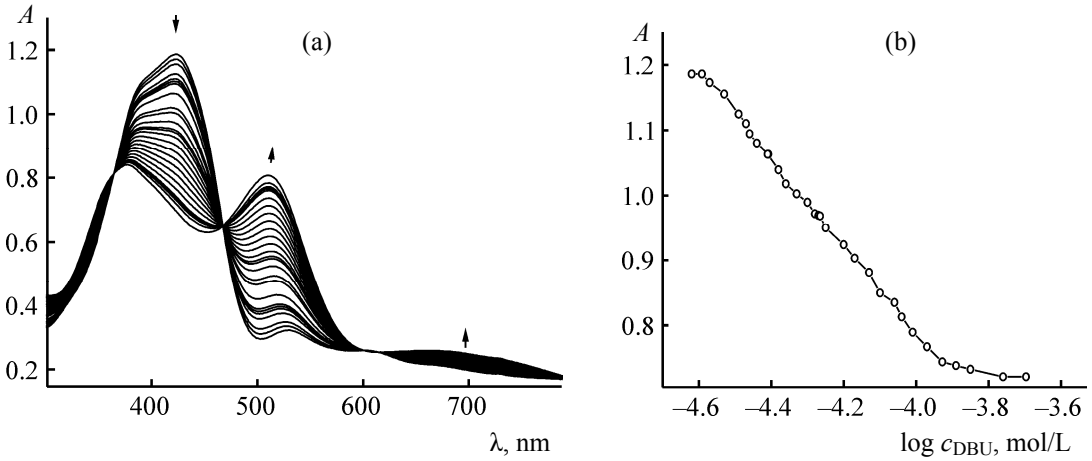


Fig. 5. (a) Changes in the EA spectrum and (b) spectrophotometric titration curve of 2,3,7,8,12,13,17,18-octamethyl-10,15,20-trinitro-5-phenylporphine **2** in system (2) at 298 K ([H_2P] = 1.13×10^{-5} M, [DBU] = 0–2.01×10^{-4} M).

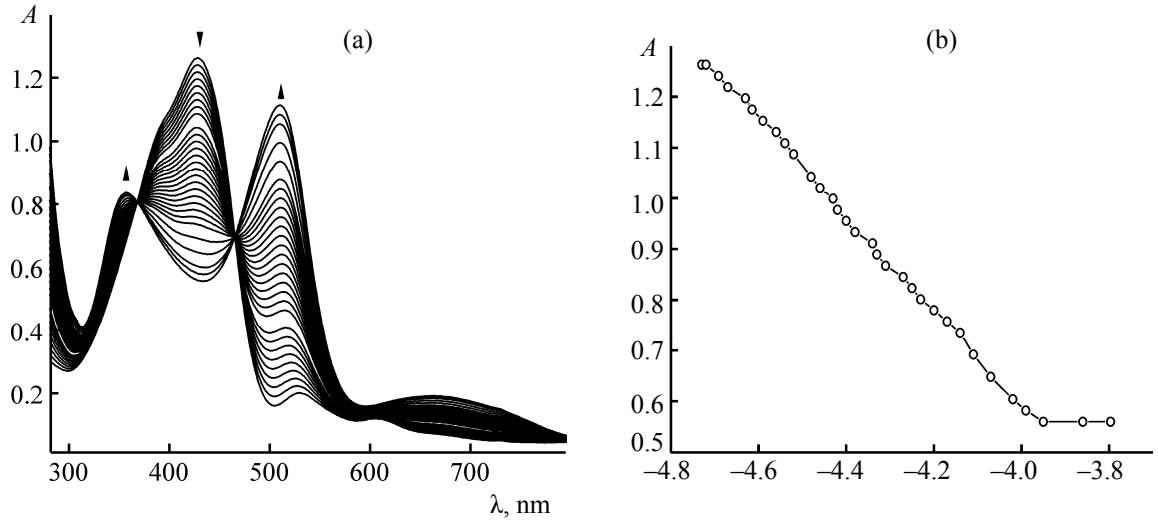


Fig. 6. (a) Changes in the EA spectrum and (b) spectrophotometric titration curve of 2,3,7,8,12,13,17,18-octamethyl-10,15,20-trinitro-5-(4-nitrophenyl)porphine **3** in system (2) at 298 K ([H_2P] = 1.42×10^{-5} M, [DBU] = 0–1.58×10^{-4} M).

As known, the electronic effects of substituents in the macroring are among factors that allow spectral observation of monocationic forms. As a rule, the step protonation and deprotonation equilibria are easily observed for porphyrins, in which the nitrogen atoms have much different electron densities. Apparently, strong polarization of the molecule will, too, favor differentiation of the cationic and anionic forms of porphyrins as acids and bases. It should be noted that the presence of isosbestic points and the character of spectral changes suggest that the changes in the concentrations of the two absorbing centers of the porphyrin molecule do not change the relative fractions of the ionized forms on deprotonation and protonation. The apparent absorbances of all the porphyrin forms involved in equilibria (1)–(4) in systems (1) and (2) were calculated using the EA spectral data and the total concentrations of each porphyrin species (see table). Having determined the number of protons that take part in the equilibrium, we could determine the character of ionization of porphyrin and calculate the step deprotonation and protonation constants. Analysis of the data in the table, in particular, the protonation and deprotonation constants of substituted porphyrins **1**–**3**, showed that our present results are in a good agreement both with the classical view on the effects of substituents, not only those introduced directly in the macroring, but also those in the phenyl "buffer," and with published data in this field. According to [21], the so-called buffer effect of the *meso*-phenyl substituents in the porphyrin macroring favors delocalization of the excess charge (both

Parameters of the EA spectra of the molecular, mono- and diprotonated, and mono- and dideprotonated forms of compounds **1**–**3** and corresponding acid and base dissociation constants in acetonitrile at 298 K

Porphyrin (form)	λ_1, nm (log ε)	λ_2, nm (log ε)	λ_3, nm (log ε)	λ_4, nm (log ε)	pK_{b2} (pK_{b1}) [$pK_{b1,2}$]	pK_{a1} (pK_{a2}) [$pK_{a1,2}$]
1 (H_2P)	389 (4.09)	514 (3.47)	588 (3.34)	646 (3.26)	6.62	4.37
1 (HP^-)	411 (4.42)	512 sh (3.57)	552 (3.59)	586 sh (3.53)	(3.64)	(5.47)
1 (P^{2-})	421 (4.46)	512 sh (3.57)	558 (3.67)	589 sh (3.57)	[10.26]	[9.84]
1 (H_3P^+)	415 (4.38)	514 (4.34)	588 (3.60)	646 (3.59)		
1 (H_4P^{2+})	448 (4.55)	–	589 (3.56)	644 (3.41)		
2 (H_2P)	421 (5.02)	529 (4.17)	–	602 (3.90)	6.06	–
2 (P^{2-})	377 (4.87)	–	511 (4.86)	700 sh (4.37)	(4.78)	–
2 (H_3P^+)	464 (5.12)		606 (4.30)	661 (4.28)	[10.84]	[8.32]
2 (H_4P^{2+})	473 (5.08)		612 (4.35)	665 (4.29)		
3 (H_2P)	428 (4.95)	530 (4.31)	–	613 (4.16)	–	–
3 (P^{2-})	357 (4.77)	510 (4.90)	–	664 sh (4.39)	–	–
3 (H_4P^{2+})	474 (5.05)	610 (4.08)	–	667 (4.01)	[11.23]	[8.06]

positive and negative) and can enhance both acidic and basic properties of tetraphenylporphine derivatives compared to the unsubstituted porphine. Quite an important parameter of spectrophotometric titration is the difference between the protonation and deprotonation constants, which reflects not only changes in the symmetry and geometry of the molecule, but also charge redistribution that affects the electron density on the endocyclic nitrogen atoms. In the present work, the difference between the protonation and deprotonation constants for processes (1) and (2) in system (1) decreases from about 3 orders of magnitude (compound **1**) to 1.28 (compound **2**) and, finally, to near zero (compound **3**). For processes (3) and (4) in system (2) this difference was slightly higher than an order of magnitude for compound **1**, which implied synchronous ionization processes. The respective difference for compounds **2** and **3** was near zero. The quantum-chemical calculations in [30] showed that *meso*-phenyl substituents, which are weak electron acceptors, withdraw the electron density from the macroring. Phenyl substitution in porphine decreases the effective electron charge on the *meso*-carbon atoms by ≈0.03 $\bar{e}$, whereas the effective charge on the nitrogen atoms of the reaction center remains almost unchanged. However, the macroring is therewith deformed due to certain isolation of the π-electron systems of the pyrrole and pyrrolenine fragments.

Analyzing the aforesaid we can conclude that the changes in the acid–base properties of the nitro derivatives of 5-phenyl-β-octaalkylporphine are associated both with the acceptor effect of the NO_2 groups, but also with the deformation of the planar macroring geometry. Thus, chemical modification of the macroring can be used to vary the acid–base properties of the macroheterocyclic ligands, and variation of the composition of the medium, along with the structural and electronic effects of substituents, can serve as an efficient tool for controlling the reactivity of porphyrins.

EXPERIMENTAL

The EA spectra were obtained on SPEK SSP-715, Cary 100, Shimadzu UV-1800 , and Hitachi UV-2000 scanning spectrophotometers. The IR spectra were measured on Thermo Nicolet AVATAR 360 FTIR spectrometer in KBr pellets. The MALDI–TOF mass spectra were run on a Shimadzu Axima Confidence instrument. The ^{1}H NMR spectra were obtained on a Bruker 500 spectrometer in $CDCl_3$. Thin-layer chromatography was performed on Silufol plates. Com-

pounds **1**–**3** were purified and identified as described in [31]. The solvent was high-purity acetonitrile (water content >0.03%), where the starting porphyrins were present in the molecular form, as evidenced by their spectra. Spectrophotometric titration with acetonitrile solutions of perchloric acid and 1,8-diazabicyclo[5.4.0]-undec-7-ene was performed on a Cary 100 Varian spectrophotometer.

The experimental and data processing procedure are described in detail in [8, 18].

Nitrosomalonic ester. A solution of 216.0 mL (0.75 mol) of malonic ester in 45 mL of acetic acid and a solution of 105 g (1.52 mol) of sodium nitrite in 200 mL of water were added in succession for over 2 h at <15°C to a solution of 14.5 g (0.49 mol) of sodium hydroxide in 150 mL of acetic acid. The mixture was allowed to stand for 3 days at room temperature and then extracted with 2 equal portions of diethyl ether. The extract was washed with water to neutral washings, dried with sodium sulfate, and evaporated to obtain ~0.71 mol of nitrosomalonic ester which was then used without further purification.

3-Methylpentane-2,4-dione. A mixture of 315 mL (3.1 mol) of acetylacetone and 200 mL (3.21 mol) of methyl iodide was gradually added to a stirred mixture of 360 g (2.6 mol) of potash and 500 mL of acetone. The mixture was refluxed for 8 h. After cooling, the precipitate was filtered off and washed with acetone. The solvent was removed by distillation, and the residue was distilled to collect the fraction with bp 160–175°C. Yield 287 g (78%).

2-Ethoxycarbonyl-3,4,5-trimethylpyrrole (6). A solution of nitrosomalonic ester (~0.71 mol) in 150 mL of acetic acid and 60 mL of water and 186 g (2.82 mol) of zinc dust were simultaneously added to a stirred solution of 81.0 g (0.71 mol) of 3-methylpentane-2,4-dione in 260 mL of acetic acid (temperature <95°C). The resulting mixture was stirred for an additional 1 h on a boiling water bath and then poured into 5 L of water. The precipitate was filtered off, washed with water, dissolved in benzene, excel zinc dust was filtered off, benzene was distilled off, and the residue was recrystallized from methanol. Yield 55.7 g (43.3%), mp 127–128°C. ^{1}H NMR spectrum, δ, ppm: 8.86 br.s (1H, NH), 4.31 q (2H, CH_2Et, J_{HH} = 7.2 Hz), 2.28 s (3H, CH_3), 2.21 s (3H, CH_3), 1.94 s (3H, CH_3), 1.37 t (2H, CH_3Et, J_{HH} = 7.2 Hz).

2,2'-[5,5'-Bis(ethoxycarbonyl)-3,3',4,4'-tetramethyl]dipyrrolylmethane (8). Bromine, 5.7 mL (0.11 mol), was gradually added to a suspension of 20.0 g (0.11 mol) 2-(ethoxycarbonyl)-3,4,5-trimethylpyrrole and 19.0 g (0.23 mol) of anhydrous sodium acetate in 150 mL of acetic acid under stirring and cooling with cold water, and the mixture was stirred for 0.5 h and poured into 1 L of water. The precipitate was filtered off and washed with water. The resulting acetoxymethylpyrrole **7** was dissolved in a mixture of 200 mL of methanol and 5 mL of HCl and refluxed under constant stirring for 3 h. The mixture was then cooled down, the precipitate was filtered off, washed with methanol, and dried in air at 70°C. Yield 10.0 g (52.5%), mp 128–129°C (methanol). ^{1}H NMR spectrum, δ, ppm: 9.03 br.s (2H, NH), 4.25 q (4H, OCH_2Et, J = 7.1 Hz), 3.84 s (2H, *ms*-CH_2), 2.24 s (6H, 3,3'-CH_3), 2.31 s (6H, 4,4'-CH_3), 1.30 t (6H, CH_3Et, J = 7.1 Hz).

2,2'-(3,3',4,4'-Tetramethyl)dipyrrolylmethane (9). A solution of 1.0 g (2.89 mmol) of dipyrrolylmethane **8** and 1.0 g (17.8 mmol) of KOH in 15 mL of ethylene glycol was refluxed for 1 h, cooled down, and poured into 150 mL of water containing 5 g of sodium-acetate trihydrate. The precipitate was filtered off, washed with water, and dried in air at room temperature. Yield 0.5 g (85.5%).

2,3,7,8,12,13,17,18-Octamethyl-5-phenylporphine (4). Concentrated hydrobromic acid, 2 mL, was added at room temperature to a stirred solution of 0.5 g (2.47 mmol) of dipyrrolylmethane **9** and 0.61 g (4.95 mmol) of 2-formyl-3,4-dimethylpyrrole in 100 mL of butanol (biladiene **10** precipitated). The mixture was stirred for 1 h and, after addition of 2.0 mL (19.8 mmol) of benzaldehyde, for an additional 4 h under reflux. Benzoquinone, 0.6 g (5.55 mmol), was then added, and the resulting mixture was refluxed for 15 min. The precipitate (240 mg) that formed after removal of butanol was filtered off, washed with water, dried in air at 70°C, and dissolved in a methylene chloride containing trifluoroacetic acid (1 mL of trifluoroacetic acid in 50 mL of methylene chloride). The solution was filtered, and the filtrate was neutralized with diethylamine (~2 mL) until its color changed from green to red. The precipitate that formed was filtered off, washed with methylene chloride, and dried in air at room temperature. Yield 240 mg. The filtrate was subjected to chromatography on alumina (Brockmann activity grade II) in methylene chloride. The eluate was evaporated, and the porphyrin was precipitated with methanol, filtered off, washed with methanol, and dried in air at room temperature. Total yield 430 mg (34.9%), R_f 0.39 (benzene). IR spectrum,

ν, cm^{-1}: 2958, 2920, 2857, 1631, 1443, 1387, 1229, 1116, 1058, 1017, 944, 831, 741, 692. EA spectrum, λ_{max}, nm (log ε): 624 (3.55), 571 (3.86), 537 (3.90), 503 (4.19), 404 (5.27). ^{1}H NMR spectrum, δ, ppm: 10.49 s (2H, 10,20-H), 10.35 s (1H, 15-H), 8.30 d (2H, 2,6-H_{Ph}, J = 6.8 Hz), 7.97–8.06 m (3H, 3,4,5-H_{Ph}), 3.60 s (12H, 12,13,17,18-CH_3), 3.33 s (6H, 2,8-CH_3), 2.28 s (6H, 3,7-CH_3), –2.83 br.s and –4.04 br.s (4H, NH). Mass spectrum (MALDI-TOF), m/z: 499.152 $[M + H]^+$.

2,3,7,8,12,13,17,18-Octamethyl-5-(4-nitrophenyl)-porphine (5) was prepared in a similar way from 0.52 g (2.57 mmol) of 3,3',4,4'-tetramethyldipyrrolylmethane **9**, 0.63 g (5.14 mmol) of 2-formyl-3,4-dimethylpyrrole, and 2.0 g (13.23 mmol) of 4-nitrobenzaldehyde. Yield 470 mg (33.6%), R_f 0.30 (benzene). IR spectrum, ν, cm^{-1}: 2977, 2921, 2857, 1644, 1590, 1519 [$\delta_{as}(NO_2)$], 1444, 1342 [$\delta_s(NO_2)$], 1289, 1162, 1141, 1048, 953, 853, 754, 696. EA spectrum, λ_{max}, nm (log ε): 625 (3.55), 572 (3.82), 538 (3.88), 504 (4.15), 403 (5.16). ^{1}H NMR spectrum, δ, ppm: 10.54 s (2H, 10,20-H), 10.42 s (1H, 15-H), 8.87 d (2H, 2,6-H_{Ar}, J = 8.5 Hz), 8.58 d (2H, 3,5-H_{Ar}, J = 8.5 Hz), 3.61 s (12H, 12,13,17,18-CH_3), 3.35 s (6H, 2,8-CH_3), 2.30 s (6H, 3,7-CH_3), –2.72 br.s (2H, NH), –3.90 br.s (2H, NH). Mass spectrum (MALDI-TOF), m/z: 544.197 $[M + H]^+$.

2,3,7,8,12,13,17,18-Octamethyl-10,20-dinitro-5-phenylporphine (1). A solution of раствор 50.0 mg (0.72 mmol) of solium nitrite in 0.5 mL of water was added to a stirred solution of 100 mg (0.20 mmol) 2,3,7,8,12,13,17,18-octamethyl-5-phenylporphine in 5.0 mL of trifluoroacetic acid. The mixture was stirred for 2 h at room temperature and then poured into 50 mL of water and neutralized with ammonium solution until a change of color. The precipitate was filtered off, washed with water, dried in air, dissolved in benzene, ad chromatographed on silica in benzene. The eluate was evaporated, and the product was precipitated with methanol. The precipitate was filtered off, washed with methanol, and dried in air at room temperature. Yield 90 mg (76.4%), R_f 0.70 (benzene). IR spectrum, ν, cm^{-1}: 2964, 2927, 2869, 1636, 1533 [$\delta_{as}(NO_2)$], 1447, 1361 [$\delta_{as}(NO_2)$], 1162, 1135, 1096, 885, 848, 793, 709. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 9.96 s (1H, 20-H), 8.02 d (2H, 2,6-H_{Ph}, J = 7.6 Hz), 7.75–7.87 m (3H, 3,4,5-H_{Ph}), 3.46 s and 3.36 s (6H, 2,18-CH_3); 3.21 s, 3.20 s, 3.19 s and 3.09 s (12H, 8,12,13,17-CH_3), 2.29 s and 2.25 s (6H, 3,7-CH_3), –3.10 br.s (1H, NH), –3.42 br.s (1H, NH). Mass spectrum, (MALDI-TOF), m/z: 589.382 $[M + H]^+$.

2,3,7,8,12,13,17,18-Octamethyl-10,15,20-trinitro-5-phenylporphine (2) was prepared in a similar way. Yield 80 mg (63.1%), R_f 0.63 (benzene). IR spectrum, ν, cm^{-1}: 3322, 2932, 2853, 1644, 1536 [$\delta_{as}(NO_2)$], 1446, 1360 [$\delta_s(NO_2)$], 1156, 1137, 873, 808, 707, 662. EA spectrum, λ_{max}, nm (log ε): 669 (3.46), 607 (3.76), 530 (4.05), 429 (4.94). ^{1}H NMR spectrum, δ, ppm: 8.08–8.12 m (2H, 2,6-H_{Ph}), 7.79–7.88 m (3H, 3,4,5-H_{Ar}), 3.01 br.s (12H, 12,13,17,18-CH_3), 2.86 br.s (6H, 2,8-CH_3), 2.03 br.s (6H, 3,7-CH_3), –2.77 br.s (1H, NH), –2.97 br.s (1H, NH). Mass spectrum (MALDI-TOF), m/z: 634.262 $[M + H]^+$.

2,3,7,8,12,13,17,18-Octamethyl-10,15,20-trinitro-5-(4-nitrophenyl)porphine (3) was prepared in a similar way. Yield 40 mg (32.7%), R_f 0.55 (benzene). IR spectrum, ν, cm^{-1}: 3328, 2929, 1644, 1596, 1540 [$\delta_{as}(NO_2)$], 1448, 1345 [$\delta_s(NO_2)$], 1137, 1093, 1010, 873, 840, 735, 688, 599. ^{1}H NMR spectrum, δ, ppm: 8.70 d (2H, 2,6-H_{Ar}, J = 8.5 Hz), 8.34 d (2H, 2,6-H_{Ar}, J = 8.5 Hz), 3.02 br.s (12H, 12,13,17,18-CH_3), 2.87 br.s (6H, 2,8-CH_3), 2.03 br.s (6H, 3,7-CH_3), –2.78 br.s (1H, NH), –3.00 br.s (1H, NH). Mass spectrum (MALDI-TOF), m/z: 679.295 $[M + H]^+$.

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