



Synthesis of Calamitic, Liquid Crystalline Porphyrins With Lateral Aromatic Branches

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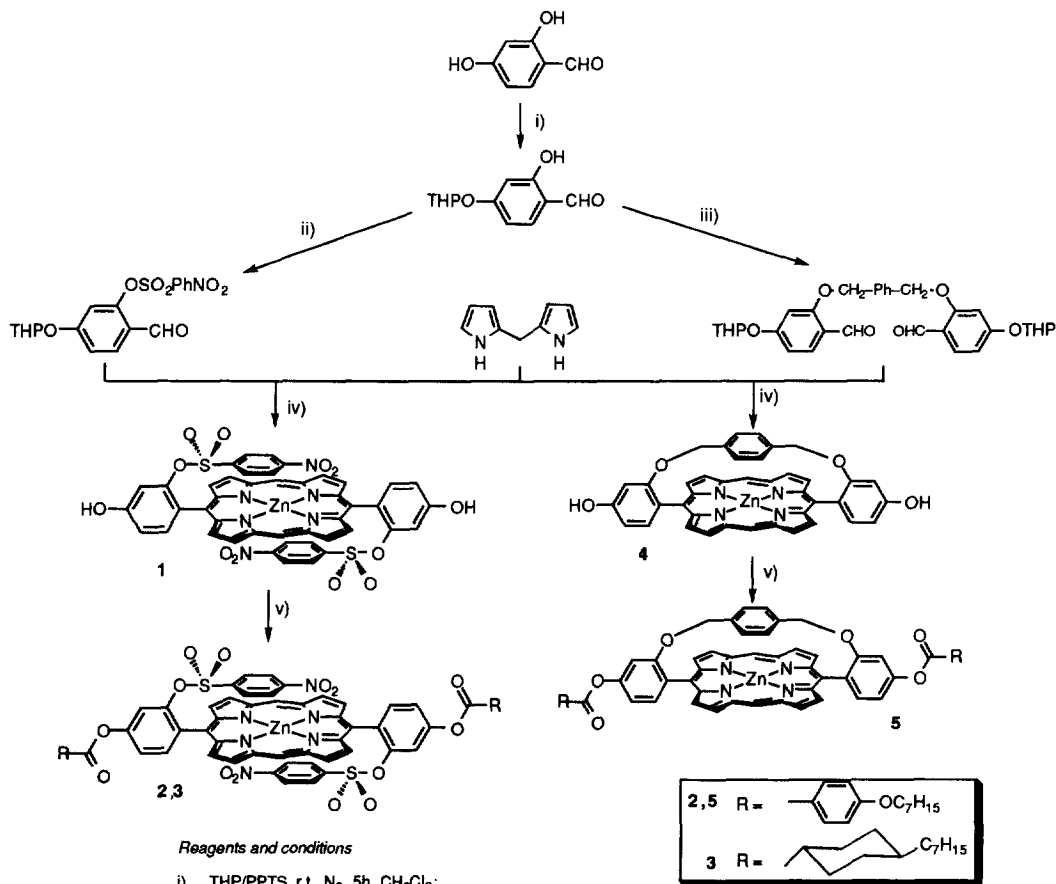
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Abstract: The lateral, electron-accepting aromatic substituent was successfully used to obtain a conformationally pure, laterally substituted liquid crystalline porphyrin. In addition, the attempt to synthesise a strapped, rod-like porphyrin showed that the planarity of the porphyrin core could be crucial in molecular design to synthesise strapped liquid crystalline porphyrin. Copyright © 1996 Elsevier Science Ltd

To date, peripherally octasubstituted porphyrins have been shown to lead, in a relatively straightforward manner, to systems showing columnar mesophases^[1a-e] because of the inherently disc-like shape of the molecular core. Later work on columnar systems was focused on *meso*-tetrasubstituted porphyrins.^[1f-g] However, in so-called calamitic liquid crystal materials, the materials are inherently rod-like and the mesophases (e.g. nematic and smectic) result from the organisation of the molecules *via* correlation of the long molecular axes. For some time, it has been known that certain classes of rod-shaped molecules can give rise to columnar phases.^[2] In spite of the above facts, the simple idea in which inherently disc-like porphyrins could be persuaded to be rod-like liquid crystals in their behaviour was first realised by us with the synthesis of 5,15-disubstituted porphyrins.^[3,4] Our recent studies have also shown that inherently disc-like porphyrins can be made to be rod-like liquid crystals with low melting points, using lateral substitution to prevent intermolecular π - π interactions.^[5] However, the different conformations of lateral substituents on the *ortho* positions of the inner benzene rings were observed, i.e., α,α - and α,β -atropisomers. The α,β -atropisomer favoured self-organisation of the liquid crystal phase, and thus exhibited a nematic phase, while the α,α -atropisomer prevented the formation of a nematic phase. In order to obtain a conformationally pure, laterally substituted liquid crystalline porphyrin, it is essential to control the conformation of lateral substituents. In this report, we describe efforts to design such materials, using intramolecular "donor-acceptor" and strapped strategies to restrict the rotation of the two inner benzene rings around the porphyrin core-phenyl bonds, which is responsible for the atropisomerism.

The synthesis of the intramolecular 'donor-acceptor' liquid crystalline porphyrins is illustrated in the scheme, in which the *ortho*-(*para*-nitrophenylsulfonyl)oxy group was used as a lateral group because of its strong electron-accepting ability.^[6] Thus, after the protection of the hydroxy group on the *para* position of 2,4-dihydroxyaldehyde, the product was reacted with *para*-nitrophenylsulfonyl chloride in dry pyridine by a previously reported method,^[6] giving a yellowish product of the aldehyde in a yield of 60%. This aldehyde was

then condensed with β ,*meso*-unsubstituted dipyrromethane^[7] in 50:50 methanol-dichloromethane with $\text{BF}_3\cdot\text{OEt}_2$ catalysis under N_2 . Oxidation with *p*-chloranil and metallation with $[\text{Zn}(\text{OAc})_2]$ gave the desired porphyrin **1** in 27% yield. Porphyrin **1** was then esterified to afford the final diester porphyrins **2-3** in 45% and 52% yields, respectively, using the DCC/DMAP method in the presence of activated molecular sieves. Porphyrins **2-3** were purified by flash column chromatography (silica gel, 230-400 mesh, dichloromethane as eluent). Similarly, the scheme also shows the route used for the synthesis of the strapped, rod-like porphyrin **5**. In the scheme, the deprotection of the THP-ether occurred in the condensation steps. This was particularly important in the synthesis of porphyrin **5** as the unprotected, strapped dialdehyde was both air sensitive and acid labile. All the porphyrin diesters were characterised by UV/Vis, ^1H NMR, (+ve)FAB MS and elemental analysis.^[8]



Scheme Synthesis of the new porphyrins

The absorption of porphyrins **2-3** shows the red-shift of both the Soret and Q bands by 1-3 nm and 2-5 nm, respectively, compared with their parent porphyrins without the two lateral aromatic branches. This indicated that the ground state interaction between the porphyrin and the nitrophenylsulfonfyl group existed due to their proximity in space. As far as porphyrin **5** is concerned, comparison of its electronic absorption with that of the

parent porphyrin without the xylyl strap, shows a red-shift of both the Soret and Q bands, greater than those of porphyrins 2-3, indicating the existence of a distorted porphyrin ring owing to the short strap of the xylene unit. A similar red-shift has been found for related, distorted porphyrins.^[9]

The ¹H NMR spectra of porphyrins 2-3 in CDCl₃ showed that the protons of two lateral phenyl groups were shifted upfield to 5.30 and 5.70 ppm (8.10 and 8.40 ppm in the starting aldehyde), which could be associated with a porphyrin ring current effect.^[6] This suggested that the α,β -atropisomer was the major form in solution, though a tiny amount of the α,α -atropisomer was found. This suggested the presence of a charge-transfer interaction between porphyrin and nitrophenylsulfonyl group which restricted the rotation of the two inner benzene rings around the porphyrin core-phenyl bonds. This has previously been observed in otherwise unsubstituted porphyrins bearing a nitrophenylsulfonyl group.^[6] It was noted that on warming, a mixture of the α,β -atropisomer (68%) and the α,α -atropisomer (32%) was observed by NMR. Comparison of porphyrin 5 with the dialdehyde indicates that the methylene and phenyl protons in the strap were shifted significantly upfield, resulting from porphyrin ring current effects. The *ortho* protons of the *meso* phenyl groups were also considerably downfield shifted to 9.10 ppm in porphyrin 5, showing that the *meso* phenyl groups were tilted so that the *ortho* protons may be switched into the deshielding area of the porphyrin ring current. Moreover, the peripheral protons in porphyrin 5 were shifted upfield with respect to its parent porphyrin (without the xylyl strap). As these protons were in the deshielding area of the ring current, the upfield shifts may be due to the decrease of the porphyrin ring current, suggesting the distortion from the planarity in porphyrin 5. Combining the distortion of the porphyrin ring with the tilted conformation of *meso* phenyl groups, it could be derived that porphyrin 5 was bent about the porphyrin core. Thus, the rod-like shape of porphyrin 5 was detrimentally changed.^[10]

The thermal behaviour of porphyrins 2, 3 and 5 was investigated by polarising optical microscopy and differential scanning calorimetry. Porphyrin 2 melted at 310 °C ($\Delta H = 71.8 \text{ kJ mol}^{-1}$) to give a nematic phase which persisted until 338 °C where decomposition occurred. The relatively narrow nematic phase range is attributed to the presence of the large lateral aromatic branches.^[11] It was found that porphyrin 3 was thermally less stable than porphyrin 2, and decomposition appeared to commence on melting at 323 °C. Thus, no mesophase was observed. It is important that no α,α -atropisomer was detected by microscopy or DSC, though the ¹H NMR demonstrated that the quantity of the α,α -atropisomer in solution increased on heating. This suggests that in this case, isomerisation between the α,α - and α,β - atropisomers occurs only in solution, in contrast to the situation with lateral alkoxy groups where we have found it to occur in the solid state.^[5] For porphyrin 5, as discussed previously, the short xylene strap resulted in a bent porphyrin core. Thus, it showed only a crystal-crystal transition at 213 °C ($\Delta H = 7.8 \text{ kJ mol}^{-1}$) before melting at 317 °C ($\Delta H = 51.9 \text{ kJ mol}^{-1}$).

In conclusion, the lateral electron-accepting substituent was successfully used to control the conformation of lateral branches in mesomorphic porphyrins; such liquid crystalline porphyrins may offer possibilities for the study of through-space electron transfer processes in the mesophase. In addition, the planarity of the porphyrin core is found to be crucial in determining the mesomorphism in porphyrins.

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References and Notes

1. a) Bruce, D.W.; in *Inorganic Materials*, ed. Bruce, D.W.; O'Hare, D.; Wiley, Chichester, **1992**; b) Gregg, B.A.; Fox, M.A.; Bard, A.J.; *J. Chem. Soc., Chem. Commun.*, **1987**, 1135; d) Gregg, B.A.; Fox, M.A.; Bard, A.J.; *J. Am. Chem. Soc.*, **1989**, *111*, 3024; e) Gregg, B.A.; Fox, M.A.; Bard, A.J.; *J. Phys. Chem.*, **1990**, *94*, 1586; f) Shimizu, Y.; Miya, M.; Nagata, A.; Ohta, K.; Matsumura, A.; Yamamoto, I.; Kusabayashi, S.; *Liq. Cryst.*, **1993**, *14*, 795; g) Ramasseul, R.; Maldivi, P.; Marchon, J.C.; Taylor, M.; Guillon, D.; *Liq. Cryst.*, **1993**, *13*, 729.
2. Malthête, J.; Nguyen, H.T.; Destrade, C.; *Liq. Cryst.*, **1993**, *13*, 171.
3. Bruce, D.W.; Dunmur, D.A.; Santa, L.S.; Wali, M.A.; *J. Mater. Chem.*, **1992**, *2*, 363.
4. Bruce, D.W.; Wali, M.A.; Wang, Q.M.; *J. Chem. Soc., Chem. Commun.*, **1994**, 2089.

5. Wang, Q.M.; Bruce, D.W.; submitted.
6. Sanders, G.M.; van Dijk, M.; van Veldhuizen, A.; van der Plas, H.C.; Hofstra, U.; Schaafsma, T.J.; *J. Org. Chem.*, **1988**, *53*, 5272.
7. Wang, Q.M.; Bruce, D.W.; *Synlett*, **1995**, 1276.
8. *Porphyrin 2*: ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD}$, warmed sample, room temperature, 250 MHz): $\delta = 0.85$ (t, 6H, 2CH₃); 1.20-1.40 (m, 12H, 6CH₂); 1.47 (m, 4H, 2CH₂); 1.82 (m, 4H, 2CH₂); 4.07 (t, 4H, 2xOCH₂); 5.33 & 5.67 [$\alpha,\beta-$, 68%, AA'XX', J = 8.9Hz] and 6.59 & 6.66 [$\alpha,\alpha-$, 32%, AA'XX', J = 9.2Hz] (8H, two lateral phenyl); 7.05 & 8.28 (m, 8H, two terminal phenyl, AA'XX', J = 8.9Hz); 7.52 [$\alpha,\alpha-$, dd, J = 8.2Hz, J' = 2.4Hz] and 7.63 [$\alpha,\beta-$, dd, J = 8.2Hz, J' = 2.4Hz] (2H); 7.81 [$\alpha,\beta-$, d, J = 2.4Hz] and 7.90 [$\alpha,\alpha-$, d, J = 2.4Hz] (2H); 8.03 [$\alpha,\alpha-$, d, J = 8.2Hz] and 8.28 [$\alpha,\beta-$, d, J = 8.2Hz] (2H); 8.69 [$\alpha,\alpha-$, d, AB, J = 4.6Hz] and 8.77 [$\alpha,\beta-$, d, AB, J = 4.6Hz] (4 β H); 9.21 [$\alpha,\alpha-$, d, AB, J = 4.6Hz] and 9.23 [$\alpha,\beta-$, d, AB, J = 4.6Hz] (4 β H); 10.14 [$\alpha,\beta-$, s] and 10.15 [$\alpha,\alpha-$, s] (2 meso-H). UV/Vis spectrum (λ_{max} , nm, CH₂Cl₂, 20°C): 412.5; 542.4; 576.4. Elemental analysis (%): C₇₂H₆₂N₆O₁₆S₂Zn found (required): C, 61.9(61.9); H, 4.4(4.5); N, 5.9(6.0); S, 4.6(4.6). (+ve) FAB MS (m/e): found: 1396 [M⁺]; required: 1396.83.
- Porphyrin 3*: ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD}$, warmed sample, room temperature, 250 MHz): $\delta = 0.87$ (t, 6H, 2CH₃); 1.10 (m, 4H, 2H_{3ax} + 2H_{5ax}); 1.27 (m, 26H, 12CH₂ + 2H₄); 1.77 (m, 4H, 2H_{2ax} + 2H_{6ax}); 1.96 (m, 4H, 2H_{3eq} + 2H_{5eq}); 2.30 (m, 4H, 2H_{2eq} + 2H_{6eq}); 2.67 (m, 2H, 2H₁); 5.33 & 5.66 [$\alpha,\beta-$, 68%, AA'XX', J = 8.9Hz] and 6.59 & 6.70 [$\alpha,\alpha-$, 32%, AA'XX', J = 9.2Hz] (8H, two lateral phenyl); 7.39 [$\alpha,\alpha-$, dd, J = 8.2Hz, J' = 2.1Hz] and 7.50 [$\alpha,\beta-$, dd, J = 8.2Hz, J' = 2.1Hz] (2H); 7.68 [$\alpha,\beta-$, d, J = 2.1Hz] and 7.77 [$\alpha,\alpha-$, d, J = 2.4Hz] (2H); 8.00 [$\alpha,\alpha-$, d, J = 8.2Hz] and 8.27 [$\alpha,\beta-$, d, J = 8.2Hz] (2H); 8.66 [$\alpha,\alpha-$, d, AB, J = 4.6Hz] and 8.75 [$\alpha,\beta-$, d, AB, J = 4.6Hz] (4 β H); 9.21 [$\alpha,\alpha-$, d, AB, J = 4.6Hz] and 9.23 [$\alpha,\beta-$, d, AB, J = 4.6Hz] (4 β H); 10.14 [$\alpha,\beta-$, s] and 10.15 [$\alpha,\alpha-$, s] (2 meso-H). UV/Vis spectrum (λ_{max} , nm, CH₂Cl₂, 20°C): 412.5; 542.4; 577.1. Elemental analysis (%): C₇₂H₇₄N₆O₁₄S₂Zn found (required): C, 62.8(62.8); H, 5.3(5.4); N, 6.0(6.1); S, 4.7(4.7). (+ve) FAB MS (m/e): found: 1376 [M⁺]; required: 1376.92.
- Porphyrin 5*: ^1H NMR ($\text{CDCl}_3/\text{CD}_3\text{OD}$, 250 MHz): $\delta = 0.91$ (t, 6H, 2CH₃); 1.26-1.50 (m, 16H, 8CH₂); 1.86 (m, 4H, 2CH₂); 3.12 & 3.17 (s, 8H, 1 phenyl + 2xOCH₂ in the strap); 4.08 (t, 4H, 2xOCH₂); 6.77 (d, 2H, J = 2Hz); 7.04 & 8.26 (m, 8H, two terminal phenyl, AA'XX', J = 8.9Hz); 7.59 (dd, 2H, J = 8.2Hz, J' = 2.3Hz); 9.06 & 9.36 (d, 8H, 8 β H, AB, J = 4.6Hz); 9.09 (d, 2H, J = 8.2Hz); 10.13 (s, 2H, 2meso-H). UV/Vis spectrum (λ_{max} , nm, CH₂Cl₂, 20°C): 416.0; 544.8; 582.8. Elemental analysis (%): C₆₈H₆₂N₄O₈Zn found (required): C, 72.0(72.4); H, 5.4(5.5); N, 4.9(5.0). (+ve) FAB MS (m/e): found: 1128 [M⁺]; required: 1128.65.
9. a) Osuka, A; Kobayashi, F.; Maruyama, K.; *Bull. Chem. Soc. Jap.*; **1991**, *64*, 1213; b) Bonar-Law, R.P.; Sanders, J.K.M.; *J. Chem. Soc., Perkin Trans. 1*, **1995**, 3085.
10. Note added in proof. The single crystal structure of a related xylyl-strapped porphyrin has recently been solved, showing the bent nature of the porphyrin core. Chen, J.; Wang, Q.M.; Arnold, J.; unpublished results.
11. Demus, D.; *Liq. Cryst.*, **1989**, *5*, 75.

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