TABLE 3. Characteristics of Porphyrins I, III-VI Synthesized

Compound	Electronic absorption spectra, λ_{max}, nm (log ε), in DMFA					Found, %				Empirical formula	Calculated, %				Yield, %
	I	II	III	IV	sorret	C	H	N	S		C	H	N	S	
I	645 (3,59)	590 (3,84)	549 (3,95)	515 (4,34)	422 (5,53)	55,6	2,5	5,7	13,7	$C_{44}H_{26}F_4N_4O_8S_4$	56,04	2,78	5,94	13,60	20
III	646 (3,50)	591 (3,67)	549 (3,83)	515 (4,19)	420 (5,50)	56,5	3,4	12,3	14,1	$C_{44}H_{34}N_8O_8S_4$	56,76	3,68	12,04	13,77	40*
IV	646 (3,52)	591 (3,70)	549 (3,86)	515 (4,23)	420 (5,57)	62,4	5,5	10,0	10,6	$C_{60}H_{66}N_8O_8S_4$	62,37	5,76	9,70	11,10	45*
V	644 (3,60)	590 (3,80)	548 (3,93)	514 (4,33)	418	59,0	4,4	9,1	10,9	$C_{60}H_{58}N_8O_{12}S_4$	59,49	4,83	9,25	10,58	75 (A); 41 (B)*
VI	648 (3,64)	591 (3,75)	550 (3,93)	516 (4,29)	418	76,0	10,7	4,0	4,8	$C_{188}H_{322}N_8O_8S_4$	76,52	11,00	3,80	4,34	70

*Based on the ammonium salt of tetra(4-sulfonatophenyl)porphin.

is diluted with water to 100 ml, centrifuged, the precipitate is washed with 100 ml of water, dried and chromatographed as in the case of IV. The yield of VI is 0.223 g (70%). R_f 0.75 (methanol—chloroform, 1:5).

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SYNTHESIS AND ELECTRONIC ABSORPTION SPECTRA OF SUBSTITUTED TETRABENZOPORPHINS

V. N. Kopranenkov, E. A. Makarova,
S. N. Dashkevich, and E. A. Luk'yanets

UDC 547.979.733

Zinc complexes of tetrabenzoporphins with substituents in the benzene fragments of the molecule were synthesized by the template tetramerization of substituted 3-carboxymethylphthalimidines or phthalimides with malonic or phenylacetic acid in the presence of zinc acetate, as well as by substitution reactions in the tetrabenzoporphin molecule. The metal-free compounds were obtained from the corresponding zinc complexes by the action of a stream of hydrogen chloride in chloroform. The electronic absorption spectra of the synthesized compounds were investigated.

Whereas the introduction of substituents into the benzene rings of phthalocyanins is an effective method for the directed alteration of their properties, to begin with the spectral ones [1], the influence of a similar substitution has been virtually unstudied in the series of tetrabenzoporphins (TBPs); this is associated with the poor availability of the substituted TBPs.

In the present communication, we describe the synthesis and electronic absorption spectra of the TBPs containing electron-donor and electron-acceptor substituents in the positions 3, 4, and 5 of the benzene rings. The substituted TBPs were synthesized from 2-naphthols by the traditional scheme of Linstead, as well as by new methods utilizing pathalimides and substitution reactions in the macrocycle.

Scientific Research Institute of Organic Intermediates and Dyes, Moscow 103787. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 773-779, June, 1988. Original article submitted December 19, 1986; revision submitted October 28, 1987.

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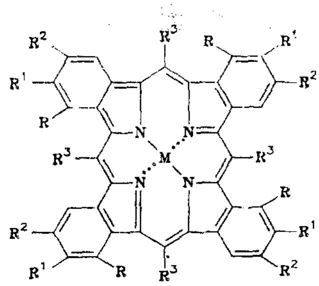
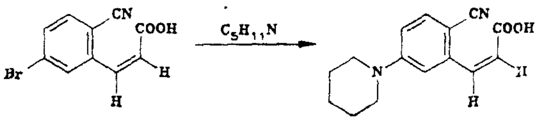


I–III, VII–XI, XX, XXI, XXIV

I–III, IX–XI, XXI, XXIV $M=Zn$; VII, VIII, XX $M=HH$; I, VII $R=R^2=R^3=H$, $R^1=C_6H_5$; II, VIII $R=R^3=H$, $R^1=R^2=C_6H_5$; III $R=CH_3$, $R^1=R^2=R^3=H$; IX three of R^1 or $R^2=Cl$, $R^3=C_6H_5$; XI, XX $R=R^2=R^3=H$, $R^1=CH_3O$; XXI $R=R^2=H$, $R^1=$ $=tert\text{-}C_4H_9$, $R^3=C_6H_5$; X two or R^1 or $R^2=Cl$, $R^3=C_6H_5$; XXIV $R^3=CH_3$, one of R^1 or $R^2=NO_2$

The zinc complexes of tetra-4-phenyl-, octa-4,5-phenyl-, and tetra-3-methyl-TBP (I)-(III) were obtained from the corresponding substituted phthalimides or their potassium derivatives and malonic acid or sodium acetate in up to 22% yield by the method which we previously developed [2]. The initial 4-phenyl- and 3-methylphthalimide (IV), (V) were synthesized according to [3, 4], and 4,5-diphenylphthalimide (V) was synthesized by the melting of the corresponding anhydride [5] with urea at 170°C. The temperature of the complex formation noticeably influences the yields of the compounds (I)-(III). The best results were obtained as follows: for compound (III) at 360°C, for (II) at 370-380°C, and for (I) at 390-400°C. At the same time, the yield of the unsubstituted TBP of zinc is virtually unchanged in the range of 340-400°C [2]. The metal-free tetra-4-phenyl- and octa-4,5-phenyl-TBP (VII), (VIII) were obtained with the yields of ~70% by the passage of a stream of hydrogen chloride through the solution of the zinc complexes (I) and (II) in chloroform at 0°C. The condensation of 4-chlorophthalimide with phenylacetic acid in the presence of zinc acetate at 360°C gave the mixture of the zinc complexes of meso-tetraphenyltri(4-chlorobenzo)benzoporphin (IX) and meso-tetraphenyldi(4-chlorobenzo)dibenzoporphin (X), which have good solubility in organic solvents, in the yields of 3.3 and 2.4%; so the partial dehalogenation and the simultaneous destruction of the macrocycle proceed in the course of the complex formation. The isolation of a mixture of chloro derivatives of TBP containing 9-11 atoms of chlorine in the molecule by boiling the unsubstituted TBP of zinc in the mixture of thionyl chloride and sulfuryl chloride was communicated in [6]. The tetra(4-methoxybenzo)porphin of zinc (XI) and the bromo-substituted zinc complex of TBP (XII) were obtained by the reaction of 5-bromo- and 6-methoxy-3-carboxymethylphthalimidines (XIII), (XIV) with zinc acetate at 280°C in a stream of inert gas. In contrast with the zinc complex of TBP [7], the formation of the compounds (XI) and (XII) is only observed in a narrow temperature range (280-290°C); their complete destruction proceeds at above 300°C. The highest and most stable yields of the products (17-19%) were obtained by performing the reaction in 1-bromonaphthalene. In the case of the phthalimidine (XIII), a mixture of the complexes with a differing content of bromine is formed as the result of the partial debromination by analogy with the chloro-substituted TBPs. However, this mixture could not be separated in the given case. The results of the elemental analysis for the series of experiments were uniform, and indicate the mean content of two bromine atoms in the molecule. The bromo derivatives of TBP were previously obtained by the bromination of the unsubstituted TBP of zinc with the mixture of phosphorus tribromide and bromine at 250°C [6]. The substitution product containing 17.5 atoms of bromine in the molecule is thereby formed. The substitution proceeds at the meso-carbon atoms and in the benzene rings.

For the synthesis of the intermediate o-cyanocinnamic acids, it was expedient to utilize, in some cases, the substitution of the available bromine atom in 5-bromo-2-cyanocinnamic acid (XV) [8], which was obtained by the traditional scheme from the accessible 6-bromo-2-naphthol. Thus, the reaction of the acid (XV) with piperidine in a polar aprotic solvent (DMF, N-methylpyrrolidone) gave 5-piperidyl-2-cyanocinnamic acid (XVI).



XV

XVI

TABLE 1. Electronic Absorption Spectra of the Tetrabenzoporphins (I)-(III), (VII)-(XII), (XIX)-(XXI), and (XXIV)

Compound	Solvent	λ_{max} (log ε) (relative intensity)
I	Chloroform	634 [1,0], 574 [0,13], 434 [2,92], 408 [0,55]
	Chloroform–pyridine, 50:1	640 (5,18), 590 (4,27), 472 (4,36), 442 (5,69), 416 (4,86)
II	Chloroform	642 (5,21), 592 (4,25), 476 (4,78), 440 (5,65), 412 (4,85)
III	Chloroform	628 [1,0], 624 пл [0,98], 580 [0,18], 428 [4,86], 400 [0,96]
	Chloroform–pyridine, 50:1	632 (5,03), 629 (5,01), 588 (4,35), 434 (5,50), 418 (5,02)
VII	Chloroform	672 (4,76), 624 (4,90), 617 (4,84), 610 пл (4,70), 580 (4,22), 462 (4,28), 442 (5,42), 423 (5,39), 395 (4,82)
VIII	Chloroform	672 [1,0], 626 [1,7], 618 [1,1], 608 пл [0,53], 572 [0,26], 444 [4,1], 424 [3,8], 394 [1,0]
IX	Benzene	641 (4,81), 597 (4,11), 451 (5,32)
X	Benzene	636 (4,88), 585 (4,14), 440 (5,33)
XI	Chloroform	632 (4,78), 626 пл (4,73), 582 (4,02), 462 (4,72), 426 (5,34), 402 (4,65)
	Polymethylmethacrylate	628 [1,0], 584 [0,35], 424 [3,33], 406 [3,26]
XII	Chloroform	628 [1,0], 566 [0,12], 428 [3,20], 404 [0,79]
	Polymethylmethacrylate	628 [1,0], 580 [0,26], 426 [2,67], 412 пл [2,30]
XIX	DMF	644 [1,0], 582 [0,56], 446 [2,75]
XX	Chloroform	662 [1,0], 614 [1,45], 608 [1,44], 600 [1,25], 564 [0,46], 430 [5,0], 418 [4,8], 386 [2,5]
XXI	Pentane	650 (4,89), 603 (2,98), 450 (5,41)
	Polymethylmethacrylate	640 [1,0], 585 [0,19], 444 [4,12], 414 [0,83]
XXIV	Benzene	638 (4,71), 594 (3,97), 438 (5,11)

When the reaction in DMF is performed in the presence of dry potassium carbonate or copper powder, the acid (XVI) is formed with a yield not greater than 5%; its yield increases to 30% in an autoclave at 180°C in the presence of nickel chloride. The best yield of compound (XVI) (60%) was achieved in boiling N-methylpyrrolidone.

The condensation of olefins with bromo- and iodo-substituted aromatic compounds in the presence of palladium catalysts with the formation of substituted styrenes having the trans configuration is known [9, 10]. By an analogous method, 5-styryl-2-cyanocinnamic acid (XVII) was obtained with a yield of 49% from the bromo-acid (XV). The cis configuration of the cinnamic acid (XVII) is retained; this was established from the PMR spectral data showing the presence of four doublets of the olefinic protons: δ 6.6 and 8.0 ppm ($J_{\alpha,\beta}$ = 16 Hz) of the trans-olefinic protons of the styryl group, and δ 7.1 and 7.7 ppm ($J_{\alpha,\beta}$ = 12 Hz) of the cis protons of the cinnamic acid fragment.

When 5-styryl-3-carboxymethylphthalimidine (XVIII), obtained by the cyclization of the cyanoacid (XVII), reacts with zinc acetate at 360°C, the tetra(4-styrylbenzo)porphin of zinc (XIX) is formed with the yield of 15%.

In contrast to the unsubstituted TBP of zinc, the chloro-, methoxy-, and bromo-substituted TBPs (IX)-(XII) have good solubility in different organic solvents (benzene, chloroform, ethanol, acetone, etc.); this was utilized for their chromatographic purification on aluminum oxide. The increase in the solubility in the case of the compounds (IX)-(XI) is explained by the non-coplanar disposition of the phenyl groups. In the case of compound (XII), it is explained by the irregular distribution of the bromine atoms in the molecule; this leads to the breaking up of the crystal lattice. We will note the increased tendency for the demetallation of these complexes in acid media by comparison with the TBP of zinc and its tert-butyl-substituted analog. Thus, if the tetra(4-tert-butylbenzo)porphin of zinc is demetallated only by the passage of hydrogen chloride into its sulfuric acid solution, then the zinc complex (XI) forms tetra(4-methoxybenzo)porphin (XX) with the yield of 70% by the reprecipitation with water from the sulfuric acid solution. The synthesized compounds were purified by chromatography on aluminum oxide.

The establishment of compounds having higher solubility than the compounds (IX)-(XII) was required for the introduction of the TBPs into thin polymeric films. Thus, compound (XXI), which is obtained by the condensation of 4-tertbutylphthalimide (XXII) with phenylacetic acid, has the solubility of not less than $5 \cdot 10^{-3}$ M in hexane, and 10^{-1} M in chloroform, owing to the presence of four tertbutyl and four meso-phenyl substituents in the molecule.

One more approach to the synthesis of TBPs substituted in the benzene fragments is provided by substitution reactions, e.g., the nitration of TBPs with substituents in the meso positions. The mixture of mono-, di-, and trinitro derivatives was previously obtained by the nitration of meso-tetraalkylporphyrins [11]. We investigated the meso-tetramethyl-TBP of zinc (XXIII), which forms the 3(4)-nitro-meso-tetramethyltetrabenzoporphin of zinc (XXIV) by nitration with the nitrating mixture in acetic acid. Products of the more extended nitration were not noted.

The electronic absorption spectra of solutions of the compounds synthesized were measured in the region of 220-750 nm (Table 1). The introduction of electron-donor or electron-acceptor substituents into the TBP molecule does not cause a significant change in the character of the spectrum in organic solvents, and only leads to some shift of the Q- and B-bands and their vibrational side bands by comparison with the unsubstituted compounds [12]. Thus, the presence of the electron-donor methoxy groups in the benzene rings of the tetra(4-methoxybenzo)porphin of zinc (XI) leads to a bathochromic shift of the Q-band by 8 nm, and of the B-band by 2 nm (Table 1). In the case of the tetramethyl- and tetraphenyl-substituted zinc complexes (I) and (III), the bathochromic shift of the Q- and B-bands is observed to be 4 and 10 nm correspondingly. In the spectrum of the octaphenyl-TBP of zinc (II), the bathochromic displacement of these bands comprises 18 and 16 nm. An analogous shift of the absorption bands in the spectrum is also observed with the introduction of four styryl groups. A distinguishing feature of the spectra of the zinc complexes containing methyl and methoxy groups is the broadening and the formation of a shoulder at the longwave Q-band (Fig. 1). For the compound (III),such a change in the spectrum is evidently associated with the presence of positional isomers of the methyl groups (3 or 6), possessing decreased symmetry. A similar separation of the Q-band was previously found for the octa-substituted porphyrazines containing donor and acceptor substituents at the same time in the molecule [13]. In contrast to the compound (III), the complex (XI), which is obtained by the Linstead scheme, should only exist in the form of one isomer. Therefore, the changes in the spectrum of this compound presented above can be explained by a decrease in the symmetry of the chromophoric part of the molecule on the introduction of strong electron-donor methoxy groups.

For the zinc complexes containing electron-acceptor substituents, e.g., (IX), (X), (XII), and (XXIV), the Q- and B-bands are shifted bathochromically up to 17 and 27 nm correspondingly by comparison with the unsubstituted compounds. The lowering of the symmetry in the case of the dihalogeno-substituted complexes (X) and (XII) is not shown in the electronic absorption spectra.

Therefore, the substituents in the benzene rings of TBP show almost the same action on the Q- and B-bands, in contrast to the phthalocyanins [14], in which the analogous substitution causes a large shift of the Q-band.

As is the case for the unsubstituted TBPs, the transition from the metallic complexes (I), (II), and (XI) to the metal-free compounds (VII), (VIII), and (XX) proceeds with the cleavage of the Q-band into two components, whereby the shortwave one is presented in the form of a triplet (Table 1). The B-band in the spectrum of the compounds (VII) and (XX) is also cleaved into two components.

EXPERIMENTAL

The electronic absorption spectra were measured on the Hitachi-356 spectrophotometer using the concentration of ~10^{-5} M. The IR spectra were registered on the UR-20 spectrometer using tablets of KBr. The mass peaks were detected on the Varian MAT CH-6 mass spectrometer with the source for the direct input of the sample, the energy of ionization of 70 eV, and the temperatures of 150-200°C for the sample vaporization block. The TLC and column chromatography were performed on Al_2O_3 of activity II according to Brockmann.

The 4-phenylphthalimide (IV) was obtained by the reaction of 4-phenylphthalic acid with ammonium carbonate at 180°C [2]; it had the mp 201°C (from benzene).

Tetra(4-phenylbenzo)porphin of Zinc (I). The mixture of 1.3 g (4.98 mmole) of the N-potassium derivative (IV), 0.8 g (7.69 mmole) of malonic acid, and 1.1 g (5.02 mmole) of zinc acetate dihydrate is heated for 1 h in a current of nitrogen at 390-400°C. It is cooled to room temperature and washed with 300 ml of hot water and 150 ml of 80% ethanol until a color-

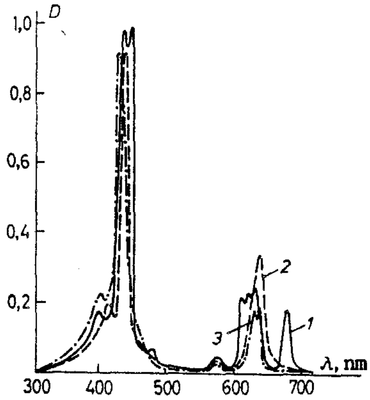


Fig. 1. The electronic absorption spectra. 1) Tetra(4-phenylbenzo)porphin (VII); 2) its zinc complex (I); 3) the zinc complex of tetra(4-methoxybenzo)porphin (XI) (in chloroform).

less filtrate is obtained. The residue is dissolved in 20 ml of pyridine; the solution is transferred to a chromatography column 3 by 40 cm and eluted with the 1:4 mixture of pyridine—chloroform. The solvent is distilled, and the residue is dissolved in 10 ml of pyridine. The solution is transferred to a chromatography column and eluted with chloroform. Compound (I) is obtained with the yield of 0.24 g (21.5%); it has the R_f 0.24 (chloroform). Found: C 82.2, H 4.2, and N 6.1%. $C_{60}H_{36}N_4Zn$. Calculated: C 82.0, H 4.1, and N 6.4.

Tetra(4-phenylbenzo)porphin (VII). A stream of hydrogen chloride is passed, for 1 h at 0°C, into a solution of 0.1 g (0.114 mmole) of compound (I) in 100 ml of chloroform. The solution is washed, in turn, with 250 ml of water, 150 ml of a 5% solution of sodium carbonate, and 200 ml of water until a neutral reaction of the rinse water is obtained; it is dried with sodium sulfate and concentrated. The residue is dissolved in 25 ml of chloroform, transferred to a chromatography column 3 by 20 cm, and eluted with chloroform. The metal-free compound (VII) is obtained with the yield of 0.07 g (70%); it has the R_f 0.33 (chloroform). Found: C 87.8, H 5.0, and N 6.7%. $C_{60}H_{38}N_4$. Calculated C 88.4, H 4.7, and N 6.9%.

4,5-Diphenylphthalimide (VI). The mixture of 1.8 g (6.02 mmole) of 4,5-diphenylphthalic anhydride [4] and 0.5 g (8.33 mmole) of dry urea is stirred for 1.5 h at 170°C. It is cooled to room temperature, and the reaction mass is washed with 500 ml of water. The residue is dried at room temperature to a constant mass, and is recrystallized from ethanol. The yield of compound (VI) is 1.5 g (85%); it has the mp 197°C. The IR spectrum is as follows: 1735, 1772 (C=O), and 3160 (N—H) cm^{-1}. Found: N 4.6%, M^+ 299. $C_{20}H_{13}NO_2$. Calculated: N 4.7%, M^+ 299.

Tetra(4,5-diphenylbenzo)porphin of Zinc (II). The mixture of 0.3 g (1.0 mmole) of compound (VI), 0.22 g (1.01 mmole) of zinc acetate dihydrate, and 0.4 g (4.88 mmole) of sodium acetate is heated for 1 h in a current of nitrogen at 370-380°C. It is cooled to room temperature, and the reaction mass is washed with 100 ml of hot water and 50 ml of aqueous ethanol (1:1). The residue is dissolved in 15 ml of chloroform; the solution is transferred to a chromatography column 3 by 15 cm and is eluted with chloroform. The yield of 0.05 g (17%) of compound (II) is obtained; it has the R_f 0.26 (chloroform). Found: C 85.3, H 4.3, and N 5.1%. $C_{84}H_{52}N_4Zn$. Calculated: C 85.3, H 4.4, and N 4.7%.

Tetra(4,5-diphenylbenzo)porphin (VIII). A stream of hydrogen chloride is passed, for 1 h at 20-25°C, into the solution of 0.03 g (0.025 mmole) of the zinc complex (II) in 20 ml of chloroform. The reaction mass is washed with 30 ml of water, 40 ml of a 5% solution of sodium carbonate, and then 25 ml of water. The solution is dried with sodium sulfate prior to its transfer to a chromatography column 3 by 20 cm and the elution with benzene. The yield of 0.02 g (71%) of compound (VIII) is obtained; it has the R_f 0.5 (chloroform).

Tetra(3-methylbenzo)porphin of Zinc (III). The mixture of 0.5 g (2.5 mmole) of the potassium derivative of 3-methylphthalimide (V) [3], 0.3 g (2.88 mmole) of malonic acid, and 0.4 g (1.83 mmole) of zinc acetate dihydrate is heated for 1 h in a stream of nitrogen at 360°C. It is cooled to room temperature and washed with 150 ml of hot water and 75 ml of aqueous ethanol (1:1). The residue is dissolved in 7 ml of pyridine, transferred to a chromatography column 3 by 15 cm, and eluted with the 4:1 mixture of chloroform–pyridine. The solvent is removed, and the residue (0.027 g) is repeatedly purified by chromatography on the same column, but eluting it with chloroform. The yield of 0.02 g (5%) of compound (III) is obtained; it has the R_f 0.25 (chloroform). Found: C 76.0 and H 4.9%. $C_{40}H_{28}N_4Zn$. Calculated: C 76.2 and H 4.5%.

6-Methoxy-3-carboxymethylphthalimidine (XIV). The solution of 2.5 g (12.4 mmole) of 4-methoxy-2-cyanocinnamic [15] in 10 ml of 10% NaOH is boiled for 3 h; it is cooled and acidified with hydrochloric acid (1:1) to the pH 5. The precipitated residue is separated and recrystallized from water. The yield of 1.68 g (62%) of (XIV) is obtained; it has the mp 198-199°C. The IR spectrum is as follows: 1671, 1718 (C=O), 3330 (N–H), and 3455 (O–H) cm^{-1}. Found: C 59.9, H 5.3, and N 6.1%. $C_{11}H_{10}NO_4$. Calculated: C 60.0, H 5.3, and N 6.3%.

Tetra(4-methoxybenzo)porphin of Zinc (XI). The mixture of 3.3 g (15.0 mmole) of the phthalimidine (XIV) and 3.3 g (15.1 mmole) of zinc acetate dihydrate in 20 ml of 1-bromonaphthalene is heated for 3 h in a stream of nitrogen at 280°C. The mixture is cooled prior to dilution with 100 ml of petroleum ether. The precipitated residue is filtered off, washed with 30 ml of petroleum ether, and dissolved in 30 ml of chloroform. It is transferred to a chromatography column 3 by 40 cm, and is eluted with chloroform. The yield of 0.44 g (17%) of compound (XI) is obtained; it has the R_f 0.16 (chloroform). Found: C 69.3, H 4.0, and N 7.7%. $C_{40}H_{28}N_4O_4Zn$. Calculated: C 69.2, H 4.1, and N 8.1%.

Tetra(4-methoxybenzo)porphin (XX). The solution of 0.04 g (0.058 mmole) of the zinc complex (XI) in 20 ml of concentrated H_2SO_4 is maintained at 0°C for 20 min; it is poured onto 250 g of ice and neutralized with aqueous ammonia to the pH 7. The precipitated residue is filtered off, washed on the filter with 250 ml of water, and dried in air. The residue (0.036 g) is dissolved in 15 ml of chloroform; the solution is transferred to a chromatography column 3 by 25 cm, and eluted with chloroform. The yield of 0.026 g (70%) of compound (XX) is obtained; it has the R_f 0.21 (chloroform). Found: C 73.9 and H 5.7%. $C_{40}H_{30}N_4O_4 \cdot H_2O$. Calculated: C 74.1 and H 5.0%.

5-Bromo-3-carboxymethylphthalimidine (XIII). The solution of 4 g (15.9 mmole) of the bromoacid (XV) [15] in 25 ml of 10% NaOH is boiled for 3 h; it is cooled and acidified with 25 ml of hydrochloric acid (1:1). The residue is filtered off and recrystallized from water. The yield of 3.4 g (79.5%) of compound (XIII) is obtained; it has the mp 181-182°C. The IR spectrum is as follows: 1710, 1725 shoulder (C=O), 3310 (N–H), and 3435 (O–H) cm^{-1}. Found: C 44.6, H 2.9, and N 4.7%. $C_{10}H_7BrNO_3$. Calculated: C 44.6, H 2.6, and N 5.2%.

Bromo-Substituted Tetrabenzoporphin of Zinc (XII). The mixture of 1.6 g (5.93 mmole) of the phthalimidine (XIII) and 1.06 g (4.84 mmole) of zinc acetate dihydrate in 20 ml of 1-bromonaphthalene is stirred at 280°C for 3 h in a stream of nitrogen. The mixture is cooled and diluted with 100 ml of petroleum ether. The residue is filtered off, washed on the filter with 30 ml of petroleum ether, dried in air, and dissolved in 25 ml of chloroform. The solution is transferred to a chromatography column 3 by 35 cm prior to the elution with the 1:1 mixture of chloroform–benzene. The yield of 0.25 g (19%) of compound (XII) is obtained; it has the R_f 0.22 (the 1:1 mixture of chloroform–benzene). Found: Br 21.6%. $C_{36}H_{18}Br_2N_4Zn$. Calculated: Br 21.8%.

Chloro-Substituted meso-Tetraphenyltetrabenzoporphins of Zinc (IX), (X). The mixture of 1.81 g (10.0 mmole) of 4-chlorophthalimide, 1.55 g (7 mmole) of zinc acetate dihydrate, and 1.5 g (10.0 mmole) of phenylacetic acid is heated for 0.5 h at 360°C. The mixture is cooled and washed with 350 ml of hot water and 250 ml of 80% ethanol until a colorless filtrate is obtained from the rinse water. The residue is dissolved in 10 ml of chloroform, and the solution is transferred to a chromatography column 3 by 50 cm filled with aluminum oxide prior to the sequential elution with chloroform, the 1:1 mixture of chloroform–benzene, and finally the 30:10:1 mixture of chloroform–hexane–pyridine. Two fractions are obtained on chromatography. The first fraction contains 0.081 g (3.3%) of the mesotetraphenyltri(4-chlorobenzo)benzoporphin of zinc (IX) having the R_f 0.18 (chloroform). Found: C 73.1, H 3.5, N 5.7, and Cl 11.0%. $C_{60}H_{33}Cl_3N_4Zn$. Calculated: C 73.4, H 3.4, N 5.7, and Cl 10.8%.

The second fraction contains 41 mg (2.4%) of the meso-tetraphenyldi(4-chlorobenzo)dibenzoporphin of zinc (X) having the R_f 0.13 (chloroform). Found: Cl 7.9 and N 5.4%. $C_{60}H_{34}Cl_2N_4Zn$. Calculated: Cl 7.5 and N 5.9%.

5-Piperidino-2-cyanocinnamic Acid (XVI). The solution of 1 g (4.0 mmole) of the acid (XV) [15] and 1.5 ml of piperidine in 10 ml of N-methylpyrrolidone is boiled for 6 h. The mixture is cooled, diluted with 20 ml of water, and acidified with hydrochloric acid (1:1) to the pH ~6. The precipitated residue is separated, dried, and chromatographed on silica gel L 40/100 (3 by 50 cm) with the 3:1 mixture of chloroform–ether for the isolation of 0.6 g (58.5%) of compound (XVI) having the mp 237-238°C (from aqueous ethanol) and the R_f 0.42 (Silufol, the 3:1 mixture of chloroform–ether). The IR spectrum is as follows: 1635 (C=C), 1690 (C=O), 2215 (C≡N), 2860, and 2940 (C–H) cm^{-1}. Found: C 70.3, H 6.4, and N 10.5% M^+ 256. $C_{15}H_{16}N_2O_2$. Calculated: C 70.3, H 6.4, and N 10.5%; M^+ 256.

5-Styryl-2-cyanocinnamic Acid (XVII). The mixture of 1.5 g (6.0 mmole) of the acid (XV), 0.8 ml of freshly distilled styrene, 1.7 ml of triethylamine, 6 mg ($2.7 \cdot 10^{-2}$ mmole) of palladium acetate, and 0.032 g ($12.2 \cdot 10^{-2}$ mmole) of triphenylphosphine in 10 ml of DMF is stirred for 3 h at 150°C. The mixture is diluted with 50 ml of water and acidified with hydrochloric acid (1:1) to the pH 3 prior to the extraction with 10 ml of chloroform and 10 ml of ether. The extracts are combined and concentrated. After the chromatography of the residue on silica gel L 40/100 (3 by 40 cm) with the 3:2 mixture of chloroform–ether, the yield of 0.8 g (49%) of compound (XVII) is obtained; it has the mp 236-237°C (from aqueous ethanol). The IR spectrum is as follows: 1632 (C=C), 1692 (C=O), and 2215 (C≡N) cm^{-1}. Found: C 78.1, H 4.7, and N 4.8%; M^+ 275. Calculated: C 78.5, H 4.8, and N 5.1%; M^+ 275.

5-Styryl-3-carboxymethylphthalimidine (XVIII). The solution of 0.5 g (1.8 mmole) of the acid (XVII) in 10 ml of 10% NaOH is boiled for 3 h, cooled, and acidified with 10% HCl to the pH 3. The yield of 0.4 g (75%) of compound (XVIII) is obtained; it has the M^+ 293.

Tetra(4-styrylbenzo)porphin of Zinc (XIX). The mixture of 0.2 g (0.7 mmole) of compound (XVIII) and 0.18 g (0.8 mmole) of zinc acetate dihydrate is heated at 360°C for 3 h. The mixture is cooled, triturated, transferred to a filter, and washed with 250 ml of hot water. The residue is reprecipitated with 150 ml of water from 15 ml of the solution in DMF. The precipitated residue is filtered off, washed on the filter with 10 ml of ethanol, and dried. The yield of 0.025 g (15%) of the zinc complex (XIX) is obtained; it has the R_f 0.8 (the 20:1 mixture of chloroform–pyridine).

meso-Tetraphenyltetra(4-tert-butylbenzo)porphin of Zinc (XXI). The mixture of 3.75 g (18.4 mmole) of 4-tert-butylphthalimide (XXII) [16], 2.72 g (20.0 mmole) of phenylacetic acid, and 3.3 g (15.0 mmole) of zinc acetate dihydrate is heated at 360°C in a stream of helium for 0.5 h. The reaction mass is cooled, triturated in a mortar, transferred to a filter, and washed with 500 ml of hot water. The residue is dried in air. It is dissolved in 20 ml of chloroform, transferred to a column 3 by 40 cm filled with aluminum oxide, eluted with chloroform, and then sequentially with the 30:10:1 mixture of chloroform–hexane–pyridine and the 60:20:1 mixture of chloroform–hexane–pyridine. The yield of 0.55 g (10.8%) of the complex (XXI) is obtained; it has the R_f 0.24 (chloroform). Found: C 82.6, H 6.4, and N 5.5%. $C_{76}H_{68}N_4Zn$. Calculated: C 82.8, H 6.2, and N 5.1%.

3(4)-Nitro-meso-tetramethyltetrabenzoporphin of Zinc (XXIV). To the solution of 0.26 g (0.216 mmole) of the disolvate of the meso-tetramethyltetrabenzoporphin of zinc (XXIII) [17] with tribenzylamine in the mixture of 50 ml of sulfolane and 250 ml of glacial acetic acid are added 60 ml of the nitrating mixture prepared from 5 ml of fuming nitric acid (d = 1.5) and 95 ml of acetic acid. The reaction mixture is held for 4 min at room temperature, poured into 500 ml of water, and neutralized with 50 ml of 5% sodium carbonate. The precipitated residue is filtered off, washed on the filter with 100 ml of water, dried in air, and further purified on a chromatography column 3 by 40 cm filled with silica gel; the elution is performed with the 1:1 mixture of ethyl acetate-hexane. The yield of 35 mg (24%) of compound (XXIV) is obtained. Found: C 70.5, H 4.3, and N 10.0%. $C_{40}H_{27}N_5O_2Zn$. Calculated: C 71.2, H 4.0, and N 10.4%.

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PORPHYRINS.

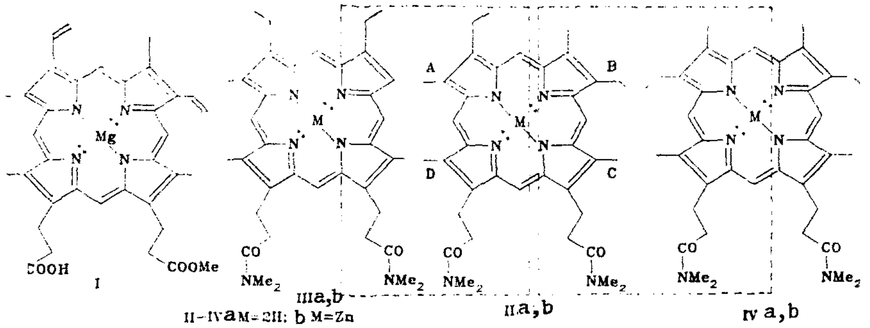
24.* IDENTIFICATION OF ISOMERIC MONOESTERS OF NATURAL PORPHYRINS BY PMR SPECTROSCOPY

G. B. Maravin and G. V. Ponomarev

UDC 547.749:543.422.25

The monomethyl esters of mono(dimethylamides) and the bisdimethylamides of mesoporphyrin-IX, mesoporphyrin-III, and mesoporphyrin-XIII have been obtained, together with their zinc complexes. A relationship has been found between the chemical shifts of the signals for $CONMe_2$ in the PMR spectra and the positions of the substituents in the porphyrin ring, enabling a correct assignment to be made for the first time of these signals to the groups in positions 13^2 and 17^2 of the porphyrin ring, to establish the structures of the isomeric monomethyl esters of mesoporphyrin-IX, and to develop a method of identifying monoesters of natural porphyrins by converting them into the monoesters of the mono(dimethylamides) of mesoporphyrin-IX, followed by examination of their PMR spectra.

The first step in the biosynthesis of chlorophyll is the formation of the monomethyl ester of the magnesium complex of protoporphyrin-IX (I), in which the presence of an esterified propionic acid residue in ring C (position 13) has not been strictly identified, but has been assumed solely by analogy with the structure of chlorophyll [2]. For this reason, the correct identification of the isomeric monomethyl esters of porphyrin (I) is of considerable interest.



The broken lines identify identical fragments of the molecule in derivatives of mesoporphyrin-IX, mesoporphyrin-III, and mesoporphyrin-XIII.

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*For Communication 23, see [1].

Institute of Biophysics, Ministry of Health of the USSR, Moscow 123182. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 780-786, June 1988. Original article submitted November 14, 1986.

0009-3127/88/2406-0637$12.50