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Chromatographic Characteristics and IR spectra of Isomeric 5,15-Diarylporphyrins*

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Abstract—The effect of ortho- and meta-isomerism on chromatographic characteristics and IR spectra of some 5,15-diarylporphyrins was investigated. For the first time separated zinc complexes of *cis*- and *trans*-isomers of 5,15-di(2-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin were analytically characterized.

The characteristic feature of porphyrins is their versatility caused by functional substitution of β-pyrrol (R^1, R^2, R^4, R^5, R^7, R^8, R^{10}, R^{11}) and (or) *ms*-bridging (R^3, R^6, R^9, R^{12}) positions [1, 2]. At unsymmetrical location of the substituents (R^1–R^{12}) isomeric forms are probable (up to twenty different structures).

Although in the literature on macrocycles a significant attention is paid to the studies of relation between the main physical and physico-chemical characteristics and molecular structure, the isomerism in porphyrins remains poorly understood [2].

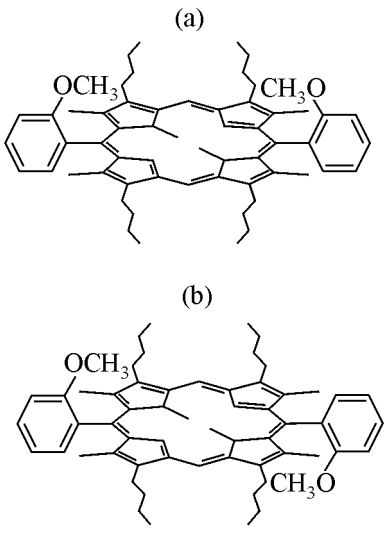

Fig. 1. *cis*- (*a*) and *trans*- (*b*) isomers of 5,15-di(2-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin.

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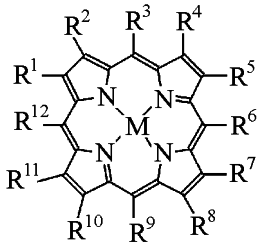
We investigated chromatographic properties and IR spectra of 5,15-di(3-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin (**I**), its zinc complex **II**, and zinc complexes of *cis*- and *trans*-isomers of 5,15-di(2-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin (**III**) and (**IV**) respectively.



R^1 = R^5 = R^7 = R^{11} = CH_3 (**I**–**V**), H (**VI**); R^2 = R^4 = R^8 = R^{10} = C_4H_9 (**I**–**IV**), CH_3 (**V, VI**); R^3 = R^9 = H (**I**–**VI**); R^6 = R^{12} = 3-$CH_3OC_6H_4$ (**I, II**), 2-$CH_3OC_6H_4$ (**III, IV**), C_2H_5 (**V**), C_6H_5 (**VI**); M = H_2 (**I, V, VI**), Zn = (**II**–**IV**).

In the synthesis of porphyrins with *ms*-phenyl groups in ortho-positions formation of atropoisomers is possible [3–6]. This is due to high steric hindrances to the rotation around the C–C bond porphyrin–phenyl originating from interaction between the *ortho*-substituent of the phenyl rings and β-methyl groups of the macrocycle. For instance, the ortho-substituted 1,15-di(2-methoxyphenyl)porphyrin can exist as two atropoisomers that are distinguished by methoxy group orientation with respect to the porphyrin plane (Fig. 1) [3]. The chromatographic characteristics of porphyrins are given in Table 1. The eluents were chosen basing on the studies carried out previously on alkyl- and aryl-substituted porphyrins [7].

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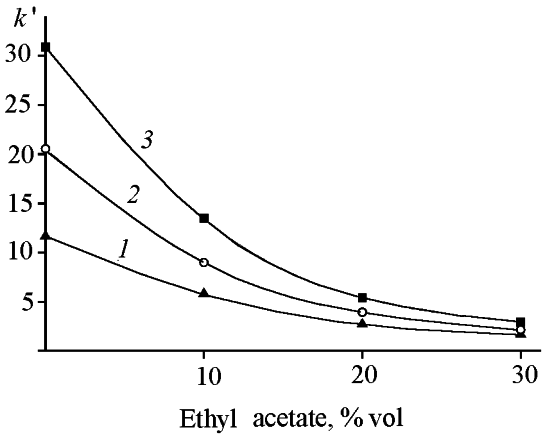

Fig. 2. Capacity factors of porphyrins **II**–**IV** as a function of ethyl acetate content in acetonitrile: (*1*) compound **III**, (*2*) compound **IV**, (*3*) compound **II**. Column Nova-Pak C_{18} (150×3.9 mm), flow rate 1 ml min^{-1}, temperature 20°C. Spectrophotometric detection, λ 410 nm.

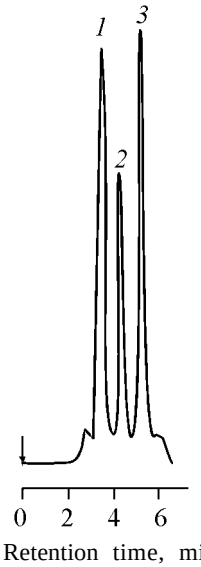

Fig. 3. Chromatogram of porphyrins mixture: (*1*) compound **III**, (*2*) compound **IV**, (*3*) compound **II**. Eluent AN–EA (90 : 10).

The order of appearance of compounds actually does not change in all the systems under study. Retention time of porphyrins grows in the series **III** < **IV** < **II** < **I**, i.e., the retention of porphyrins on nonpolar adsorbents increases with growing number of carbon atoms in the side substituents. Note that this series is consistent with the data of [7]. Porphyrin **I** contains longer alkyl chains and is stronger retained than 5,15-diethyl-2,3,7,8,12,13,17,18-octamethyl= porphyrin (**V**) and 5,15-diphenyl-2,8,12,18-tetra= methylporphyrin **VI**. Introduction into the macroring of a zinc atom decreases the retention compared to that of free ligand. Practically all chromatographic systems studied ensured separation of the *ortho*- and *meta*-isomers of the zinc complexes of 5,15-di-(methoxyphenyl)porphyrins **II**–**IV**, and also separation of atropoisomers of zinc complexes of 5,15-di(2-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin (**II, III**). The methoxy groups in the ortho-position of the phenyl *ms*-substituents prevent their free rotation, and therefore the benzene rings are normal to the macroring plane. With the *meta*-isomer apparently no hindrance to free rotation exists, and the phenyls may be situated in the same plane as macroring. The latter fact increases the interaction of porphyrin with the sorbent surface. This perhaps ix the reason of the stronger retention of *meta*-isomer compared to ortho-isomer. The atropoisomer in the cis-form is characterized by weaker retention on the reversed phase compared to the *trans*-isomer. This may be due to higher polarity of the *cis*-isomer increasing its affinity to the eluent.

The dependence of capacity factors of porphyrin zinc complexes on the ratio ethyl acetate–acetonitrile in the eluent is shown in Fig. 2. The growing amount of ethyl acetate in the eluent regularly results in decrease in the retention times and in narrowing of peaks. Even at 30% of ethyl acetate in the eluent separation both of atropoisomers and *ortho*- and *meta*-isomers (Fig. 3) occurs. These complexes are well separated on all columns under study when the eluents used are sufficiently selective. But the best results were obtained on sorbent Nova-Pak C_{18} for the selectivity of separation and peak resolution for, e.g., atropoisomers at elution with acetonitrile–ethyl acetate (90 : 10) was better (α 1.11; 1.31 and 1.55; R_s 0.43; 1.11 and 2.80 for columns Nucleosil C_{18}, μ-Bondapak C_{18} and Nova-Pak C_{18} respectively). It is due probably to the very fine grains of the sorbent Nova-Pak C_{18} (3 μm).

It should be noted that for separation and determination of free of metals porphyrins the column μ-Bondapak C_{18} 300 × 3.9 mm is more suitable than Nova-Pak C_{18} (150 × 3.9 mm). On the column Nova-Pak C_{18} the peaks of free porphyrins are more eroded than on μ-Bondapak C_{18} (eluent acetonitrile–ethyl acetate, 90 : 10). When these eluents are used in 70 : 30 ratio, the peaks of ligands on Nova-Pak C_{18} are completely eroded. Good results can be attained both with columns of ordinary length and with microcolumns (64 × 2 mm).

A valuable information on the structure of newly synthesized compounds can be deduced from IR

Table 1. Capacity factors of porphyrins **I**–**V**[a]

Compd. no.	Column 150 × 3.9 mm, Nova Pak C_{18}				Column 300 × 3.9 mm, μ-Bondapak ¢$_{18}$			Column 64 × 2 mm, Nucleosil ¢$_{18}$	
	AN	AN–EA, 90:10	AN–EA, 80:20	AN–EA, 70:30	AN–EA, 90:10	AN–AC, 40:60	AN–MEK, 30:70	AN	AN–EA, 90:10
I	41.3	29.8	–	–	19.9	4.4	1.7	12.1	3.4
II	30.9	13.5	5.4	2.9	10.7	2.7	1.6	5.2	2.3
III	11.6	5.8	2.7	1.6	6.1	2.1	1.4	2.5	1.3
IV	20.5	9.0	3.9	2.2	8.0	2.3	1.4	3.7	1.6
V	12.1	4.1	10.1	–	5.1	2.5	1.5	2.5	1.2
VI	28.3	9.8	13.2	–	9.1	3.6	1.5	–	2.3

[a] Eluents: AN, acetonitrile; EA, ethyl acetate; AC, acetone; MEK, methyl ethyl ketone.

Table 2. Vibration frequencies of CH bonds in phenyl fragments of porphyrin **I**–**IV, VI**, cm^{-1} (¤ßr pellets)

Compd. no.	γ_{CH}[a]				δ_{CH}
I	880 (1CH)	780 (3CH)	–	–	1165, 1062
II	878 (1CH)	777 (3CH)	–	–	1164, 1060
III			750 (4CH)		1170, 1053
IV	–	–	760 (4CH)	–	1169, 1050
VI	–	–	–	745 (5CH)	1170, 1050

[a] The number of neighbor C–H bonds is indicated in parentheses.

spectra. In the IR spectra of porphyrins appear the effects due to the increase in the symmetry of the molecule at complexing with metal, and to its decrease on the chemical modification of the ligand structure. Proceeding from the previous investigations on 5,15-diarylporphyrins [3, 8, 9] it should be noted that in the study of isomerism in compounds **I**–**IV** the most interesting are the vibrations of atoms in the phenyl moieties: bending vibrations of C–H bonds and skeleton vibrations of C–C bonds (Table 2).

Out-of-plain bending vibrations (γ_{CH}) of the neighboring C–H bonds in benzene rings strongly interact, and therefore the position of the corresponding absorption bands characterizes the number of adjacent C–H bonds in the ring. 5,15-Diphenylporphyrin **VI** has a strong band at 745 cm^{-1} [9] that is characteristic of interaction between five neighbor C–H bonds, i.e. of monosubstituted benzene. *meta*-Substituted diphenylporphyrins **I, II** have absorption bands at 780 (three neighbor C–H bonds) and 880 cm^{-1} (single C–H bond). In the spectrum of *ortho*-substituted diphenylporphyrins **III, IV** is present a band at 750–760 cm^{-1} (four adjacent C–H bonds).

To the in-plane bending vibrations δ_{CH} of phenyl moieties in porphyrins **I**–**IV** belong the medium bands at 1170 and 1050 cm^{-1}.

To the skeleton vibrations of the C–C bonds in the benzene rings of porphyrin **VI** correspond three bonds of growing intensity at 1100, 1180, and 1200 cm^{-1} [9]. In the spectra of *ortho*-isomers **III, IV** the presence of atropoisomers causes the splitting of the band at 1200 cm^{-1}. In the spectra of meta-derivatives **I, II** the most intense single band appears at 1190 cm^{-1}.

EXPERIMENTAL

Porphyrins **I**–**IV** were synthesized along procedures [3]. All compounds were subjected to double chromatographic purification, first on a column packed with alumina, then with silica gel, eluent benzene. Then the compounds were recrystallized from a mixture benzene–hexane, 1 : 4.

As eluents in HPLC method were used the following solvents (in parentheses are listed polarity and selectivity group): acetonitrile (6.2; 6), ethyl acetate

(4.3; 6), methyl ethyl ketone (4.5; 6), acetone (5.4; 6), and their mixtures. The chromatographic properties of porphyrins were studied on porphyrin solutions in ethyl acetate of concentration ~1.10^{-5} M. The chromatographic behavior of substances was studied on Waters chromatograph (USA), stainless-steel columns: 300 × 3.9 mm, sorbent μ-Bondapak C_{18}, grains 10 μm, dead time 1.4 min; 150 × 3.9 mm, sorbent Nova-Pak C_{18}, grains 3 μm, dead time 1.3 min; eluent flow rate 1 ml min^{-1}, sample volume 2–5 μl, detector spectrophotometer, λ 410 nm. Also was used microcolumn chromatograph Milikhrom 4, stainless-steel column 64 × 2 mm, sorbent Nucleosil C_{18}, grains 5 μm; eluent flow rate 50 μl min^{-1}, sample volume 5–15 μl, detector spectrophotometer, λ 404 nm. Columns maintained at 20°C. The dead time was determined from the erosion front on the chromatogram. In the microcolumn the retention volume of nonsorbed component 170 μl. The chromatographic behavior of substances was evaluated by capacity factor (k'), selectivity factor (α), and resolution (R_s).

The organic solvents were purified by standard methods [10]. IR spectra were registered on spectrophotometer Specord M-80 from KBr pellets.

5,15-Di(3-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin (I). Yield 45%. IR spectrum (cm^{-1}): ν_{NH} 3318 m, δ_{NH} 965 m, γ_{NH} 702 w, $\nu_{CH(ms\text{-}H)}$ 2980 m, $\delta_{CH(\beta\text{-}alk)}$ 1482 ©, $\gamma_{CH(\beta\text{-}alk)}$ 845 m.

Zinc-5,15-di(3-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin (II). Yield 95%. IR spectrum (cm^{-1}): $\nu_{CH(ms\text{-}H)}$ 2975 m, $\delta_{CH(\beta\text{-}alk)}$ 1478 s, $\gamma_{CH(\beta\text{-}alk)}$ 842 m.

***cis*-Zinc-5,15-di(2-methoxyphenyl)-3,7,13, 17-tetramethyl-2,8,12,18-tetrabutylporphyrin (III).** Yield 48%. IR spectrum (cm^{-1}): $\nu_{CH(ms\text{-}H)}$ 2960 m, $\delta_{CH(\beta\text{-}alk)}$ 1480 s, $\gamma_{CH(\beta\text{-}alk)}$ 844 m.

***trans*-Zinc-5,15-di(2-methoxyphenyl)-3,7,13,17-tetramethyl-2,8,12,18-tetrabutylporphyrin (IV).** Yield 47%. IR spectrum (cm^{-1}): $\nu_{CH(ms\text{-}H)}$ 2962 m, $\delta_{CH(\beta\text{-}alk)}$ 1481 s, $\gamma_{CH(\beta\text{-}alk)}$ 845 m.

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