Porphyrins meso-Substituted with Phenanthrene and 1,10-Phenanthroline

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Meso-tetrakis(9-phenanthryl)porphyrin and meso-tetrakis(1,10-phenanthrolin-4-yl)porphyrin were obtained and characterized by spectroscopy methods. The porphyrin containing phenanthroline substituents was formed with much smaller yield. It showed much slower progress of metallation with Cu(I) and Zn(II) ions than the phenanthreneporphyrin. While attachment of phenanthrene did not result in any meaningful changes in the uv vis spectrum when compared to other meso-substituted tetraarylporphyrins (except that of [2.2]paracyclophanylporphyrin), the appearance of two N centers in each meso substituent substantially altered porphyrin absorption in the 530-600 nm region. Although the 1 H nmr 300 MHz spectra of both porphyrins showed the same deshielding of β-pyrrole protons, the shielding of NH protons was more advanced in phenanthrolineporphyrin.

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Impressive number of new meso-substituted porphyrin systems being synthesized each year does not diminish interest in this class of compounds, neither does it make the quest for new porphyrins less substantiated. In this preliminary communication we describe the meso-tetrakis-(9-phenanthryl)porphyrin, **1**, and meso-tetrakis(1,10-phenanthrolin-4-yl)porphyrin, **2**, Figure 1, which we obtained for a number of reasons. From the sterical point of view they should not show meaningful differences: porphyrin **1** can be considered as a derivative of a porphyrin that is meso-substituted with 1-naphthyl and has the third ring cocondensed in the naphthalene 3 and 4 positions; in **2**, the third ring is attached to the respective 5, 6 positions of a 4-aza analogue of 1-naphthyl. In both cases, the new ring is oriented away from the porphine core and does not impose any steric hindrance on it. Because of this, comparisons of the ease of formation and metallation at the porphine center, very much like comparison of the electronic and the nmr spectra, is substantiated and could reveal the influence of the nitrogen atomic centers in the three-ring substituents on a number of phenomena.

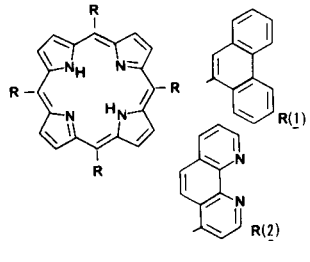

Figure 1. Porphyrins under consideration: meso-tetrakis(9-phenanthryl)-porphyrin, **1**, and meso-tetrakis(1,10-phenanthrolin-4-yl)porphyrin, **2**.

The well known preference of phenanthrene to undergo oxidation to a 9,10-quinone might allow us and other researchers interested in the possibility of the formation of the quinonoid bond systems encompassing both meso-substituent and porphine, to apply porphyrin **1** as a useful model. Such a possibility also concerns porphyrin **2**. The mentioned quinonoid system of bonds might include the 1,10-phenanthrolin-4-yl substituent in the manner characteristic for the ketone form of 4-hydroxy-1,10-phenanthroline [1]. In this case the H atom at C(23) would be displaced to the N(1) center of phenanthroline which is attached to the meso C(15) position. It is also worth mentioning that joining the 1,10-phenanthroline units to porphine creates a possibility of dealing with porphyrins capable of extended complexation of metals by the N centers located outside the porphine core. One can expect increased interest in this type of complexation following the report on hydroxyquinoline-substituted porphyrin [2].

The attachment of phenanthrene and phenanthroline substituents raises the question of a number of expected atropoisomers of the resulting porphyrins. If the substituents are located perpendicularly to the plane of the porphine core, as might be expected by analogy to the porphyrins meso-substituted by phenyls, the obtained porphyrins will by achiral; this would not be the case if the dihedral angle is different than 90°. Free rotation of each of the three-ring substituents is impossible due to the steric hindrance resulting from overlapping in the co-planar conformer of the β-pyrrole hydrogen atoms on those attached to the C(8) and C(5) centers of the substituents in **1** and **2**, respectively. Due to the fact of tetra-substitution, there is a possibility, though, of the closure of the porphyrin ring with the steric positions of all substituents fixed in the chain skeleton when it is still open. For the perpendicular porphyrins one should expect the UUUU, UUUD, UUDD and UDUD atropoisomers (U and D denoting the up and down location of the substituents as referred to porphyrin plane, U and D being interchangeable).

As far as the dipole monents are concerned, the extreme isomers should be UDUD and UUUU shown in Figure 2,

the former having $\mu = 0$, the latter greatest value. However, this differentiation would practically matter only for the phenanthrolineporphyrin **2**. The meso-substituents are divided in it by the "rotating" C(meso)-C(phenanthroline) bond into the U fragment and the D fragment in the 4:1 ratio (considering the length of the "rotating" arm) while this division for the phenanthreneporphyrin **1** represents only the 3:2 ratio. To the polarity of some isomers of **2** contributes also the fact that the "center of gravity" of two nitrogen centers present in each phenanthroline substituent can never be coplanar with the porphine core. It should be also emphasized that the difference in polarity of the extreme atropoisomers of **2** could be enhanced by engaging each 1,10-phenanthroline unit in metal complexation with a ligand of a specific structure, *e.g.*, with monophenanthrolinyltri(substituted)phenyl-1-porphyrin.

The calculations of the energy differences between the expected isomers of **1** and **2** are now in progress, following the procedure successfully applied in this laboratory [3-5] to stereoisomers of the [2.2]paracyclophanylporphyrin.

Tlc separations carried out as described in Experimental, yielded only one fraction in the case of meso-tetrakis-(9-phenanthryl)porphyrin being referred to as porphyrin **1**. This is not surprising in view of very small differences in polarity of the atropoisomers of that porphyrin, see Figure 2. Contrary to this, the meso-tetrakis(1,10-phenanthrolin-4-yl)porphyrin appeared as two closely located and partially interfering tlc fractions assigned to the UUUD and UUUU isomers. The fraction that was slightly less polar was much more abundant. It is denoted in the following discussion as phenanthrolineporphyrin **2**, and is expected to represent the UUUD isomer with the addition of UUUU.

The ^{1}H nmr 300 MHz spectra show that the three-ring meso-substituents basically preserve their spectral characteristics in porphyrins spectra. In the spectrum of **1** there is a region of strongly deshielded "bay" protons clearly separated from the remaining phenanthrene protons, the latter visible as mostly overlapping signals, similar to the

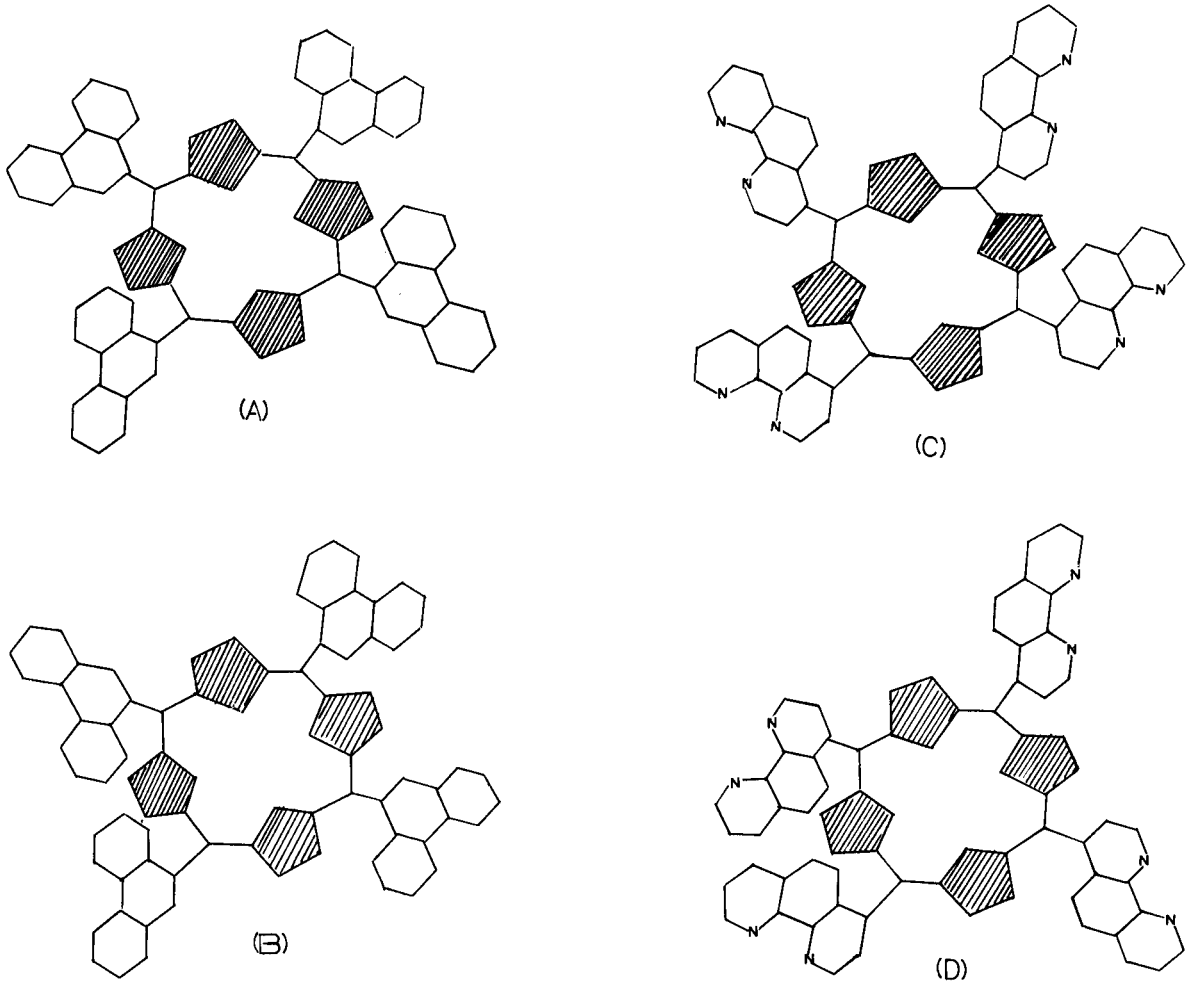

Figure 2. Atropoisomers of porphyrins **1** and **2**. Out of four possible iso mers: UUUU, UUUD, UUDD and UDUD (see text) those are shown which are respectively the most and the least polar, for **1**: UUUU (A) and UDUD (B), for **2**: UUUU (C) and UDUD (D).

spectra of alkylphenanthrenes [6]. In the spectrum **2**, a characteristic pattern of well separated signals of all protons is visible with the protons adjacent to the nitrogen centers in phenanthroline showing strongest deshielding, compare, *e.g.*, [7]. β-Pyrrole protons in **1** and **2** reveal very similar chemical shifts, 8.60 ppm and 8.54 ppm, respectively, that reflects nearly the same anisotropy effects imposed by the phenanthrene and phenanthroline substituents. This is not the case, though, for the signals of the NH protons. Although they are strongly shielded in both porphyrins: −2.11 ppm *vs* −2.32 ppm, the effect of shielding resulting from the ring current in porphine core substituted with phenanthroline is distinctly more pronounced than in case of the phenanthrene substitution. The spectrum of **2**, contrary to **1**, reveals the presence of atropoisomers distinguishable by the 300 MHz instrument, as proven by the slightly shifted "double image" of most signals; the NH signals also have somewhat different characteristics, see Figure 3. The differences in chemical shifts of the respective protons in the UUUD and UUUU atropoisomers of **2** are like those described by Abraham *et al.* [8] for the atropoisomers of meso-tetra(2-methoxy-1-naphthyl)porphyrin. They are, however, smaller than the differences described for the atropoisomers of meso-tetraphenylporphyrins substituted in the benzene rings, compare *e.g.*, [9]. It is no surprise that phenanthrene and phenanthroline units, both less bulky substituents than [2.2]paracyclophane, do not exhibit the influence on the chemical shift values of porphine β-pyrrole protons and NH protons comparable to that characterising paracyclophanylporphyrins [10].

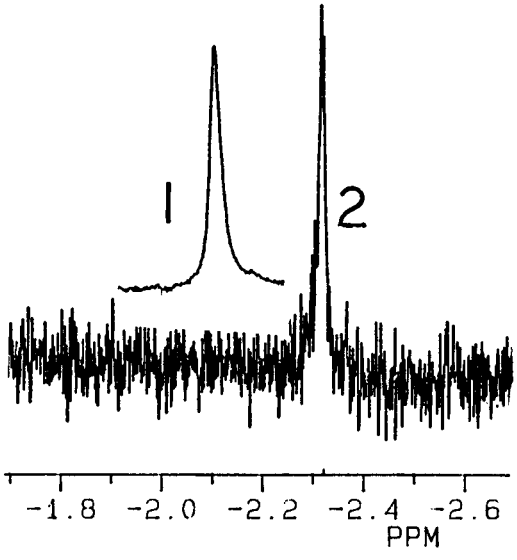

Figure 3. The ^{1}H nmr 300 MHz (deuteriochloroform) signals of the NH protons in porphyrins **1** and **2**.

The electronic spectra of porphyrins **1** and **2** exhibit remarkable differences. Although the positions of the Soret band and the longest wavelength band are similar: 424 vs 423 nm, and 645 vs 643 nm for **1** and **2** respectively, the whole character of these spectra in the absorption region between these extremes is different, see Figure 4. The uv-vis spectrum of **1** is similar to that of meso-tetraphenylporphyrin, the bands showing bathochromic shifts only of a few nm, and reversing their relative intensities for bands II and III. The spectrum of **2** has a pattern of bands rather unusual for the porphyrins in the range of 530-600 nm. Three bands present there show much smaller differentiation of intensity than the two bands visible in the spectrum of **1**, that together with their broad character gives a spectrum with strongly overlapping bands.

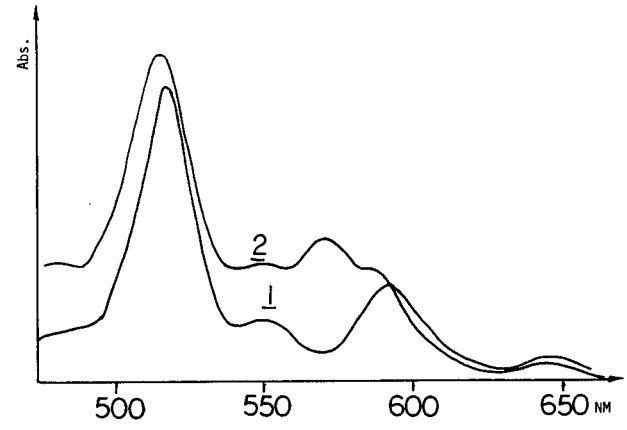

Figure 4. Visible region of the absorption spectra of meso-tetrakis-(9-phenanthryl)porphyrin, **1**, and meso-tetrakis(1,10-phenanthrolin-4-yl)-porphyrin, **2**, in chloroform.

There is a remarkable difference in the yields of porphyrins **1** and **2**. The yield of phenanthrolineporphyrin was 10 times lower than that of phenanthreneporphyrin (the latter being *ca.* 6%) when the propionic acid method of synthesis was used [11]. However, when Lindsey method [12], usually increasing the yield, was applied as in [3], the phenanthrolineporphyrin was not found among the products. These complex phenomena deserve explanation.

Even more striking differences appear in the process of metallation in the porphine core. Under circumstances in which the N centers of phenanthroline substituents are not involved in complexation, the metallation with Cu(I) of porphyrin **2** takes place slowly, not instantly as in case of porphyrin **1**; also metallation with Zn(II) proceeds much more slowly for phenanthrolineporphyrin than phenanthreneporphyrin, see Figure 5. It is characteristic that in the first stage of metallation of **2**, its three-band pattern of vis absorption in the 530-600 nm region changes first to that containing two bands, and only then takes a shape characteristic for metalloporphyrins.

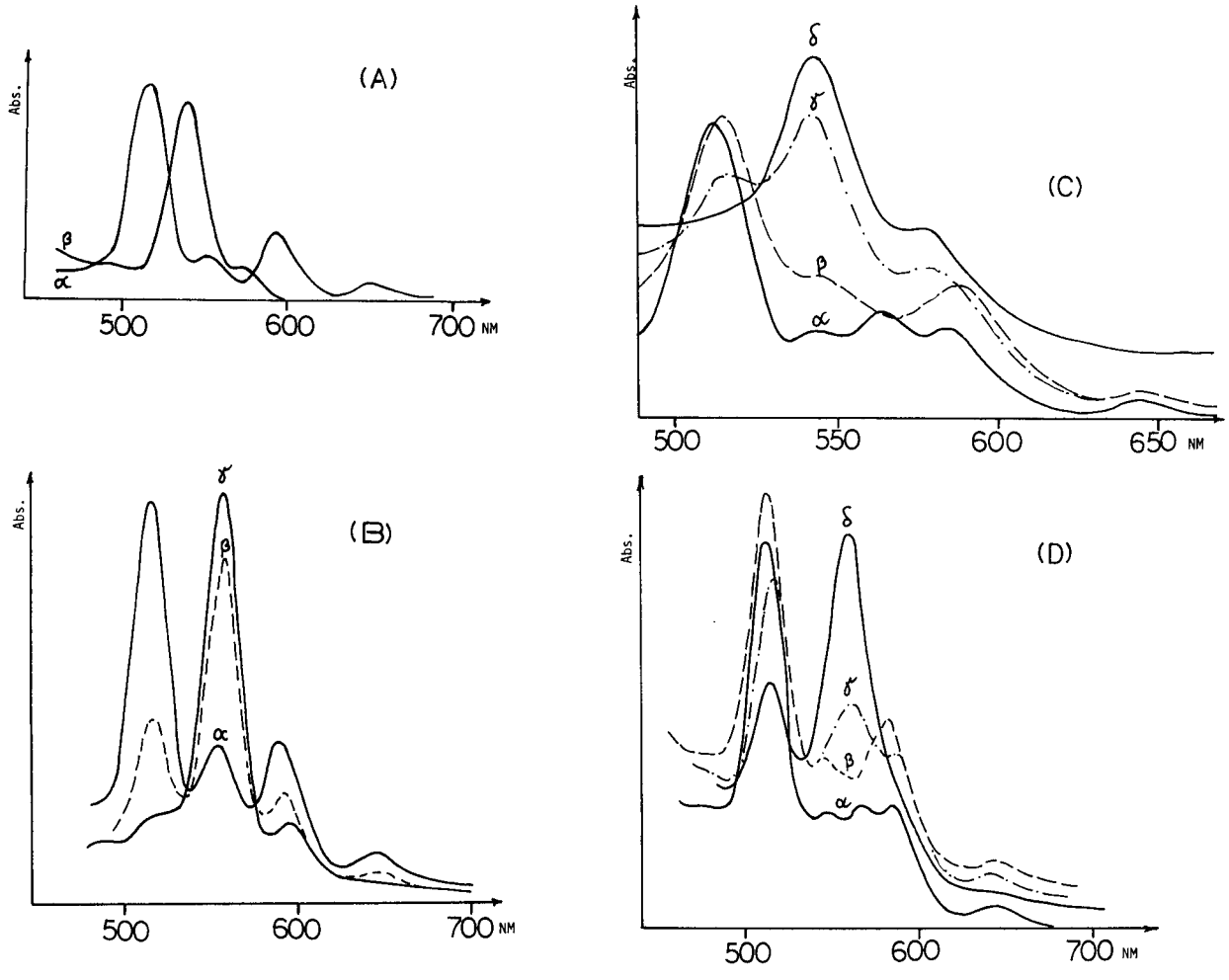

Figure 5. Visible region of the absorption spectra of the solutions of **1** and **2** in chloroform-methanol 98:2 v/v, mixed with methanol solutions of copper(I) chloride and zinc(II) acetate: (A) **1** before mixing, α, and immediately after mixing, β, with Cu(I) ions; (B) **1** before and immediately after mixing, α, with Zn(II) ions, after 20 minutes, β, and after 80 minutes, γ; (C) **2** before, α, and immediately after mixing, β, with Cu(I) ions, after 30 minutes, γ, and after 80 minutes, δ; (D) **2** before, α, and immediately after mixing, β, with Zn(II) ions, after 80 minutes, γ, and after 4 hours, δ.

EXPERIMENTAL

The following chemicals and materials were used: phenanthrene-9-carboxaldehyde, 97% (Aldrich); pyrrole, 99% (Aldrich), freshly distilled; propionic acid, 99% (Aldrich); 4-methyl-1,10-phenanthroline, 99% (Aldrich); selenium dioxide obtained from selenium powder, 99.5% (Aldrich) and concentrated nitric acid; Celite 521 (Aldrich) as a filter agent; Florisil 60/200 mesh (Applied Science Laboratories) for column chromatography; aluminum oxide, cationotropic, activity grade 1 (M. Woelm) for chromatography; Kieselgel 60 tlc plates, 2 mm (E. Merck) and aluminum oxide F-254 neutral type F pre-coated tlc sheets, 0.20 mm (EM Reagents).

Mass spectrometry was performed on a fast atom bombardment Micromass 70/70 mass spectrometer model V6 with an 11/250 data system. 1 H nmr spectra were recorded on a Bruker-IBM AF (300 MHz) Fourier transform spectrometer. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 4c uv-vis spectrophotometer model C 688-0002.

Synthesis.

meso-Tetrakis(9-phenanthryl)porphyrin (**1**).

Basically the method of Adler *et al.* [11] was applied with some steps previously applied in this laboratory to the synthesis of [2.2] paracyclophanylporphyrin [3]. To the mixture of 9-phenanthrenecarboxaldehyde (618 mg, 3 mmoles) and propionic acid (60 ml), pyrrole (0.3 ml, 4.3 mmoles) was added in one portion under reflux. The solution, yellow after mixing, soon became brownish-red and finally almost black. The refluxing was continued for 1.5 hours. After distilling off the propionic acid in a rotary evaporator, the black residue was dissolved in chloroform (50 ml), and Florisil (19 g) was added. Repeated vacuum evaporation left the dry residue which was placed on top of a chromatography column filled with Florisil. As a result of elution with methylene chloride, three fractions were collected, 200 ml each. The first two fractions contained porphyrin as checked by the characteristic uv vis pattern of the Soret band followed by four longer wavelength bands. Evaporation to dryness gave 75 mg of deep-violet pow-

dered substance. Further separation was carried on the aluminum oxide tlc plates with 1-bromobutane. The porphyrin fraction which moved with the front of the solvent was rechromatographed twice in the same way. The yield of meso-tetrakis(9-phenanthryl)porphyrin **1**, was 45 mg (ca. 6%); fab ms: 1014 calcd mass (M), 1015 $(M+H)^+$; ^1H nmr (deuteriochloroform): 300 MHz δ 8.94 (tr, 4H, 5-H), 8.70-8.50 (m, 4H, 4-H), 8.57 (s, 8H, β-pyrrole H), 8.02 (d, 4H, 1-H), 7.90-7.56 and 7.21 (m, 24H, 2-, 3-, 6-, 7-, 8-, 10-H), −2.11 (s, 2H, NH); uv-vis (chloroform): λ max nm 645, 590, 551, 517, 424 Soret, (chloroform:methanol 98:2 v/v): 645, 590, 551, 517, 426 Soret, (benzene): 647, 591, 550, 517, 425 Soret.

Anal. Calcd. for $C_{76}H_{46}N_4$: C, 89.91; H, 4.57; N, 5.52. Found: C, 89.52; H, 4.56; N, 5.22.

1,10-Phenanthroline-4-carboxaldehyde.

Although this is an already known compound [13], the available literature data are somewhat fragmentary [14]. Freshly prepared selenium dioxide (750 mg) was dissolved with heating in dioxane (10 ml) containing 4% water. To this solution, 4-methyl-1,10-phenanthroline (900 mg) dissolved in 60 ml of water-free dioxane was added for 2 hours. The reaction mixture was then refluxed for 3 hours and filtered while still hot, through a Celite 521 layer, ϕ5 cm, 5 cm. From the filtrate dioxane was distilled off until the volume was decreased by 2/3. This crucial step had to be carried on gently because otherwise the 1,10-phenanthroline-4-carboxaldehyde which began to precipitate, underwent decomposition, even an explosive one, due to the reaction with dioxane peroxides formed during the oxidation. For this reason evaporation to dryness (compare, *e.g.*, [14]) should be avoided. From the concentrated solution a pulver-like white-gray substance precipitated. It was filtered off and dried in air. It was the desired reaction product containing a negligible impurity of selenium. It was used directly to the synthesis of porphyrin **2**, see below. From the remaining solution left in an open dish, fine colorless needles of the 1,10-phenanthrene-4-carboxaldehyde crystallized after a few days, mp 195-199° dec; ^1H nmr (deuteriochloroform): 300 MHz 10.55 (s, 1H, CHO), 9.44 (d, 1H, 2-H), 9.21 (dd, 1H, 9-H), 8.98 (d, 1H, 5-H), 8.26 (dd, 1H, 7-H), 7.97 (d, 1H, 3-H), 7.94 (d, 1H, 6-H), 7.66 (dd, 1H, 8-H).

The annoying aspect of this reaction is the appearance of metallic selenium throughout the whole process. Although filtration through Celite reduced its presence much more drastically than multiple centrifugation, the traces of this metal could even be seen in the capillary tube after determination of the melting point of the final crystalline product.

meso-Tetrakis(1,10-phenanthrolin-4-yl)porphyrin (**2**).

To the refluxing mixture of the unpurified 1,10-phenanthroline-4-carboxaldehyde (416 mg, 2 mmoles) dissolved in propionic acid (60 ml), pyrrole (0.14 ml, 2 mmoles) was added under reflux and heating was continued for 1 hour. After cooling and adding 20 g of aluminum oxide, it was evaporated to dryness. The residue was placed onto the chromatography column filled with basic aluminum oxide and eluted with methanol. The first 400 ml of the reddish eluate which emerged from the column were evaporated to dryness. The black residue was dissolved in 50 ml of chloroform and the solution washed with 5% water solution of sodium hydroxide and water. After drying over anhydrous sodium sulfate it was concentrated by evaporation to about 2 ml and placed on tlc silica-gel plates. Elution with methanol resulted in a spectacular system of bands: yellow (Rf 0.87-0.94), pink (0.77-0.84), yellow (0.64-0.71), violet (0.22-0.59), yellow (0.08-0.20) and black (0-0.02). The porphyrin was present only in the bottom yellow band, and also, to some extent, in the adjacent black band near the starting line. None of the bands in the Rf region 0.22-0.94 showed a uv-vis spectrum typical for porphyrins. The process of development had to be carried on very slowly because the porphyrin fraction left the starting line last. This fraction after dissolving in methanol-chloroform 1:1 v/v solution and evaporation to dryness left a greenish residue which glittered like porphyrin, and gave the porphyrin-type uv spectrum. Further purification was conducted on aluminium oxide tlc plates (0.2 mm) with a chloroform-methanol (50:1) mixture as an eluent. The broad band obtained was divided into upper and bottom parts. The fraction collected in the latter, after concentrating and repeated elution with methanol-water (10:1 v/v) on the tlc kieselguhr plates was characterized by much lower Rf values than the starting, slightly less polar upper fraction. It is expected that they represented, respectively, the UUUU isomer with the addition of UUUD, and the UUUD isomer with the addition of UUUU. A very small yield of the UUUU(UUUD) fraction did not allow its investigation at present. The yield of UUUD(UUUU) fraction was 3 mg (*ca.* 0.6%); fab ms: 1023 calcd mass (M), 1024 $(M+H)^+$; ^1H nmr (deuteriochloroform, the region *ca.* 7.2 ppm rechecked in deuterioacetone): 9.56 (dd, 4H, 9-H), 9.32 (d, 4H, 2-H), 8.54 (dd, 8H, β-pyrrole H), remaining phenanthroline protons: 8.41 (dd, 4H), 8.02 (dd, 4H), 7.75-7.67 (m, 4H), 7.45 (d, 4H), 7.22 (d, 4H), −2.32 (s, 2H, NH); uv vis (chloroform): λ 643, 584, 568, 547, 515, 423 Soret; (chloroform-methanol 98:2 v/v): 644, 586, 568, 546, 514, 423 Soret.

Anal. Calcd. for $C_{68}H_{38}N_{12}$: C, 79.82; H, 3.74; N, 16.43. Found: C, 79.51; H, 3.56; N, 16.81.

Metallation of Porphyrins.

Metallation of porphyrins **1** and **2** was carried out by mixing directly in the absorption cuvette of the uv-vis spectrometer, at room temperature, the solution of porphyrin in chloroform:methanol 98:2 v/v with the methanol solution of copper(I) chloride, copper(II) acetate or zinc acetate dihydrate; uv-vis (chloroform-methanol 98:2 v/v): λ max nm **1**-Cu(I): 575, 541, 421 Soret; **1**-Zn(II): 596, 559, 432 Soret; **2**-Cu(I): 576, 545, 423 Soret; **2**-Cu(II): 563, 543, 423 Soret; **2**-Zn(II): 560, 515, 434 Soret.

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