Tetrahedron Letters No. 49, pp 4477 - 4480, 1976. Pergamon Press. Printed in Great Britain.

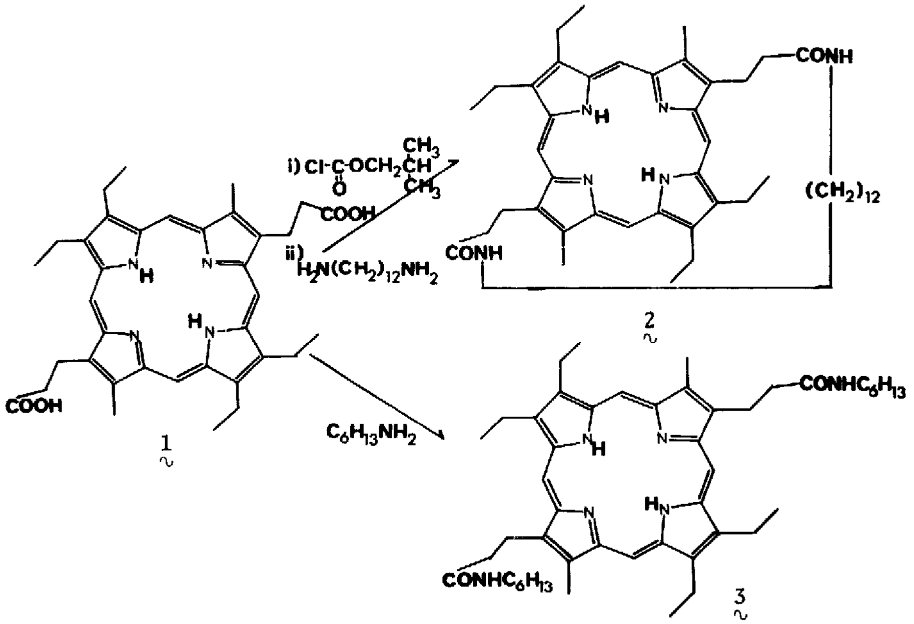
CYCLOPHANE PORPHYRIN - I

Hisanobu Ogoshi*, Hiroshi Sugimoto, and Zen-ichi Yoshida,
Department of Synthetic Chemistry, Kyoto University, Sakyo, Yoshida,
Kyoto, 606, Japan

(Received in Japan 13 September 1976; received in UK for publication 20 October 1976)

The metal complex of cyclophane porphyrin has been considered to be a candidate of model compound for heme-proteins. First cyclophane porphyrin of the ETIO type has been reported by Traylor and his coworkers.[1] However, its physicochemical behavior has never been discussed. Second cyclophane porphyrin named by "capped porphyrin" has been prepared by Baldwin[2] and his coworkers. The latter porphyrin can be regarded as a derivative of α,β,γ,δ-*meso*-tetraphenylporphin. It has been noted that the redox potentials of porphyrin and metalloporphyrin are dependent upon the peripheral substituents on porphin.[3] Therefore, it is particularly interesting to prepare the ETIO type cyclophane porphyrin which is structurally closer to the naturally occurring porphyrin. We wish to report briefly the synthesis of a new cyclophane porphyrin substituted with alkyl groups at the β-positions of four pyrrolic rings and its zinc(II) complex.

To a mixture of 1,2,5,6-tetraethyl-3,7-dimethyl-4,8-bis(2-carboxyethyl)-porphin[4] **1**, isobutyl chloroformate and triethylamine in dry tetrahydrofuran was added 1,12-dodecanediamine. The reaction mixture in high dilution was stirred for 5 hr at room temperature. After the solvent was removed under reduced pressure, the thin layer chromatography of the residue on silica gel with methylene chloride-acetone(6:1) gave purple red powder of cyclophane porphyrin **2** (16%), Anal. Calcd. for $C_{48}H_{66}N_6O_2$: C, 76.15; H, 8.52; N, 11.10. Found: C, 75.95; H, 8.58; N, 10.96. Mass spectrum shows a molecular peak at m/e 758. Molecular weight determined by the vapor-pressure osmometry was found to be 749. Infrared absorptions at 3300, 1640, 1550 cm^{-1} are due to the amide groups. Similar condensation of 1 with n-hexylamine afforded bis-n-hexylamide derivative 3 (92%). Anal. Calcd. for $C_{48}H_{68}N_6O_2$: C, 76.14; H, 8.54; N, 11.09. Found: C, 76.02; H, 8.57; N, 10.98. The zinc complexes



4 and 5 were prepared by treatment of 2 and 3 with zinc acetate in methanol respectively. Visible spectra of 2, 3, 4 and 5 are summarized in Table 1. Owing to low solubility of the free bases in the usual nmr solvents, the nmr spectra of the zinc complexes were measured in pyridine-d_5 as shown in Figure 1. Eight protons of the dodecamethylene group of 4 appear at τ 9.90 and 10.25 as two multiplets. Shifts to higher magnetic field are readily explained in terms of the anisotropy due to diamagnetic ring current of macrocycle in comparison with the proton chemical shifts of the n-hexyl groups of the reference complex 5.

Investigations on the synthesis of cyclopane porphyrins and their metal complexes are in progress.

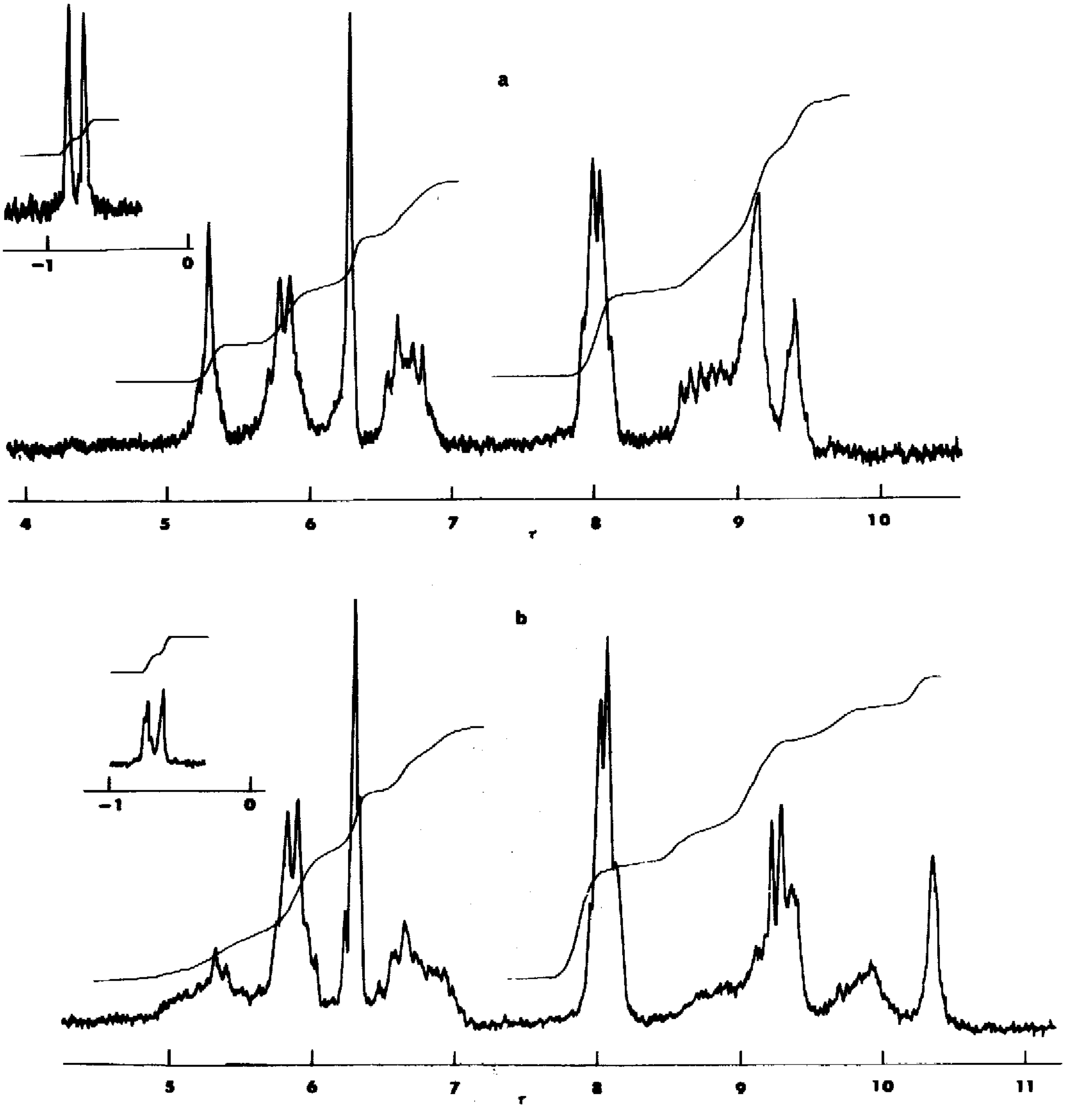


Figure 1. The 100-MHz ^1H NMR spectra of (a) the zinc(II) complex of the reference porphyrin and (b) that of the cyclophane porphyrin in pyridine-d_5 solution at 31.5°.

Table 1. Visible spectra of porphyrin and their Zn(II) complexes.

Compound	λmax(logε) in $CHCl_3$
2	401(4.85), 500(3.97), 535(3.86), 568(3.62), 622(3.56)
3	401(4.84), 500(3.97), 535(3.88), 568(3.62), 622(3.55)
4	401(5.32), 538(4.01), 571(4.11)
5	401(5.33), 538(4.01), 571(4.13)

References and Notes

(1) H. Dieckman, C. K. Chang, and T. G. Traylor, J. Am. Chem. Soc.,93,4068 (1971).

(2) J. Almog, J. E. Baldwin, and J. Huff, J. Am. Chem. Soc.,97,227(1975).

(3) J. H. Fuhrhop, K. Kadish, and D. G. Davis, J. Am. Chem. Soc.,95,5140 (1973). J. W. Buchler, "Porphyrins and Metalloporphyrins", Ed. K. M. Smith, Elsevier Scientific Publishing Co., (1975), P. 220.

(4) H. Ogoshi, H. Sugimoto, S. Sanada, E. Watanabe, and Z. Yoshida, Chem. Lett., No. 5, 427(1975).

Nomenclature of **1** according to the IUPAC rule is expressed as 7,17-bis (2-carboxyethyl)-2,3,12,13-tetraethyl-8,18-dimethylporphin.