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Synthesis of Totally Rigid Covalently Linked Bis-Porphyrin Systems for Studying Long–Range Electron Transfer and Energy Transfer Processes

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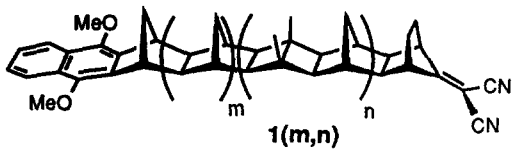
Abstract: The synthesis of novel rigid covalently linked bis-porphyrin systems, **3 – 5**, and the monoporphyrin model, **6**, is described. The synthetic strategy entails formation of *o*–phenylenediamine units, **11**, and their reaction with the dioxotetraphenylchlorin, **12**.

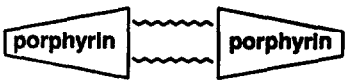
Considerable progress has been made recently in understanding the factors that govern long range electron and energy transfer processes.[1] This has been made possible largely through the construction of rigid, covalently linked polychromophoric, Donor–{bridge}–Acceptor systems in which the chromophores are fixed at well defined separations and orientations, thereby enabling the determination of the distance and orientation dependence of ET to be made with the minimum of ambiguity.[2,3] In this respect, systems such as **1(m,n)**, because of the symmetry and rigidity of the polynorbornyl bridge, have provided much valuable insight.[3] It would be desirable to synthesize a variety of rigidly linked bis–porphyrin molecules, **2**, built around the polynorbornyl bridge, whose length and configuration can be systematically varied, since they would be useful models for investigating electron and energy transfer processes that are associated with the "special pair" in the bacterial photosynthetic reaction centre.[4]

We report the synthesis of the rigid bis–porphyrins, **3 – 5**. Crystal structure studies on related systems[6b,6d] suggest that, in **3** and **4**, the angle between the planes of the porphyrin units is *ca* 100°, and the edge–to–edge separation between the two chromophores is *ca* 5.2 Å (for **3**) and 7.6 Å (for **4**). For **5**, the rings are *ca* 6 Å apart and are canted towards each other by *ca* 23°. The synthesis of the monoporphyrin model compound, **6**, is also reported. Although other bis–porphyrin systems have been synthesized and studied,[4,5b] molecules **3 – 5** are unique in terms of their combined symmetry and total rigidity, and by the fact that they are connected to each other by a saturated bridge, rather than a conjugated bridge.

† Deceased January 24, 1993. A tragic loss of a fine young chemist and friend.



1(m,n)



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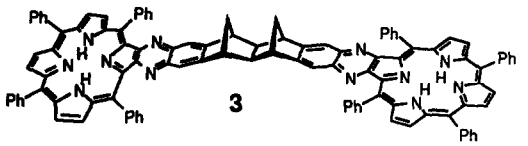

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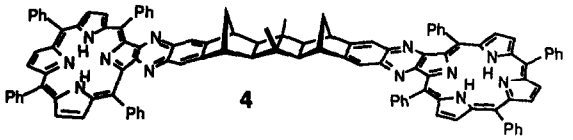

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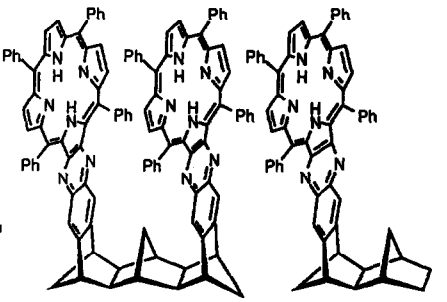
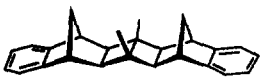
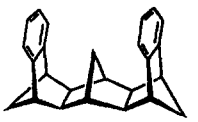


5 6

3a



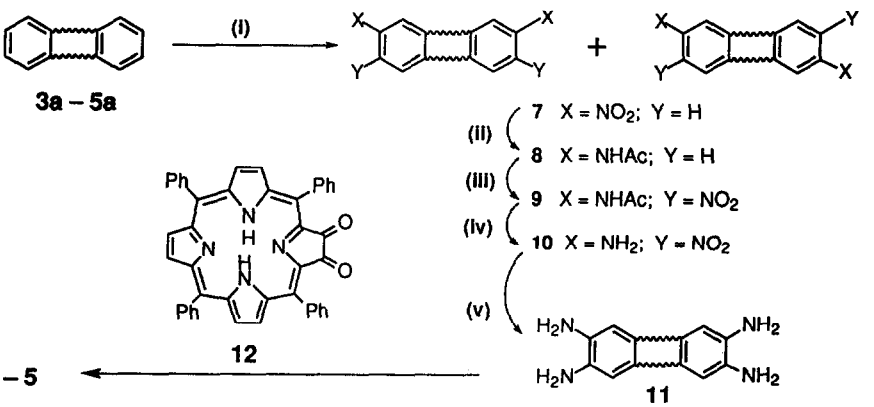
4a



5a

6a

Scheme



Reagents: (i) $Cu(NO_3)_2$, Ac_2O, 0° C; 3–5 h; (ii) Zn, AcOH/Ac_2O (10:1), reflux, 17 h; (iii) AcOH/Ac_2O (1:1), HNO_3, 0° C, 1 h; (iv) $NH_2NH_2.H_2O$, reflux, 17 h; (v) $NH_2NH_2.H_2O$/EtOH (1:10), 10% Pd/C, reflux, 30 – 90 min.

The strategy is shown in the Scheme and is based on Crossley's synthesis of conjugatively bridged bis–porphyrin systems through reaction of dioxochlorin, **12**,[5a] with benzene–1,2,4,5–tetramine.[5b] The starting point is the appropriate dibenzo system, **3a – 5a**; these compounds are readily obtained from the corresponding dienes employing known annelation techniques.[6] Nitration of the dibenzo compound ($Cu(NO_3)_2$, Ac_2O)[7] gave a *ca* 50:50 mixture of two diastereomeric dinitro compounds, **7** in which each aromatic ring was mononitrated (*ca* 83% yield). This mixture was not separated since both diastereomers eventually give the desired symmetrical tetra–amines, **11**.

Reductive acylation of the mixture of dinitro compounds, **7**, (Zn/AcOH), followed by nitration gave the mixture of bis-*o*-nitroamides, **9** (*ca* 63% yield). The bis–aminonitro compounds, **10**, were obtained by treatment of **9** with hydrazine hydrate (*ca* 66% yield). Reduction of **10** to the tetra–amine, **11**, was achieved using hydrazine hydrate and 10% Pd/C (*ca* 64% yield). The ^1H nmr spectra of these amines indicated restoration of C_{2v} molecular symmetry. For example, the four aromatic protons in each tetra–amine occur as a sharp singlet, at δ ($CDCl_3$) 6.54, and 6.50 ppm for the precursors of **3** and **4**, respectively, and at 6.30 ppm for the precursor of **5**. Treatment of tetra–amine **11** with dione **12**[5,7] gave the respective bis–porphyrin, **3 – 5** in *ca* 12% overall yield from the dibenzo systems, **3a – 5a**.[8] In a similar fashion, the monoporphyrin system, **6**, was synthesized from the dimethanoanthracene, **6a**.[8]

The ^1H nmr spectra of **3 – 6** reveal that the quinoxoline protons and the three sets of pyrrole protons in **5** are shielded, by about 0.3 ppm, compared to the corresponding protons in the monoporphyrin system, **6**, and in the bis–porphyrin molecules, **3** and **4**. This observation suggests that the near cofacial arrangement of the porphyrin rings in **5** results in shielding of the protons of one ring by the ring current of the other. The N–H protons in **5** are likewise shielded, by 0.4 ppm with respect to the N–H protons in **3** and **4**, and by 1.3 ppm, with respect to those in **6**. As expected,[6b] the methylene CH_2 protons of the central norbornyl bridge in **5** occur at high field (δ –1.53), which is due to the combined ring current effects of both rings. The chemical shift of the corresponding methylene proton that points towards the porphyrin ring in the monoporphyrin system, **6** is less pronounced of course (δ –0.70).

The electronic interactions in **3 – 5**, and their metalated derivatives, is under active investigation and the photophysics of these interesting systems will be reported shortly.

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REFERENCES AND NOTES

1. (a) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265–322. (b) Miller, J. R.; Closs, G. L. *Science* **1988**, *240*, 440. (c) Wasielewski, M. R. Photoinduced Electron Transfer, Part D, Fox, M. A.; Chanon, M. Eds.; Elsevier: Amsterdam, 1988; chap. 1.4. (d) Paddon–Row, M. N.; Verhoeven, J. W. *New. J. Chem.* **1991**, *15*, 107.
2. (a) Calcaterra, L. T.; Closs, G. L.; Miller, J. R. *J. Am. Chem. Soc.*, **1983**, *105*, 670. (b) Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.*, **1986**, *90*, 3673. (c) Joran, A. D.; Leland, B. A.; Geller, G. G.; Hopfield, J. J.; Dervan, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 6090. (d) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562. (e) Stein, C. A.; Lewis, N. A.; Seitz, G. *J. Am. Chem. Soc.*, **1982**, *104*, 2596.

3. (a) Penfield, K. W.; Miller, J. R.; Paddon–Row, M. N.; Cotsaris, E.; Oliver, A. M.; Hush, N. S. *J. Am. Chem. Soc.*, **1987**, *109*, 5061. (b) Hush, N. S.; Paddon–Row, M. N.; Cotsaris, E.; Oevering, H.; Verhoeven, J. W.; Heppener, M. *Chem. Phys. Lett.* **1985**, *117*, 8. (c) Warman, J. M.; de Haas, M. P.; Paddon–Row, M. N.; Cotsaris, E.; Hush, N. S.; Oevering, H.; Verhoeven, J. W. *Nature* (London) **1986**, *320*, 615. (d) Oevering, H.; Paddon–Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E.; Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.*, **1987**, *109*, 3258. (e) Oliver, A. M.; Craig, D. C.; Paddon–Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.*, **1988**, *150*, 366. (f) Lawson, J. M.; Craig, D. C.; Paddon–Row, M. N.; Kroon, J.; Verhoeven, J. W. *Chem. Phys. Lett.* **1989**, *164*, 120. (g) Kroon, J.; Verhoeven, J. W.; Paddon-Row, M. N.; Oliver, A. M. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1358.

4. (a) Osuka, A.; Nakajima, S.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. *J. Am. Chem. Soc.* **1993**, *115*, 4577. (b) Sessler, J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618.

5. (a) Crossley, M. J.; King, L. J. J. *Chem. Soc., Chem. Commun.* **1984**, 920. (b) Crossley, M. J.; Burn, P. L. *J. Chem. Soc., Chem. Commun.* **1987**, 39.

6. (a) Paddon–Row, M. N.; Cotsaris, E.; Patney, H. K. *Tetrahedron* **1986**, *42*, 1779. (b) Craig, D. C.; Paddon–Row, M. N.; Patney, H. K. *Aust. J. Chem.* **1986**, *39*, 1587. (c) Paddon–Row, M. N.; Patney, H. K.; Pasupuleti, L. *Aust. J. Chem.* **1982**, *35*, 307. (d) Craig, D. C.; Paddon–Row, M. N. *Aust. J. Chem.* **1987**, *40*, 1951.

7. Antolovich, M.; Keyte, P. J.; Oliver, A. M.; Paddon–Row, M. N.; Kroon, J.; Verhoeven, J. W.; Jonker, S. A.; Warman, J. M. *J. Phys. Chem.* **1991**, *95*, 1933.

8. **Data: Compound 3:** Mp > 300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ –2.62 (4H, s), 1.78 (2H, d, *J* 10.2 Hz), 1.96 (2H, s), 2.75 (2H, d, *J* 11.3 Hz), 3.76 (4H, s), 7.51 (4H, s), 7.71 – 7.80 (20H, br m), 7.92 (4H, t, *J* 7.4 Hz), 8.07 – 8.20 (16H, br m), 8.70 (4H, s), 8.90 (4H, d, *J* 5.1 Hz), 8.94 (4H, d, *J* 5.1 Hz). Anal. Calcd for $C_{108}H_{70}N_{12}$: C, 84.45; H, 4.60; N, 10.95. Found: C, 83.80; H, 4.56; N, 10.68.

   Compound 4: Mp > 300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ –2.60 (4H, s), 1.15 (6H, s), 1.82 (2H, d, *J* 9.2 Hz), 2.08 (4H, s), 2.11 (2H, d, *J* 9.2 Hz), 3.57 (4H, s), 7.55 (4H, s), 7.70 – 7.80 (20H, br m), 7.90 (4H, t, *J* 7.4 Hz), 8.13 (8H, br d, *J* 6.8 Hz), 8.20 (8H, d, *J* 6.2 Hz), 8.69 (4H, s), 8.90 (4H, d, *J* 5.1 Hz), 8.94 (4H, d, *J* 5.1 Hz). Anal. Calcd for $C_{114}H_{78}N_{12}$: C, 84.73; H, 4.87; N, 10.40. Found: C, 84.28; H, 4.88; N, 10.02.

   Compound 5. Mp > 300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ –3.02 (4H, s), –1.53 (2H, s), 1.73 (2H, d, *J* 8.8 Hz), 1.81 (2H, d, *J* 8.8 Hz), 1.83 (2H, s), 2.22 (4H, s), 3.43 (4H, s), 7.23 (4H, s), 7.60 – 8.08 (40H, v br m), 8.47 (4H, s), 8.66 (4H, d, *J* 5.0 Hz), 8.70 (4H, d, *J* 5.0 Hz). Anal. Calcd for $C_{113}H_{76}N_{12}.H_2O$: C, 83.78; H, 4.85; N, 10.38. Found: C, 83.36; H, 4.75; N, 10.27.

   Compound 6. Mp > 300 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ –1.70 (2H, s), –0.70 (1H, d, *J* 10.5 Hz), 0.075 (1H, d, *J* 10.6 Hz), 1.02 – 1.04 (2H, br m), 1.26 – 1.31 (2H, br m), 1.80 (2H, br s), 1.96 (2H, br s), 2.29 (2H, br s), 3.53 (2H, s), 7.50 (2H, s), 7.64 – 8.00 (10H, v br m), 8.08 (2H, v br m), 8.24 – 8.32 (8H, v br m), 8.73 (2H, s), 8.94 (2H, d, *J* 5.0 Hz), 8.98 (2H, d, *J* 5.0 Hz). Anal. Calcd for $C_{60}H_{44}N_6$: C, 84.87; H, 5.23; N, 9.91. Found: C, 84.48; H, 5.17; N, 9.88.

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