# Facile Aerial Oxidation of a Porphyrin. Part 4.† Unsymmetrical *meso*-Tetra Aryl Porphyrins with 3,5-Di-t-Butyl-4-Hydroxyphenyl and 4-Hydroxyphenyl Substituents

**Lionel R. Milgrom* and Nasrin Mofidi**
*School of Inorganic and Physical Chemistry, Kingston Polytechnic, Penrhyn Road, Kingston-upon-Thames KT1 2EE*
**Christopher C. Jones**
*Department of Chemistry, Imperial College of Science and Technology, Exhibition Road, London SW7 2AZ*
**Anthony Harriman**
*Davy Faraday Laboratory, Royal Institution, 21 Albemarle Street, London W1X 4BS*

A series of porphyrins (**2a**)–(**5a**), unsymmetrically substituted in their *meso*-positions with 3,5-di-t-butyl-4-hydroxyphenyl(DtB4HP) and 4-hydroxyphenyl (4HP) groups, has been synthesised and characterised. The two di-DtB4HP di-4HP isomeric porphyrins, (**3a**) and (**4a**) (called '*cis*' and '*trans*', respectively), in particular are distinguishable by $^1H$ n.m.r. spectroscopy. In basified dichloromethane (DCM) solutions, the porphyrins undergo drastic colour and u.v.–visible changes which, in 1 mol dm$^{-3}$ methanolic potassium hydroxide, is indicative of irreversible aerial oxidation that is slower and less extensive than for the symmetrically tetrakis-DtB4HP substituted porphyrin (**1**). Cyclic voltammetry supports this, indicating that in basified DCM solutions, one-electron oxidation of porphyrins (**2a**)–(**5a**) becomes increasingly more difficult than for (**1**), as the DtB4HP groups are replaced by 4HP. An explanation of the relative redox activity of these porphyrins compared with (**1**), is offered in terms of the different electron-releasing properties of the two types of phenolic substituent.

In recent years, we and other workers have undertaken the investigation of the facile aerial oxidation of porphyrins *meso*-substituted with redox-active groups.[1] Porphyrin (**1**) in basic solutions, for example, undergoes facile two-electron oxidation to (**7**). Reduction back to (**1**) again may be achieved either chemically[2] or electrochemically.[3] Possible applications of such a redox cycle include electrocatalytic oxygen reduction in fuel cells[4] and *in situ* generation of hydrogen peroxide.

We wished to extend these investigations to immobilised derivatives of (**1**) covalently-bound to solid supports. This would require the synthesis of porphyrins containing different substituents; some with redox activity and others with functionality. We have previously synthesised a wide range of derivatised porphyrins (for studies in solar energy conversion), based on the readily functionalisable *meso*-tetrakis(4-hydroxyphenyl)porphyrin.[5] We have also reported a one-pot synthesis of unsymmetrical porphyrins and their facile separation by flash chromatography.[6] By combining these two approaches, we thought it possible to produce porphyrins containing both redox-active and functional moieties, the latter through which attachment to solid supports could be achieved. This paper, therefore, reports the synthesis and some properties of unsymmetrical tetra-aryl porphyrins containing both 3,5-di-t-butyl-4-hydroxyphenyl (DtB4HP) and 4-hydroxyphenyl (4HP) groups.

## Results and Discussion

Porphyrins (**2a**)–(**5a**) were obtained by the Rothemund reaction[7] of 4-methoxybenzaldehyde and 3,5-di-t-butyl-4-hydroxybenzaldehyde with pyrrole in refluxing propionic acid. After column chromatography on neutral alumina (eluting with DCM), the mixture of porphyrins was treated with a solution of 1 mol dm$^{-3}$ boron tribromide in DCM (−80 °C) to demethylate the 4-methoxyphenyl groups.[8]

Separation of similar mixtures of porphyrins had previously been achieved using preparative thin-layer chromatography (t.l.c.)[9] and flash chromatography.[6] We found, however, that with the mixture of porphyrins described here, column chromatography on silica gel (column grade) was adequate, eluting with mixtures of diethyl ether and hexane. Porphyrins (**1**)–(**4a**) were eluted from the column separately with a 65:35 ether–hexane mixture, while (**5a**) was eluted by increasing the ether ratio to 80:20.

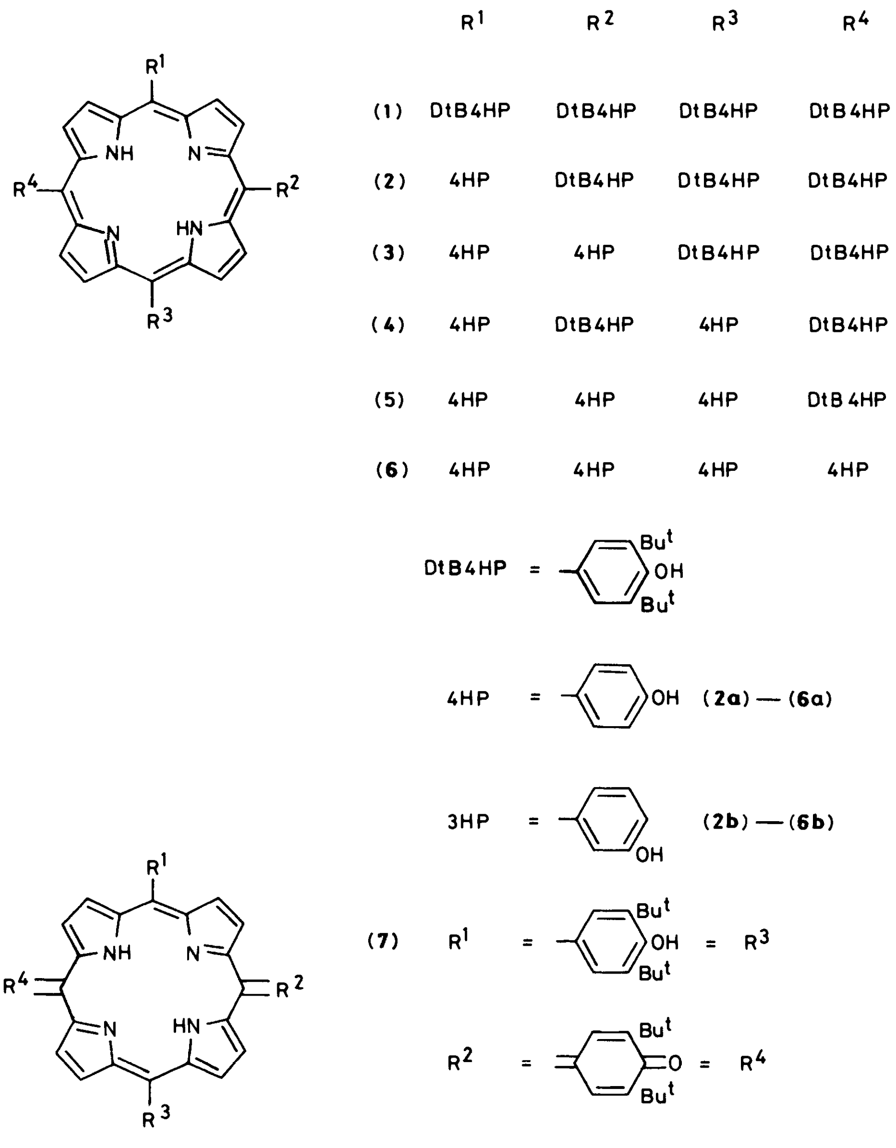
The porphyrins were characterised using f.a.b.s., u.v.–visible and $^1H$ n.m.r. spectroscopy. In particular, the n.m.r. spectra were useful for distinguishing the two di-DtB4HP di-4HP isomers (**3a**) ('*cis*') and (**4a**) ('*trans*').[6b,‡] The pyrrole β-protons in these isomers are in two slightly different environments, depending on the positioning of the DtB4HP and 4HP *meso*-substituents to each other. The '*cis*' isomer (**3a**) has a mirror plane of symmetry through two diagonally opposed porphyrin nitrogen atoms (Figure 1) which gives a possible four different β-proton environments. The '*trans*' isomer (**4a**) has mirror planes through two opposite *meso*-positions Figure 1 which gives only two possible β-proton environments. The $^1H$ n.m.r. spectrum of (**3a**) (in $CD_2Cl_2$) does indeed show four different β-proton resonances (centred on δ 8.89), but the $^1H$ n.m.r. spectrum of (**4a**) (in [$^2H_6$]acetone) shows only a broadened singlet (at δ 8.91).

Porphyrins (**2a**)–(**5a**) in DCM, gave u.v.–visible spectra typical of *meso*-tetra-aryl-substituted porphyrins,[10] *i.e.*, a strong B band (around 420 nm) and four Q bands (500–650 nm), the intensities of which decreased with increasing wavelength. Addition of either tetra-n-butylammonium hydroxide (tnBAH) or potassium hydroxide (KOH—both bases

---

† For part 3, see ref. 1(*i*).

‡ We thank a referee for suggesting the alternative terms, 'adjacent' (for '*cis*') and 'opposite' (for '*trans*').



| | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| **(1)** | DtB4HP | DtB4HP | DtB4HP | DtB4HP |
| **(2)** | 4HP | DtB4HP | DtB4HP | DtB4HP |
| **(3)** | 4HP | 4HP | DtB4HP | DtB4HP |
| **(4)** | 4HP | DtB4HP | 4HP | DtB4HP |
| **(5)** | 4HP | 4HP | 4HP | DtB4HP |
| **(6)** | 4HP | 4HP | 4HP | 4HP |

Scheme.

Table 1. U.v.-visible spectra of porphyrins (1)–(5a) in basified DCM

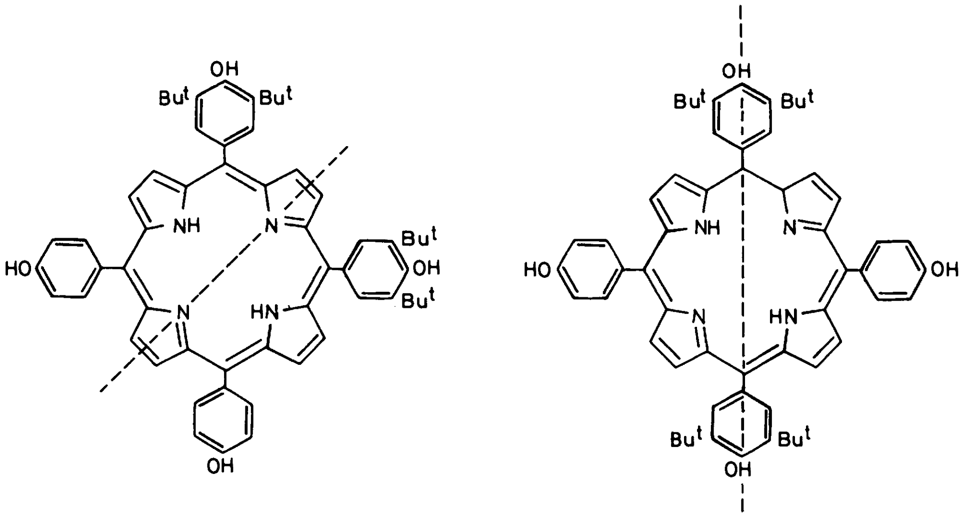
| Porphyrin | 1 mol dm$^{-3}$ tnBAH–MeOH[a] | 1 mol dm$^{-3}$ KOH–MeOH[a] |
|---|---|---|
| **(1)** | 437[b] (19.5), 551 (60.8) | 801 (102.1) |
| **(2a)** | 405 (36.7), 459 (36.8)<br>791 (24.6) | 428 (70.4), 527 (9.6)<br>572 (10.2), 663 (6.2) |
| **(3a)** | 411 (76.3), 450 (60.5)<br>773 (41.9) | 425 (119.6), 526 (17.4)<br>571 (20.8), 662 (14) |
| **(4a)** | 412 (51.0), 460 (41.1)<br>768 (21.4) | 429 (55.9), 579 (11.9)<br>659 (8.8) |
| **(5a)** | 430 (57.4), 598 (8.9)<br>680 (8.95) | 430 (72.8), 595 (6.1)<br>653 (5.2), 709 (4.3) |

[a] 10 Drops of base added to porphyrin stock solutions. [b] Absorption wavelengths in nm; decadic extinction coefficients (× $10^{-3}$) in parentheses.

as 1 mol dm$^{-3}$ solutions in methanol; 10 drops), however, led to drastic colour and spectroscopic changes (Table 1 and Figure 2). Initially, the colour of the solutions changed to deep green, accompanied in the u.v.–visible spectra by intensity decreases, broadening and/or splitting of the B band, collapse of the four Q bands, and in some cases, appearance of a broad absorption at long wavelength. Porphyrins (**2a**)–(**5a**) in 1 mol dm$^{-3}$ KOH–MeOH and (**5a**) in 1 mol dm$^{-3}$ tnBAH–MeOH initially have u.v.–visible spectra that resemble (**6a**) in 1 mol dm$^{-3}$ KOH–MeOH,[5] *i.e.*, collapse of the Q bands into two or three broader bands centred around 600 and 680 nm, and a broadened, red-shifted B band of decreased intensity. Porphyrins (**2a**)–(**4a**) in 1 mol dm$^{-3}$ tnBAH–MeOH, on the other hand, have split B bands of decreased intensity, straddling the original neutral porphyrin B band, and a broad absorption, centred around 750–800 nm, replacing the original Q bands. In contrast, porphyrin (**1**) in degassed, basified DCM, loses its B band completely (Figure 2).

The spectral changes shown by (**2a**)–(**5a**) are reminiscent of those occurring in some metal complexes of (**1**) [*e.g.* Pd(II), Pt(II), V(IV)=O, Sn(IV), Cu(II)][1i] which on basification undergo little aerial oxidation. The broad absorption at long wavelength probably represents mixing of diquinomethide-type structures (*e.g.* Figure 3) into the porphyrin ground state.

We investigated the meaning of these spectral changes in



(3a)

(4a)

**Figure 1.** Porphyrins (3a) and (4a) showing mirror planes of symmetry in each molecule and the pyrrole β-proton $^1H$ n.m.r. resonances

terms of possible aerial oxidation of the porphyrins, by modifying a technique used previously,[1i] *i.e.*, acidification of the basified solutions with trifluoroacetic acid (TFA), and observation of the intensity of the returned B band. In the previous work,[1i] we investigated metal complexes of (**1**). In this present work, the porphyrins are metal-free, so that acidification with TFA produces the B band of the porphyrin dication (*ca.* 450 nm) and not that of the neutral porphyrin.

Stock solutions of the porphyrins (**2a**)–(**5a**) were prepared in DCM ($2 \times 10^{-5}$ mol dm$^{-3}$) and an aliquot of each taken, placed in a cuvette, acidified with one drop of TFA, and the u.v.–visible spectrum recorded. This shows the spectrum of the porphyrin dication prior to oxidation. An undegassed mixture of tnBAH–MeOH (10 drops) or 1 mol dm$^{-3}$ KOH–MeOH (10 drops) was added to the stock solutions, and aliquots withdrawn and acidified every 5 min over a period of 1.5 h. Some aerial oxidation of the porphyrins was deemed to have occurred, over this period, if a significant decrease in the intensity of the returned dicationic B band occurred after acidification.

Our results (Figure 4) indicate that the stock solutions basified with 1 mol dm$^{-3}$ tnBAH–MeOH underwent very little aerial oxidation. However, the stock solutions basified with 1 mol dm$^{-3}$ KOH–MeOH did show marked reductions in B band intensity, after acidification with TFA, during the first 30 min. Once again, this behaviour contrasts with that of free-base porphyrin (**1**) in undegassed basified DCM solutions, which shows rapid (1–3 min) and complete disappearance of the B band on acidification with TFA. The transition-metal complexes of (**1**)[1i] mentioned earlier do, however, show the slower and less extensive autoxidation behaviour of (**2a**)–(**5a**).

Cyclic voltammetry was performed on ethanolic and DCM solutions of (**2a**)–(**5a**), under neutral and basified conditions. The results are shown in Table 1 and Figure 5. The first half-wave potentials are lower in DCM than ethanol, in particular, under basified conditions. Under neutral conditions, there is a small increase in the first half-wave potentials, in both ethanol and DCM, with increasing number of DtB4HP groups in the porphyrin. In basified DCM solutions, this trend is dramatically reversed, with the first half-wave potentials markedly decreasing with increasing number of DtB4HP groups in the porphyrin, the lowest value being for (**1**). Thus the ease of one-electron oxidation of the porphyrins in basified DCM increases along the series: (**6a**) $\simeq$ (**5a**) < (**4a**) < (**3a**) < (**2a**) < (**1**).

An explanation of the u.v.–visible and cyclic voltammetric data may depend on the way the two bases variously affect the deprotonation of the different phenolic OH groups, and how efficiently the resulting phenoxides can delocalise their electron density into the porphyrin ring. This last point has previously been discussed as a possible prerequisite for aerial oxidation of the (**1**) to occur.[1a,g,i] The delocalised charge could disrupt the aromatic stability of the porphyrin ring, leading to oxidation of the whole system. Alternatively, in (**1**), delocalisation of the phenoxide negative charge could lead to diquinomethide-type structures, as in Figure 3, effectively blocking electron donation by the other substituents, which would then be easily oxidised by air.

That the first half-wave potentials of (**2a**)–(**5a**) are higher in basic ethanol than basified DCM, would indicate that the more polar ethanol is somehow hindering delocalisation of electron density onto the porphyrin rings, probably by hydrogen-bonding to the phenoxide anions. Also, the decrease in first half-wave potentials with increasing number of DtB4HP groups, probably indicates that these groups have greater electron-releasing power into the porphyrin ring than the unsubstituted 4HP groups. This is not unreasonable as the inductive electron-donating effect of the t-butyl substituents in the DtB4HP groups would be added to the mesomeric donating effect of the phenoxide oxygen. And because of the steric crowding around this oxygen, there would be less solvent stabilisation of this phenoxide compared with that formed from 4HP groups. This could explain why porphyrin (**1**) undergoes rapid aerial oxidation in basified solutions, whereas porphyrin (**6a**) does not. It could also explain the differences in relative ease of aerial oxidation of porphyrins (**2a**)–(**5a**) with the two different bases, as indicated by the u.v.–visible data.

It is known that bulky *ortho* alkyl substituents attached to phenol lower the redox potential[11] and decrease the acidity.[12] Also, 1 mol dm$^{-3}$ tnBAH–MeOH probably basifies DCM solutions more strongly than 1 mol dm$^{-3}$ KOH–MeOH (due, in the first case, to the loss of primary solvation of the hydroxide ion by formation of contact ion pairs[13]). We propose, therefore, that 1 mol dm$^{-3}$ tnBAH–MeOH in DCM deprotonates both the DtB4HP and 4HP *meso*-substituents, while 1 mol dm$^{-3}$ KOH–MeOH in DCM *initially* deprotonates the less sterically hindered 4HP groups only. Since in tnBAH–MeOH the deprotonated DtB4HP groups are better electron donors than the deprotonated 4HP groups,[14] the former will delocalise their phenoxide electron density onto the porphyrin ring (*via* the

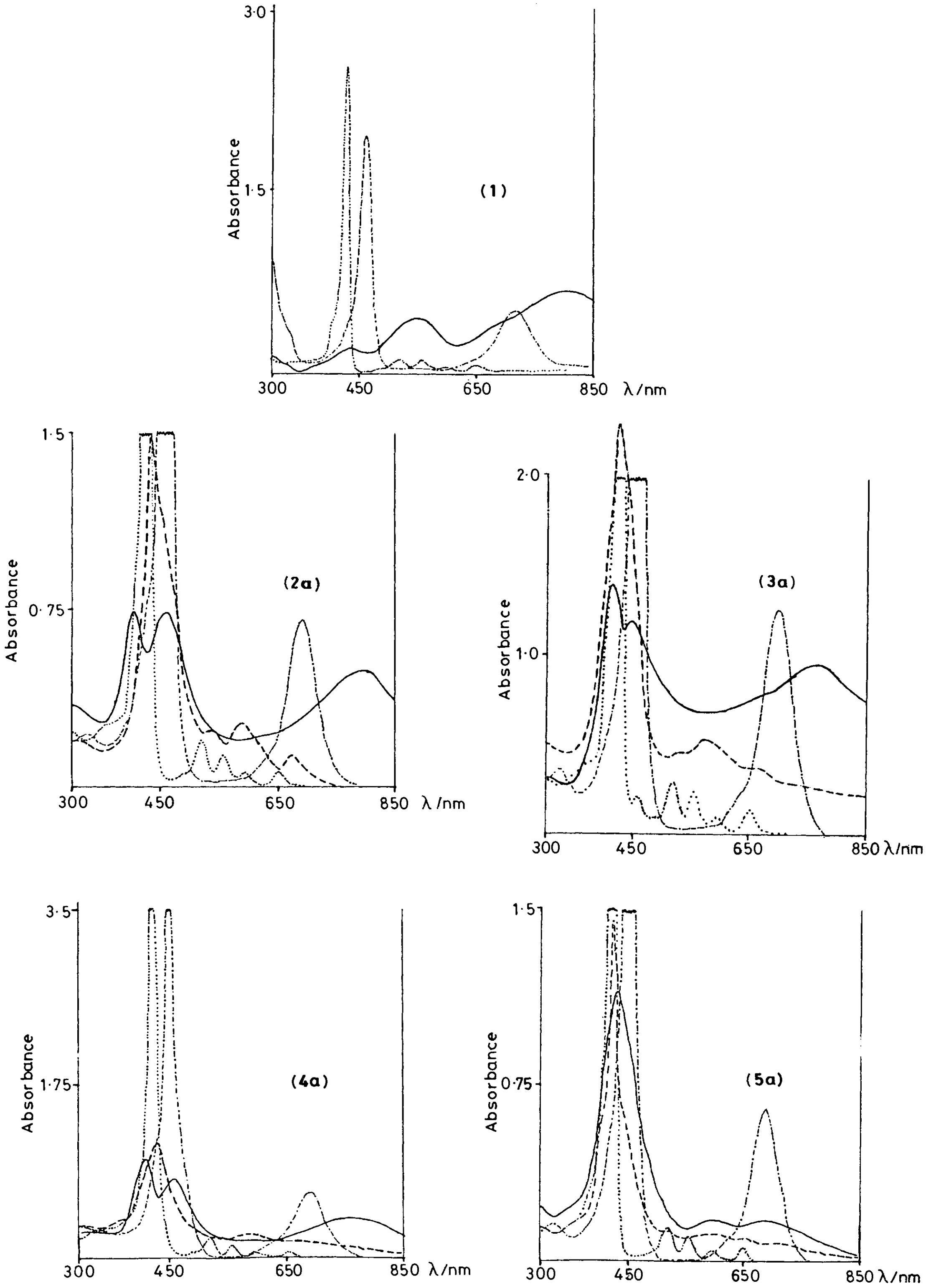


**Figure 2.** U.v.–visible spectra of porphyrins (**1**)–(**5a**) in neutral (· · · ·), acidified (TFA, – · – · –), basified (1 mol dm$^{-3}$ tnBAH–MeOH, ———), and basified (1 mol dm$^{-3}$ KOH–MeOH, – – – –) DCM

electron-deficient *meso*-carbons[15]) more efficiently than the latter. This would make the deprotonated DtB4HP groups less readily oxidisable. On the other hand, in 1 mol dm$^{-3}$ KOH–MeOH, the deprotonated 4HP groups would have less opposition to donating their phenoxide electron density onto the porphyrin ring, due to the initial absence of competing deprotonated DtB4HP groups. This would mean that, once the DtB4HP groups had deprotonated, there would be less opportunity for them to delocalise their phenoxide electron density into the now electron-rich porphyrin ring. Consequently, they would be more readily oxidised.

A simple test of this argument would be to synthesise an

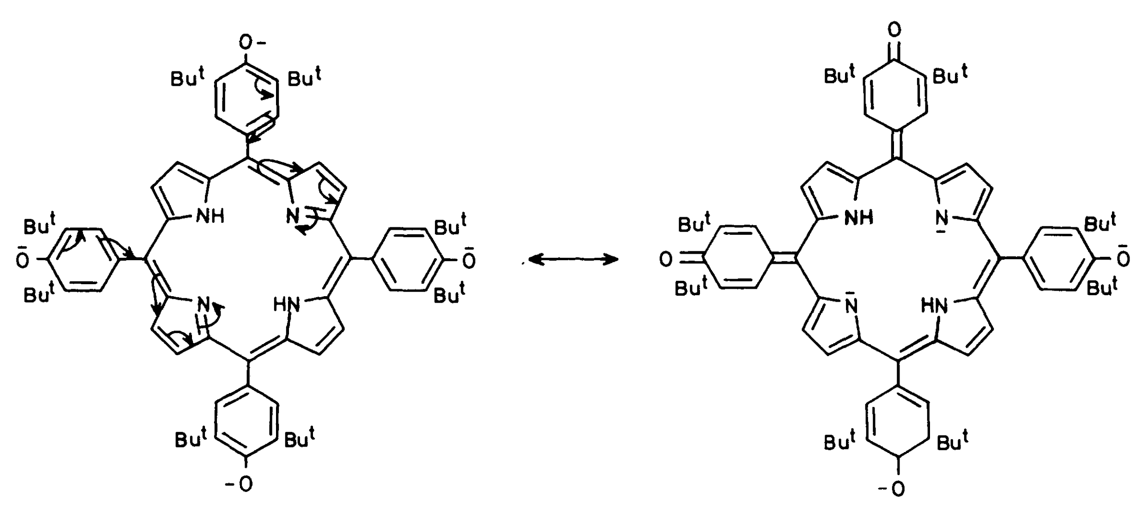


Figure 3. Aromatic and diquinomethide resonance forms of porphyrin (**1**)

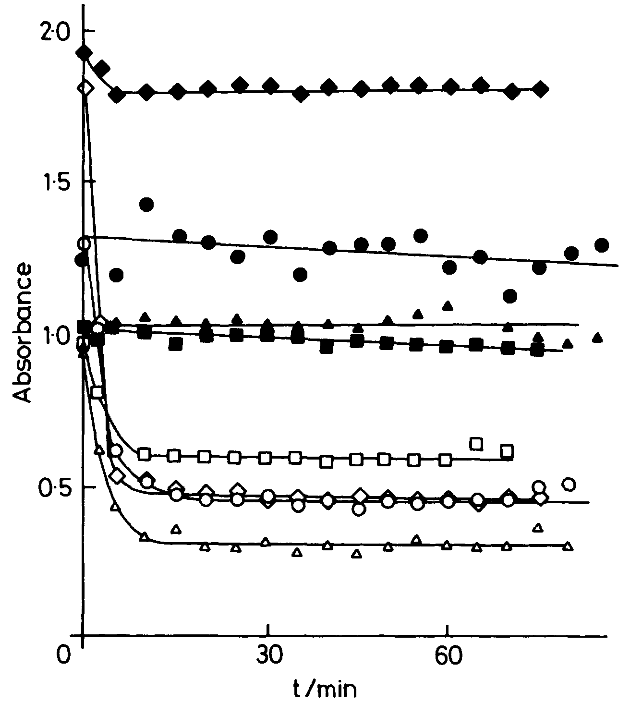


**Figure 4.** Decrease in regenerated dicationic porphyrin B band, the abscissa representing time elapsed after addition of base (open figures, 1 mol dm$^{-3}$ KOH–MeOH; closed figures, 1 mol dm$^{-3}$ tnBAH–MeOH: $t = 0$), before acidification with TFA: (**2a**), (**3a**), (**4a**), and (**5a**)

analogous series of unsymmetrical porphyrins (**2b**)–(**5b**) in which the 4HP substituents of the earlier series were replaced by 3HP groups. Previous work[5] has shown that porphyrin (**6b**) in 1 mol dm$^{-3}$ KOH–MeOH gives a normal *meso*-tetra-aryl-type spectrum. This is because the phenoxide electron density is now unable to delocalise into the porphyrin ring, so leaving the porphyrin optical state unaffected. Consequently, in basified solutions, unsymmetrical porphyrins (**2b**)–(**5b**) should have redox and u.v.–visible characteristics determined solely by the availability of electron density from the deprotonated DtB4HP groups. We would predict, therefore, that this series of porphyrins should be less amenable to aerial oxidation in basified DCM solutions, as the DtB4HP phenoxide electron density can be more easily accommodated on the porphyrin ring, without competition from the 3HP phenoxide electron density.

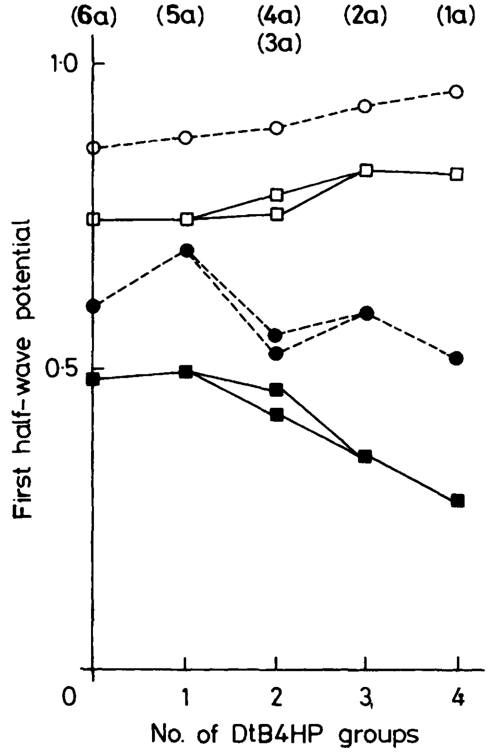


**Figure 5.** Cyclic voltammograms in neutral (open figures) and basic (closed figures) ethanol (circles) and DCM (squares). The added base was degassed NaOEt in ethanol (10$^{-2}$ mol dm$^{-3}$)

In an exploratory study, we have synthesised porphyrins (**2b**)–(**5b**), separated (**2b**)–(**4b**), and characterised (**2b**), analytically and spectroscopically. Porphyrins (**3b**) and (**4b**) have, at present, been characterised by f.a.b.s only. Preliminary results on the aerial oxidation of this series, using the basification and acidification procedure previously mentioned, indicate that DCM solutions of (**3b**) and (**4b**) are appreciably stable with the two bases, while (**2b**) is only partially aerially oxidised with 1 mol dm$^{-3}$ KOH–MeOH [less so than (**2a**) under similar conditions]. Further details on this series will be published at a later date.

A feature of the cyclic voltammetry for porphyrins (**3a**) and (**4a**), is their small difference in first half-wave potential (Figure 5). This indicates that, within an overall trend of increasing ease of porphyrin oxidation (EtOH[neutral] < DCM[neutral] < EtOH[basic] < DCM[basic]), and except in neutral EtOH, it is harder to remove an electron from the '*trans*' isomer (**4a**) than the '*cis*' isomer (**3a**), by approximately 0.03 V. As mentioned earlier, the overall trend probably reflects the relative differences in the ability of EtOH and DCM to solvate the porphyrins two different types of phenol and phenoxide substituents. The more subtle variations in first half-wave potential between the '*trans*' and '*cis*' isomers may reflect the relative positioning of the DtB4HP and 4HP groups on the porphyrin ring affecting the overall polarity of the macrocycle: the '*cis*' isomer will be more polar than the '*trans*'. This could be exacerbated by the different electron releasing powers of the two phenolic substituents, '*cis*' DtB4HP groups being better placed to release electron density into the porphyrin ring than a '*trans*' configuration (Figure 6).

We observed weak e.s.r. spectra for porphyrins (**2a**)–(**4a**) in DCM ($\sim 10^{-2}$ mol dm$^{-3}$), basified with 1 mol dm$^{-3}$ tnBAH–MeOH (Figure 7). Porphyrin (**5a**) was e.s.r.-silent. The e.s.r. spectra of these compounds showed marked differences compared with that of porphyrin (**1**) under similar conditions. The latter gives a 1:2:1 triplet [Figure 7(a)] of superhyperfine multiplets [Figure 7(b)]. This is interpreted as due to unpaired electron density, isolated on the e.s.r. timescale on a DtB4HP group, interacting with two equivalent aryl protons and, at longer range, the 18 equivalent protons of the t-butyl groups.[11]

**Table 2.** First half-wave potentials (V *versus* s.c.e.[a]) of porphyrins (**1**)–(**6a**) in neutral and basic[b] ethanol and DCM

Porphyrin half-wave potentials

| | Ethanol | | DCM | |
|---|---|---|---|---|
| Porphyrin | Neutral | Basic | Neutral | Basic |
| (**1**) | 0.95 | 0.51 | 0.81 | 0.28 |
| (**2a**) | 0.925 | 0.59 | 0.82 | 0.35 |
| (**3a**) | 0.89 | 0.52 | 0.75 | 0.42 |
| (**4a**) | 0.89 | 0.55 | 0.78 | 0.46 |
| (**5a**) | 0.875 | 0.69 | 0.74 | 0.49 |
| (**6a**) | 0.855 | 0.60 | 0.74 | 0.48 |

[a] Saturated calomel electrode. [b] By addition of sodium ethoxide.

The e.s.r. spectra of porphyrins (**2a**)–(**4a**) are weaker and more complex. Our interpretation of them, at this stage, is therefore tentative.

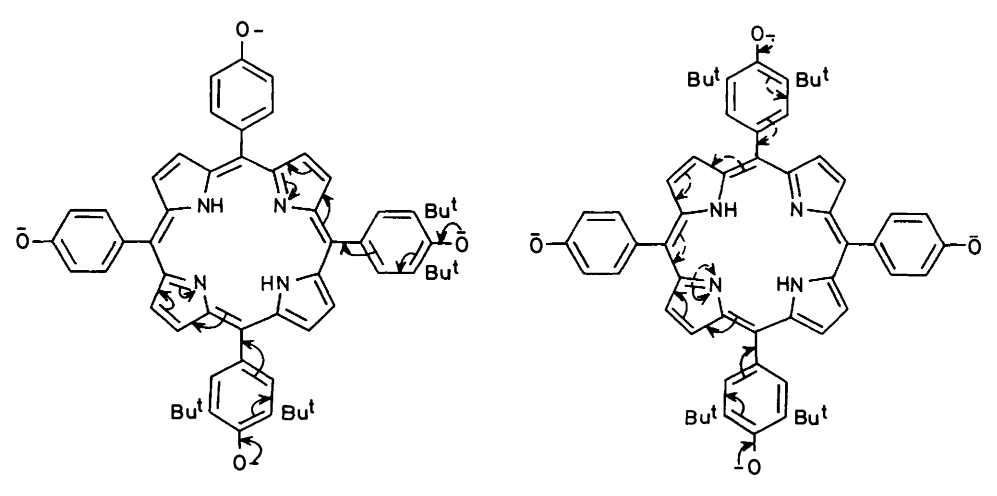
The e.s.r. spectrum of (**2a**) appears as a triplet on which is superimposed a broader component. This second component is more intense at higher concentrations and, for (**3a**) and (**4a**), completely dominates as a broad doublet, reminiscent of the spectra obtained for the Ni(II) complex of (**1**).[1i] We are, as yet, unable to account satisfactorily for these e.s.r. spectra. However, crystal structure data on the Pd(II) complex of (1)[1g] indicate hydrogen-bonding between DtB4HP groups in the solid state. Also, the decay of the triplet e.s.r. spectrum for the Sn(IV) complex of (**1**), in neutral DCM, shows second-order kinetics[1i] indicating a bimolecular mechanism (possibly *via* peroxy-linked radical dimers) for the radical-decay process. It is not inconceivable, therefore, that in the solution concentrations used for the e.s.r. studies, porphyrins (**2a**)–(**4a**) may be forming hydrogen-bonded dimers; the labile hydrogen-bonded hydrogen accounting for the doublet e.s.r. spectrum and its broadness. We hope to report on this at a later date.

## Conclusions

Substitution of one or more of the DtB4HP groups in porphyrin (**1**) with 4HP groups yields a series of unsymmetrical porphyrins (**2a**)–(**5a**). Their lability to dissolved oxygen in basified solutions is noticeably reduced, compared with the free-base parent porphyrin (**1**), but similar to certain of its metal complexes. As a result, by attaching these porphyrins to solid supports, *via* their 4HP groups, it should be possible to utilise these porphyrins' reducing ability (*e.g.*, for production of hydrogen peroxide, and in the operation of fuel cells) in a more rational manner compared with free-standing homogeneous solutions of the more reactive porphyrin (**1**). Experiments along these lines are now clearly possible.

## Experimental

Chromatographic separations of the porphyrins were performed on columns made from slurries of neutral alumina (Brockmann activity grade III, B. D. H.) or silica gel (Kieselgel 60, Merck). Thin layer chromatography plates (Merck) were obtained ready-made. Pyrrole, substituted benzaldehydes, propionic acid, 1 mol dm$^{-3}$ boron tribromide in DCM, 1 mol dm$^{-3}$



(3a) (4a)

**Figure 6.** Relative placing of DtB4HP groups on porphyrin ring could affect their electron-releasing power into the macrocycle

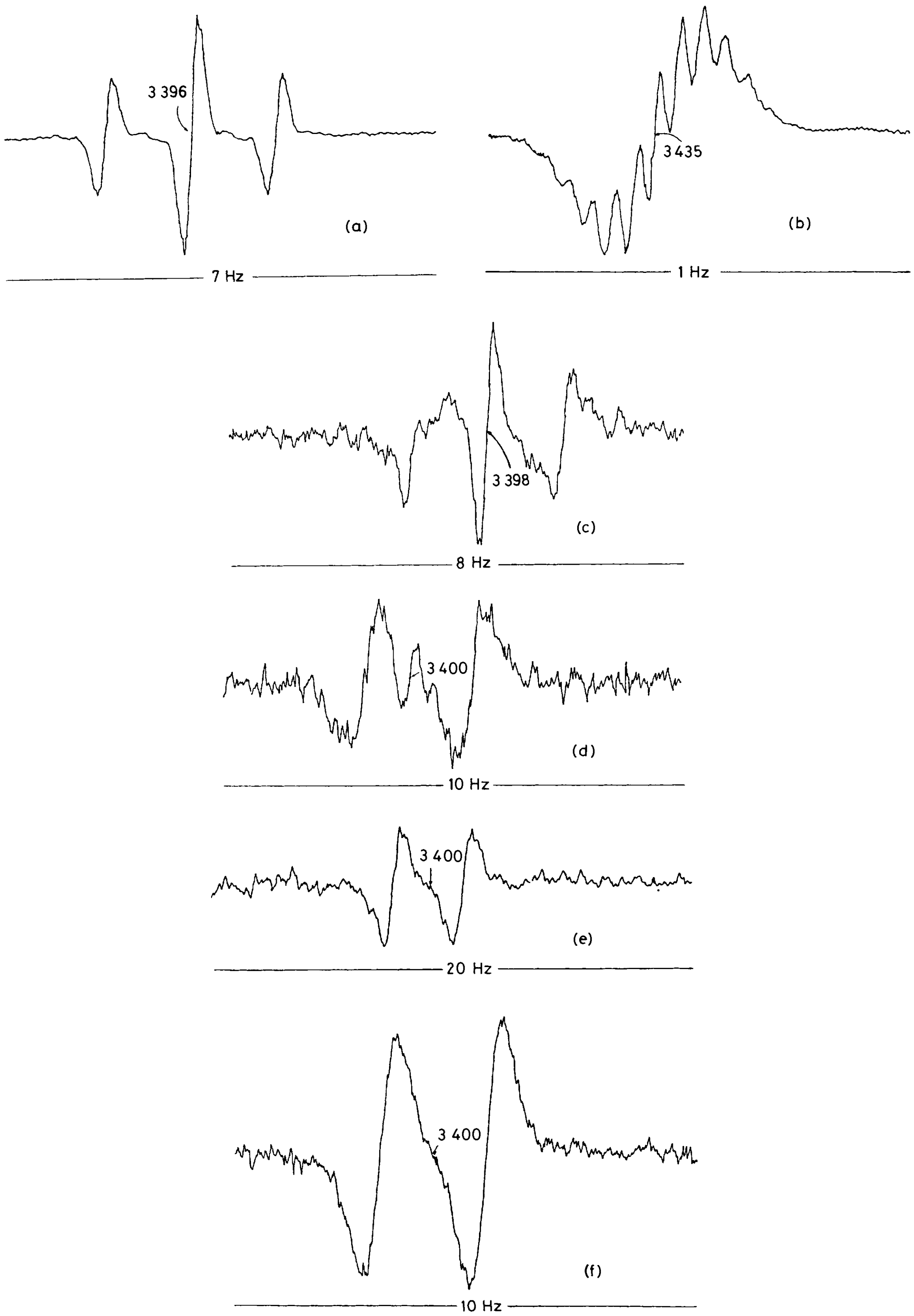


**Figure 7.** E.s.r. spectra of porphyrins: (**1**); (a) and (b); (**2a**); (c) and (d); (**3a**); (e), (**4a**); (f). Porphyrin (**5a**) is e.s.r.-silent

tnBAH in methanol, and TFA were purchased from Aldrich and used as supplied. Chloroform, DCM, methanol, diethyl ether, and hexane were reagent grade (B. D. H.). DCM for demethylation reactions, was dried and distilled from calcium hydride. $^1$H N.m.r. spectra were run on a Bruker WP80 instrument in $CDCl_3$ or $CD_2Cl_2$ using $SiMe_4$ as an internal reference. E.s.r. spectra were run on a Bruker ER 200t instrument using freshly prepared solutions of the porphyrins in DCM (*ca.* $10^{-2}$ mol dm$^{-3}$) to which had been added several drops of 1 mol dm$^{-3}$ tnBAH–MeOH. A solid solution of Mn(II)-doped (190 p.p.m.)

MgO was used as an external reference. Cyclic voltammograms were performed in neutral and basic, dried, nitrogen-degassed ethanol and DCM, with tetra-n-butylammonium fluoroborate (0.1 mol dm$^{-3}$) as the supporting electrolyte. For the basic solutions, sodium ethoxide in ethanol ($10^{-2}$ mol dm$^{-3}$) was added, after being purged with nitrogen. All u.v.–visible spectra were recorded on a Shimadzu u.v.–260 spectrophotometer. Stock solutions of the porphyrins were prepared in DCM ($2 \times 10^{-5}$ mol dm$^{-3}$; 100 cm$^3$) and their spectra run. A solution of 1 mol dm$^{-3}$ tnBAH–MeOH or 1 mol dm$^{-3}$ KOH–MeOH (10 drops) was then added to each stock solution and their spectra run again. Acidification (to test the amount of aerial oxidation) was performed by withdrawing aliquots of these basic solutions, placing them in a cuvette, and adding TFA (1 drop). The u.v.–visible spectra were then rerecorded.

*Synthesis of Porphyrins* (**2a**)–(**5a**).—4-Methoxybenzaldehyde (5.6 cm$^3$, 50 mmol) and 3,5-di-t-butyl-4-hydroxybenzaldehyde (11.75 g, 50 mmol) were added to propionic acid (500 cm$^3$) and the mixture brought to reflux. Pyrrole (7.0 cm$^3$, 100 mmol) was then added, the mixture refluxed for a further 1.5 h, concentrated to one fifth of its original volume, and then allowed to cool overnight. The purple slurry of mixed porphyrins was then filtered, and washed with methanol. The dark propionic acid residues were concentrated to yield a second crop. The total crude material was dissolved in the minimum amount of DCM, chromatographed on neutral alumina, and the red band of mixed porphyrins eluted with DCM. The eluant was collected and crystallised with methanol (2.78 g). Part of this solid (500 mg) was demethylated using an excess of boron tribromide in DCM (1 mol dm$^{-3}$; 30 cm$^3$) at $-80$ °C, as reported previously.[1d,5,6] the mixture was then neutralised with triethylamine, extracted into ethyl acetate, washed with water, and the ethyl acetate layer was separated, dried ($MgSO_4$), filtered, and evaporated to dryness. The residue was taken into the minimum of diethyl ether and applied to a column of silica gel and eluted with a solvent mixture consisting of 65:35 diethyl ether–hexane. The first fraction eluted from the column was concentrated and precipitated with hexane to give a purple amorphous powder of the *porphyrin* (**1**) (15 mg). All subsequent fractions were checked for purity by t.l.c. The second fraction from the column was concentrated and precipitated with hexane to give a purple amorphous powder of the *porphyrin* (**2a**)* (50 mg), $\lambda_{max.}$(MeOH) ($\varepsilon$/dm$^{-3}$ mol$^{-1}$ cm$^{-1}$) 421 (182.7), 518 (8.0), 556 (6.0), 594 (2.9), and 651 nm (3.0); $\lambda_{max.}$ (MeOH plus two drops TFA) 457 (107.8) and 694 nm (32); *m/z* [Found ($M^+$) 1 014, requires 1 014]. The third fraction from the column was concentrated and crystallised with hexane as purple microcrystals to give the *porphyrin* (**4a**) (35 mg) $\lambda_{max.}$(MeOH) ($\varepsilon$/dm$^{-3}$ mol$^{-1}$ cm$^{-1}$) 420 (223.9), 518 (10.3), 555 (7.8), and 651 nm (4.4); $\lambda_{max.}$ (MeOH plus two drops TFA) 455 (134.3) and 694 nm (35.5); *m/z* [Found ($M + 1$) 903, requires 903]; $\delta_H$([$^2H_6$]acetone; $SiMe_4$) 2.83 (s, t-butyl H, 36 H), 7.22, 7.33, 8.02, and 8.13 (AB spin system centred on 7.68, $J_{AB}$ = 8.8 Hz for aromatic protons on 4HP groups, 8 H), 8.07 (s, aromatic protons on DtB4HP groups), and 8.89 (s, pyrrole β-protons, 8 H). The fourth fraction was eluted from the column, evaporated to dryness, taken into DCM, filtered, and crystallised with hexane to give purple microcrystals of *porphyrin* (**3a**), (250 mg) $\lambda_{max.}$($CH_2Cl_2$) ($\varepsilon$/dm$^{-3}$ mol$^{-1}$ cm$^{-1}$) 421 (633.9), 517 (15.0), 557 (12.1), 595 (5.4), and 651 nm (7.3); $\lambda_{max.}$ ($CH_2Cl_2$ plus two drops TFA) 454 (384.2) and 699 nm (60.5) *m/z* [Found ($M + 1$) 903, requires 903]; $\delta_H$ ($CD_2Cl_2$; $SiMe_4$) 1.63 (s, t-butyl H, 36 H), 5.58 [s, OH(DtB4HP), 2 H], 7.12, 7.22, 8.00, and 8.11 (AB spin system centred on 7.61, $J_{AB}$ 8.8 Hz for aromatic protons on 4HP groups), 8.05 (s, aromatic protons on DtB4HP groups, 8 H), 8.86, 8.88, 8.90, and 8.93 (q, pyrrole β-protons, 8 H). The fifth fraction was eluted from the column by increasing the ether–hexane ratio to 80:20. The eluant was concentrated and crystallised with hexane to give purple microcrystals of *porphyrin* (**5a**) (300 mg), $\lambda_{max.}$(MeOH) ($\varepsilon$/dm$^{-3}$ mol$^{-1}$ cm$^{-1}$) 419 (258.9), 517 (9.2), 555 (7.9), 591 (3.3), and 650 nm (4.6); $\lambda_{max.}$ (MeOH plus two drops TFA) 452 (156.7) and 700 nm (43.5); *m/z* [Found ($M + 1$) 791, requires 791]; $\delta_H$([$^2H_6$]acetone; $SiMe_4$) $-2.72$ (s, NH, 2 H), 2.83 (s, t-butyl H, 18 H), 7.22, 7.33, 8.02, and 8.13 (AB spin system centred on 7.68, $J_{AB}$ 8.8 Hz due to aromatic protons on 4HP groups, 12 H), 8.07 (s, protons on DtB4HP group, 2 H), and 8.89 (s, pyrrole β-protons, 8 H).

*Synthesis of compounds* (**2b**)–(**4b**).—This synthesis was the same as for the previous set of porphyrins, except that 3-methoxybenzaldehyde replaced 4-methoxybenzaldehyde. After purification of the mixed porphyrins, by chromatography on neutral alumina, the solid residue was demethylated with 1 mol dm$^{-3}$ boron tribromide in DCM as before (4.06 g). A portion (500 mg) of this mixture was taken into the minimum amount of THF, applied to the top of a column of silica gel, and eluted with a 60:40 mixture of THF–hexane.

The first fraction off the column was *porphyrin* (**1**) which was discarded. The second fraction off the column was concentrated and crystallised with hexane to give purple microcrystals of *porphyrin* (**2b**) (120 mg) (Found: C, 80.4; H, 7.9; N, 5.0; $C_{68}H_{78}N_4O_4$ requires C, 80.47; H, 7.69; N, 5.52%); $\lambda_{max.}$($CH_2Cl_2$) ($\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$) 422 (450.5), 520 (19.8), 559 (16.2), 595 (13.2), and 655 nm (12.7); $\lambda_{max.}$ ($CH_2Cl_2$ plus two drops TFA) 459 (241.5) and 700 nm (58.3); *m/z* [Found ($M + 1$) 1 015 requires 1 015]; $\delta_H$([$^2H_6$]acetone; $SiMe_4$) $-2.81$ (br s, NH, 2 H), 2.93 (s, t-butyl H, 54 H), 7.75 (s, aromatic protons on DtB4HP groups 6 H), and 7.68 (multiplet centre due to aromatic protons of 3HP groups). The third and fourth fractions were eluted from the column, concentrated, and separated as oils with hexane to give respectively, the *porphyrin* (**4b**) *m/z* [Found: ($M + 1$) 903, requires *m/z* 903]; and the *porphyrin* (**3b**) *m/z* [Found ($M + 1$) 903, requires 903].

## Acknowledgements

L. R. M. wishes to thank Professor A. Davies and Professor J. Utley for illuminating discussions during the course of this work. C. C. J. thanks the Royal Commission for the Exhibition of 1851 for support. We also thank Dr. J. M. Ballantine, of the S.E.R.C. Mass Spectroscopy Unit at Swansea for running f.a.b.s. spectra.

## References

1 (*a*) L. R. Milgrom, *Tetrahedron*, 1983, **39**, 3895; (*b*) T. G. Traylor, K. B. Nolan, and R. Hildreth, *J. Am. Chem. Soc.*, 1983, **105**, 6149; (*c*) T. G. Traylor, K. B. Nolan, R. Hildreth, and T. A. Evans, *Heterocycles*, 1984, **21**, 249; (*d*) W. J. Albery, P. N. Bartlett, C. C. Jones, and L. R. Milgrom, *J. Chem. Res.*, 1985, (*S*) 364; (*M*) 3810; (*e*) K. B. Nolan, *J. Chem. Soc., Chem. Commun.*, 1986, 760; (*f*) L. A. Kotorlenko, D. N. Vovk, and V. N. Yakovich, *Koord. Khim.*, 1986, **12**, 1204; (*g*) A. J. Golder, L. R. Milgrom, K. B. Milgrom, K. B. Nolan, and D. C. Povey, *J. Chem. Soc., Chem. Commun.*, 1987, 1788; (*h*) T. Ozawa and A. Hanaki, *Inorg. Chim. Acta*, 1987, **130**, 231; (*i*) L. R. Milgrom, C. C. Jones, and A. Harriman, *J. Chem. Soc., Perkin Trans. 2*, 1988, 71.

2 See ref. 1(*a*).

3 M. Lyons and L. R. Milgrom, unpublished work and ref. 1(*g*).

4 (*a*) D. Ozer, R. Parash, F. Broitman, U. Mar, and A. Bettelheim, *J. Chem. Soc., Faraday Trans. 1*, 1984, 1139 and references therein; J. P. Collman, N. H. Hendricks, K. Kim, and C. S. Bencosme, *J. Chem. Soc., Chem. Commun.*, 1987, 1537.

5 L. R. Milgrom, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2535.

---

* All CHN analyses confirmed the assigned structures.

6 (*a*) A.-C. Chan, J. Dalton, and L. R. Milgrom, *J. Chem. Soc., Perkin Trans. 2*, 1982, 707; (*b*) L. R. Milgrom, *J. Chem. Soc., Perkin Trans. 1*, 1984, 1483.

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

8 J. F. McOmie and M. W. Watts, *Tetrahedron*, 1968, **24**, 2289, and refs. 5 and 6(*a*).

9 J. A. Anton and P. A. Loach, *J. Heterocycl. Chem.*, 1975, **12**, 573.

10 See, M. Gouterman in 'The Porphyrins,' ed. D. Dolphin, Academic Press, New York, 1978–1979, vol. 3, pp. 1–165.

11 See, H. Musso in 'Oxidative Coupling of Phenols,' eds. W. I. Taylor and A. R. Battersby, Edward Arnold (London) 1967, p. 62.

12 See, 'Rodd's Chemistry of Carbon Compounds,' ed. S. Coffey, Elsevier (Amsterdam) 1971, vol. 3A p. 296.

13 M. Krell, M. C. R. Symons, and J. Barthel, *J. Chem. Soc., Faraday Trans 1*, 1987, **83**, 3419.

14 J. Utley, personal communication.

15 See, J. W. Buchler, ref. 10, vol. 1, p. 389.

*Received* 23rd *February* 1988; *Paper* 8/00717I