Meso-[2.2]paracyclophanyltriphenylporphyrin: A Simple Representative of Cyclophanylporphyrins

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(*R* + *S*)*Meso*-[2.2]Paracyclophanyltriphenylporphyrin **3**, a member of a novel class of cyclophanylporphyrins, was obtained and characterized by spectroscopic and electrochemical methods. Compared to *meso*-tetra[2.2]paracyclophanylporphyrin **1**, it represents a simplified structure designed for the investigation of electronic interactions between the [2.2]paracyclophane moiety and porphyrin core and for use in metallation reactions.

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Meso-tetra[2.2]paracyclophanylporphyrin **1** obtained recently in our laboratory [1] differs significantly from *meso*-tetraphenylporphyrin **2** in that paracyclophanyl substituents take the place of the phenyl rings. This representative of a novel class of cyclophanylporphyrins shows marked alteration of the electronic structure of the porphyrin core [2,3] because of the electron-donating character of [2.2]paracyclophane [3,4]. However, the hindered rotation about four direct bonds between the paracyclophanyl units (at C4 or C5 atom centers) and the *meso*-carbon atom centers of porphine makes possible as many as 39 stereoisomers, some of them representing enantiomeric pairs, others the *meso*- forms [3]. Because of this complicated situation the need became apparent for a [2.2]paracyclophanylporphyrin containing only one paracyclophanyl unit, PCP. This would simplify the evaluation of electronic effects resulting from linking [2.2]paracyclophane to porphine and could represent an interesting model for many mimetic- and catalytic-type studies.

With this realization, the preparation of (*R* + *S*)*meso*-[2.2]paracyclophanyltriphenylporphyrin **3** was undertaken. We report here the reaction conditions and the separation procedure of this compound. We also present the results of spectroscopic and cyclovoltammetric studies of **3**, as well as the calculated π-electron density values on the atom centers of its porphyrin core. Comparison of the experimental and theoretical data with those previously obtained for **1** [1,2,3] and for **2** helps to evaluate the particular role of [2.2]paracyclophane as a *meso*-substituent of porphine. The isolated (*R* + *S*) **3** does not form crystals suitable for X-ray examination. It was necessary, therefore, to take advantage of the results of geometry optimization [4], see Figure 1, in order to deal with the experimental spectral data and reach the π-electron density distribution values.

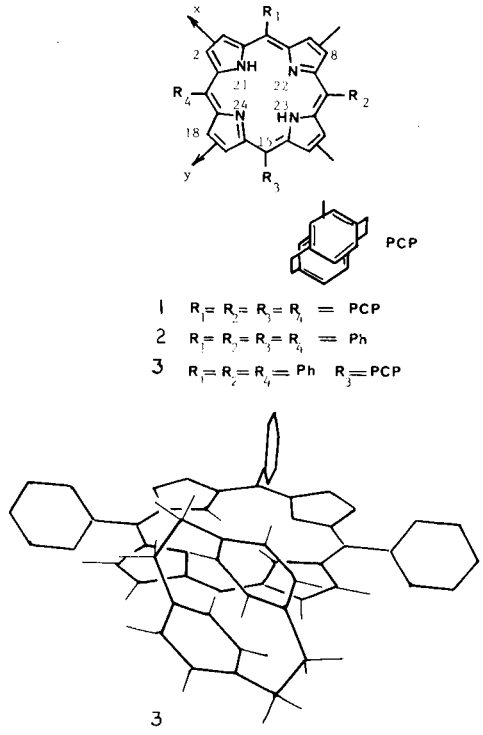

Figure 1. *Meso*-[2.2]paracyclophanyltriphenylporphyrin **3** under investigation and other *meso*-substituted porphyrins considered: *meso*-tetra-[2.2]paracyclophenylporphyrin **1** and *meso*-tetraphenylporphyrin **2**. The location of the PCP substituent in **3** corresponds to the three-dimensional presentation shown above. Atoms to which the calculated π-electron density values refer are shown by the numbers.

Cyclophaneporphyrin **3** was obtained by mixed condensation of pyrrole with benzaldehyde and [2.2]paracyclophane-4-carbaldehyde according to the general procedure of Adler and Longo [5]. We found previously that the newer approach to synthesis of *meso*-substituted porphyrins proposed by Lindsey *et al.* [6] was also of great value

in the preparation of **1** [2]. It furnished the final product with higher yield and the purification procedures were easier than in [5]. In the synthesis of **3** attention had to be paid, however, to the separational procedure, and every additional component of the final reaction was disadvantageous. The Lindsey method was, therefore, less suitable as it used a quinone, not air (as in [5]), for the oxidant of the intermediate porphyrinogen. It was characteristic that the condensation of [2.2]paracyclophane-4-carbaldehyde with pyrrole according to the first method, when carried out at a much lower concentration than described in [5], resulted in significantly higher yield of **1** [2]. As the dependence of concentration on the yield had not yet been investigated for this procedure, we had to establish the influence of the concentration of benzaldehyde and paracyclophane aldehyde (applied in the synthesis of **3**), when used separately, on the yield of the respective products, **2** and **1**. The results were promising as seen from the point of view of the attempted cross-condensation; there was no notable difference in porphyrin yield although [2.2]paracyclophane-4-carbaldehyde represented pronounced steric hindrance as well as unknown reactivity. Comparison of the electrophilicity of the carbonyl group in both aldehydes based on theoretical calculations [2] and the evaluation of the steric hindrance factor suggested, accordingly, a small difference in reactivity of these aldehydes. The general conclusion was, therefore, that benzaldehyde and paracyclophane aldehyde should be applied in a 3:1 ratio when the reaction is aimed at the maximum yield of **3**.

The main difficulty was still the isolation of only one component from the reaction mixture, where the presence of six products of closely related structure and similar properties was a prior existing reality. Accompanying polymeric materials, always present in the reaction mixture, caused well-known difficulties when porphyrin did not crystallize from the propionic acid medium. Because of all that, column chromatography was used in the first step of purification of the crude material obtained from cross-condensation. Well-balanced elution power of methylene chloride altered by pentane and ethyl acetate admixtures in precisely established proportions resulted in the separation of all low-molecular-weight components in the forerun, as well as in removal of most of the highly polymerized by-products left on the Florisil bed. The final result at this stage of purification was material which contained only porphyrins.

Separation of **3** from the mixture of five accompanying porphyrins was additionally complicated by the atropoisomerism of **1**. This phenomenon, known to us because of previous investigations [2,3], resulted in the formation of numerous isomeric species differentiated by their polarity. There was well-grounded anticipation that the two- and three-substituted [2.2]paracyclophanyl porphyrins would also exist in a number of atropoisomeric individuals. This made it necessary to apply preparative tlc as the only possible way to tackle this task. The developing phase applied had to have not only good resolving properties but also had to give reproducible results. Although many two- and three-component developing mixtures appeared to have sufficient resolving properties, the reproducibility was poor and the results were often changeable. The scanning of a great number of halogenated hydrocarbons chosen from a wide variety of aliphatic and aromatic series had shown their valuable properties as developing solvents in tlc of porphyrins. The only disadvantage among some members of this class of compounds was instability against moisture, resulting in the generation of acidic products of hydrolysis. As the R_f values are greatly influenced by *p*H, all precautions had to be taken to avoid the risk. Polyhalogenated species containing two geminal halogen atoms (or even three), like dichloromethylene or chloroform, were particularly disadvantageous. In other cases, *e.g.*, when 1-bromobutane or fluorobenzene was used, this difficulty was nonexistent. As an analytical tool quick and precise enough for identification of the required component located on the tlc plate, the spectrophotometric approach proved to be useful and of the necessary accuracy also for determining the purity grade of any isolated material. The general idea was based on the previously found [2] linear character of bathochromic shifts and hypochromic effects caused by each [2.2]paracyclophanyl substituent replacing the phenyl group in every *meso*-position in the porphyrin macrocycle. This gave rise to the analytical procedure based on the measurement of absorption at 419 nm, representing λ max for **2**, and 429 nm, corresponding to λ max calculated for *meso*-di[2.2]paracyclophanyldiphenylporphyrin. The symmetrical shapes of Soret bands for **2** and **1** within the 10 nm region approximate the maximum absorption wavelength value gave reasonable support for acceptance of the values of the first derivative on the absorption curve as a measure of the purity grade, see Figure 2. Some preliminary experiments proved the applicability of this approach, as well as its advantage in isolation and further purification. It was also shown that the absorption measurements at the wavelengths, 419 nm, 424 nm and 429 nm, and the calculated differential quotients, A_{424}/A_{419} and A_{424}/A_{429}, furnished precise evaluation of the amount of contaminating admixtures of **2** and *meso*-di[2.2]paracyclophanyldiphenylporphyrin the two components characterized by similar properties. The strategy applied to the separation of the products of this particular cross-condensation could be used in other cases of porphyrin syntheses. This presented analytical approach for monitoring the process of purification might be useful as well.

The electronic absorption spectrum of **3** shows in the visible region the characteristic porphyrin pattern of four

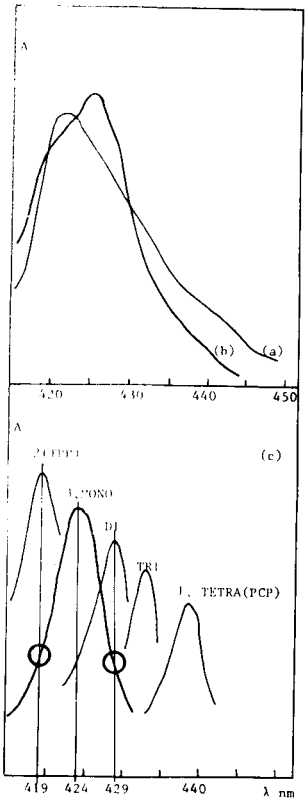

Figure 2. The Soret band region in: (a) the crude product of cross-condensation of pyrrole with benzaldehyde and *meso*-[2.2]paracyclophane-4-carbaldehyde; (b) partially purified *meso*-[2.2]paracyclophanyltriphenylporphyrin **3**; (c) the spectra of pure *meso*-tetraphenylporphyrin and the porphyrins in which the phenyl rings were replaced by one, two, three and four [2.2]paracyclophane units. The values of first derivatives were taken for **3** at the points shown by the circles.

bands in addition to the Soret band absorption, see Figure 3. When compared to **2**, rather small differences in band intensities appear that make both spectra very similar and resemble the *etio*-type spectra of non-*meso*-substituted porphyrin derivatives [7]. They differ markedly from the pattern of the **1** spectrum, mainly due to the reverse ratio of intensities of the III and IV bands that marks the spectrum of the latter paracyclophanylporphyrin more like the *rhodo*-type spectrum (see Experimental; for theoretical explanation see [4]). All bands in the spectrum of **3** are bathochromatically shifted as compared to **2**, with the shifts of the respective I-IV bands amounting to 7 nm, 7 nm, 6 nm, 5 nm and the shift of the Soret band 7 nm (in benzene). These shifts are on the average one-third smaller than the shifts in **1** *vs.* **2**. Comparison of the cyclophanylporphyrin **3** spectrum with the spectra of *meso*-tetrakisbiphenylporphyrin and *meso*-tetrakis(2-phenylethenyl)porphyrin [1] shows that the shifts of bands I-IV are greater in **3** by 2-3 nm. However, a marked difference is observed in the Soret band. This band in the latter two porphyrins, representing different degrees of π-electron interaction of the *meso*-substituents with porphine, shows the same transition energy as **2**, but differs (by 7 nm) from that of the Soret band in **3**. Characteristically the Soret band in **3** is broader at its half-width by 15% as compared to **2**, which we attributed [4] to the split of the short wavelength A → B transition. The latter is due to the unique electronic structure of [2.2]paracyclophane [8] which replaced one of four phenyls in **2**.

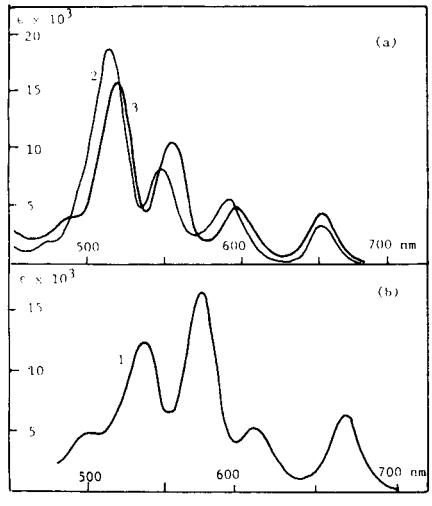

Figure 3. Characteristic shape of the visible absorption spectra of: (a) *meso*-tetraphenylporphyrin **2** and *meso*-[2.2]paracyclophanyltriphenylporphyrin **3**; (b) *meso*-tetra[2.2]paracyclophanylporphyrin **1**.

The ^{1}H nmr (300 MHz) spectrum of **3**, Figure 4, reveals the mutual influence of the [2.2]paracyclophane and porphyrin constituents. Eight β-pyrrole protons lose their magnetic equivalence typical for **2**. The attachment of the two-deck PCP substituent at an angle of *ca.* 38° [4] *versus* the porphyrin macrocycle of the only energetically stable conformer substantially alters the location of the zero shielding surface and exposes one β-proton in particular to exceptionally strong deshielding at 10.15 ppm. Also a second proton at 9.16 ppm is located in the (−) shielding zone, while the remaining ones appear approximately in the same region as the β-protons of **2**. The shielding effect, characteristic for aromatic protons of [2.2]paracyclophane molecules alone (6.37 ppm), for which the stacking of two benzene rings is responsible, becomes at least partially compensated by the deshielding influence of the ring current in the attached porphyrin core. In particular, two protons appear at a much lower field, at 7.23 ppm and 7.01 ppm, while the remaining five protons give reasonably well-resolved signals in the 6.9-6.6 ppm range. The shielding and deshielding zones of the porphyrin core substantially alter the chemical shift values of the methylene groups in the PCP bridges. Instead of the eight equivalent protons at 3.05 ppm typical for [2.2]paracyclophane, two pairs of protons experience stronger deshielding (3.62

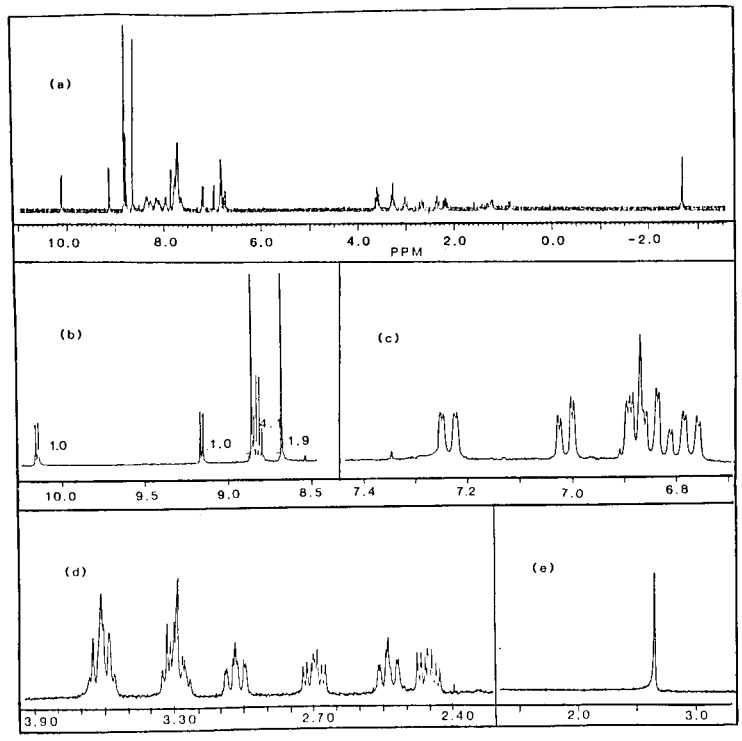

Figure 4. The ^{1}H nmr spectrum (300 MHz) of *meso*-[2.2]paracyclophanyltriphenylporphyrin **3**: (a) the whole range; (b) the range of β-pyrrole protons; (c) the range of aromatic protons of [2.2]paracyclophane substituents; (d) the range of aliphatic protons in ethane bridges of these substituents; (e) NH protons.

ppm, 3.20 ppm) and three pairs show stronger shielding. The latter is particularly obvious for the protons appearing at 2.21 ppm, and the former for the protons in bridges located more apart from the porphyrin core. In fact, the distance between the strongest deshielded aliphatic PCP protons and the porphyrin core in **3** is comparable to the distance between the porphyrin core and the aromatic *para* protons of the phenyl substituents in **2**; both types of protons show downfield shifts of *ca.* 0.5 ppm, although in different ranges at the ppm values. The signals from 15 protons of the three phenyl rings in **3** prove that each of them experiences a different influence of the PCP substituent. The phenyl ring adjacent to PCP, toward which the vertical axis of the double-deck PCP substituent is tilted upward, see Figure 1, contains protons more deshielded (when compared to **2**) than those belonging to the second adjacent phenyl ring located in the position opposite to PCP. As a result of this, the signal from the *ortho* protons in **2**, which is a singlet at 8.30 ppm, appears in **3** as a set of irregular multiplets in the range of 8.40-8.20 ppm; the signal from the *meta* and *para* protons of **2**, which is a singlet at 7.80 ppm, appears in the form of irregular multiplets at 8.0, 7.9 and 7.8 ppm. Finally, at room temperature, two central NH protons appear as a small broadened singlet at −2.64 ppm (*vs.* −2.72 ppm in **2**) which proves that only a slight weakening of the strong shielding characteristic for protons located inside the porphyrin core takes place.

In a qualitative evaluation of some of the observed phenomena we took advntage of the "network approach" of Abraham [9] in which the porphyrin ring is broken down into a number of current loops (four pyrrole rings and four, formally distinguished, inner hexagons with the equivalent dipoles placed at the center of each loop). This double-dipole approximation resulted in good agreement of the observed and calculated chemical shifts for the protons of the β-methyl groups [9] and also predicted a low-field shift of the NH protons at the center of the porphyrin core. Also this approach made it possible to take into account the distribution of charge because the observed protonation shifts for *meso*- and β-protons appeared to be more related to π-electron density at these positions than to the ratios of the ring current shifts at the respective protons.

In the case of **3** the high symmetry of the **2** system and of many systems investigated in [9] disappeared as a result of the displacement of one phenyl by a PCP unit. The nonperpendicular location of benzene layers in PCP *versus* the porphyrin core plane, contrary to **2**, increased the electronic interaction between PCP and porphine [4] and al-

tered the π-electron density at the positions of the β-pyrrole carbon atoms. For **2** and **1** the calculations [10] point to nearly identical density values at two β-positions for each pair of oppositely situated pyrrole rings: $q^{\pi} = 1.024$ and 1.018 *vs.* $q^{\pi} = 1.026$ and 1.019, respectively. Contrary to that in **3** all centers become differentiated. The greatest, $q^{\pi} = 1.042$, is reached at the C(18) center located in one of the rings adjacent to PCP, see Figure 1. The second and third high values, 1.030 and 1.028, respectively, appear at the C(2) and C(8) centers located symmetrically in the pyrrole rings non-adjacent to PCP; these two positions were also favored by MINDO/3 [10]. All other centers show much lower π-electron densities, on the average of 0.04 lower, while for **2** the difference between the values appearing was an order of magnitude smaller than for **3**. This alteration of π-electron density, much greater for **3** than **2**, might be connected with the greater downfield shifts of two β-pyrrole protons in the nmr spectrum of **3** compared to **2**, as well as the broadened range in which the signals of the β-protons appear in **3**. The decrease in shielding of NH protons in **2** as the result of displacement of one phenyl by the PCP unit ($\delta = -2.72 \rightarrow -2.64$ ppm) becomes enhanced as the result of displacement of all phenyls by the PCP units [1,2] ($\delta = -2.64 \rightarrow 2.04$ ppm). However, even when the place of one phenyl in **2** is taken by the PCP unit, the distribution of the π-electron density (CNDO/2) is altered on the nitrogen centers in the porphyrin core of **3**, and this in turn influences the current loop (dipoles) connected in the "network approach" to the ring current. In **2** the value of q^{π} N(22), N(24) = 1.262 e and is lower by 0.389 than the density on the density on the N(H) centers N(21), N(23). However, in **3** the q^{π} values on N(24) located in the pyrrole ring adjacent to the PCP unit and the more distant N(22) center become strongly differentiated: q^{π} N(24) = 1.282, q^{π} N(22) = 1.247. The q^{π} values on the N(H) centers in both **3** and **2** are practically the same: for **3** q^{π} N(23) = 1.649 and q^{π} N(21) = 1.646; for **2** q^{π} N(21), N(23) = 1.648.

The cyclovoltammograms of **3** in 1,2-dichloroethane reveal consecutive reduction steps to anion radical $\mathbf{3}^{\cdot -}$ and dianion $\mathbf{3}^{2-}$, with these two one-electron additions occurring at half-wave potentials of -1.24 and -1.53 V *vs.* SCE. For the electrode oxidation three oxidation waves appear, the first one at $E_{1/2} = 0.95$ V. This potential is lower than that of **2**, 1.05 V, and of most derivatives of **2** substituted in the phenyl rings [11], which proves that the [2.2]paracyclophanyl substituent facilitates oxidation. This fact is even more convincingly demonstrated by the first oxidation potential of **1** as low as 0.55 V [12]. The loss of two electrons corresponding to subsequent generation of cation radical and dication, $\mathbf{3} \rightarrow \mathbf{3}^{\cdot +} \rightarrow \mathbf{3}^{2+}$, would agree with the commonly accepted mechanism of oxidation of porphyrins [13]. However, none of the investigated porphyrins represented the paracyclophanylporphyrin system like the **3**. Therefore, in attributing the third oxidation wave it is necessary to consider the role of the [2.2]paracyclophane unit in electron detachment.

Cyclophane systems are not easily oxidized electrochemically [14], even though the formation of cation radicals and their dimers from 4,5,7,8-tetramethyl[2.2]-paracyclophane is known in the electrolytic oxidation at low temperature [15]. We found that [2.2]paracyclophane could be oxidized irreversibly in 1,2-dichloroethane at a potential of about 1.60 V, *i.e.*, at a potential of *ca.* 0.20 V higher than the third oxidation wave of **3**. The possible detachment of the third electron from the PCP unit of **3** would result in creating in it the cation radical $PCP^{\cdot +}$ with the possibility of subsequent dimerization. In fact, the electrode oxidation of **3** resulted in the formation of a conductive polymeric film. Its nature suggests, though, that polymerization rather than dimerization took place. The nature of this phenomenon requires further investigation. At present a working hypothesis seems reasonable in which a quinonoid system of bonds is formed in a fragment of the molecule of **3** in which the PCP is included. This happens as a result of the detachment of two protons and two electrons, the latter compensating the electron deficiency of the $\mathbf{3}^{2+}$ dication. The benzoquinonyl structural fragment of bonds formed in the PCP unit (from which the second benzene ring not connected directly with porphine could possibly be detached) would have the ability to form the polymeric paracyclophanoquinonyl-porphyrin or xylylenyl-porphyrin. This assumption can be sustained in view of the results of Bruchin *et al.* [15] who demonstrated by ms the tendency of the cation radical of 4,5,7,8-tetra-methylparacyclophane to form the species of *p*-xylylene, easily undergoing polymerization.

EXPERIMENTAL

Spectroscopic and Electrochemical Methods.

Electronic spectra were recorded on a Perkin-Elmer Lambda 4c uv-vis spectrophotometer, model C688-0002; ^{1}H nmr spectra were recorded on a Bruker-IBM AF (300 MHz) Fourier transform spectrometer. Mass spectrometry was performed on a fast atom bombardment model V6 Micromass 70/70 mass spectrometer with an 11/250 data system. Cyclic voltammetric and differential-pulse voltammetric measurements were made with an IBM EC 225 voltammetric analyzer.

Chemicals and Materials.

[2.2]Paracyclophane, dichloromethyl methyl ether and propionic acid puriss. p.a. were used as obtained from Fluka. Benzaldehyde and pyrrole (Aldrich) were distilled before use. Methylene chloride, 1,2-dichloroethane, chloroform, petroleum ether and ethyl acetate (EM Science) were used as received. 1-Bromobutane 99% (Aldrich) was washed with saturated sodium hydrogen carbonate solution, dried over anhydrous potassium carbonate and freshly distilled before use for chromatography. Thin-layer chromatography: for monitoring purposes DC-Fertigplatten Kiesel-gel $60F_{254}$ plates of 0.25-mm layer thickness were used. Preparative separations were performed on PSC-Fertigplatten Kiesel-gel 60 (Merck) plates without fluorescent indicator, 2.0-mm layer

thickness. Column chromatography was performed on silica-gel Type 6 (Merck) and Florisil (Applied Sciences) 60/200 mesh.

1,2-Dichloroethane for electrochemical use was purchased from Fisher Scientific Company as hplc grade, and spectroscopic grade *N,N*-dimethylformamide was purchased from Aldrich. The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), obtained from Eastman was twice recrystallized from ethanol, dried and stored *in vacuo* at 40°. Aqueous 25% tetramethylammonium hydroxide, TEAH, solution was obtained from Eastman and used as received.

Syntheses.

(a) [2.2]Paracyclophane-4-carbaldehyde.

[2.2]Paracyclophane-4-carbaldehyde was prepared according to [16]. For the crude product of mp 134-139° at least four spots of by-products, R_f = 0.13, 0.33, 0.45 and 0.53 (1-bromobutane), were seen on tlc as well as unreacted starting material, R_f = 0.78. The crude product was recrystallized from *n*-butanol and from acetic acid to give chromatographically pure aldehyde (R_f = 0.29, bromobutane as developer), mp 142-145°.

(b) Cross-condensation of Pyrrole, Benzaldehyde and [2.2]Paracyclophane-4-carbaldehyde.

Paracyclophane aldehyde (2.36 g, 10 mmoles) and benzaldehyde (3.2 ml, 30 mmoles) were dissolved in 350 ml of propionic acid. The solution was heated under reflux in a 1-l round-bottom flask equipped with a magnetic stirrer, and 2.8 ml pyrrole (40 mmoles) in 50 ml propionic acid was added in one portion. The reaction mixture turned instantly dark and was refluxed and mixed for better aeration for 1 hour. The propionic acid was distilled off *in vacuo*. Triethylamine (1 ml) was then added and the resultant solid black material washed twice with 50 ml portions of absolute ethanol. The dry product was dissolved in a 1,2-dichloroethane/chloroform mixture (1:1), and 40 g of silica-gel was added. The suspension was warmed (50°) and mixed for 30 minutes and then evaporated to dryness. The resultant black powder was put on top of a chromatographic column packed with 200 g of silca-gel and then washed with dichloroethane/petroleum ether (1:1) to remove the low-molecular-weight, fast-moving impurities. The porphyrin fraction was eluted with dichloromethane/ethyl acetate (9:1). After rotary evaporation 2.7 g of partially purified material was obtained, yield 36%.

(c) Separation and Purification of *Meso*-[2.2]paracyclophanyltriphenylporphyrin (**3**).

Partially purified product (0.27 g) from cross-condensation was dissolved in 80 ml of 1,2-dichloroethane, and 30 g of Florisil was added. The slurry was dried by rotary evaporation and placed on top of a chromatographic column packed with 120 g Florisil. The column was washed with dichloromethane and 500 ml of eluent containing a small amount of uncharacterized yellow oily material was discharged. The bright green porphyrin fraction moved very slowly. The fractional separation of this material was then performed using dichloromethane/ethyl acetate (100:1) mixture. Ten fractions of 100 ml each were collected and evaporated *in vacuo*. Each fraction was analyzed by tlc with 1-bromobutane as developer. Well-separated spots of R_f = 0.68 and 0.57 were identified spectrophotometrically in the Soret band region as corresponding to **2** and **3**, respectively. The fractions which were reasonably rich in the component with R_f = 0.57 (usually fractions II to VII) were taken to preparative tlc purification.

(d) Purification of *Meso*-[2.2]paracyclophanyltrophenylporphyrin (**3**).

Preliminary enriched material (50 mg) obtained from column chromatography was put on a preparative plate, 20 x 20 cm, and developed in 1-bromobutane. The band, usually well separated, of R_f between 0.55 and 0.60 was removed from the plate and the silica-gel extracted with chloroform. The solution was centrifuged and evaporated *in vacuo*. A small portion was dissolved in benzene and the absorption was measured at 419 nm, 424 nm and 429 nm. The values of $A_{424}/A_{419} < 1.50$ and $A_{424}/A_{429} < 1.55$ indicated the need for further purification. The purification was repeated until the above two ratios were reached.

The overall yield of purple, metallic material was 0.012 g, *i.e.*, 4.4% calculated on partially purified product and 1.6% of the starting pyrrole.

Fast atom bombardment ms showed the presence of the parent ion, M^+ = 745 m/e and no presence of m/e peaks at 875 and 614 which would correspond, respectively, to *meso*-di[2.2]paracyclophanyldiphenylporphyrin and *meso*-tetraphenylporphyrin **2**. All of these appeared in the ms spectrum of the crude product; ^{1}H nmr: 300 MHz spectrum showed the presence of β-pyrrole protons, 10.14 (d, 1 H), 9.15 (d, 1 H), 8.82 (m, 4 H), 8.62 (s, 2 H), phenyl protons, 8.39, 8.31, 8.20, 8.13 (all m, 6 *ortho*-H), 7.90, 7.77 (br s and m, respectively, 9 *meta* + *para* H), paracyclophanyl aromatic protons, 7.23 (br d, 1 H), 7.01 (br d, 1 H), 6.89-6.76 (irreg m, 5 H), aliphatic protons, 3.62 (br t, 2 H), 3.31 (irreg t, 2 H), 3.05 (irreg t, 1 H), 2.69 (m, 1 H), 2.38 (irreg t, 1 H), 2.21 (m, 1 H); pyrrole NH protons, −2.64 (s, 2 H); uv-vis (benzene): λ max 652 nm (log 3.64), band I, 596 nm (3.67), band II, 555 nm (4.01), band III, 519 nm (4.20), band IV, 424 nm (5.63), Soret band; ir (potassium bromide): 3313 br vs, 3054 m, 3024 m, 2954 s, 2922 vs, 2889 s, 2851 s, 1596 m-s, 1559 m-s, 1555 m, 1468 s-m, 1441 s-m, 1348 s-m, 1261 s-m, 1222 m, 1177 s, 1153 vs, 1099 br vs, 1071 s, 1031 m, 1003 s-m, 972 s-m, 963 s, 800 vs, 729 vs, 700 vs, 674 m, 659 m, 597 m, 515 m, 419 m (weak peaks are omitted); half-wave potentials in V vs. sce (dichloroethane, TBAP as a supporting electrolyte), −1.24, −1.53 (reduction waves), 0.95, 1.18 (anodic peak potential), 1.42 (oxidation waves).

Anal. Calcd. for $C_{54}H_{40}N_4$: C, 87.07; H, 5.41; N, 7.52. Found: C, 86.9; H, 5.6; N, 7.6.

REFERENCES AND NOTES

[+] On sabbatical leave from Poznan Technical University, Poland.

[1] L. Czuchajowski and M. Lozynski, *J. Heterocyclic Chem.*, **25**, 349 (1988).

[2] L. Czuchajowski, S. Goszczynski and A. K. Wisor, *J. Heterocyclic Chem.*, **25**, 1343 (1988).

[3] L. Czuchajowski, S. Goszczynski and A. K. Wisor, submitted.

[4] L. Czuchajowski, J. E. Bennett, S. Goszczynski, D. E. Wheeler, A. K. Wisor and T. Malinski, *J. Am. Chem. Soc.*, **110**, ... (1988).

[5] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour and L. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

[6] J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Marguerettaz, *J. Org. Chem.*, **52**, 827 (1987).

[7] K. M. Smith in "Porphyrins and Metalloporphyrins", K. M. Smith, ed, Elsevier, Amsterdam, 1975, p 21.

[8a] F. Vogtle and P. Neumann, *Top. Curr. Chem.*, **48**, 67 (1974). [b] L. Czuchajowski and A. K. Wisor, *J. Mol. Struct. (Theochem.)*, **165**, 163 (1988).

[9a] R. J. Abraham, *J. Mol. Phys.*, **4**, 145 (1961); [b] R. J. Abraham, S. C. M. Fell and K. M. Smith, *Org. Magn. Reson.*, **9**, 367 (1977); [c] R. J. Abraham, *J. Magn. Reson.*, **43**, 491 (1981).

[10] CNDO/2 and MINDO/3 calculations were performed as in ref [4] on Cray system applying authors' versions of programs in FORTRAN.

[11] J. H. Fuhrhop, K. M. Kadish and D. G. Davis, *J. Am. Chem. Soc.*, **95**, 5140 (1973).

[12] L. Czuchajowski, S. Goszczynski, D. E. Wheeler, A. K. Wisor, J. E. Bennett and T. Malinski, 196th National ACS Meeting, Los Angeles, Sept. 1988, ORGN 248.

[13] J. H. Fuhrhop, *Struct. Bonding (Berlin)*, **18**, 1 (1974).

[14] J. F. Liebman in "Cyclophanes", S. M. Rosenfeld, ed, Academic Press, New York, 1983, p 42.

[15a] J. Bruchin, F. Gerson and H. Ohya-Nishiguchi, *Helv. Chim. Acta*, **60**, 2471 (1977); [b] J. Bruchin, F. Gerson and H. Ohya-Nishiguchi, *J. Chem. Soc., Perkin Trans. II*, 1045 (1980); see Scheme 2 on p 1049.

[16] H. Hopf and F. W. Raulfus, *Isr. J. Chem.*, **25**, 210 (1985).