Tetrahedron Letters,Vol.28,No.47,pp 5829-5832,1987
Printed in Great Britain

0040-4039/87 $3.00 + .00
Pergamon Journals Ltd.

SYNTHESIS OF AN OBLIQUE BIS-PORPHYRIN SYSTEM CONTAINING A 1,10-PHENANTHROLINE SPACER

Sylvie Noblat, Christiane O. Dietrich-Buchecker, and Jean-Pierre Sauvage

Laboratoire de Chimie Organo-Minérale, UA 422, Institut de Chimie, 1, rue Blaise Pascal,
F-67000 Strasbourg-Cedex, France

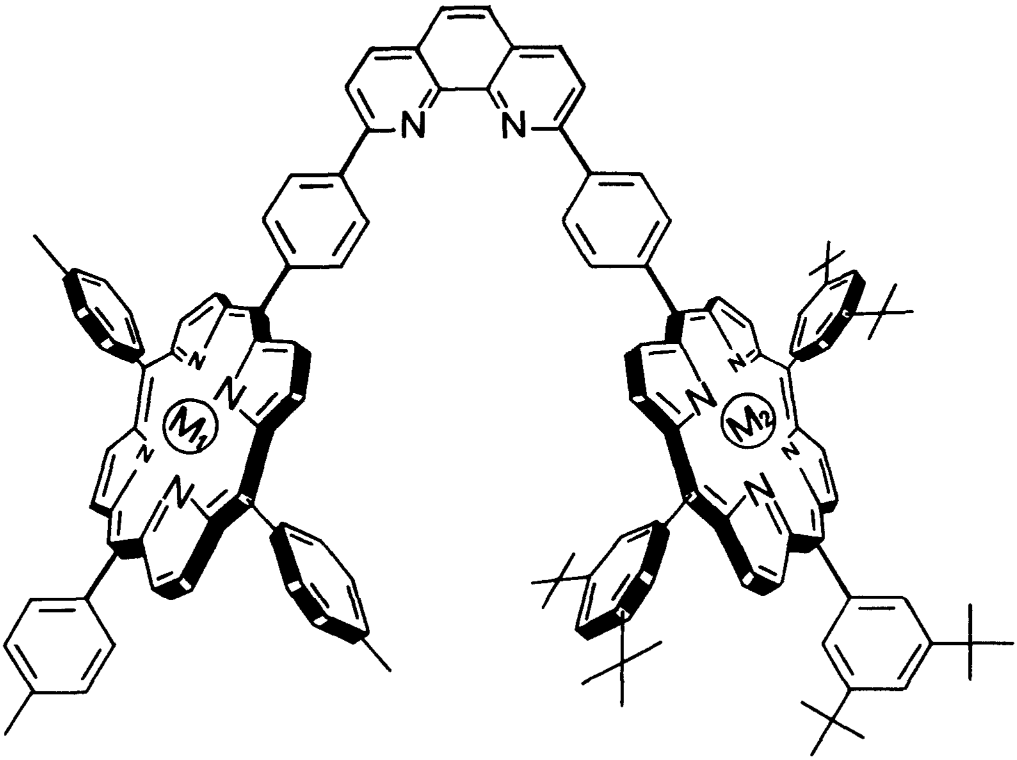
Abstract:

A molecule consisting of two porphyrin rings (free base or Zn complex) rigidly held by a 1,10-phenanthroline nucleus has been made ; the centre-to-centre separation is about 13 Å.

Understanding the factors which govern electron transfer processes in natural photosynthesis might be noticeably improved by studying synthetic systems that mimic parts of the biological structures. A recent crystallographic analysis of a bacterial reaction centre[1] (**Rhodopseudomonas viridis**) shows the intringuing mutual arrangement of the tetrapyrrolic rings : except for the special pair of bacteriochlorophylls, each tetrapyrrole forms an interplane angle of 64° or 70° with its closest neighbour, the centre-to-centre separation being 13 Å or 11 Å.[1] It might be conjectured that this special arrangement is of particular importance with respect to the charge separation process.

In order to build synthetic analogues of the bacterial reacting centre, several approaches using multi-porphyrin systems have recently been reported.[2,3] However, the number of molecular arrays whose rigidity is sufficient to ensure control of the distance and orientation of the respective tetrapyrrolic subunits is highly limited.[4,5]

We now report the synthesis of a novel type of "gable" like[6] diporphyrin, as represented in Figure 1.



1 : $M_1 = M_2 = 2H$

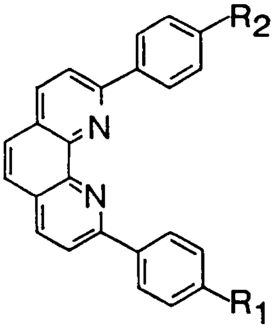
2 : $M_1 = Zn$, $M_2 = 2H$

3 : $M_1 = M_2 = Zn$

FIGURE 1

Compounds **1-3** display geometrical features reminiscent of those found in the bacterial reacting centre. Owing to the prefered planar geometry of the 2,9-diphenyl-1,10-phenanthroline fragment,[7] both tetrapyrrole units are likely to adopt an oblique disposition. The rotation axis of the two porphyrins should form an angle of 60° and their centre-to-centre separation is about 13 Å (CPK models).

Compounds **1-3** have been made from 1,10-phenanthroline following a synthetic strategy close to that previously used by Tabushi et al. for making a gable-porphyrin.[6] The precursors are represented in Figure 2. New compouds gave good elemental analysis; ^1H NMR, UV visible and mass spectra are also consistent with their structures.



4 : $R_1 = R_2 = CH_3$
5 : $R_1 = CHBr_2$, $R_2 = CH_2Br$
6 : R_1 = CHO, $R_2 = CH_2OCOC_2H_5$
7 : R_1 = TrTP, $R_2 = CH_2OCOC_2H_5$
8 : R_1 = TrTP, $R_2 = CH_2OH$
9 : R_1 = TrTP, R_2 = CHO
10 : R_1 = Zn^{II}TrTP, R_2 = CHO

FIGURE 2

1,10-phenanthroline is reacted with 4-lithiotoluene (4 equivalents) in toluene for 45 min. at room temperature. After hydrolysis, MnO_2 oxidation following a previously published procedure[8] and chromatographic separation (Silica ; toluene-CH_3OH), **4** is obtained as a white solid (mp 197-199) in 65% yield. Bromination of **4** to **5** by N-bromo succinimid (3 equivalents ; refluxing benzene for 30 min) is performed under light irradiation (λ 320 nm ; 0.5 hrs). After filtration, washing (H_2O) and solvent evaporation, the crude product containing **5** is directly treated by NaOH in refluxing propionic acid. After work-up and chromatographic purification (Silica ; CH_2Cl_2-AcOEt), **6** is isolated as a white solid (mp 38-40) in 37% yield from **4**. Adlers reaction[9] applied to a 1:12:13 mixture of **6**, p-tolualdehyde and pyrrole in refluxing CH_3CH_2COOH for 4 hrs, followed by column chromatography (Silica ; toluene-AcOEt) and repeated crystallization (C_6H_6-EtOH) leads to a 16% yield of the monoporphyrin **7**, [λ_{max} (log ε) (CH_2Cl_2) : 418 (5.29), 517 (4.16), 552 (3.95), 592 (3.64), 648 nm (3.72) ; M^+ 996 ; mp 300], in addition to tetra-p-tolyl-porphyrin.

Hydrolysis of **7** (aqueous NaOH 1.8 M/DMF, 1:4 v/v; RT; 45 min) furnishes **8** in 80% after flash chromatography (silica ; toluene-CH_3OH).

Oxidation of the benzylic alcohol function of **8** is efficiently performed by activated MnO_2 in large excess (CH_2Cl_2 ; RT under argon ; 1 hr). **9** is thus obtained as a violet solid [98% yield from **8** ; ^1H NMR spectrum ($CDCl_3$) shows characteristic peaks at δ 10.10 ppm (CHO) and -2.71 ppm (porphyrinic NH) ; λ_{max} (CH_2Cl_2) : 420, 518, 554, 592, 647 nm].

Quantitative conversion of **9** to its zinc(II) complex **10** is performed by an excess of $Zn(OAc)_2.2H_2O$ in refluxing $CHCl_3/CH_3OH$ (98:2). The role of the zinc atom within the tri-p-tolyl porphyrin (TrTP) subunit of **10** is to protect the corresponding coordination site and further allow preparation of dissymetric systems. When 63 equivalents of 3,5 diterbutyl-benzaldehyde[10] are reacted with one equivalent of **10** and 64 equivalents of pyrrole in boiling propionic acid for 20 hrs, a mixture of several porphyrinic compounds is obtained. After repeated chromatographic separations on silica a surprisingly high yield of bis-porphyrins is obtained : 0.15 equivalents for **1** (15%) and 0.10 equivalents for 2 (10%).[11] In addition, 2.5 equivalents of tetra(3,5-di-t-butylphenyl) porphyrin and 1,4 equivalents of its zinc complex are isolated. Structural assignement of 1 is based on mass spectroscopy (FAB using a tetraglyme matrix, M + H^+ 1784.8, $C_{127}H_{118}N_{10}$ requires 1784,4), ^{1}H NMR and electronic spectra [λ_{max} (log ϵ) (CH_2Cl_2) : 419 (5.60), 517 (4.26), 553 (4.05), 592 (3.75), 648 nm (3.79) ; mp 113-115].

Reaction of 1 or 2 with an excess of $Zn(OAc)_2.2H_2O$ leads to quantitative formation of 3, as shown by ^{1}H NMR, mass and UV-visible spectroscopy. [3 : λ_{max} (log ϵ) (CH_2Cl_2) : 420 (5.29), 550 (4.00), 589 nm (3.36) ; M + H^+ : 1912.1]. The chemical structure of 2 is demonstrated by the presence of patterns characteristic of both a Zn(II) porphyrin and a free tetrapyrrolic cycle in the visible spectrum [λ_{max} (log ϵ) (CH_2Cl_2) : 420 (5.57) ; 517 (4.00), 551 (4.15), 591 (3.68), 648 nm (3.40) ; M + H^+ : 1848.6].

Acknowledgements: We thank the CNRS for financial support, Dr. P. Mathis (CEA, Saclay) for discussions. Dr. A. Van Dorsselaer and Mr. R. Hueber are also gratefuly acknowledged for mass spectral analyses.

References

1 J. Deisenhofer, O. Epp, K. Miki, R. Huber, and H. Michel, J. Mol. Biol., 1984, **180**, 385.

2 G. Dubowchik, and A.D. Hamilton, J. Chem. Soc., Chem. Commun., 1985, 904.
G. Dubowchik, and A.D. Hamilton, J. Chem. Soc., Chem. Commun., 1986, 1391.

3 M.R. Wasielewski, M.P. Niemczyk, and W.A. Svec, Tetrahedron Lett., 1982, 3215.

4 G. Dubowchik, and A.D. Hamilton, J. Chem. Soc., Chem. Commun., 1987, 293.

5 J.A. Cowan, J.K.M. Sanders, G.S. Beddard, and R.J. Harrison, J. Chem. Soc., Chem. Commun., 1987, 55.

6 I. Tabushi, and T. Sasaki, Tetrahedron Lett., 1982, 1913.
I. Tabushi, S. Kugimiya, and T. Sasaki, J. Am. Chem. Soc., 1985, **107**, 5159.

7 M. Cesario, C.O. Dietrich-Buchecker, J. Guilhem, C. Pascard, and J.P. Sauvage, J. Chem. Soc., Chem. Commun., 1985, 244.

8 C.O. Dietrich-Buchecker, P.A. Marnot, and J.P. Sauvage, Tetrahedron Lett., 1982, **23**, 5291.

9 A.D. Adler, F.R. Longo, J.D. Finarelli, J. Goldmacher, J. Assour, and L. Korsakoff, J. Org. Chem., 1967, **32**, 476.

10 M.S. Newman, and L.F. Lee, J. Org. Chem., 1972, **37**, 4468.This aldehyde was used in order to increase the solubility of the final product.

11 The protecting effect of Zn^{2+} is only partial since the free base 1 is obtained in significant yield. However, detailed mass spectral analysis (FAB) of 2 shows that Zn^{2+} is indeed located in the TrTP site ; exchange of Zn^{2+} between the two porphyrinic rings is minor.

(Received in France 25 August 1987)