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Synthesis of Monohydroxy–Substituted Diarylporphyrins and Their Binding Ability towards Aminobenzoic Acids

Nugzar Zh. Mamardashvili,[@] and Mikhail O. Koifman

Institute of Solution Chemistry of Russian Academy of Sciences, 153045 Ivanovo, Russia
[@]Corresponding author E-mail: ngm@isc-ras.ru

Synthesis of some new monohydroxy-substituted diarylporphyrins with different positions of the reactionary center in the macrocycle was performed. An ability of their zinc complexes to bind methyl esters of ortho-, meta- and para-aminobenzoic acids in toluene was studied by spectrophotometric titration and ^{1}H NMR spectroscopy.

Keywords: Zinc diarylporphyrinate, synthesis, binding ability, methyl ester of aminobenzoic acid, hydrogen bond, spectrophotometric titration, ^{1}H NMR spectroscopy.

Introduction

Porphyrins are widely used for binding of amino acids which usually occurs due to donor-acceptor interaction between NH-groups of amino acid and Zn^{II} atom of metalloporphyrinate.[1,2] In the case of zinc porphyrinates with OH groups the possibility of additional hydrogen bonds formation between the hydroxyl groups of porphyrinate and oxygen atom of amino acid appears. Hydrogen bonds in the resulting molecular complex make it significantly more stable.

When porphyrins form hydrogen bonds with amino acids (or with other biological objects) they are considered to be capable of recognizing the given substrates, and the higher the complex stability, the better is the recognizing ability of this porphyrin.

This work is devoted to the synthesis of new monohydroxysubstituted zinc porphyrinates with different positions of reactionary centres and investigation of their binding ability towards amino acids. To this end we used synthetic approach on the basis of key 10-arylsubstituted *a,c*-biladiene dihydrobromides which according to the literature data are widely employed for obtaining of mono-functionalized porphyrins.[3-6] By the method of spectrophotometric titration and ^{1}H NMR spectroscopy a binding ability of the zinc porphyrinates (ZnP) regarding to the methyl esters of *ortho*- (**L$_1$**), *meta*- (**L$_2$**), and *para*- (**L$_3$**) aminobenzoic acids in toluene have been studied.

Experimental

During the research were used commercially available aromatic aldehydes (2-hydroxybenzaldehyde, 2-hydroxymethylenoxybenzaldehyde and 4-hydroxyphenylen-(4-methylenoxy)benzaldehyde from Sigma and OttavaChemicals. 2,18-Dimethyl-3,7,8,12,13,17-hexaethyl-10-phenylbiladiene-*a,c* dihydrobromide was obtained as described earlier.[7] Zinc 10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrinate was obtained as described in [8]. Electronic absorption spectra were obtained in toluene using Cary 100 spectrophotometer. IR-spectra were obtained in tablets of KBr using spectrometer Specord M-80. The mass spectra (electronic impact, 70 eV) were obtained on an MKh-1310 instrument (ion source temperature 150-200 ^{0}C). Reactions were monitored by thin layer chromatography and spectrophotometry. Neutral alumina (Merck; Brockmann activity grade II) was used for column chromatography.

*10-Phenyl-20-(2-hydroxyphenylen)-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrin (**2**).* A solution of 2,18-dimethyl-3,7,8,12,13,17-hexaethyl-10-phenylbiladiene-*a,c* dihydrobromide (5.0 g, 0.6 mmol), 2-hydroxybenzaldehyde (0.10 ml, 1 mmol) and hydrobromic acid (1 ml, 46 %) was heated under reflux for 4 h in 50 ml of methanol. Iodine (0.10 g) was then added and the mixture was refluxed for additional 15 min. After cooling, the precipitate was filtered off, washed with methanol and dried. The crude porphyrin was dissolved in methylene chloride and subjected to chromatography on alumina (Brockmann activity grade II), with methylene chloride-methanol mixture (1:1) as an eluent. The eluate was partly evaporated, and the porphyrin was precipitated with methanol (0.11 g, 30% yield). R_f 0.27, (Al_2O_3, eluent - benzene). *m/z* (ESI): 675 (91 %) [(*M*+H)+]. UV-vis (toluene) λ_{max} nm (lgε): 628 (3.06), 578 (3.59), 551 (3.23), 515 (4.14), 412 (4.98). ^{1}H NMR ($CDCl_3$, 295 K) δ ppm: 10.11 (2H, s, *meso*-H), 7.50 (3H, m, Ar-H_{ortho}), 7.33 (1H, d, Ar-H_{meta}), 7.24 (3H, t, Ar-H_{meta}), 7.12 (2H, t, Ar-H_{para}), 5.09 (1H, s, -OH), 2.97-2.92 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.28 (6H, s, $CH_{3(2,18)}$), 1.11 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$), -3.03 (2H, bd. s., NH). IR (KBr) cm^{-1}: ν_{NH} 3310, ν_{OH} 3213, δ_{OH} 1451, δ_{NH} 969, γ_{NH} 697, ν_{CH} 2980, δ_{CH} 1502, γ_{CH} 830.

10-Phenyl-20-(2-hydroxymethylenoxy)phenylen-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrin (**3**) and 10-phenyl-20-[4-hydroxyphenylen-(4-methylenoxy)phenylen]-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrin (**4**) were obtained similarly.

*10-Phenyl-20-(2-hydroxy-methylenoxy)phenylen-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrin (**3**).* Yield 20 %. R_f 0.31 (Al_2O_3, eluent - benzene). *m/z* (ESI): 705 (96%) [(*M*$^+$H)$^+$]. UV-vis (toluene) λ_{max} nm (lgε): 629 (3.29), 581 (3.85), 552 (3.40), 517 (4.36), 411 (5.08). ^{1}H NMR ($CDCl_3$, 295 K) δ ppm: 10.19 (2H, s, *meso*-H), 7.70 (3H, m, Ar-H_{ortho}), 7.53 (1H, d, Ar-H_{meta}), 7.47 (3H, t, Ar-H_{meta}), 7.32 (2H, t, Ar-H_{para}), 5.89 (1H, s, -OH), 3.61 (2H, s, OCH_2), 2.18-2.12 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.58 (6H, s, $CH_{3(2,18)}$), 1.09 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$), -3.01 (2H, bd.s., NH). IR (KBr) cm^{-1}: ν_{NH} 3315, ν_{OH} 3217, δ_{OH} 1455, $\nu_{s\ C\text{-}O\text{-}C}$ 1260, $\nu_{as\ C\text{-}O\text{-}C}$ 1232, δ_{NH} 969, γ_{NH} 697, ν_{CH} 2986, δ_{CH} 1501, γ_{CH} 837.

*10-Phenyl-20-[4-hydroxyphenylen-(4-methylenoxy) phenylen]-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrin (**4**).* Yield 23%. R_f 0.37, (Al_2O_3, eluent - benzene). *m/z* (ESI): 780

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(83%) [(M^+H)$^+$]. UV-vis (toluene) λ_{max} nm (lgε): 630 (3.32), 583 (3.92), 553 (3.45), 518 (4.44), 412 (5.11). ^{1}H NMR ($CDCl_3$, 295 K) δ ppm: 10.23 (2H, s, *meso*-H), 7.52 (4H, d, Ar-H_{ortho}), 7.22 (4H, d, Ar-H_{meta}), 5.17 (1H, s, -OH), 3.71 (2H, s, OCH_2), 2.20-2.16 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.52 (6H, s, $CH_{3(2,18)}$), 1.12 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$), -3.05 (2H, bd.s., NH). IR (KBr) cm^{-1}: ν_{NH} 3320, ν_{OH} 3227, δ_{OH} 1460, $\nu_{s\ C\text{-}O\text{-}C}$ 1276, $\nu_{as\ C\text{-}O\text{-}C}$ 1243, δ_{NH} 971, γ_{NH} 691, ν_{CH} 2990, δ_{CH} 1510, γ_{CH} 841.

*Zinc 10-phenyl-20-(2-hydroxyphenylen)-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrinate (**5**)*. 10 times excess of zinc acetate was added to the solution of 10-phenyl-20-(2-hydroxyphenyl)-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrin (30 mg) in dimethylformamide (70 ml) and the reactionary mixture was heated under reflux for 30 min. On cooling the solution was diluted with water (1:1), the precipitated substances were filtered off and dried at room temperature. The crude porphyrin was dissolved in methylene chloride and subjected to chromatography on alumina (Brockmann activity grade II), with methylene chloride-hexane mixture (1:1) as an eluent. The eluate was partly evaporated, and the porphyrin was precipitated with methylene chloride-methanol mixture (1:2) (24.70 mg, 83% yield). R_f 0.40, (Al_2O_3, eluent – benzene). UV-vis (toluene) λ_{max} nm (lgε): 578 (3.56), 542 (3.99), 410 (4.92). IR (KBr) cm^{-1}: ν_{NH} 3320, ν_{OH} 3210, δ_{OH} 1448, δ_{NH} 978, γ_{NH} 689, ν_{CH} 2987, δ_{CH} 1512, γ_{CH} 838. ^{1}H NMR ($CDCl_3$, 295 K) δ ppm: 10.13 (2H, s, *meso*-H), 7.52 (3H, m, Ar-H_{ortho}), 7.31 (1H, d, Ar-H_{meta}), 7.22 (3H, t, Ar-H_{meta}), 7.10 (2H, t, Ar-H_{para}), 5.11 (1H, s, -OH), 3.00-2.82 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.22 (6H, s, $CH_{3(2,18)}$), 1.15 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$). ^{1}H NMR for the complex **5-L$_1$** ($CDCl_3$, 295 K) δ ppm: 10.10 (2H, s, *meso*-H), 7.49 (3H, m, Ar-H_{ortho}), 7.28 (1H, d, Ar-H_{meta}), 7.17 (3H, t, Ar-H_{meta}), 7.05 (2H, t, Ar-H_{para}), 6.28 (2H, m, L-H), 5.11 (1H, s, -OH), 4.53 (3H, s, L-OCH_3), 3.83 (2H, t, L-H), 3.02-2.86 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.23 (6H, s, $CH_{3(2,18)}$),1.56 (2H, s, L-NH_2), 1.18 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$).

Zinc 10-phenyl-20-(2-hydroxymethylenoxy)phenylen-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrinate (**6**) and zinc 10-phenyl-20-[4-hydroxyphenylen-(4-methylenoxy)phenylen]-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrinate (**7**) were obtained similarly.

*Zinc 10-phenyl-20-(2-hydroxymethylenoxy)phenylen-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrinate (**6**)*. Yield 86%. R_f 0.49, (Al_2O_3, eluent - benzene). UV-vis (toluene) λ_{max} nm (lgε): 579 (3.57), 540 (3.98), 412 (4.91). IR (KBr) cm^{-1}: ν_{NH} 3311, ν_{OH} 3217, δ_{OH} 1455, $\nu_{s\ C\text{-}O\text{-}C}$ 1260, $\nu_{as\ C\text{-}O\text{-}C}$ 1232, δ_{NH} 973, γ_{NH} 698, ν_{CH} 2984, δ_{CH} 1501, γ_{CH} 839. ^{1}H NMR ($CDCl_3$, 295 K) δ ppm: 10.05 (2H, s, *meso*-H), 7.55 (3H, m, Ar-H_{ortho}), 7.31 (1H, d, Ar-H_{meta}), 7.20 (3H, t, Ar-H_{meta}), 7.02 (2H, t, Ar-H_{para}), 5.92 (1H, s, -OH), 3.61 (2H, s, OCH_2), 2.78-2.54 (12H, m, $CH_2CH_{3\ (3,7,8,12,13,17)}$), 2.28 (6H, s., $CH_{3(2,18)}$), 1.04 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$). ^{1}H NMR for the complex **6-L$_2$** ($CDCl_3$, 295 K) δ ppm: 10.02 (2H, s, *meso*-H), 7.51 (3H, m, Ar-H_{ortho}), 7.32 (1H, d, Ar-H_{meta}), 7.19 (3H, t, Ar-H_{meta}), 7.00 (2H, t, Ar-H_{para}), 6.70 (1H, s, -OH), 6.35 (3H, m, L-H), 4.55 (3H, s, L-OCH_3), 3.81 (1H, s, L-H), 3.57 (2H, s, OCH_2), 2.72-2.50 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.24 (6H, s., $CH_{3\ (2,18)}$), 1.70 (2H, s, L-NH_2), 1.01 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$).

Zinc 10-phenyl-20-[4-hydroxyphenylen(4-methylenoxy)-phenylen]-2,18-dimethyl-3,7,8,12,13,17-hexaethylporphyrinate (7). Yield 84%. R_f 0.53, (Al_2O_3, eluent – benzene). UV-vis (toluene) λ_{max} nm (lgε): 581 (3.63), 543 (3.97), 410 (5.15). IR (KBr) cm^{-1}: ν_{NH} 33160, ν_{OH} 3222, δ_{OH} 1462, $\nu_{s\ C\text{-}O\text{-}C}$ 1266, $\nu_{as\ C\text{-}O\text{-}C}$ 1247, δ_{NH} 971, γ_{NH} 690, ν_{CH} 2993, δ_{CH} 1510, γ_{CH} 841. ^{1}H NMR ($CDCl_3$, 295 K) δ ppm: 10.21 (2H, s, *meso*-H), 7.54 (4H, d, Ar-H_{ortho}), 7.23 (4H, d, Ar-H_{meta}), 5.17 (1H, s, -OH), 3.74 (2H, s, OCH_2), 2.21-2.17 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.4 (6H, s., $CH_{3(2,18)}$), 1.10 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$). ^{1}H NMR for the complex **7-L$_1$** ($CDCl_3$, 295 K) δ ppm: 10.19 (2H, s, *meso*-H), 7.51 (4H, d, Ar-H_{ortho}), 7.20 (4H, d, Ar-H_{meta}), 6.22 (2H, m, L-H), 5.63 (1H, s, -OH), 4.53 (3H, s, L-OCH_3), 3.86 (2H, t, L-H), 3.71 (2H, s, OCH_2), 2.18-2.12 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.3 (6H, s., $CH_{3(2,18)}$), 1.53 (2H, s, L-NH_2), 1.07 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$). ^{1}H NMR for the complex **7-L$_2$** ($CDCl_3$, 295 K) δ ppm: 10.20 (2H, s, *meso*-H), 7.56 (4H, d, Ar-H_{ortho}), 7.24 (4H, d, Ar-H_{meta}), 6.37 (3H, m, L-H), 5.47 (1H, s, -OH), 4.55 (3H, s, L-OCH_3), 3.84 (1H, s, L-H), 3.76 (2H, s, OCH_2), 2.23-2.15 (12H, m, $CH_2CH_{3(3,7,8,12,13,17)}$), 2.51 (6H, s., $CH_{3(2,18)}$), 1.65 (2H, s, L-NH_2), 1.13 (18H, t, $CH_2CH_{3(3,7,8,12,13,17)}$).

The reactions of **L$_1$-L$_3$** with ZnP were studied by spectrophotometric titration method on the increasing and decreasing wavelengths as described earlier.[9,10] Before titration, a solution of ZnP in toluene with $6\cdot10^{-6}$ M concentration and a solution of amino acid with a fixed concentration were placed into 1 cm quartz cell (the measurements were performed at 20 ^{0}C). The optical density was measured on two wavelengths, where its changes were almost the same. The stability constant (K_a) was calculated as follows:

$$k_a = \frac{[ZnPL]}{[ZnP][L]} = 1/c\left(\frac{\Delta A^i_{\lambda_1}}{\Delta A^0_{\lambda_1}}\frac{\Delta A^0_{\lambda_2}}{\Delta A^i_{\lambda_2}}\right),$$

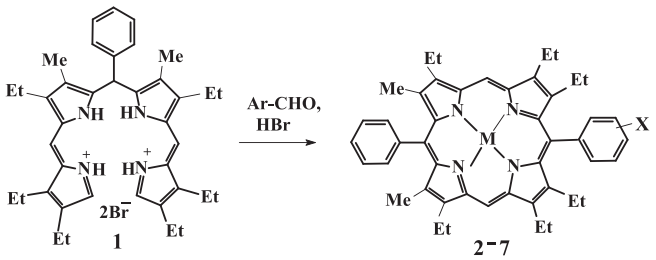
where λ_1 is the wavelength with decreasing intensity, λ_2 is the wavelength with growing intensity, c is the concentration of amino acid, A^0 is the maximum change of optical density at the given wavelength, A^i is the optical density of solution at the given wavelength and at the given concentration. The error of K_a determination was ± 10%.

The cocentration interval of amino acid ester solutions, where the changes of the optical density are observed, ranges from $(7\text{-}10)\cdot10^{-6}$ M to $(7\text{-}10)\cdot10^{-4}$ M depending on the porphyrinate type. The smaller the concentration interval with the observed changes in the optical density the better is the recognizing capability of porphyrinate.

The dependence of the formation of amino acid - ZnP associates on the position of hydroxy-substituents in a macrocycle was confirmed by the method of ^{1}H NMR spectroscopy. ^{1}H NMR spectra were recorded on a Bruker AC-500 spectrometer at 500.17 MHz. Chemical shifts are given in ppm from tetramethylsilane (TMS); solvent - deuterochloroform.

Results and Discussion

By the reaction of 10-phenylsubstituted *a,c*-biladiene dihydrobromide **1** with corresponding aromatic aldehydes new mono-hydroxysubstituted porphyrins **2-4** were obtained. The strength of organic acids (trifluoroacetic acid, chloroacetic acid, acetic acid) used as the catalyst only slightly effects on the yield of the target products **2-4**. Hydrobromic acid is the most convenient and provides the optimum yield (30%).



X = 2-OH (**2,5**), 2-OCH_2OH (**3,6**), 4-$OCH_2C_6H_4$(4-OH) (**4,7**);
M = H_2 (**2-4**), Zn (**5-7**)

Heating of the porphyrins **2-4** with zinc acetate in dimethylformamide allowed obtaining zinc porphyrinates

5-7 with the yield of 85%. The spectral characteristics of **2-7** are in full agreement with the proposed structures.

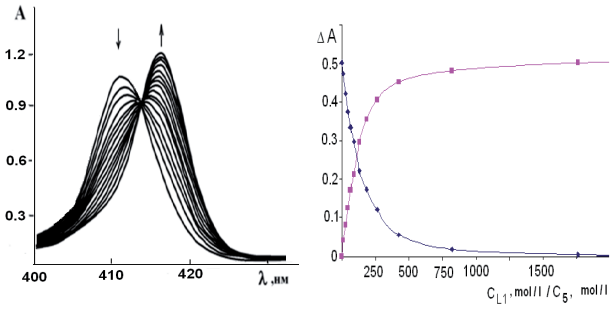


Figure 1. a) Changes of the UV-vis spectra of **5** upon addition of $\mathbf{L_1}$ in toluene; b) binding isotherm of the complexation ($C_{porph.}$ = 6.2·10^{-6} M, C_{ester} = 0÷8.6 ·10^{-3} M).

The Figure 1 shows changes of the electron absorption spectrum in the Soret region upon addition of $\mathbf{L_1}$ methyl ester to porphyrinate **5**. The presence of isosbestic points in the UV-vis spectra of the reactionary system, one step titration curve of the complexation and the data of ^{1}H NMR spectroscopy of **5** - $\mathbf{L_1}$ complex indicate the formation of complex **8** with reagents ratio of 1:1**.** Since the processes of extra coordination of amino acids to zinc porphyrinates were the subjects of our previous studies[9,10] we shall not consider this topic in details in this work.

The stability constants determined for **8** are similar for the complexes **9** between zinc 10,20-diphenyl-2,8,12,18-tetramethyl-3,7,13,17-tetraethylporphyrinate **10** (porphyrin without hydroxy-group) and $\mathbf{L_1}$-$\mathbf{L_3}$ (Table 1). Basing on the results we can conclude that **8** and **9** are the complexes with a single binding point (through coordination to Zn^{II}).

By comparison of the obtained K_a values with published data for analogous complexes of tetraphenylporphyrin in toluene, we should admit that $\mathbf{L_1}$-$\mathbf{L_3}$ are less strong extraligands than piperidine (K_a = 80900 M^{-1}), imidazole (K_a = 24000 M^{-1}) and quinoline (K_a = 16900 M^{-1}) but considerably stronger than pyrrole (K_a = 200 M^{-1}), methanol (K_a = 5 M^{-1}) and other alcohols.[10,11] The ligands $\mathbf{L_1}$-$\mathbf{L_3}$ are most similar to pyridine (K_a = 5000 M^{-1}) in their extra coordination properties.

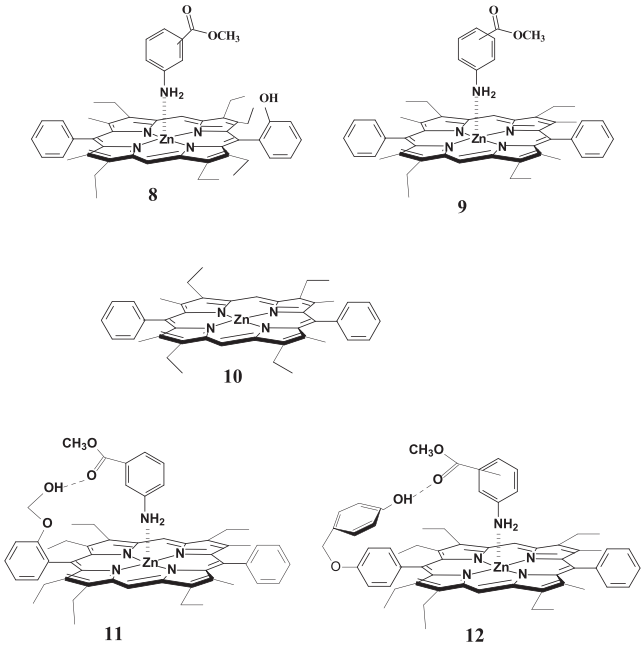


Table 1. Stability constants (K_a*, M^{-1}) of zinc porphyrinates **5-7** and **10** with amino acids methyl esters in toluene at 20^{0}C.

Porphyrinate	$\mathbf{L_1}$	$\mathbf{L_2}$	$\mathbf{L_3}$
5	1020	1050	990
6	980	3380	960
7	2420	1730	870
10	1009	1023	979

* The error of K_a determination is ~7%

Changes of the electron absorption spectra upon addition of $\mathbf{L_1}$-$\mathbf{L_3}$ to the porphyrinate **6** or **7** are similar to that during

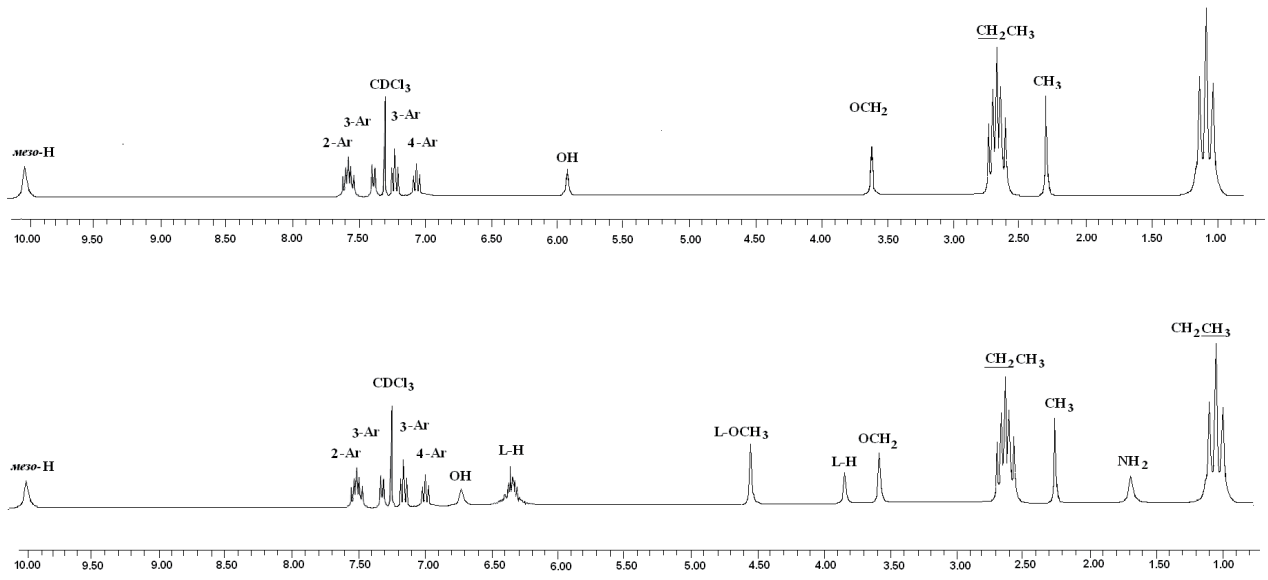
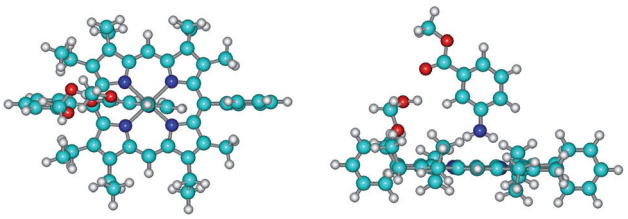


Figure 2. ^{1}H NMR spectra of **6** and **6**-$\mathbf{L_2}$ (**11**) in $CDCl_3$ at 25 ^{0}C.

the complexation of **5** with $\mathbf{L}_{1.}$ But the reactionary system saturation occurs at less concentration of the reagents and the interactions are characterized by higher stability constants (Table 1). A sharp increasing of the stability constants in the systems **6**-$\mathbf{L}_2$, **7**-$\mathbf{L}_1$ and **7**-$\mathbf{L}_2$ could be explained by the formation of the complexes **11**, **12** with two binding points through coordination to Zn^{II} and additional hydrogen bonding between hydroxy-group of porphyrinate and oxygen atom of amino acid.



a) **b)**

Figure 3. Top (a) and side (b) views of structure of complex **11** optimized by semi-empirical method AM1.

Formation of the complexes was also studied by ^{1}H NMR spectroscopy. In the spectra of complex **11** the OH signal is shifted downfield by 0.8 ppm (Figure 2). The similar shifts (δ = 0.5 and 0.3 ppm, correspondingly) were observed for the complexes **12**. According to the literature data[1] and results of our own calculations (Figure 3), the formation of the strong hydrogen bonds between the carbonyl oxygen atom of amino acid and hydrogen atom of porphyrinate's hydroxy-group is confirmed.

Conclusions

Thus, the developed synthetic methods allow obtaining hydroxysubstituted porphyrinates, which due to the good geometrical conformity between the reactionary centers of the reagents are able to coordinate *ortho*- and *meta*-aminobenzoic acids simultaneously through the central metal cation and hydroxy group on the macrocycle's periphery. Selectivity and high sensitivity of porphyrins to low-energy effects make the tetrapyrrolic macrocycles to be the ideal candidates for the substrates determination, separation and extraction.

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