cis–trans Isomerisation and Atropisomerism of Octaethyl 1,2-bis(coproporphyrinyl)ethylene Ester

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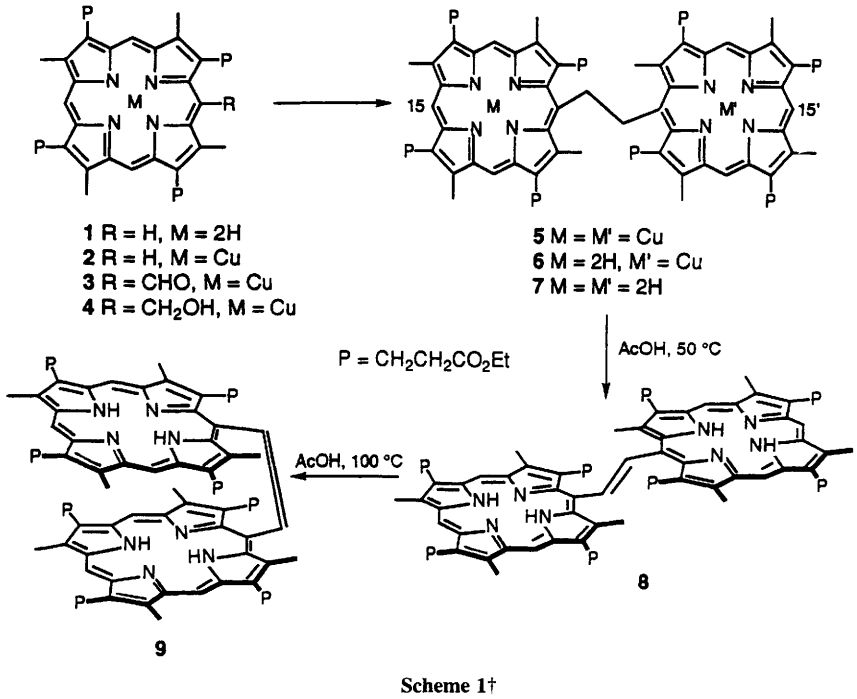
Oxidation of the ethane-bridged dimer of coproporphyrin-I proceeds stereoselectively to produce only the sterically unhindered *trans*-ethylene-bridged atropisomer, which undergoes thermal isomerisation to give two atropisomers of the *cis*-dimer.

Porphyrin dimers with a well-defined structural organization serve as the most reliable models to study the primary charge separation process in photosynthesis.[1]. For this purpose we have recently prepared a series of *trans*- and *cis*-ethylene-bridged porphyrin dimers.[2–5] In order to study further the mechanism of the facile oxidation of the ethane-bridged dimers[2–4] and the *cis–trans* isomerisation[5] of the ethylene-bridged dimers, we have synthesized new porphyrin dimers of the unsymmetrically substituted coproporphyrinyl-I ester **1** using the reported methods.[3,5,6] Application of the coproporphyrin derivatives allow the individual atropisomers of these dimers to be distinguished, and their influence on the reaction course of chemical transformations to be studied. Here, we report the *cis–trans* isomerisation and atropisomerism of coproporphyrin dimers studied by ^{1}H NMR.

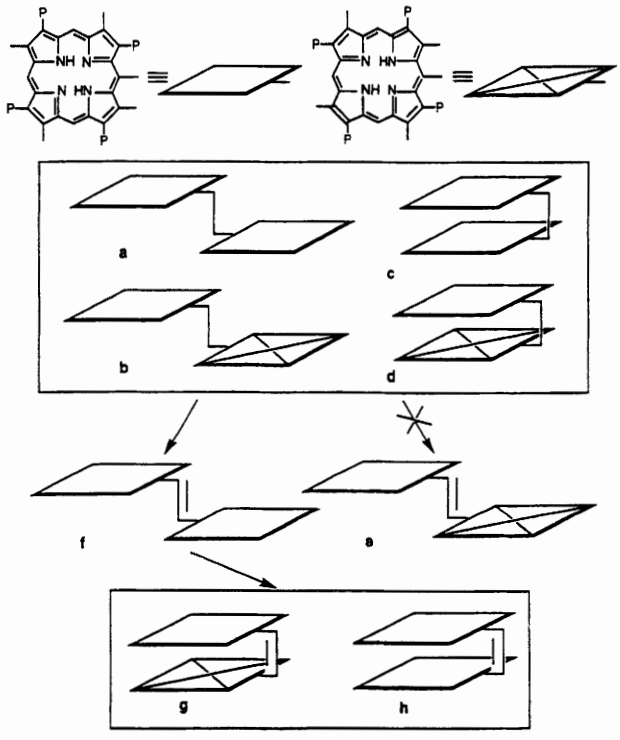
The synthetic route is shown in Scheme 1. The Cu complex **2** obtained by treatment of the free base **1** with $Cu(OAc)_2$ was formylated by the Vilsmeier reaction, followed by the reduction of **3** with $NaBH_4$ in MeOH–$CHCl_3$ to give the hydroxy derivative **4** in a total yield of 75%. Dimerization of **4** into **5** was carried out according to the literature method[3,5] in 46% yield and **5** was demetallated with H_2SO_4–TFA to yield the ethane dimer **7** in 65% yield. In contrast to the facile demetallation in other types of ethane porphyrins[3,6,7] and chlorins,[8] the demetallation of **5** proceeds slowly‡ and in a step-wise manner through heterodimer **6**,§ probably due to steric hindrance caused by propionic ester residues. Oxidation of **7** in AcOH at 30–40 °C produced the *trans*-dimer **8** in a quantitative yield. Increasing the temperature to 60 °C yielded a mixture of **8** and **9** in 76 and 8% yields, respectively.

The presence of the two different types of substituents in the coproporphyrin-I derivatives suggests the existence of four conformers **a**–**d** for **7** and two pairs of atropisomers, **e** and **f** for **8** and **g** and **h** for **9** (Scheme 2). In the ^{1}H NMR spectrum of **7**¶ there are five singlets in the *meso*-proton region in a 2 : 1 : 1 : 1 : 1 ratio indicating the existence of atropisomers. A signal at δ 9.85 with 2 H intensity, assigned to protons at the 15,15′-positions, is not strongly affected by atropisomerism. While the other four *meso*-protons at the 10,10′,20,20′-positions must be greatly dependent on the internal disposition of macrocycles in dimer **7** that is different for each atropisomers. Owing to this dependence, considerable upfield shifts of these protons (by 2 ppm), caused by the folded *syn*-conformations **c** and **d** in dimer **7**, have been observed. The presence of four complex multiplets from the bridged CH_2–CH_2 protons, which interact with each other in the corresponding pairs, also indicates the existence of atropisomers **a**, **b**, **c** and **d**.

Oxidation of ethane **7** into the *trans*-dimer **8** occurred only from conformer **a**; the formation of the less sterically hindered atropisomer **f**‖ has been exclusively observed during and after the reaction. The assignment of the structure of **f** (**8**) was done by ^{1}H-^{1}H ROESY and ^{1}H-^{1}H COSY spectra. The ^{1}H NMR spectrum of this atropisomer showed that all the signals of the



Scheme 1†



Scheme 2

CH_2COEt groups at the 3,3′-positions were shifted upfield by 1.33 ppm compared to those of the other propionic chains due to the ring current effect of the neighbouring porphyrin ring. Strong COSY peaks from the upfield shifted CH_2CH_2CO triplets at the 3,3′-positions and the CH_2CH_2CO overlapping triplets were observed. By using a spin-locking field technique the positive NOE cross peak in the ROESY spectrum due to through space interactions between the CH_3 protons at the 7,7′-positions and the CH_2CH_2CO propionic chain protons at the 3′,3-positions, correspondingly, were detected indicating that these methyl groups were located under and above the propionic residues in close proximity to their methylene fragments. These data were in good agreement with the X-ray analysis[9] of the *trans*-isomer of octaethylporphyrin. No positive cross peaks in the ROESY spectrum from other CH_3 protons at the 2,2′,12,12′,17,17′-positions and CH_2CH_2CO protons from the propionic chains at the 8,8′,13,13′,18,18′-positions were observed.

Heating **8** in boiling AcOH led to an equilibrium mixture of *trans*- and *cis*-forms in a 23 : 77 ratio indicating the energetic advantage of the *cis*-isomer owing to π-π interactions of porphyrin rings and the large steric hindrance between the lateral propionic substituents in the *trans*-isomer. Similar behaviour has even been observed for sterically less-hindered octaethylporphyrin dimers by ^{1}H NMR[2,5] and X-ray[9,10] analyses. On the basis of the ^{1}H NMR spectrum of *cis*-dimer **9**** it may be concluded that isomerisation of *trans*-**8** to *cis*-dimer **9** occurs by rotation of the porphyrin rings in the intermediate state to produce stable atropisomers **g** and **h** in a 2 : 1 ratio, the less-sterically hindered isomer **g** is formed in a larger amount. The positions of the *meso*, CH=CH and CH_3 protons are different in each atropisomers. Atropisomers **g** and **h** were not able to transform thermally to each other due to sterical hindrance, although this may be possible through back isomerisation to the *trans*-isomer.

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Footnotes

† Only one atropisomer of **9** is shown; all atropisomers are presented in Scheme 2.

‡ Full demetallation is completed after 6 h.

§ Usually monometallated ethane-bridged dimers are prepared by H_2SO_4–CF_3CO_2H treatment according to G. V. Ponomarev and A. M. Shul'ga, SU Pat. 1172923 (1985); *Chem. Abstr.*, 1986, **104**, 186243a.

¶ *Selected spectroscopic data* for 7: ^{1}H NMR ($CDCl_3$ 360 MHz) δ 9.85 (s, 2 H, 15,15′-meso-H), 8.89, 8.54, 8.49, 8.10 (all s, 4 H, 10,10′,20,20′-*meso*-H), 5.55, 5.40, 5.12, 4.96 (all m, 4 H, CH_2CH_2), 4.56–1.75 (m, 48 H, CH_2CH_2CO and CH_2CH_3), 3.72, 3.70, 3.45, 3.38, 3.06, 2.74, 1.78, 1.38 (all a, 24 H, CH_3), 1.26–0.99 (m, 24 H, CH_2CH_3), −3.90, −4.99, −5.01 (all br s, 4 H, NH); MS (EI) *m/z* 1561 [(M+ 3)$^+$, 50%], 1489 (8), 794 (15), 780 (100), 766 (30), 708 (22).

‖ *Selected spectroscopic data* for **8**: ^{1}H NMR ($CDCl_3$, 360 MHz) δ 10.10, 10.09, 9.90 (all s, 6 H, *meso*-H), 8.52 (s, 2 H, CH=CH), 4.40–4.38, 4.26, 3.31–3.23, 2.42 (overlapping t, t, 32H, CH_2CH_2CO), 4.25–4.21, 3.03 (overlapping q, q, 16 H, CH_2CH_3), 3.71, 3.67, 3.63, 3.20 (all s, 24 H, CH_3), 1.26, 1.24, 1.22, −0.07 (all t, 24 H, CH_2CH_3), −2.56 (br s, 4 H, NH); MS (EI) *m/z* 1560 [(M + 4)$^+$ 100%], 780 (40).

** *Selected spectroscopic data* for **9** (Integral intensities of the signals have been calculated for the mixture of **g** and **h** atropisomers in 2 : 1 ratio); ^{1}H NMR ($CDCl_3$, 360 MHz) for **g**: δ 9.72, 9.59, 8.71, 7.30 (all s, 16 H, *meso*-H, CH=CH), 3.61, 3.55, 3.30, 1.44 (all s, 48 H, CH_3); for **h**: 9.70, 9.60, 8.12, 7.93 (all s, 8 H, *meso*-H, CH=CH), 3.63, 3.21, 3.07, 2.12 (all s, 24 H, CH_3); for **g** and **h**: 4.50–2.00 (overlapping m, 144 H, CH_2CH_2CO and CH_2CH_3), 1.28–1.05 (overlapping t, 72 H, CH_2CH_3), −4.70, −4.90, −5.53, −5.70 (all br s, 12 H, NH); MS (EI) *m/z* 1560 [(M + 4)$^+$ 100%], 780 (50).

References

1 M. R. Wasielewski, *Chem. Rev.*, 1992, **92**, 435.
2 G. V. Ponomarev and A. M. Shul'ga, *Khim. Geterocycl. Soed.* 1986, 278.
3 A. M. Shul'ga and G. V. Ponomarev, *Khim. Geterocycl. Soed.*, 1988, 339.
4 V. V. Borovkov, G. V. Ponomarev, A. Ishida, T. Kaneda and Y. Sakata, *Chem. Lett.*, 1993, 1409.
5 G. V. Ponomarev, V. V. Borovkov, K. Sugiura, Y. Sakata and A. M. Shul'ga, *Tetrahedron Lett.*, 1993, **34**, 2153.
6 G. V. Ponomarev and A. M. Shul'ga, *SU Pat.*, 1172922, (1985); *Chem. Abstr.*, 1986, **104**, 168272e.
7 D. Arnold, A. W. Johnson and M. Winter, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1643.
8 K. M. Smith, G. M. F. Bisset and M. J. Bushell, *Bioorg. Chem.*, 1980, **9**, 1.
9 R. Kitagawa, Y. Kai, G. V. Ponomarev, K. Sugiura, V. V. Borovkov, T. Kaneda and Y. Sakata, *Chem. Lett.*, 1993, 1071.
10 M. O. Senge, K. R. Gerzevske, M. G. H. Vicente, T. P. Forsyth and K. M. Smith, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 750.