CHEMISTRY LETTERS, pp.641-644, 1977. Published by the Chemical Society of Japan

METALLOPORPHYRINS. II.[1] SYNTHESIS AND VISIBLE SPECTRA OF BIS- AND TRIS-PORPHYRINS AND THEIR METAL COMPLEXES

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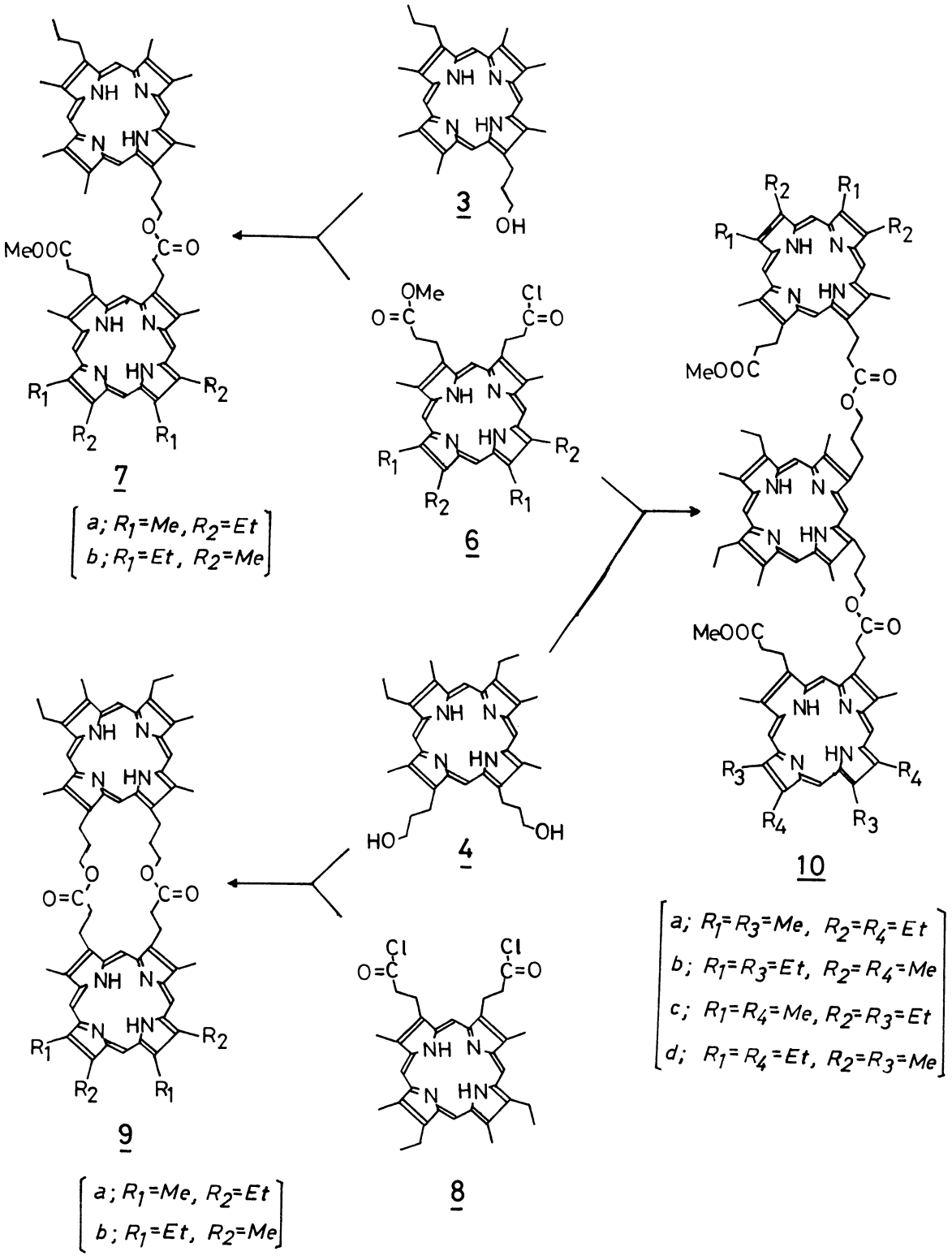
The acyl chloride of monomethyl ester of mesoporphyrin-IX (6) was treated with porphyrins having monohydroxy and dihydroxy groups (3 and 4) to afford single-bridged bis- and trisporphyrins (7 and 10), respectively. The diacyl chloride of mesoporphyrin-IX (8) was treated with the dihydroxy porphyrins (4) to give double-bridged bisporphyrin (9). The visible spectra of the free base and the metal complexes of the multiporphyrins are found to be distinguishable from those of mesoporphyrin-IX dimethylester (5) and its metal complexes. The chromophores in the multiporphyrin systems interact strongly intramolecularly.

The aggregation of porphyrins and metalloporphyrins have been attracting current interest[2] particularly in relation to the photochemical function of chlorophylls in the photosynthesis. In order to reveal the effect of aggregation on the photochemical behaviors of metalloporphyrins, our efforts have been focused on the preparation of bis- and tris(metalloporphyrins). Bis-(metalloporphyrins) have been synthesized recently in connection with the intramolecular energy transfer.[3] During our investigation some publications concerning our interest have appeared; while covalently linked pyrochlorophyllide a dimer[4a] and chlorophyll a dimer[4b] have been prepared and characterized as biomimetic models, cyclophane porphyrin has been synthesized.[5] These works led us to present our studies on the synthesis of bis- and trisporphyrins and their metal complexes, which show characteristic visible absorption spectra owing to the intramolecular dimer formation.

Porphyrins having such mono- and difunctional groups as carboxy and hydroxy groups are required for the synthesis of bis- and trisporphyrins when the macrocycles are linked by ester bonding. Mesoporphyrin-IX monomethyl ester (1) was employed as a monocarboxy porphyrin on account of the availability and the solubility, although 1 may be a mixture of two position isomers.

In order to obtain a monohydroxy porphyrin, 2-(2-ethoxycarbonylethyl)-3,7,8,13,17,18-hexamethyl-12-propylporphin (2) was prepared according to the stepwise method.[6] The key intermediate, 3,4-dimethylpyrrole-2-aldehyde, was


3
6
7
a; R1=Me, R2=Et
b; R1=Et, R2=Me
4
8
9
a; R1=Me, R2=Et
b; R1=Et, R2=Me
10
a; R1=R3=Me, R2=R4=Et
b; R1=R3=Et, R2=R4=Me
c; R1=R4=Me, R2=R3=Et
d; R1=R4=Et, R2=R3=Me

available from 3,4-dimethylpyrrole prepared readily according to the procedure reported by the present author.[7] The $LiAlH_4$ reduction of 2 in THF gave 2-(3-hydroxypropyl)-3,7,8,17,18-hexamethyl-12-propylporphin (3) in a 93.5% yield. 3,7-Bis(3-hydroxypropyl)-2,8,13,18-tetramethyl-12,17-diethylporphin (4) as a dihydroxy porphyrin was prepared by the $LiAlH_4$ reduction of mesoporphyrin-IX dimethyl ester.[8]

The monomethyl ester (1) was converted into the acyl chloride (6) with use of purified thionyl chloride. The acyl chloride in dichloromethane was added dropwise to a solution of 3 in the presence of triethylamine. The solution was washed with water and dried over K_2CO_3. After evaporating the solvent, the mixture of two isomers of bisporphyrin (7) was purified on silica gel plates using dichloromethane as an eluent. The yield was 55%.

To a highly diluted dichloromethane solution of 6 was added the diacyl chloride of mesoporphyrin-IX (8) in one portion, followed by the addition of excess triethylamine. The reaction mixture was treated in the same manner as described above and chromatographed on a silica gel column using dichloromethane as an eluent. The main red fraction was evaporated to dryness. The product was rechromatographed on a silica gel column, and the double-bridged bisporphyrin (9) was thus obtained in a 28% yield. The product showed a single spot on a silica gel plate.

A solution of monoacyl chloride (6) in dichloromethane was added to a solution of 4 in the presence of triethylamine. The product was chromatographed on a silica gel column. Chloroform was used as an eluent. The initial main fraction was evaporated to dryness, and the residue was purified by means of TLC. The yield of the trisporphyrin (10) was 50%. The trisporphyrin may be a mixture of four isomers, while the TLC on silica gel showed only one spot.

The molecular weight determination allowed us to ascribe the multiporphyrins to the proposed structures. The theoretical molecular weights of the single-bridged bisporphyrin (7), the double-bridged bisporphyrin (9), and the single-bridged trisporphyrin (10) are 1057, 1069, and 1676, respectively, while the molecular weights determined by means of the vapor pressure osmometry were 1003, 1042, and 1590, respectively. The infrared spectra of these multiporphyrins possess no carbonyl band other than the ester carbonyl band at 1735 cm^{-1}.

The visible spectra of the free base multiporphyrins as well as their Zn and Cu complexes are presented in Table 1. The visible spectra of the multi-porphyrins are no longer superposed on that of 5 in particular with respect to the absorption coefficient. Of the absorption bands of bis(metalloporphyrins), the Soret band exhibits significant blue shift in comparison with the metal complexes of 5. These phenomena indicate the presence of the interaction between two macrocycles in the multiporphyrins and the metal complexes. Our results are keenly contrastive with the properties of the cyclophane porphyrin and its zinc complex, which have been reported to demonstrate no remarkable interaction between two chromophores.[5] The visible spectra of the mixtures of 5 and 7 at

various mixing ratios demonstrate isosbestic points, when the concentrations of 5 and 7 are so adjusted that the total concentration *per macrocycle* remains constant. The spectra of the metal complexes represented the same result. The difference of the electronic spectra of the bisporphyrins and their metal complexes from those of monomeric mesoporphyrin-IX diester and the metal complexes are therefore due to the intramolecular dimer formation. The splitting of the Soret band of the trisporphyrin metal complexes into two peaks suggests the presence of both monomeric and dimeric states.

Table 1. The visible spectra of multiporphyrins and their metal complexes in chloroform.

porphyrin	free base; λ^{max} ($\varepsilon \times 10^{-4}$)	Zn complex	Cu(II) complex
mesoporphyrin-IX diMe ester(5)	400, 498, 534, 567, 622. (17.5) (1.37) (0.96) (0.65) (0.47)	403, 534, 571. (29.3) (1.51) (1.93)	398, 525, 562. (38.7) (1.29) (2.47)
single-bridged bisporphyrin(7)	398, 502, 535, 570, 623. (24.0) (2.12) (1.50) (1.06) (0.72)	390, 539, 574 (31.2) (2.04) (2.74)	387.5, 531, 566. (31.0) (1.94) (3.39)
double-bridged bisporphyrin(9)	392, 502, 532.5 570, 624.5. (24.5) (2.00) (1.30) (1.10) (0.64)	389.5, 539, 573 (28.6) (1.94) (2.56)	387.5, 530.5,565. (31.0) (2.04) (3.44)
single-bridged trisporphyrin(10)	398, 503.5 536.5 573, 627.5. (36.9) (3.30) (2.28) (1.62) (1.10)	390, 399, 538, 574. (39.4) (37.1) (3.00) (3.83)	389, 397, 529, 565. (37.1) (44.4) (2.88) (4.87)

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(Received March 31, 1977)