The Synthesis of Bichromophoric Rigid Norbornylogous Systems Containing the Porphyrin Group as One of the Chromophores

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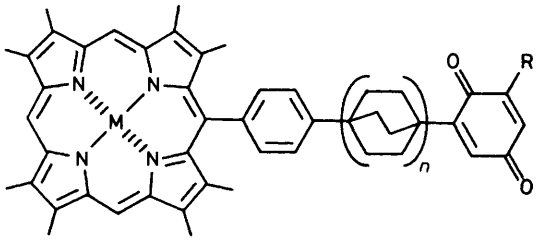
The synthesis of three novel systems in which the porphyrin group is fused to a norbornyl unit, or to an extended linearly fused system of norbornyl and bicyclo[2.2.2]octyl units, is described. The compounds are: 7,10,13,16-tetraphenyl-1,2,3,4-tetrahydro-1,4-methanobenzo[*g*]quinoxalino[2,3-*b*]porphyrin (**7a**), 1,4-dimethoxy-8,11,14,17-tetraphenyl-5,20-dihydro-5,20-methanonaphtho-[2,3-*g*]quinoxalino[2,3-*b*]porphyrin (**3**), and (5α,5aβ,5bα,5cβ,6α,21α,21aβ,21bα,21cβ,22α)-1,4-dimethoxy-5b,21b-dimethyl-9,12,15,18-tetraphenyl-5,5a,5c,6,21,21a,21c,22-octahydro-5,22:6,21-dimethanonaphtho[2‴,3‴:3″,4″]cyclobuta[1″,2″:3′,4′]cyclobuta[1′,2′:4,5]benzo[1,2-*g*]quinoxalino[2,3-*b*]porphyrin (**4**). In each case, the porphyrin unit is linked to the norbornyl ring through a quinoxaline group, and this was formed through condensation of 17,18-dioxo-5,10,15,20-tetraphenylchlorin (**6**) and the appropriate norbornyl-*o*-phenylenediamine (**5d**), (**22a**), or (**22b**).

Single electron transfer (ET) is, perhaps, the most fundamental of all chemical reactions, and plays a pivotal role in a variety of synthetic and biological processes, occurring under both thermal[1–6] and photochemical[7–24] conditions. It is therefore hardly surprising that considerable effort from many groups continues to be spent on probing the mechanistic features of ET.[1–25] During the past few years, measurements of intramolecular electron transfer dynamics have provided deeper insight into the effect of distance, energy, and orientation on electron transfer rates.[3–6,10–24] In this respect, investigations of ET using model compounds containing two chromophores that are held in fixed orientation with respect to each other, and at well defined separations by a hydrocarbon 'spacer', have proved to be of particular value.[13–17] Of the many chromophores which have been used for ET studies, the porphyrin-donor and quinone-acceptor chromophores are particularly popular,[18–24] partly because they feature in many biological ET systems, but also because the thermodynamics of the ET process in the porphyrin–quinone dyad can be easily controlled through judicious choice of the complexing metal.

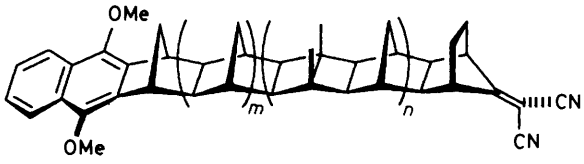
Of relevance to the work described herein, we cite the recent study of ET dynamics carried out by Joran and his co-workers, using the series of compounds (**1**; M = H_2, Zn), in which the porphyrin and quinone chromophores are separated by 0, 1, or 2 bicyclo[2.2.2]octane spacers.[23,24] It was found that the intramolecular photoinduced ET rate was substantial even for (**1c**), in which the edge-to-edge distance between the chromophore separation is estimated to be 14 Å. Such a substantial long-range ET rate is no doubt due to through-bond orbital interactions[26] between the chromophores and the bicyclo[2.2.2]octyl relays. Although compounds (**1a–c**) have provided some impressively fast ET rate data, they suffer from two disadvantages. First, there is some conformational ambiguity with respect to the relative orientation between the porphyrin and quinone chromophores; presumably the quinone group can adopt several stable conformations with respect to the porphyrin group. Consequently, the measured ET rates for these compounds are a composite resulting from all stable orientations. In other words, precise information about the dependence of ET dynamics on the relative orientation of the chromophores cannot be obtained with certainty from these experiments. Secondly, model calculations indicate that the bicyclo[2.2.2]octyl group is not a very effective relay for through-bond interactions;[27] the choice of a more effective relay should therefore result in even more spectacular ET rate data. We have investigated ET dynamics in the series of compounds (**2**) in which the 'norbornylogous' spacer consists of linearly fused combinations of norbornyl and bicyclo[2.2.0]-hexyl units.[3,13–17] The norbornylogous spacer does not suffer from the two above mentioned disadvantages; the two chromophores in (**2**) are conformationally frozen, and a wealth of experimental data indicates that the spacer acts as a very efficient through-bond relay.[28,29] In this paper, we report the synthesis of (**3**), (**4**), and (**7a**), the former two molecules representing the first two members of a series of bichromophoric norbornylogues containing a porphyrin moiety rigidly attached to a norbornyl ring through a quinoxaline group.

The overall synthetic strategy is outlined in Scheme 1 for the synthesis of the monochromophoric model compound (**7a**). Rigid fusion of the porphyrin group to the norbornyl ring was to be achieved through the quinoxaline nucleus, the synthesis of which should easily be realized from the reaction between the known 17,18-dioxo-5,10,15,20-tetraphenylchlorin, (**6**),[30] and 6,7-diaminobenzonorbornene (**5d**). This reaction has its precedent in the recently reported synthesis of laterally bridged bisporphyrin systems, formed from the condensation between dioxochlorins, such as (**6**), and benzene-1,2,4,5-tetramine.[31] The synthesis of (**7a**) was quite straightforward. Nitration of benzonorbornene (**5a**) with $Cu(NO_3)_2$–Ac_2O gave the known 6-nitro compound (**5b**) in good yield.[32] Treatment of (**5b**) with fuming nitric acid and sulphuric acid gave the desired 6,7-dinitro material (**5c**) in 24% yield. This method had been previously used to synthesize other 6,7-dinitro analogues of (**5c**).[33] The symmetric structure of (**5c**) followed from its ^1H n.m.r. spectrum, which revealed only a sharp singlet for the two aromatic protons at δ 7.66. The ^1H n.m.r. spectrum of the crude reaction mixture also displayed two weak signals, of equal intensity, at δ 7.56 and 8.34. Presumably, this can be attributed to the presence of a small amount of the 5,7-dinitro isomer. Unfortunately, dinitration of (**5a**) could not be achieved in one step; nitration of (**5a**) with fuming nitric acid under a variety of conditions gave mainly tarry products, accompanied by only poor yields of dinitro material (**5c**). Reduction of (**5c**), using a mixture of Pd–C and $NaBH_4$, gave the unstable diamino compound (**5d**), which was not characterized but immediately treated with the dioxochlorin (**6**) to give (**7a**) in 81% yield. The

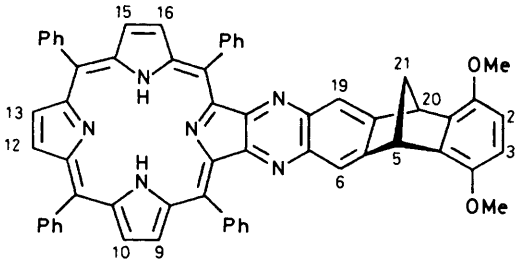


(1)

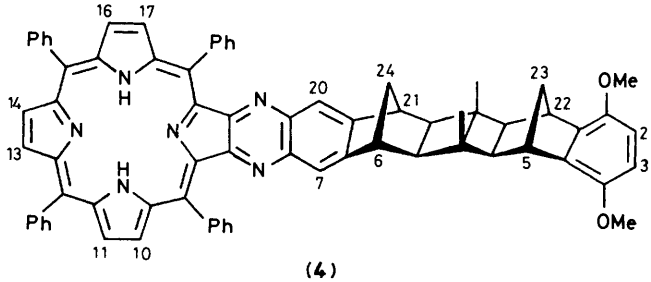
a; n = 0
b; n = 1
c; n = 2



(2)



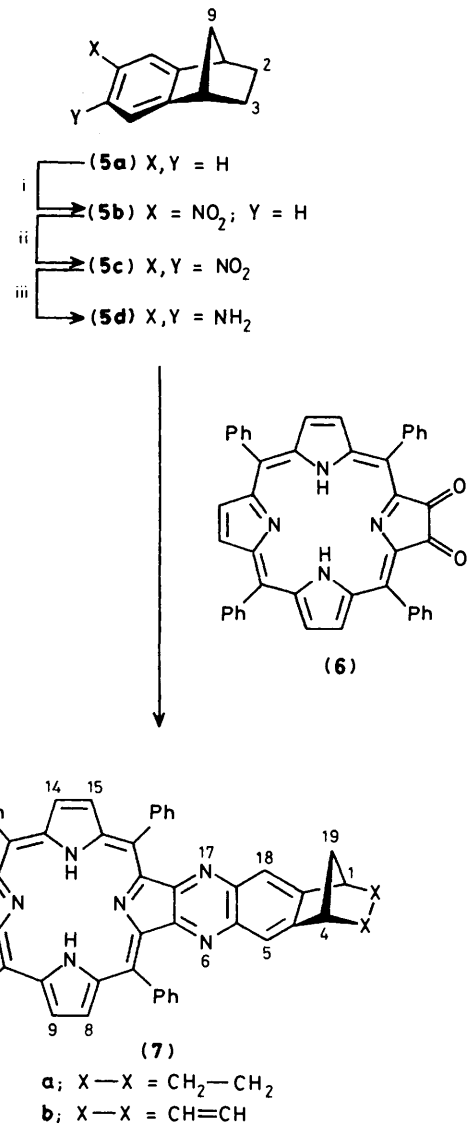
(3)



(4)

structure of (**7a**) was verified by its 500 MHz ^{1}H n.m.r. spectrum, *inter alia:* sharp singlets at δ −2.54 (2NH), 7.57 (5- and 18-H), 8.74 (11- and 12-H), and an AB system at 8.96 (J 4.95 Hz, 8- and 9-H, and 14- and 15-H).

Two pathways for the synthesis of (**3**) and (**4**) can be devised which differ in the sequence of the annellation of the porphyrin and dimethoxybenzene groups to the norbornyl framework. In the first approach, one could begin with benzonorbornadiene (**8a**) and attach the porphyrin group through the sequence of steps outlined in Scheme 1. Benzene annellation[34] of the resulting product (**7b**) or the extended norbornylogue derived therefrom (*vide infra*), followed by oxidation of the benzene ring, should lead to (**3**) and (**4**). Unfortunately, we were unable to secure sufficient quantities of either (**8c**) or (**8e**) to make this pathway viable. Although the mononitro compound (**8b**) can easily be prepared,[32] further nitration of this material using a variety of nitrating agents led only to the formation of tars. Prior reduction of (**8b**) to (**8d**) and nitration of this material likewise gave only extremely low yields of (**8e**). The dinitro compound (**8c**) has been obtained as a by-product from a



(5a) X,Y = H
(5b) X = NO_2; Y = H
(5c) X,Y = NO_2
(5d) X,Y = NH_2

(6)

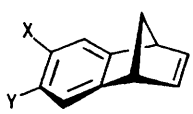
(7)

a; X—X = CH_2—CH_2
b; X—X = CH=CH

Scheme 1. *Reagents:* i, $Cu(NO_3)_2$–Ac_2O; ii, fuming HNO_3; iii, Pd–C, $NaBH_4$.

solvolysis reaction,[33] but not in sufficient yield to warrant pursuing this approach.

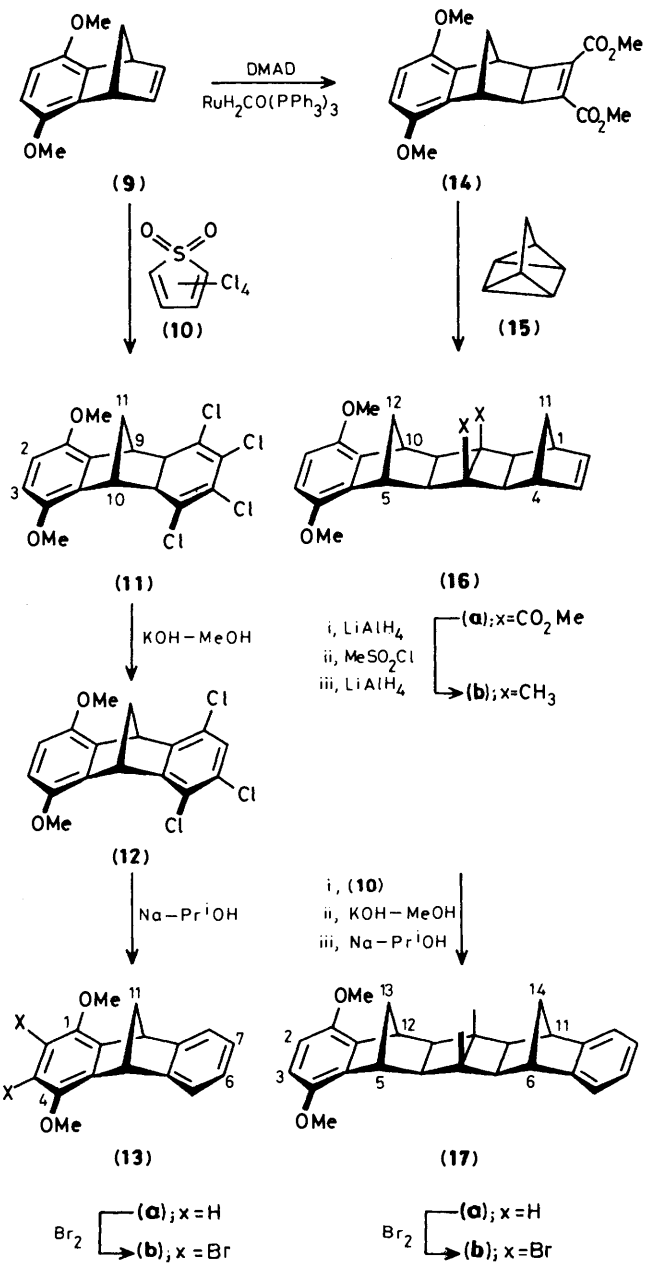
The second approach is outlined in Scheme 2. The key material is the known 5,8-dimethoxybenzonorbornadiene (**9**).[35]



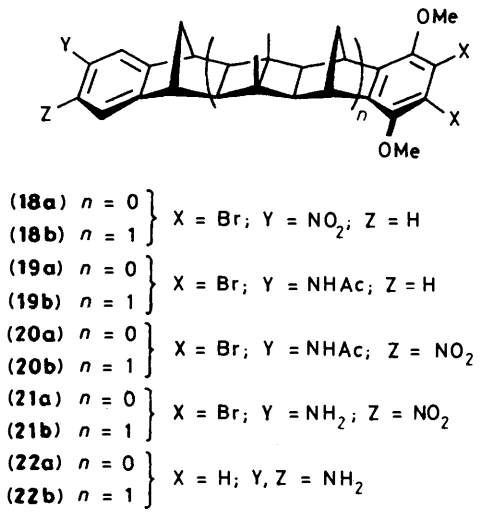
(8)

a; X, Y = H
b; X = NO_2, Y = H
c; X Y = NO_2
d; X = NHAc, Y = H
e; X = NHAc, Y = NO_2

Benzene ring annellation[34] of this compound was achieved using tetrachlorothiophene dioxide (**10**).[36] Treatment of (**9**) with (**10**) in refluxing toluene cleanly gave (**11**) in 90% yield.



Scheme 2.



Aromatization of this compound, through dehydrohalogenation, to give (**12**) was effected under standard conditions.[37] Reductive dechlorination[38] of (**12**) gave (**13a**) in good yield. In order to synthesize the required diamino compound (**22a**), it is necessary to nitrate the benzene ring in preference to the dimethoxybenzene ring. Since the latter ring is inherently much more reactive than the former towards electrophilic substitution, the dimethoxybenzene ring must therefore be protected. This was done through bromination of (**13a**) to give (**13b**). The remaining synthetic steps presented no problems. Nitration [$Cu(NO_3)_2$] of (**13b**) gave (**18a**), and this was reduced (Zn–AcOH) to give (**19a**). Nitration of (**19a**) (HNO_3–AcOH–Ac_2O), to give (**20a**), followed by treatment with hydrazine hydrate led to the formation of the *o*-aminonitro compound (**21a**). Conversion of (**21a**) into (**22a**) was effected in one step using hydrazine hydrate and Pd–C in ethanol. The diamine (**22a**) is quite unstable and could not be purified. However, its ^1H n.m.r. spectrum clearly revealed the symmetry of the system: two sharp singlets at δ 6.46 and 6.75 resulting from the protons attached to the diamino and dimethoxy aromatic rings respectively. Reaction of (**22a**) with (**6**) gave (**3**) in 82% yield. The C_s symmetry of (**3**) is revealed by its 500 MHz ^1H n.m.r. spectrum: sharp singlets at δ 7.69 and 8.72, respectively, due to the quinoxaline protons (6- and 19-H) and the equivalent pair of porphyrin protons, 12- and 13-H. The bridgehead protons, 5- and 20-H, appear as a single line at δ 4.77, and the two methoxy groups are equivalent (δ 3.84).

Extension of the norbornyl framework, to produce (**17a**) from (**9**) (Scheme 2), follows recently established methodology.[17,29,39,40] Ruthenium-catalysed thermal (2 + 2) cycloaddition[39] of dimethylacetylene dicarboxylate (DMAD) to (**9**) cleanly gave the adduct, (**14**), which underwent the expected[40] thermal (2 + 2 + 2) cycloaddition with quadricyclane, (**15**), to give (**16a**). The adduct (**16a**) was converted into the dimethyl analogue (**16b**), through the diol (**16**; X = CH_2OH) and $LiAlH_4$ reduction of the bismesylate derivative of the diol. Benzene annellation of (**16b**), using the same procedure as that employed for the formation of (**13a**), gave (**17a**). Bromination of this compound to give (**17b**), and its subsequent conversion into (**22b**), *via* (**18b**)–(**21b**), followed essentially the same procedures as those used in the synthesis of (**22a**) from (**18a**) (*vide infra*). The target compound, (**4**), was formed in 62% yield from (**22b**) and (**6**). The ^1H n.m.r. spectrum of (**4**) is fully consistent with the structure for (**4**) (see Experimental section).

The synthesis of higher homologues of (**2**) and (**3**), their oxidation to the corresponding porphyrin–quinone dyads, and kinetic measurements of intramolecular photoinduced ET in these quinones, form the basis for future work in these laboratories.

Experimental

General.—M.p.s were taken on a Kofler hot-stage and are uncorrected. ^1H N.m.r. spectra were recorded either at 60 MHz, using a Varian 360L machine, or at 500 MHz, using a Bruker AM-500 spectrometer. All n.m.r. spectra were measured using $CDCl_3$ as solvent. Visible electronic spectra were recorded on a Hitachi U-3200 spectrophotometer; all spectra were obtained using CH_2Cl_2 as the solvent.

6,7-*Dinitro*-1,2,3,4-*tetrahydro*-1,4-*methanonaphthalene* (**5c**).— Fuming nitric acid (0.34 g, *ca.* 5.4 mmol) was very carefully and slowly added to a rapidly stirred solution of (**5b**)[32]

(1.0 g, 5.3 mmol) in sulphuric acid (18 mol dm^{-3}, 1.0 g). The dark mixture was heated on a steam bath for 5 min. Ice–water (20 cm^3) was added to the cooled mixture and the precipitated solid was collected and recrystallized from (1:1) CH_2Cl_2–petroleum to give the dinitro compound (**5c**) (0.3 g, 24%), m.p. 149 °C; δ_H(500 MHz; $CDCl_3$) 1.21 (2 H, m, 2-H_{endo}, 3-H_{endo}), 1.68 (1 H, d, *J* 9.4 Hz, 9-H), 1.88 (1 H, dt, *J* 1.9, 9.4 Hz, 9-H), 2.06 (2 H, m, 2-H_{exo}, 3-H_{exo}), 3.55 (2 H, s, 1-, 4-H), and 7.66 (2 H, s, 5-, 8-H) (Found: C, 56.7; H, 4.4; N, 11.8. $C_{11}H_{10}N_2O_4$ requires C, 56.4; H, 4.3; N, 12.0%).

7,10,13,16-*Tetraphenyl*-1,2,3,4-*tetrahydro*-1,4-*methanobenzo*[g]*quinoxalino*[2,3-b]*porphyrin* (**7a**).—To a stirred mixture of (**5c**) (0.1 g, 0.43 mmol) and Pd–C (10%, 0.1 g) in CH_2Cl_2 (7 cm^3) and methanol (7 cm^3) under nitrogen, was added $NaBH_4$ (0.32 g, 8.4 mmol) in small portions. During the addition the solution turned dark red and then faded. After the addition was complete, the mixture was stirred for 30 min. The mixture was filtered and the filtrate evaporated. The residue was dissolved in CH_2Cl_2 (20 cm^3) and washed with water (10 cm^3). The organic layer was dried and evaporated to give diamine (**5d**) (0.06 g, 81%) which was not purified further; δ_H(60 MHz; $CDCl_3$) 1.2–2.0 (6 H, m), 3.35 (2 H, s, 1-, 4-H), 2.9–3.9 (2 H, vbr, NH_2), and 6.63 (2 H, s, 5-, 8-H).

A solution of the diamino compound (**5d**) (0.06 g, 0.34 mmol) in CH_2Cl_2 (10 cm^3) was added to a stirred solution of dioxochlorin (**6**) (0.25 g, 0.39 mmol) in CH_2Cl_2 (25 cm^3). The dark green mixture turned red and it was stirred for 30 min. The mixture was evaporated and the residue was chromatographed (silica, 50% petroleum–CH_2Cl_2 eluant) and the first fraction was collected and evaporated. The resulting solid was recrystallized from CH_2Cl_2–methanol, to give (**7a**) (0.23 g, 85%), m.p. >300 °C; δ_H(500 MHz; $CDCl_3$) −2.54 (2 H, s, 2 × NH), 1.36 (2 H, m, 2-H_{endo}, 3-H_{endo}), 1.74 (1 H, d, *J* 8.9 Hz, 19-H), 1.89 (1 H, d, *J* 9.0 Hz, 19-H), 2.05 (2 H, m, 2-H_{exo}, 3-H_{exo}), 3.62 (2 H, s, 1-, 4-H), 7.57 (2 H, s, 5-, 18-H), 7.75–7.85 (10 H, m, ArH), 7.91 (2 H, t, *J* 7.6 Hz, 2 × H_{para}), 8.18 (4 H, m, ArH), 8.25 (4 H, d, *J* 6.4 Hz, 4 × H_{ortho}), 8.74 (2 H, s, 12-, 13-H), 8.94 (2 H, half of AB system, *J* 4.9 Hz, 9- and 16-H, or 10- and 15-H), and 8.98 (2 H, half of AB system, *J* 4.9 Hz, 19- and 16-H, or 10- and 15-H); $\lambda_{max.}$ 433 (ε 134 000), 490 (2 100), 524 (98 000), 558 (2 300), 597 (4 400), and 649 nm (540) (Found: C, 84.1; H, 4.6; N, 10.5. $C_{55}H_{38}N_6$ requires C, 84.4; H, 4.9; N, 10.7%).

1,4-*Dimethoxy*-9,10-*dihydro*-9,10-*methanoanthracene* (**13a**).—A solution of 1,2,3,4-tetrachlorothiophene-1,1-dioxide[36] (**10**) (8.3 g, 31 mmol) and (**9**)[35] (5.5 g, 27 mmol) in toluene (80 cm^3) was refluxed for 48 h. Removal of the solvent under reduced pressure gave crude (**11**) (9.0 g, 90%) which was not purified further; δ_H(60 MHz; $CDCl_3$) 1.95 (1 H, d of AB system, *J* 11 Hz, 11-H), 2.82 (2 H, s, 8a-, 10a-H), 3.81 (6 H, s, 2 × OCH_3), 4.12 (2 H, s, 9-, 10-H), and 6.66 (2 H, s, 2-, 3-H).

A mixture of (**11**) (8.0 g, 22 mmol) and KOH (2.3 g, 41 mmol) in 95% ethanol (20 cm^3) was refluxed for 3 h. The solvent was removed and the solid washed with water (to remove inorganic salts) to give crude (**12**) (6.8 g, 94%) which was not purified further; δ_H(60 MHz; $CDCl_3$) 2.47 (2 H, m, 2 × 11-H), 3.80 (6 H, s, 2 × OCH_3), 4.83 (2 H, m, 9-, 10-H), 6.58 (2 H, s, 2-, 3-H), and 7.07 (1 H, s, 6-H).

Small pieces of sodium metal (14 g, 600 mmol) were slowly added to (**12**) (6.6 g, 20 mmol) in a refluxing mixture of THF (330 cm^3) and propan-2-ol (990 cm^3). The solution was refluxed for a further 4 h after the addition of sodium was complete. The solution was evaporated to dryness. T.l.c. analysis of the residue revealed the presence of starting material, and so the reduction was repeated. The residue from the repeated reduction, now free of starting material, was dissolved in CH_2Cl_2 (300 cm^3) and the solution was washed with water (100 cm^3). The organic layer was dried and evaporated to give (**13a**) (4.2 g, 84%), m.p. 141 °C (from CH_2Cl_2–methanol); δ_H(500 MHz; $CDCl_3$) 2.45 (1 H, d part of AB system, *J* 7.9 Hz, 11-H), 2.48 (1 H, d part of AB system, *J* 7.9 Hz, 11-H), 3.78 (6 H, s, 2 × OCH_3), 4.54 (2 H, s, 9-, 10-H), 6.48 (2 H, s, 2-, 3-H), 6.93 (2 H, m, 2 × ArH), and 7.32 (2 H, m, 2 × ArH) (Found: C, 80.7; H, 6.5. $C_{17}H_{16}O_2$ requires C, 80.9; H, 6.4%).

2,3-*Dibromo*-1,4-*dimethoxy*-6-*nitro*-9,10-*dihydro*-9,10-*methanoanthracene* (**18a**).—Bromine (1.4 g, 8.8 mmol) in CH_2Cl_2 (5 cm^3) was added dropwise to a solution of (**13a**) (1.1 g, 4.4 mmol) in CH_2Cl_2 (25 cm^3) at 25 °C. The solution was stirred in the dark for 5 h after which it was washed with aqueous sodium thiosulphate (10%, 15 cm^3) and water (15 cm^3). The organic layer was dried and evaporated to give the crude dibromo compound (**13b**) (1.7 g, 95%) which was not purified further; δ_H(60 MHz; $CDCl_3$) 2.55 (2 H, br s, 2 × 11-H), 3.90 (6 H, s, 2 × OCH_3), 4.65 (2 H, br s, 9-, 10-H), 6.9–7.15 (2 H, m, 2 × ArH), and 7.25–7.50 (2 H, m, 2 × ArH).

Copper(II) nitrate trihydrate (0.53 g, 2.2 mmol) was added to a solution of (**13b**) (1.8 g, 4.4 mmol) in acetic anhydride (18 cm^3) and the resulting mixture was stirred at room temperature for 18 h. The mixture was poured onto ice (50 g) and aqueous ammonia (15 mol dm^{-3}, 36 cm^3). The dark blue, oily mixture was extracted with CH_2Cl_2 (4 × 50 cm^3), and the combined organic extracts were washed with water (50 cm^3), dried ($MgSO_4$), and evaporated. Column chromatography of the residue [silica, 20 g; 65% benzene–light petroleum (b.p. 60–80 °C)] gave a thick oil which was recrystallized from benzene–methanol to give (**18a**) (1.7 g, 85%), m.p. 148 °C; δ_H(500 MHz; $CDCl_3$) 2.58 (1 H, d, part of AB system, *J* 8.6 Hz, 11-H), 2.61 (1 H, d, part of AB system, *J* 8.6 Hz, 11-H), 3.85 (3 H, s, OCH_3), 3.88 (3 H, s, OCH_3), 4.69 (1 H, s, 9- or 10-H), 4.71 (1 H, s, 9- or 10-H), 7.46 (1 H, d, *J* 8.0 Hz, 8-H), 7.98 (1 H, dd, *J* 2.3, 8.0 Hz, 7-H), and 8.14 (1 H, d, *J* 2.3 Hz, 5-H) (Found: C, 45.3; H, 3.1; N, 3.0. $C_{17}H_{13}Br_2NO_4$ requires C, 44.9; H, 2.9; N, 3.1%).

6-*Acetamido*-2,3-*dibromo*-1,4-*dimethoxy*-7-*nitro*-9,10-*dihydro*-9,10-*methanoanthracene* (**20a**).—A mixture of (**18a**) (1.0 g, 2.2 mmol) and zinc powder (2.0 g, 31 mmol) in glacial acetic acid (20 cm^3) and acetic anhydride (3 cm^3) was refluxed for 18 h. The mixture was neutralized with aqueous ammonia (17 mol dm^{-3}, *ca.* 40 cm^3) and filtered. The filtrate was extracted with CH_2Cl_2 (3 × 20 cm^3) and the combined extracts were dried and evaporated to give crude (**19a**) (1.0 g, 97%) which was not purified further; δ_H(60 MHz; $CDCl_3$) 1.96 (3 H, s, CH_3CON), 2.39 (2 H, m, 2 × 11-H), 3.9 (6 H, br s, 2 × OCH_3), 4.53 (2 H, m, 9-, 10-H), and 6.5–7.4 (4 H, m, 3 × ArH, NH).

To a stirred solution of (**19a**) (1.0 g, 2.1 mmol) in glacial acetic acid (7.5 cm^3) and acetic anhydride (7.5 cm^3) was added dropwise nitric acid (15 mol dm^{-3}, 0.4 g, 6.1 mmol). The solution was stirred for 0.5 h and then neutralized with aqueous ammonia (15 mol dm^{-3}, *ca.* 30 cm^3). The resulting mixture was extracted with CH_2Cl_2 (4 × 30 cm^3) and the combined organic extracts were washed with water (30 cm^3), dried, and evaporated. Column chromatography of the residue (silica, CH_2Cl_2) gave (**20a**) (0.8 g, 73%), m.p. 97 °C; δ_H(500 MHz; $CDCl_3$) 2.26 (3 H, s, CH_3CO), 2.52 (1 H, d, part of AB system, *J* 8.7 Hz, 11-H), 2.57 (1 H, d, part of AB system, *J* 8.7 Hz, 11-H), 3.85 (3 H, s, OCH_3), 3.86 (3 H, s, OCH_3), 4.63 (1 H, s, 9- or 10-H), 4.68 (1 H, s, 9- or 10-H), 8.11 (1 H, s, 5-H), 8.79 (1 H, s, 8-H), and 10.53 (1 H, br s, NH) (Found: C, 44.7; H, 3.2; N, 5.6. $C_{19}H_{16}Br_2N_2O_5$ requires C, 44.6; H, 3.15; N, 5.5%).

1,4-*Dimethoxy*-8,11,14,17-*tetraphenyl*-5,20-*dihydro*-5,20-*methanonaphtho*[2,3-g]*quinoxalino*[2,3-b]*porphyrin* (**3**).—A solution of (**20a**) (0.5 g, 1 mmol) in hydrazine hydrate (85%, 12 cm^3) was heated at 70 °C for 17 h. Most of the hydrazine

hydrate was removed under reduced pressure and the residue was dissolved in CH_2Cl_2 (30 cm^3) and washed with water (2 × 15 cm^3). The organic layer was dried and evaporated to give crude (**21a**) (0.4 g, 87%) which was not purified further; δ_H(500 MHz; $CDCl_3$) 2.38 (1 H, d, *J* 8.5 Hz, 11-H), 2.48 (1 H, d, *J* 8.5 Hz, 11-H), 3.84 (3 H, s, OCH_3), 3.85 (3 H, s, OCH_3), 4.50 (1 H, s, 9- or 10-H), 4.53 (1 H, s, 9- or 10-H), 6.33 (2 H, v br s, NH_2), 6.81 (1 H, s, 5-H), and 7.97 (1 H, s, 8-H).

A mixture of (**21a**) (0.3 g, 0.6 mmol), hydrazine hydrate (10 cm^3, 0.29 mol), Pd–C (10%, 90 mg), and ethanol (95%, 60 cm^3) was refluxed with stirring for 17 h. The hot solution was filtered and the filtrate was evaporated. The residue was dissolved in CH_2Cl_2 (30 cm^3) and the resulting solution was washed with water, dried, and evaporated to give the diamino compound (**22a**) (0.1 g, 56%). This material is quite unstable and could not be purified sufficiently for analysis; δ_H(60 MHz; $CDCl_3$) 2.38 (2 H, m, 2 × 11-H), 3.8 (10 H, v br s, 2 × OCH_3, 2 × NH_2), 4.41 (2 H, br s, 9-H, 10-H) 6.50 (2 H, s, 1-, 4-H), and 6.75 (2 H, s, 6-, 7-H).

A solution of the dioxochlorin (**6**) (0.24 g, 0.37 mmol) in CH_2Cl_2 (40 cm^3) was added to a magnetically stirred solution of (**22a**) (0.1 g, 0.35 mmol) in CH_2Cl_2 (50 cm^3). The resulting mixture was stirred for 0.5 h during which it turned a deep red colour. The solution was concentrated (10 cm^3) and passed through a silica column (30 g, CH_2Cl_2). The eluant was evaporated and the residue was dissolved in CH_2Cl_2–petroleum (2:3, 50 cm^3). This solution was passed through a silica column (100 g) and eluted with 3:2 CH_2Cl_2–petroleum (b.p. 60–80 °C). The eluant was evaporated, and the residue recrystallized from CH_2Cl_2–methanol (the compound tends to aggregate, and so must be dissolved in fairly large amounts of CH_2Cl_2 before addition of methanol) to give the porphyrin–dimethoxybenzene compound (**3**) (0.26 g, 82%), m.p. > 300 °C; δ_H(500 MHz; $CDCl_3$) −2.58 (2 H, s, 2 × NH), 2.52 (1 H, d, *J* 8.2 Hz, 21-H), 2.64 (1 H, d, *J* 8.2 Hz, 21-H), 3.84 (6 H, s, 2 × OCH_3), 4.77 (2 H, s, 5-, 20-H), 6.49 (2 H, s, 2-, 3-H), 7.69 (2 H, s, 6-, 19-H), 7.75–7.82 (10 H, m, ArH), 7.93 (2 H, t, *J* 7.6 Hz, 2 × H_{para}), 8.1–8.2 (4 H, m, ArH), 8.23 (4 H, d, *J* 6.8 Hz, 4 × H_{ortho}), 8.72 (2 H, s, 12-, 13-H), 8.92 (2 H, half of AB system, *J* 5 Hz, 9- and 16-H, or 10 -and 15-H), and 8.94 (2 H, half of AB system, *J* 5 Hz, 9- and 16-H, or 10- and 15-H); $\lambda_{max.}$ 434 (ε 149 000), 491 (2 500), 524 (11 400), 558 (2 550), 597 (5 100), 648 (530), and 686 nm (300) (Found: C, 82.2; H, 4.6; N, 9.6. $C_{61}H_{42}N_6O_2$ requires C, 82.2; H, 4.7; N, 9.4%).

Dimethyl (2aα,3β,8β,8aα)-4,7-*Dimethoxy*-2a,3,8,8a-*tetrahydro*-3,8-*methanocyclobuta*[b]*naphthalene*-1,2-*dicarboxylate* (**14**).—A magnetically stirred solution of (**9**)[35] (38.4 g, 190 mmol), DMAD (27.5 g, 193 mmol), and $RuH_2CO(PPh_3)_3$[39,41] (0.6 g, 0.64 mmol) in benzene (200 cm^3) was refluxed under nitrogen for 24 h. Ethanol (250 cm^3) was added to the cooled mixture. The resulting precipitate was collected and recrystallized from ethanol to give (**14**) (56.1 g, 86%), m.p. 172–173 °C; δ_H(500 MHz; $CDCl_3$) 1.71 (1 H, d part of AB system, *J* 10.2 Hz, 9-H), 1.75 (1 H, d part of AB system, *J* 10.2 Hz, 9-H), 2.76 (2 H, s, 2a-, 8a-H), 3.50 (2 H, s, 3-, 8-H), 3.79 (3 H, s, OCH_3), 3.83 (3 H, s, OCH_3), and 6.62 (2 H, s, 5-, 6-H) (Found: C, 66.2; H, 5.9. $C_{19}H_{20}O_6$ requires C, 66.3; H, 5.85%).

Dimethyl (1α,4α,4aβ,4bα,4cβ,5α,10α,10aβ,10bα,10cβ)-6,9-*Dimethoxy*-1,4,4a,4c,5,10,10a,10c-*octahydro*-1,4:5,10-*dimethanobenzo*[3′,4′]*cyclobuta*[1′,2′:3,4]*cyclobuta*[1,2b]*naphthalene*-4b,10b-*dicarboxylate* (**16a**).—A magnetically stirred solution of (**14**) (56 g, 0.19 mol) in quadricyclane (**15**) (20 g, 0.22 mol) was refluxed for 72 h. Acetone (100 cm^3) was added to the cooled mixture and the resulting precipitate was collected and recrystallized from acetone to give (**16a**) (61.2 g, 72%), m.p. 196–197 °C; δ_H(500 MHz; $CDCl_3$) 1.14 (1 H, d, *J* 9.8 Hz, 11-H), 1.51 (1 H, d, *J* 10.3 Hz, 12-H), 1.89 (1 H, d, *J* 9.8 Hz, 11-H), 2.07 (2 H, br s), 2.29 (2 H, br s), 2.33 (1 H, d, *J* 10.3 Hz, 12-H), 2.86 (2 H, t, *J* 1.6 Hz, 1-, 4-H), 3.56 (2 H, br s, 5-, 10-H), 3.77 (6 H, s, 2 × OCH_3), 3.79 (6 H, s, 2 × OCH_3), 6.04 (2 H, t, *J* 1.8 Hz, 2-, 3-H), and 6.60 (2 H, s, 7-, 8-H) (Found: C, 71.4; H, 6.6. $C_{26}H_{28}O_6$ requires C, 71.5; H, 6.5%).

(1α.4α,4aβ,4bα,4cβ,5α,10α,10aβ,10bα,10cβ)-6,9-*Dimethoxy*-4b,10b-*dimethyl*-1,4,4a,4c,5,10,10a,10c-*octahydro*-1,4:5,10-*dimethanobenzo*[3′,4′]*cyclobuta*[1′,2′:3,4]-*cyclobuta*[1,2-b]-*naphthalene* (**16b**).—To a solution of (**16a**) (51.2 g, 117 mmol) in dry THF (350 cm^3), under nitrogen, was added $LiAlH_4$ (9.2 g, 242 mmol) in small portions. The mixture was refluxed for 18 h. To the cooled mixture was added successively water (9 cm^3) (**CAUTION**!), 15% aqueous NaOH (9 cm^3), and water (27 cm^3). The mixture was then filtered and the filtrate dried and evaporated under reduced pressure to give the diol (**16**; X = CH_2OH) (43 g, 95%) which was not purified further; $\nu_{max.}$(Nujol) 3 250 cm^{-1}.

To a cooled solution (−5 °C) of the diol (**16**; X = CH_2OH) (42.3 g, 110 mmol) in dry pyridine (250 cm^3) was added slowly methanesulphonyl chloride (27 g, 236 mmol). The resulting solution was kept at −5 °C for 72 h, after which it was poured onto crushed ice and then extracted with CH_2Cl_2 (3 × 200 cm^3). The organic extract was washed successively with 1 mol dm^{-3} HCl (100 cm^3) and saturated aqueous $NaHCO_3$, and then dried, and evaporated to give the dimethanesulphonate (**16**; X = CH_2OMs) (53 g, 94%) which was not purified.

A magnetically stirred mixture of the dimethanesulphonate (**16**; X = CH_2OMs) (53 g, 105 mmol) and $LiAlH_4$ (8.5 g, 223 mmol) in dry THF (350 cm^3) was refluxed for 18 h. Use of an identical work-up procedure to that described above for the synthesis of the diol (**16**; X = CH_2OH) gave (**16b**) (26.5 g, 72%), m.p. 178–179 °C (from methanol); δ_H(500 Mz; $CDCl_3$) 0.90 (6 H, s, 2 × CH_3), 1.18 (1 H, d, *J* 8.8 Hz, 11-H), 1.38 (1 H, d, *J* 8.8 Hz, 11-H), 1.58 (1 H, d t, *J* 1.5, 8.8 Hz, 12-H), 1.68 (2 H, s), 1.77 (1 H, d, *J* 9.44 Hz, 12-H), 1.91 (2 H, s), 2.74 (2 H, t, *J* 1.5 Hz, 1-, 4-H), 3.52 (2 H, br s, 5-, 10-H), 3.75 (6 H, s, 2 × OCH_3), 5.98 (2 H, t, *J* 1.8 Hz, 2-, 3-H), and 6.59 (2 H, s, 7-, 8-H) (Found: C, 82.4; H, 8.2. $C_{24}H_{28}O_2$ requires C, 82.7; H, 8.1%).

(5α,5aβ,5bα,5cβ,6α,11α,11aβ,11bα,11cβ,12α)-1,4-*Dimethoxy*-5b,11b-*dimethyl*-5,5a,5c,6,11,11a,11c,12-*octahydro*-5,12:6,11-*dimethanonaphtho*[2″,3″:3′,4′]*cyclobuta*[1′,2′:3,4]*cyclobuta*-[1,2-b]*naphthalene* (**17a**).—A magnetically stirred solution of (**16b**) (9.7 g, 27.8 mmol) and 2,3,4,5-tetrachlorothiophene 1,1-dioxide[36] (**10**) (7.1 g, 27.9 mmol) in toluene (150 cm^3) was refluxed for 18 h. Ethanol (150 cm^3) was added to the cooled solution and the resulting precipitate was filtered to give crude adduct (14.8 g, 98%) resulting from Diels–Alder reaction between (**16b**) and (**10**), followed by cheletropic loss of SO_2. A suspension of the adduct (14.8 g, 27.5 mmol) and KOH (3 g, 54 mmol) in ethanol (250 cm^3) was refluxed for 18 h. Evaporation of the solvent (reduced pressure) gave a solid which was washed with water (to remove inorganic salts) and dried to give the crude 7,8,10-trichloro derivative of (**17a**) (13.8 g, 100%).

To a refluxing solution of the crude trichloro derivative (13.8 g, 27.5 mmol) in THF (100 cm^3) and propan-2-ol (150 cm^3) were added small pieces of sodium (total amount 20 g, 0.87 mol) over 2 h. The mixture was refluxed for a further 18 h. The cooled mixture was carefully treated with sufficient ethanol to destroy any unchanged sodium, and then diluted with ice-cold water (500 cm^3). The resulting solution was extracted with CH_2Cl_2 (3 × 250 cm^3), and the combined organic extracts (after washing with water and drying) were evaporated to give (**17a**) (9.2 g, 84%), m.p. 154–156 °C (from methanol); δ_H(500 MHz; $CDCl_3$) 1.00 (6 H, s, 2 × CH_3), 1.58 (1 H, d, *J* 9.0 Hz, 13- or 14-H), 1.63 (1 H, d, *J* 9.5 Hz, 13- or 14-H), 1.79 (1 H, d, *J* 9.2 Hz, 13- or 14-H), 1.84 (1 H, d, *J* 9.3 Hz, 13- or 14-H), 1.88 (4 H, br s, 6a-,

6c-, 12a-, 12c-H), 3.25 (2 H, s, 6-, 11-H), 3.51 (2 H, s, 5-, 12-H), 3.77 (6 H, s, 2 × OCH_3), 6.56 (2 H, s, 2-, 3-H), 7.01–7.03 (2 H, m, 2 × ArH), and 7.10–7.12 (2 H, m, 2 × ArH) (Found: C, 84.2; H, 7.7. $C_{28}H_{30}O_2$ requires C, 84.4; H, 7.6%).

(5α,5aβ,5bα,5cβ,6α,11α,11aβ,11bα,11cβ,12α)-8-*Acetamido*-1,4-*dimethoxy*-5b,11b-*dimethyl*-9-*nitro*-5,5a,5c,6,11,11a,11c,12-*octahydro*-5,12:6,11-*dimethanonaphtho*[2″,3″:3′,4′]*cyclobuta*-[1′,2′:3,4]*cyclobuta*[1,2-b]*naphthalene* (**20b**).—A solution of (**17a**) (5.3 g, 13.2 mmol), and bromine (4.2 g, 26.4 mmol) in CH_2Cl_2 (90 cm^3) was stirred at room temperature, in the dark, for 5 h. The solution was washed with saturated aqueous sodium thiosulphate, dried, and evaporated to give the dibromo compound (**17b**) (7.3 g, 99%), m.p. 153–157 °C, which was not purified further; δ_H(500 MHz; $CDCl_3$) 1.02 (6 H, s, 2 × CH_3), 1.65 (2 H, m, 13-, 14-H), 1.84 (2 H, m, 13-, 14-H), 1.91 (2 H, s), 1.96 (2 H, s), 3.29 (2 H, s, 6-, 11-H), 3.55 (2 H, s, 5-, 12-H), 3.81 (6 H, s, 2 × OCH_3), 7.04 (2 H, m, 2 × ArH), and 7.13 (2 H, m, 2 × ArH).

Copper(II) nitrate trihydrate (3.3 g, 13.7 mmol) was added to a stirred solution of (**17b**) (3.8 g, 6.8 mmol) in acetic anhydride (38 cm^3) and CH_2Cl_2 (38 cm^3). The mixture was left at room temperature until t.l.c. showed no starting material (*ca.* 4 h). The mixture was then poured slowly into aqueous ammonia (15 mol dm^{-3}, 80 cm^3), and ice was added to maintain the temperature below 44 °C. The resulting mixture was extracted with CH_2Cl_2 (4 × 40 cm^3), and the combined organic extracts were washed with water (40 cm^3), dried, and then evaporated to give (**18b**), which was not purified further; δ_H(60 MHz; $CDCl_3$) 1.02 (6 H, s, 2 × CH_3), 1.5–2 (8 H, m), 3.37 (2 H, br s, 5-, 12-H, or 6-, 11-H), 3.55 (2 H, br s, 5-, 12-H, or 6-, 11-H), 3.78 (6 H, s, 2 × OCH_3), 7.18 (1 H, d, *J* 9 Hz, 10-H), and 7.8–8.1 (2 H, m, 7-, 9-H).

Zinc powder (2 g, 31 mmol) was added to a stirred solution of (**18b**) (2 g, 3.3 mmol) in glacial acetic acid (80 cm^3) and acetic anhydride (10 cm^3). The mixture was stirred for 18 h at room temperature, after which it was neutralized with aqueous ammonia (15 mol dm^{-3}, *ca.* 90 cm^3). The resulting mixture was extracted with CH_2Cl_2 (3 × 50 cm^3), washed with water (50 cm^3), dried, and evaporated to give (**19b**) (1.7 g, 83%) which was not purified further; δ_H(60 MHz; $CDCl_3$) 1.0 (6 H, s, 2 × CH_3), 1.7–1.95 (8 H, m), 2.0 (3 H, s, CH_3CO), 3.20 (2 H, br s, 5-, 12-H, or 6-, 11-H), 3.52 (2 H, br s, 5-, 12-H, or 6-, 11-H), 3.80 (6 H, s, 2 × OCH_3), 6.9 (2 H, m, 2 × ArH), 7.32 (1 H, m, ArH), and 7.8 (1 H, v br s, NH).

Nitric acid (15 mol dm^{-3}, 0.5 cm^3, 7.5 mmol) was added very slowly to an ice-cold solution of (**19b**) (1.7 g, 2.8 mmol) in glacial acetic acid (10 cm^3) and acetic anhydride (10 cm^3). The solution was stirred at 0 °C for 1 h, after which ice and aqueous ammonia (40 cm^3) were added, and the mixture was then extracted with CH_2Cl_2 (4 × 50 cm^3). The combined organic extracts were washed with water (50 cm^3), dried, and evaporated to give (**20b**) (0.55 g, 30%), m.p. 159 °C; δ_H(500 MHz; $CDCl_3$) 1.02 (6 H, s, 2 × CH_3), 1.65 (1 H, d, *J* 10.0 Hz), 1.70 (1 H, d, *J* 9.7 Hz), 1.83 (1 H, d, *J* 9.7 Hz), 1.84–1.95 (3 H, m), 1.97 (2 H, s, 5a-, 11c-H), 2.26 (3 H, s, CH_3CO), 3.34 (1 H, s, 6- or 11-H), 3.39 (1 H, s, 6- or 11-H), 3.56 (2 H, s, 5-, 12-H), 3.82 (6 H, s, 2 × OCH_3), 7.94 (1 H, s, 7-H), 8.55 (1 H, s, 10H), and 10.50 (1 H, br s, NH) (Found: C, 54.5; H, 4.6; N, 4.1. $C_{30}H_{30}Br_2N_2O_5$ requires C, 54.7; H, 4.6; N, 4.25%).

(5α,5aβ,5bα,5cβ,6α,21α,21aβ,21bα,21cβ,22α)-1,4-*Dimethoxy*-5b,21b-*dimethyl*-9,12,15,18-*tetraphenyl*-5,5a,5c,6,21,21a,21c,22-*octahydro*-5,22:6,21-*dimethanonaphtho*-[2‴,3‴:3″,4″]*cyclobuta*[1″,2″:3′,4′]*cyclobuta*[1′,2′:4,5]-*benzo*[1,2-g]*quinoxalino*-[2,3-b]*porphyrin* (**4**).—A stirred suspension of (**20b**) (0.55 g, 0.84 mmol) in hydrazine hydrate (85%, 15 cm^3) was heated at 90 °C for 17 h. Use of the same work-up procedure as that described above for the preparation of (**21a**) gave the nitroamine (**21b**) (0.46 g, 89%); δ_H(60 MHz; $CDCl_3$) 0.90 (6 H, s, 2 × CH_3), 1.2–2.0 (8 H, m), 3.11 (2 H, br s, 5-, 12-H, or 6-, 11-H), 3.48 (2 H, br s, 5-, 12-H, or 6-, 11-H), 3.78 (6 H, s, 2 × OCH_3), 6.2 (2 H, br s, NH_2), 6.55 (1 H, s, 7-H), and 7.76 (1 H, s, 10-H).

A mixture of (**21b**) (0.46 g, 0.75 mmol), hydrazine hydrate (7 cm^3), and Pd–C (10%, 0.1 g) in ethanol (95%, 20 cm^3) was refluxed for 17 h. Use of the same work-up procedure as that described above for the preparation of (**22a**) gave the diamine (**22b**) (0.2 g, 63%) as an air-sensitive solid; δ_H(60 MHz; $CDCl_3$) 0.93 (6 H, s, 2 × CH_3), 1.27–1.9 (8 H, m), 3.08 (2 H, br s, 5-, 12-H, or 6-, 11-H), 3.50 (2 H, br s, 5-, 12-H, or 6-, 11-H), 3.50 (2 H, NH_2, D_2O), 3.78 (6 H, s, 2 × OCH_3), 6.50 (2 H, s, 2-, 3-H or 7-, 10-H), and 6.58 (2 H, s, 2-, 3-H, or 7-, 10-H).

A solution of (**6**) (0.34 g, 0.53 mmol) in CH_2Cl_2 (50 cm^3) was added to a solution of diamine (**22b**) (0.2 g, 0.47 mmol) in CH_2Cl_2 (30 cm^3), and the resulting mixture was stirred for 30 min. The solvent was removed under reduced pressure and the residue was chromatographed on silica (75 g) using CH_2Cl_2 as an eluant. The first crude fraction was evaporated and the residue dissolved in 1:1 CH_2Cl_2–light petroleum (b.p. 60–80 °C) and rechromatographed on silica (120 g), using 3:7 light petroleum–CH_2Cl_2 as eluant, to give (**4**) (0.3 g, 62%), m.p. >300 °C (from CH_2Cl_2–methanol); δ_H(500 MHz; $CDCl_3$) −2.52 (2 H, s, 2 × NH), 1.10 (6 H, s, 2 × CH_3), 1.64 (1 H, d, *J* 9.0 Hz), 1.80 (1 H, d, *J* 9.6 Hz), 1.85 (1 H, d, *J* 8.9 Hz), 1.97 (2 H, s), 2.08 (1 H, d, *J* 9.6 Hz), 2.10 (2 H, s), 3.55 (2 H, s, 5-, 22-H or 6-, 21-H), 3.59 (2 H, s, 5-, 22-H or 6-, 21-H), 3.78 (6 H, s, 2 × OCH_3), 6.56 (2 H, s, 2-, 3-H), 7.56 (2 H, s, 7-, 20-H), 7.76–7.84 (10 H, m, ArH), 7.93 (2 H, t, *J* 7.6 Hz, 2 × H_{para}), 8.1–8.23 (4 H, v br hump, ArH), 8.26 (4 H, d, *J* 6.0 Hz, 4 × H_{ortho}), 8.76 (2 H, s, 13-, 14-H), 8.96 (2 H, d, *J* 5.0 Hz, 10-, 17-H or 11-, 16-H), and 9.01 (2 H, d, *J* 5.0 Hz, 10-, 17-H or 11-, 16-H); $\lambda_{max.}$ 434 (ε 148 000), 490 (2 500), 524 (11 500), 558 (2 550), 597 (5 100), 649 (610), and 688 nm (478) (Found: C, 83.1; H, 5.1; N, 8.0. $C_{72}H_{56}N_6O_2$ requires C, 83.4; H, 5.4; N, 8.1%).

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References

1 J. R. Miller, J. V. Beitz, and R. K. Huddleston, *J. Am. Chem. Soc.*, 1984, **106**, 5057, and references cited therein.
2 T. T. Li and M. J. Weaver, *J. Am. Chem. Soc.*, 1984, **106**, 6107.
3 K. W. Penfield, J. R. Miller, M. N. Paddon-Row, E. Cotsaris, A. M. Oliver, and N. S. Hush, *J. Am. Chem. Soc.*, 1987, **109**, 5061.
4 L. T. Calcaterra, G. L. Closs, and J. R. Miller, *J. Am. Chem. Soc.*, 1983, **105**, 670.
5 J. R. Miller, L. T. Calcaterra, and G. L. Closs, *J. Am. Chem. Soc.*, 1984, **106**, 3047.
6 G. L. Closs, L. T. Calcaterra, N. J. Green, K. W. Penfield, and J. R. Miller, *J. Phys. Chem.*, 1986, **90**, 3673.
7 D. Creed and R. A. Caldwell, *Photochem. Photobiol.*, 1985, **180**, 715.
8 H. Kuhn, *J. Photochem.*, 1979, **10**, 111.
9 D. Mobius, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 848.
10 P. Pasman, J. W. Verhoeven, and Th. de Boer, *Chem. Phys. Lett.*, 1978, **59**, 381.
11 P. Pasman, N. W. Koper, and J. W. Verhoeven, *Recl. Trav. Chim. Pays-Bas*, 1982, **101**, 363.
12 M. R. Wasielewski, M. P. Niemczyk, W. A. Svec, and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 5562.
13 N. S. Hush, M. N. Paddon-Row, E. Cotsaris, H. Oevering, J. W. Verhoeven, and M. Heppener, *Chem. Phys. Lett.*, 1985, **117**, 8.

14 J. M. Warman, M. P. de Haas, M. N. Paddon-Row, E. Cotsaris, N. S. Hush, H. Oevering, and J. W. Verhoeven, *Nature (London)*, 1986, **320**, 615.
15 J. M. Warman, M. P. de Haas, H. Oevering, J. W. Verhoeven, M. N. Paddon-Row, A. M. Oliver, and N. S. Hush, *Chem. Phys. Lett.*, 1986, **128**, 95.
16 J. W. Verhoeven, M. N. Paddon-Row, N. S. Hush, H. Oevering, and H. Heppener, *Pure Appl. Chem.*, 1986, **58**, 1285.
17 H. Oevering, M. N. Paddon-Row, M. Heppener, A. M. Oliver, E. Cotsaris, J. W. Verhoeven, and N. S. Hush, *J. Am. Chem. Soc.*, 1987, **109**, 3258.
18 M. R. Wasielewski, M. P. Niemczyk, W. A. Svec, and E. B. Pewitt, *J. Am. Chem. Soc.*, 1985, **107**, 1080.
19 T. A. Moore, D. Gust, P. Mathis, J.-C. Mialocq, C. Chachaty, R. V. Bensasson, E. J. Land, D. Doizi, P. A. Liddell, W. R. Lehman, G. A. Nemeth, and A. L. Moore, *Nature (London)*, 1984, **307**, 630.
20 P. A. Liddell, D. Barrett, L. R. Makings, P. J. Pessiki, D. Gust, and T. A. Moore, *J. Am. Chem. Soc.*, 1986, **108**, 5350.
21 D. Gust, T. A. Moore, L. R. Makings, P. A. Liddell, G. A. Nemeth, and A. L. Moore, *J. Am. Chem. Soc.*, 1986, **108**, 8028.
22 D. Gust, T. A. Moore, P. A. Liddell, G. A. Nemeth, L. R. Makings, A. L. Moore, D. Barrett, P. J. Pessiki, R. V. Bensasson, M. Rougee, C. Chachaty, F. C. De Schryver, M. Van der Auweraer, A. R. Holzwarth, and J. S. Connolly, *J. Am. Chem. Soc.*, 1987, **109**, 846.
23 A. D. Joran, B. A. Leland, G. G. Geller, J. J. Hopfield, and P. B. Dervan, *J. Am. Chem. Soc.*, 1984, **106**, 6090.
24 A. D. Joran, B. A. Leland, P. M. Felker, A. H. Zewail, J. J. Hopfield, and P. B. Dervan, *Nature (London)*, 1987, **327**, 508.
25 H. B. Gray, *Chem. Soc. Rev.*, 1986, **15**, 17.
26 (*a*) R. Hoffmann, *Acc. Chem. Res.*, 1971, **4**, 1; (*b*) R. Gleiter, *Angew. Chem., Int. Edn. Engl.*, 1974, **13**, 696; (*c*) M. N. Paddon-Row, *Acc. Chem. Res.*, 1982, **15**, 245.
27 M. N. Paddon-Row, unpublished data.
28 (*a*) M. N. Paddon-Row, H. K. Patney, R. S. Brown, and K. N. Houk, *J. Am. Chem. Soc.*, 1981, **103**, 5575; (*b*) M. N. Paddon-Row, H. K. Patney, J. B. Peel, and G. D. Willett, *J. Chem. Soc., Chem. Commun.*, 1984, 564; (*c*) F. S. Jørgensen, M. N. Paddon-Row, and H. K. Patney, *ibid.*, 1983, 573; (*d*) V. Balaji, L. Ng, K. D. Jordan, M. N. Paddon-Row, and H. K. Patney, *J. Am. Chem. Soc.*, 1987, **109**, 6957.
29 M. N. Paddon-Row, E. Cotsaris, and H. K. Patney, *Tetrahedron*, 1986, **42**, 1779.
30 M. J. Crossley and L. G. King, *J. Chem. Soc., Chem. Commun.*, 1984, 920.
31 M. J. Crossley and P. L. Burn, *J. Chem. Soc., Chem. Commun.*, 1987, 39.
32 M. W. Galley and R. C. Hahn, *J. Org. Chem.*, 1976, **41**, 2006.
33 H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *J. Am. Chem. Soc.*, 1969, **91**, 4512.
34 M. N. Paddon-Row, H. K. Patney, and L. N. Pasupuleti, *Aust. J. Chem.*, 1982, **35**, 307.
35 (*a*) D. S. C. Chang and N. Filipescu, *J. Am. Chem. Soc.*, 1972, **94**, 4170; (*b*) J. Meinwald and G. A. Wiley, *J. Org. Chem.*, 1958, **23**, 3667.
36 M. S. Raasch, *J. Org. Chem.*, 1980, **45**, 856.
37 W. P. Lay, K. Mackenzie, and J. R. Telford, *J. Chem. Soc. C*, 1971, 3199.
38 B. V. Lap and M. N. Paddon-Row, *J. Org. Chem.*, 1979, **44**, 4979.
39 T. Mitsudo, K. Kokuryo, T. Shinsugi, Y. Nakagawa, Y. Watanabe, and Y. Takegami, *J. Org. Chem.*, 1979, **44**, 4492.
40 R. N. Warrener, I. G. Pitt, and D. N. Butler, *J. Chem. Soc., Chem. Commun.*, 1983, 1340.
41 N. Ahmad, J. J. Levison, and S. D. Robinson, *Inorg. Synth.*, 1974, **15**, 48.

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