

Porphyrin System Containing  
[2.2]Paracyclophane Units

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*Meso*-tetrakis([2.2]paracyclophanyl)porphyrin was obtained from [2.2]paracyclophanecarbaldehyde and pyrrole. Replacement of phenyl groups in *meso*-tetraphenylporphyrin by paracyclophanyl substituents remarkably influences the electronic structure of the molecule, causing bathochromic shifts of all uv-vis absorption bands, and changing the ring current of the porphyrin core. The shifts in the electron spectrum are substantially greater than those observed for other porphyrin derivatives characterized by their extended  $\pi$ -electron systems, such as *meso*-tetrakis(2-phenylethenyl)porphyrin and *meso*-tetrakisbiphenylporphyrin.

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Great interest in the chemistry of cyclophanes and porphyrins has been demonstrated in many papers. Some of them deal with so called cyclophane porphyrins [1,2], where the porphyrin ring represents one of the stacked structural units of the bi- or tri-layered molecule. Yet, no compounds are known containing the structural units of a cyclophane, like for example that of [2.2]paracyclophane joined to the porphyrin ring. In these compounds a substantial alteration of the  $\pi$ -electron system of both components, the porphyrin core and the attached paracyclophane units, could be expected with all the consequences regarding the properties of the cyclophanylporphyrins and their metallated derivatives.

We report the synthesis of *meso*-tetrakis([2.2]paracyclophanyl)porphyrin, **1**, from (**R** + **S**)-paracyclophanecarbaldehyde and pyrrole. The reaction conditions were similar to those applied by Adler *et al.* [3] in obtaining *meso*-tetraphenylporphyrin, **2**. This proved that the double-layered structure of paracyclophanecarbaldehyde and its properties, different from other arylcarbaldehydes, were not an obstacle to the formation of *meso*-tetraparacyclophanylporphyrin. Tlc proved to be a valuable method for separation of polymeric by-products as well as for purification of the cyclophanylporphyrin **1**. Although the formation of well separated bands was confusing at first, some of them proved to be atropoisomers of **1** because of the same  $M^+$   $m/e$  values. In fact, two atropoisomers,  $M^+ = 1134$  (ms-fab), were found of  $R_F$  0.68-0.65 and 0.32-0.29. Only the first one was obtained in an amount allowing the thorough investigation described below. The X-ray diffraction investigation will be undertaken by us after obtaining the enantiomeric [2.2]paracyclophanecarbaldehyde. This would facilitate the study of the atropoisomers of the product **1** and elucidation of their three-dimensional structure.

The  $^1\text{H}$ -nmr (300 MHz) spectrum of the atropoisomer under investigation shows that the NH protons are less shielded (by *ca.* 0.8 ppm) than the NH protons of *meso*-te-

traphenylporphyrin **2**; in addition to that, they appear as two singlets at room temperature. This proves that a substantial decrease of the ring current in the porphyrin ring in **1** is due to the influence of the paracyclophane units and to perturbation of the tautomeric exchange [4], both phenomena requiring further investigation. The steric reasons connected with the existence of two layers in each paracyclophenyl substituent, with only one of the layers joined directly to the porphyrin (and non-coplanar to the latter), contributes to the non-equivalency of  $\beta$  H-atoms of the adjacent pyrrole rings in **1**, contrary to **2**. It is also characteristic that the  $\beta$  proton which is most deshielded appears at a field distinctly lower than the  $\beta$  protons in **2**. The multiplet signals of the aromatic protons of paracyclophanyl substituents range from  $\delta$  7.15 ppm to 6.22 ppm while the signal for the molecule of [2.2]paracyclophane appears at  $\delta$  6.37 ppm. This fact points to a deshielding influence of the heteroaromatic porphyrin core on the attached paracyclophane units. Also, the ring current of the porphyrin core causes substantial differentiation of signals of the aliphatic protons in paracyclophane bridges.

Replacement of phenyl rings in tetraphenylporphyrin **2** by the paracyclophanyl units strongly influences the uv-vis spectrum of **1**. All bands, including the Soret band, become bathochromatically shifted with regard to **2** on an average of about 20 nm. In order to gather more experimental data for theoretical treatment of this phenomenon [5], two other *meso*-tetrasubstituted porphyrins were prepared and examined, see Table 1 and Figure 1. They were *meso*-tetrakisbiphenylporphyrin **3**, and *meso*-tetrakis(2-phenylethenyl)porphyrin **4**. Compound **3** is a substance that formally contains the same number of benzene rings as **1**, whereas compound **4** represents a more extended  $\pi$ -electron conjugation than **2**. The spectra of both show bathochromic shifts much more limited than in **1**, and only a little larger than in **2** (the spectrum of the latter serving as a reference). The attachment of 2,5-dimethylphenyl substituents, representing the formal "halves" of the 2.2 pa-

racyclophane, compound **5**, practically does not alter the spectrum of **2**.

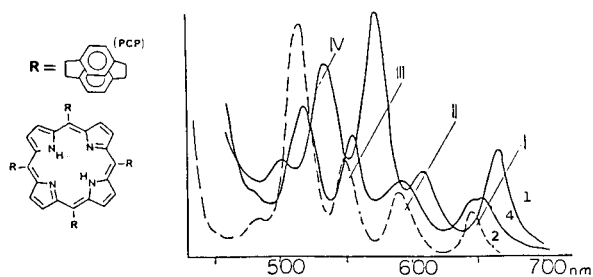


Figure 1. Visible region of the spectra of meso-tetrakis(2.2/paracyclophanyl)porphyrin **1**, meso-tetraphenylporphyrin **2** and meso-tetrakis(2-phenyl-ethenyl)porphyrin **4**.

Table I

The Bathochromic Shifts, in nm, of the Bands in the UV-VIS Spectra (in  $C_2H_4Cl_2$ ) of meso-Tetrasubstituted Porphyrins with the Bands in the Spectrum of meso-Tetraphenylporphyrin, **2**, as the Reference

Meso-Substituted Porphyrin (see Figure 1)	Reference Bands [a] and Shifts, in nm				
	I	II	III	IV	Soret band
<b>1</b> R = [2.2]paracyclophane	21	16	25	21	20
<b>2</b> R = Ph (reference)	0	0	0	0	0
<b>3</b> R = $-C_6H_4-C_6H_5$	6	3	5	3	1
<b>4</b> R = $-CH=CH-Ph$	4	3	6	3	0
<b>5</b> R = 2,5-diMeC <sub>6</sub> H <sub>3</sub>	1	1	-3	0	0

[a] I 645 nm, II 589 nm, III 549 nm, IV 514 nm, Soret band 417 nm (compound **2**).

Because of the obvious change in the electronic structure of **1** when compared to **2**, it was not surprising that the longest wavelength bands in the electronic spectra of the metallated meso-tetracyclophanylporphyrins were energetically lower than in metallated meso-tetraphenylporphyrins. For instance, for the metallation with Mn(III), the respective values are 689 vs 618 nm, for Fe(III) 719 vs 692 nm (the compounds in the form of M(III)Cl porphyrins).

The preliminary spectro-electrochemical investigation [6] demonstrated that [2.2]paracyclophanyl substituents essentially alter other properties of **1** and metallated **1**. They lower the oxidation potential, a property needed for a porphyrin system to act as a sensitizer [7]. Also, changes in the ability of base ligation, dioxygen binding and catalytic properties should be expected when they are compared to

many derivatives of meso-tetraphenylporphyrins and to other porphyrin systems. The corresponding research is in progress [5].

## EXPERIMENTAL

The mixture of paracyclophane-carbaldehyde [8] (4 mmoles), pyrrole (4 mmoles), and 30 ml of propionic acid was refluxed for 6 hours. Propionic acid was evaporated under vacuum. The residue was dissolved in 150 ml of methylene chloride and refluxed with 8 g of silica gel for 5 minutes. After filtration, the concentrated solution was chromatographed on Merck preparative plates (1.5 mm) with ethylene chloride as eluent. The uppermost fraction,  $R_f$  0.68 to 0.65, was collected, yield 7%.

Anal. Calcd. for  $C_{84}H_{70}N_4$ : C, 88.9; H, 6.2; N, 4.9. Found: C, 89.1; H, 6.1; N, 4.9.

The positive ion fast-atom-bombardment (6 KeV argon) mass spectrum showed the expected P + 1 pseudo-parent ion  $m/e$  1135; *m*-nitrobenzyl alcohol was used as a solvent. The uv-vis spectrum in ethylene chloride showed the bands at 666, 605, 574, 535 nm and the Soret band at 437 nm, see Figure 1. The ir spectrum (potassium bromide medium-weak and weak bands omitted): 3440 vs, 3033, 3010, 2950, 2924 vs, 2851, 1623, 1600, 1587, 1555, 1500, 1458, 1435, 1409, 1342, 1224, 1154, 1089, 1011, 980, 956, 923, 898, 877, 800 vs, 722 s, 634, 597 and 464  $cm^{-1}$ . The  $^1H$ -nmr spectrum at 300 MHz was not well resolved and not easily assignable in the range  $\delta$  9 to 8 ppm. In deuteriochloroform (TMS) it showed  $\beta H$  of the pyrrole units  $\delta$  10.42 br s, 9.90 br s; signals  $\delta$  8.77 br s and 8.4-8.15 m; aromatic protons of the paracyclophane units  $\delta$  7.15-6.60 m 6.43-6.22 m; aliphatic protons of ethane bridges  $\delta$  3.60 m, 3.40 m, 3.08 m, 2.87 m; NH protons  $\delta$  -1.93 and -2.29 ppm.

The meso-substituted porphyrins **3** and **4** were obtained in essentially the same manner as **1**; for **3**,  $R_f$  0.68-0.59 (methylene chloride as eluent), yield below 1%; for **4**,  $R_f$  0.98 (after shaking with sodium bicarbonate, ethylene chloride as eluent), yield below 1%.

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