Tetrahedron Letters No. 2, pp 169 - 172, 1977. Pergamon Press. Printed in Great Britain.

CYCLOPHANE PORPHYRIN-III. DOUBLE PORPHYRINS

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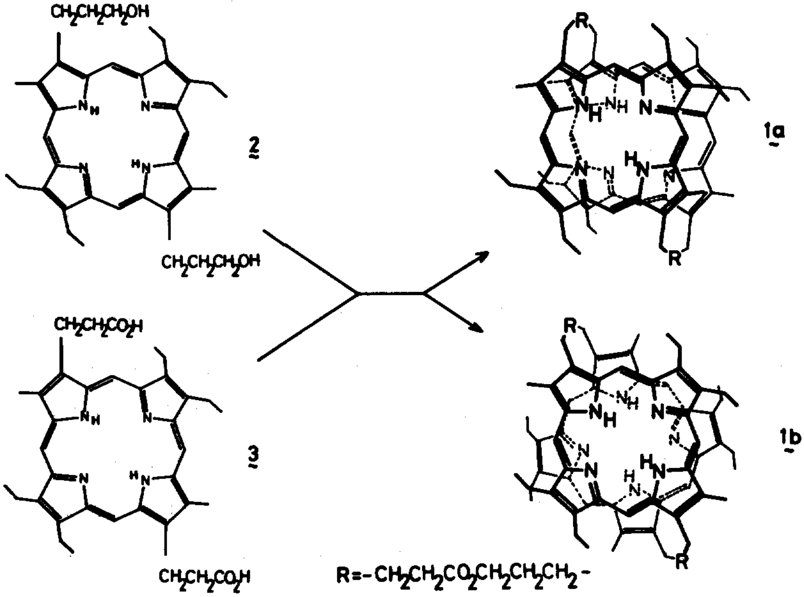
(Received in Japan 2 October 1976; received in UK for publication 2 December 1976)

Interaction between metalloporphyrins in the aggregated state is particularly interesting due to the chemical relevance to energy transfer in chlorophylls (magnesium dihydroporphyrin) during photosynthesis.[1] Recently the covalently linked metalloporphyrins have been prepared in order to fix the geometry of the two chromophores,[2] whereas intermolecular energy transfer in solution involves randomly oriented molecules. The bridged porphyrins have been obtained from the condensation of 2-chlorocarboxyethyl-12,17-diethyl-3,7,8,-13,18-pentamethylporphin with p-phenylenediamine or ethylenediamine. They have assumed the interaction between the two metalloporphyrin rings in terms of a slight reduction of the triplet life time. We wish to report the first cyclophane porphyrin consisting of two porphyrin rings and its zinc(II) complex for the purpose of constructing more rigid systems.

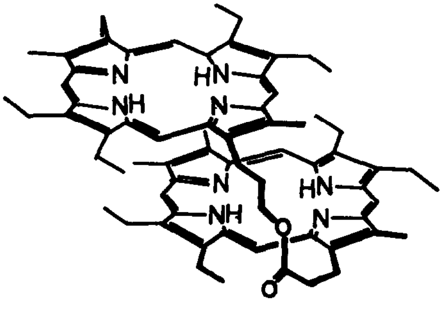
Cyclophane porphyrin **1** has been prepared by condensation of 7,17-bis-(3-hydroxypropyl)-2,3,12,13-tetraethyl-8,18-dimethylporphin **2** and 7,17-bis-(2-carboxyethyl)-2,3,12,13-tetraethyl-8,18-dimethylporphin **3**.[3] The porphyrin **3** was treated with isobutyl chloroformate in tetrahydrofuran. To highly diluted reaction mixture was added dropwise the tetrahydrofuran solution of **2** under argon atmosphere. The reaction mixture was washed with aqueous NH_4Cl solution, dried over Na_2SO_4 and condensed to dryness. Thus obtained solid was chromatographed on thin layer of silica gel with CH_2Cl_2-acetone(6/1; v/v). The fraction at R_f=0.7 gave red crystals of cyclophane porphyrin **1** (yield 11%). Molecular weight of the bridged porphyrin was determined to be 1071 by means of vapor-pressure osmometry. Calculated value of **1** requires 1125.46 for

$C_{72}H_{84}N_8O_4$. Infrared spectrum of **1** shows a strong absorption at 1735 cm^{-1} assignable to the carbonyl stretching mode of the ester group. Visible absorption maxima of **1** are found at 400nm(logε 5.04), 499(3.88), 533(3.78), 563(3.66), and 620(3.51). The cyclophane porphyrin **1** including two centrosymmetric porphyrin rings **2** and **3** gives two chiral stereoisomers represented

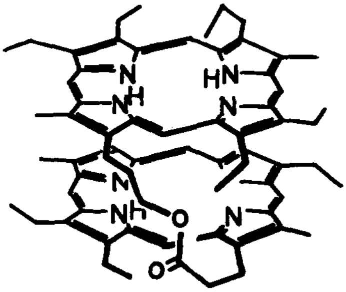


as *syn* **1a** and *anti* **1b** forms with respect to geometry of two methyl groups at 8 and 18 positions. For the structure of **1a**, two sets of two methyl groups of both porphyrins are at the pseudo-geminal configuration.[4] The *anti* form **1b** can be obtained by rotating either of the two porphyrin rings by 180° around the axis through 7 and 17 positions. Separation of two stereoisomers by using TLC was unsuccessful.

Treatment of mixture of **1a** and **1b** with zinc acetate gave the Zn(II) complexes of cyclophane porphyrin **4a** and **4b**. Visible spectrum of the mixture of **4a** and **4b** in CH_2Cl_2 shows absorption maxima at 401, 531 and 568, which verifies complete incorporation of Zn^{+2} into both porphyrins of **1a** and **1b**. Fig. 1 shows the nmr spectra of the free bases **1a** and **1b** in $CDCl_3$ and the Zn(II) complexes **4a** and **4b**. Since the meso protons of **2** and **3** have two signals respectively, the meso protons of two stereoisomers should exhibit eight



SYN. 1a



ANTI. 1b

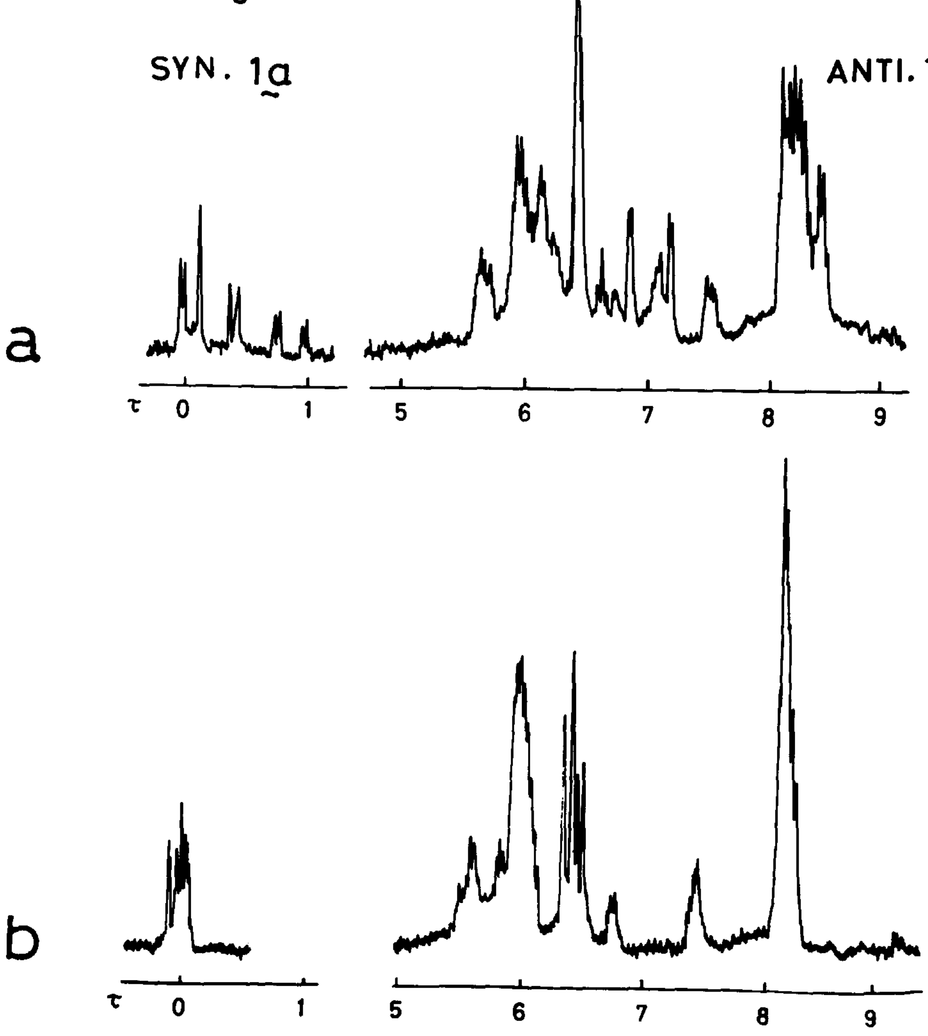


Fig. 1 The 220 MHz nmr spectra at 31.5°. (a) The cyclophane porphyrin free base 1 in $CDCl_3$. (b) The Zn(II) complex 4 in pyridine-d_5.

signals. The meso protons of the free base in 220 MHz nmr spectrum are resolved into nine signals at τ -0.03(2H), 0.00(2H), 0.11(4H), 0.36(2H), 0.43 (2H), 0.73(1H), 0.80(1H), 0.90(1H), and 0.99(1H). Integral ratio of these peaks suggests the formation of equal amount of the two stereoisomers. The separation of signals due to the meso protons of 2 is 0.20 ppm and the corresponding signals of 3 are superposed at τ 0.00 as a single peak. Therefore marked separation of the chemical shifts and splitting into more than eight signals as is seen in Fig. 1 are attributed to mutual diamagnetic ring current effect of two porphyrins on the meso protons. In contrast with the free base, chemical shifts of the meso protons of the Zn(II) complex are centered at τ 0.00 in narrower region of 0.2 ppm. It is suggested that two Zn(II) porphyrin rings of 4 constitutes rather complete face-to-face configuration. On the other hand, parallel sliding of two porphyrin rings in the free base towards the opposite directions, that is, partial face-to-face configuration results in higher magnetic field shifts of two meso protons owing to the ring current of the faced porphyrin. Furthermore, similar trend has been observed for the chemical shifts of the methyl groups.

From a study of Corey-Pauling-Kolton molecular model, the intramolecular distance between two Zn(II) porphyrins was estimated to be 7 Å. However, no remarkable interaction between two chromophores has been observed on the basis of its electronic spectrum. The visible spectrum of the Zn(II) complex can be expressed by superposition of the respective Zn(II) complexes of 2 and 3. Further syntheses of cyclophanes of double porphyrins are in progress.

REFERENCES AND NOTES

(1) R. K. Clayton, Molecular Physics in Photosynthesis, Blaisdell, New York (1965), Chap. 1-4 and 12-13.

(2) F. P. Schwarz, M. Gouterman, Z. Muljiami, and D. Dolphin, Bioinorganic Chem., **2**, 1 (1972).

(3) H. Ogoshi, H. Sugimoto, S. Sanada, E. Watanabe, and Z. Yoshida, Chem. Lett., 427 (1975).

(4) H. J. Reich and D. J. Cram, J. Am. Chem. Soc., **91**, 3505 (1969).