# SYNTHESIS OF TETRA(4-SULFONATOPHENYL)PORPHIN DERIVATIVES

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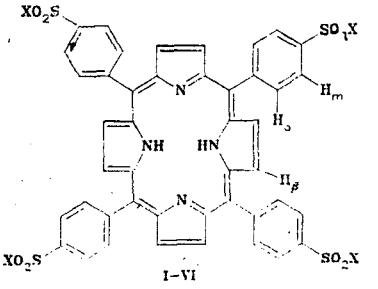
Corresponding sulfonamides were obtained by the action of ammonia and amines on tetra(4-sulfonatophenyl)porphin fluorides and chlorides. Their structure was confirmed by IR, PMR, and electronic spectra.

Despite the comprehensive research on the physicochemical properties of tetraphenylporphin-sulfonic acid, their derivatives (acid halides, amides, etc.) have not as yet been investigated. Sulfonyl halides and sulfonamides of tetraphenylporphin may serve as starting materials for the synthesis of numerous derivatives.

Sulfonated tetraphenylporphins can be obtained firstly by the Rothemund reaction from pyrrole and the corresponding aldehyde $XO_2SC_6H_4CHO$ [1, 2], and secondly, from the available [3] tetra(4-sulfonatophenyl)porphin by converting the $-SO_3H$ groups into $-SO_2Cl$ and further into $-SO_2F$, $-SO_2NR_2$, etc. Direct introduction of the $-SO_2Cl$ and $-SO_2F$ groups into tetraphenylporphin by the action of chloro- or fluorosulfonic acid has not yet been shown. The above two methods have limitations, and therefore the acid fluorides of tetraphenylporphin-sulfonic acids, obtained from formylbenzenesulfonyl fluorides and pyrrole [2] are of interest as key compounds. The strength of the S-F bond determines the stability of the aromatic sulfonyl fluorides to hydrolysis in neutral and acid media, to the action of oxidizing and reducing agents. For tetra(4-fluorosulfonylphenyl)porphin (I), the substitution of fluorine proceeds somewhat more easily than with benzene- and toluenesulfonyl fluorides [4], so that it is easier to convert, for example, to sulfonamides. To obtain amides, we can also use tetra(4-chlorosulfonylphenyl)porphin (II), formed by the action of thionyl chloride on a suspension of an ammonium salt of tetra(4-sulfonatophenyl)porphin in DMFA (in the absence of DMFA, the reaction does not go), in view of its instability to hydrolysis, compound II was rapidly converted into amides III-V. Attempts to convert an unpurified sodium salt of tetra(4-sulfonatophenyl)porphin containing a considerable amount of sodium sulfate into II by the action of $POCl_3$ or thionyl chloride in DMFA were unsuccessful.




I-VI

I X=F, II X=Cl, III X=$NH_2$, IV X=$N(C_2H_5)_2$, V X = morpholyl VI X = $N(C_{18}H_{37})_2$

The structure of the compounds obtained was confirmed by the data of PMR (Table 1) and IR (Table 2) spectroscopy. The PMR spectra of porphyrins I, III, V in trifluoroacetic acid have certain characteristic features, since in acidic solvents the molecules of porphyrins are doubly protonated. While in neutral solutions, the macrocycle is planar, during the formation of a dication it strongly deforms, which causes a weakening of the ring current and a shift of the β-proton signals into a weak field [5]. The signals of benzene ring protons have a doublet structure (SSCC 9-10 Hz) characteristic of para-substituted benzenes.

The electronic absorption spectra of the compounds studied (Table 3) belong to the "etio-type," the band intensities are arranged in the following series: Sorret >> IV > III > II > I.

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TABLE 1. Chemical Shifts, δ (ppm) in PMR Spectra of Porphyrins I, III-VI in Trifluoroacetic Acid

| Compound | $H_\beta$ | $H_o$ | $H_M$ (J, Гц) | $H_N$ |
|---|---|---|---|---|
| $H_2$TPP* | 8,70 | 8,07 | 7,60 | −2,81 |
| $H_2$TPP | 8,45 | 8,17 | 7,64 | −2,38 |
| I | 8,61 | 8,59 | 8,35 (10,5) | −2,53 |
| III | 8,63 | 8,52 | 8,35 (9) | −1,90 |
| IV* | 8,73 | 8,30 | 8,16 (9) | −2,91 |
| V | 8,61 | 8,57 | 8,20 (9) | −1,87 |
| VI* | 8,76 | 8,42 | 8,27 (9) | −2,94 |

*In $CDCl_3$.

TABLE 2. Characteristic Frequencies ($cm^{-1}$) in IR Spectra of Porphyrins I, III-VI

| Compound | $\nu_{as\ S-O}$ | $\nu_{s\ S-O}$ | $\nu_{S-N}$ [$\nu_{S-F}$] | $\delta_{S-O}$ |
|---|---|---|---|---|
| I | 1412 | 1220 | [786] | 613 |
| III | 1350 | 1163 | 733 | 594 |
| IV | 1357 | 1158 | 742 | 597 |
| V | 1355 | 1174 | 750 | 595 |
| VI | 1422 | 1172 | 735 | 609 |

As in other tetraarylporphins with electron-acceptor substituents the positions of the band maxima differ slightly from the spectrum of tetraphenylporphin $H_2$TPP [6].

The sulfonamides of tetraphenylporphin dissolve much better in organic solvents than does compound I. Compound III is soluble in acetone, and VI, even in hexane.

## EXPERIMENTAL

The PMR spectra were run on a Tesla BS-497 spectrometer (100 MHz), using HMDS as an internal standard. Saturated solutions of porphyrins I, III, V in trifluoroacetic acid were used, since the solubility of these compounds in neutral solvents is insufficiently high. The IR spectra were obtained on a IKS-29 spectrophotometer (in mineral oil), and the electronic spectra on a Specord M-40 UV-VIS spectrophotometer. The TLC was carried out on Silufol plates.

Tetra(4-fluorosulfonylphenyl)porphin was obtained according to [2].

Tetra(4-chlorosulfonylphenyl)porphin (II). A 300 mg portion (0.03 mmole) of the ammonium salt of tetra(4-sulfonatophenyl)porphin, dried at 120°C to a constant weight, is suspended in 50 ml of dry DMFA, and 3 ml (40 mmoles) of thionyl chloride are added. The mixture is stirred for 3 h at 50°C, and poured into 100 g of ice. The precipitate of porphyrin II is filtered, washed with 20 ml of ice water and immediately used for the preparation of the amides.

Tetra(4-sulfamoyl)porphin (III). A freshly prepared II (0.2 g) is boiled for 10 min with 5 ml of 25% of aqueous ammonia. The mixture is diluted with water to 100 ml, the precipitate is filtered, washed with 50 ml of water, dried at 100°C, and dissolved in 30 ml of acetone. The solution is filtered, concentrated to 5 ml and 15 ml of ethanol are added. The precipitate obtained is filtered, and dried at 80°C. The yield of III is 74 mg (40%).

Tetra[4-N,N-diethylsulfamoyl)phenyl]porphin (IV). A precipitate of II, obtained from 0.3 g of an ammonium salt of tetra(4-sulfonatophenyl)porphin, is boiled for 10 min with 5 ml of diethylamine. The mixture is diluted with 100 ml of water, the precipitate formed is filtered, washed with water, dried and dissolved in 30 ml of chloroform. The chloroform solution is chromatographed on L100/250 silica gel with elution by a 10:1 chloroform–methanol mixture. The eluate is concentrated to 15 ml, and compound IV is precipitated by adding 60 ml of methanol. $R_f$ 0.48 (methanol–chloroform, 1:20). Yield, 0.154 g (45%).

Tetra(4-morpholinosulfonylphenyl)porphin (V). A). A mixture of 400 mg (0.424 mmole) of tetra(4-fluorosulfonylphenyl)porphin in 50 ml of morpholine is stirred for 4 h at 120-130°C. Morpholine is distilled off in vacuo, the residue is washed with 100 ml of water, dried, and chromatographed as in the case of IV. The yield of V is 0.385 g (75%). $R_f$ 0.42 (methanol–chloroform, 1:10).

B) The precipitate of II obtained from 0.3 g of the ammonium salt of tetra(4-sulfonatophenyl)porphin is boiled for 10 min with 5 ml of morpholine. The mixture is diluted with water to 50 ml and centrifuged. The precipitate is separated, washed with water, dried, and chromatographed as in the case of IV. The yield of V is 0.147 g (41%).

Tetra[4-(N,N-bisoctadecylsulfamoyl)phenyl]porphin (VI). A mixture of 100 mg (0.106 mmole) of bis(octadecylamine and 20 ml of pyridine is boiled for 48 h. When cool, the mixture

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

| Compound | Electronic absorption spectra, $\lambda_{max}$, 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


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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.


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