Tetrahedron Vol. 38, No. 1, pp. 27 to 39, 1982
Printed in Great Britain.

0040-4020/82/010027-13$03.00/0

SYNTHESES AND OXYGENATION OF IRON(II) "STRAPPED" PORPHYRIN COMPLEXES

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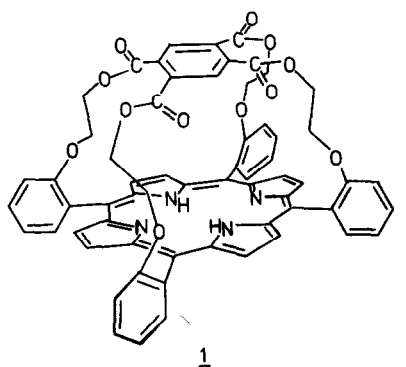
(*Received in U.K. 22 October* 1981)

Abstract - A general route to 'strapped' porphyrins which are bridged between diagonally opposite meso-positions is described. Studies on the oxygenation and carbonylation of their iron(II) complexes have shown that they are inferior to 'capped' porphyrins as models for the oxygen-carrying haemoproteins. The results reported herein suggest that strapping structures which do not enforce well-defined and rigid cavities for oxygen binding afford little protection against irreversible oxidation of (dioxygen) (porphyrin) iron(II) complexes.

In the preceding paper we reported the synthesis of 'capped' metalloporphyrins which serve as models for the oxygen-carrying haemoproteins, haemoglobin and myoglobin.[1] In this paper we report our alternate approach to reversible-oxygen carriers based on 'strapped' porphyrins.[2]

Steric encumbrance about the oxygen binding-site is a requirement for reversible oxygenation at room temperature of both the oxygen-carrying haemoproteins and substances designed to mimic them.[3] A number of synthetic chelates based on the porphyrin nucleus have been reported, however only the iron(II) complexes of 'capped' porphyrins[1,4,5,6] [e.g. (1)] 'picket-fence' porphyrins[7] [e.g. (2)] have so far shown reversible oxygenation behaviour at ambient temperature for any length of time.



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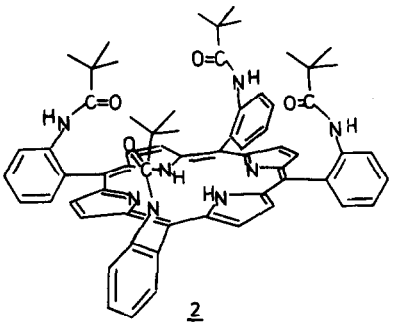

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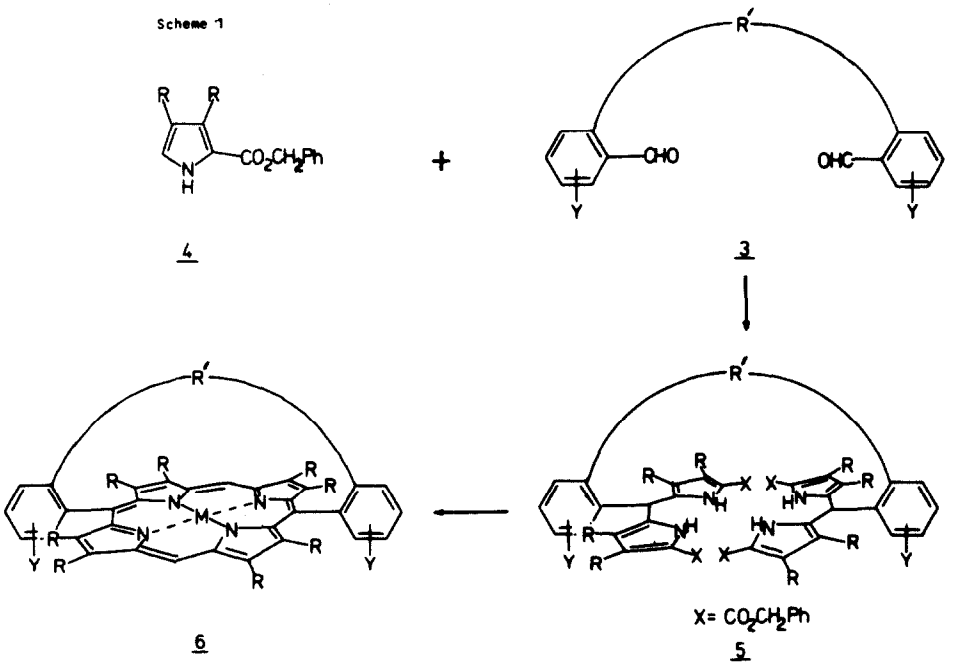
Less hindered iron(II) porphyrins react with excess nitrogenous base, generally 1-methylimidazole or pyridine to form a (2:1) complex [$Fe^{II}Por(B)_2$] or haemochrome which is insenstive to dioxygen. Reversible hinging of dioxygen may be exhibited in aprotic solvents in the presence of only modest excesses of base at low temperatures (ca. -50°) and low concentration of porphyrin (ca. 10^{-4}M) but rapid irreversible oxidation to μ-oxo dimers occurs at ambient temperature.[8,9,10] The irreversible autoxidation of complexes (1) and (2) occurs through oxygenation of the 4-coordinate iron species on the unprotected face, which is present in low equilibrium concentration.[5,11]

The other approach at providing the necessary protection of the oxygen binding site has centred on our 'strapped' porphyrin approach in which a strand is attached linking diagonal positions on the porphyrin periphery in order to provide steric encumbrance.

Two approaches to 'strapped' porphyrins have been reported, differing in the timing of attachment of the strap. The first involves attachment of the strap after the porphyrin nucleus was constructed. Thus 'bridged'[12], 'crowned'[13], and 'cyclophane'[14] porphyrins have been synthesized from porphyrins with diagonal terminally-functionalized side-chains by condensation of these functional groups with another bifunctional molecule to form the bridge. Very high dilution conditions were necessarily required in these reactions to prevent excessive intermolecular polymerization. The second approach has involved synthesis of the 'strapped' porphyrins from 'strapped' acyclic precursors. Traylor has followed this strategy in the synthesis of his first 'cyclophane' porphyrin which was prepared as a copper(II) complex.[15] A bis(bromodipyrromethene) linked via β-pyrrolic positions was converted to the porphyrin however no attempt was made to study the behaviour of a ferrous derivative of it with dioxygen. A drawback of this synthesis was that a number of transformations was required of intermediate pyrroles in the sequence which made the route unattractive as a general route to 'strapped' porphyrins.

Our synthesis of 'strapped' porphyrins was based on MacDonald's pyrromethane route to porphyrins.[16] Our strategy is schematically outlined in Scheme 1. The starting dialdehyde (3) with two potential functional groups upon which a base-bearing second strap could later be attached, is condensed with a pyrrole-2-carboxylic acid derivative (4) at the unsubstituted α-position to give a bridged or 'strapped'-bis(pyrromethane) (5). Generation of the free tetraacid and condensation with a 'one carbon unit', either formic acid or trimethyl orthoformate leads to a centrosymmetric 'strapped' porphyrin (6). Further condensation of the porphyrin with a base-bearing strap would lead to a doubly-strapped porphyrin. Introduction of the top strap early in the synthesis serves to hold the pyrromethanes in close proximity thus favouring intramolecular condensation leading to porphyrin over intermolecular polymerization. This approach to 'single-strapped' porphyrin (6) has the advantage over other syntheses of avoiding the need for high dilution conditions. Furthermore the strap can be derived from the use of any dialdehyde of an appropriate size as a starting material, thus there is the

Scheme 1



potential to adjust the size and polarity of the oxygen-binding cavity. We have used this strategy to construct a number of 'strapped' porphyrins with varying bulk in the strap.

In practice the 'strapped' approach to reversible oxygen-carriers has not been a success since no compound has yet been prepared which avoids the problems of haemochrome formation and irreversible μ-oxo dimer formation.

Synthesis of 'Strapped' Porphyrins

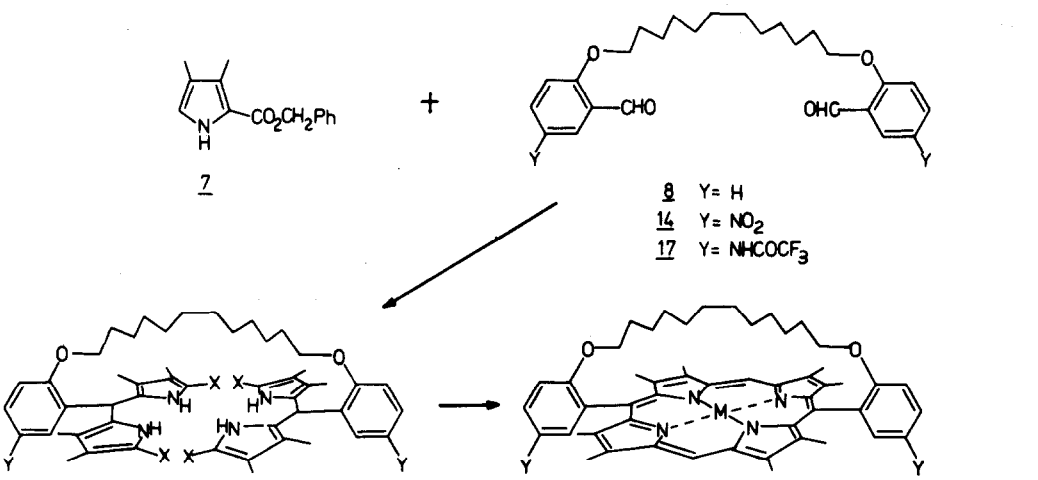
Benzaldehydes have been used as the starting material for the dialdehyde (3) throughout since meso-phenylpyrromethanes are less acid labile than the corresponding meso-alkyl compounds.[17] Benzyl 3,4-dimethyl-pyrrole-2-carboxylate (7) was the simplest suitably substituted pyrrole for the formation of the 'strapped'-bis(pyrromethanes).

The synthesis of an 'alkyl-strapped' porphyrin (11) in which the alkyl chain is derived from 1,12-dibromododecane is shown in Scheme 2. The alkyl chain was chosen for the top strap to minimize possible strain on the porphyrin ring. Condensation of the anion of salicylaldehyde with 1,12-dibromododecane in DMF gave the 'alkyl-strapped'-dialdehyde (8) in 65% yield. Acid-catalysed condensation of (8) with the pyrrole (7) gave high yields of the desired 'alkyl-strapped'-bis(pyrromethane) (9), hydrogenolysis of which gave the unstable tetraacid (10). Consequently the tetraacid was not purified but was condensed immediately with trimethyl orthoformate with trichloro-acetic acid as catalyst in the presence of zinc acetate to give the 'alkyl-strapped' porphyrin (11) in 23% overall yield from salicylaldehyde. The crude porphyrin was obtained as a mixture of the free-base porphyrin (11) and the zinc complex (12).

The porphyrin was conveniently isolated as the zinc derivative so the crude porphyrin mixture was converted entirely to (12) by further treatment with zinc acetate in methanol and isolated as bright red-violet crystals in 42% yield by chromatography. Elemental analysis and field-desorption mass spectrometry gave a molecular formula, $C_{52}H_{58}N_4Zn$.

Zinc porphyrins are relatively acid-labile and the metalloporphyrin (12) was demetallated in nearly quantitative yield by brief treatment with anhydrous hydrogen bromide. The 'strapped' porphyrin (11) was obtained as a very high melting (m.p. >300°) dark-red crystalline solid, which had limited solubility in organic solvents other than trifluoroacetic acid and other carboxylic acids.

The ^{1}H NMR spectrum of the porphyrin (11) in trifluoroacetic acid clearly demonstrated that the alkyl-chain spanned the porphyrin ring. The resonances of 16 of the 24 protons in the C_{12}-methylene chain fell in the region δ 0.5 to δ-0.9, a strong upfield shift only in accord with these protons lying above the



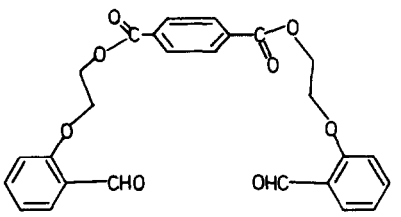
porphyrin plane and thereby being exposed to the powerful diamagnetic anisotropy of the aromatic nucleus. The peaks due to the methyl protons resonated as two sharp singlets of 12 protons each at δ 2.70 and 3.52, indicating that the protons on four of the methyl groups were shifted upfield by the diamagnetic ring current of the two meso-phenyl rings which are perpendicular to the porphyrin plane.[18] The visible spectrum of (11) had four satellite bands I-IV, and a Soret bands at $\lambda_{max}(CH_2Cl_2)$ ($\log_{10}\varepsilon$) :628 (3.08), 576(3.76), 541(3.64), 507(4.12), 409 nm (5.26) respectively and was of the phyllo-type, i.e. band IV > II > III > I, indicative of substitution at both the meso and β-positions of the porphyrin ring.[19]

The bifunctionalized 'strapped' porphyrin (16) was obtained with slight modification to the above route in 22% overall yield from 5-nitrosalicylaldehyde (13). The sodium salt of 5-nitrosalicylaldehyde was condensed with 1,12-dibromododecane in DMF at 120° to yield the 'strapped'-bis(nitrobenzaldehyde) (14) in 75% yield. Better yields of (14) were obtained when the sodium salt was prepared in a separate step by treatment of 5-nitro-salicylaldehyde with aqueous sodium hydroxide than when it was generated *in situ* using sodium hydride. The direct approach to (16) was not very successful. Acid catalysed condensation of the dialdehyde (14) with pyrrole (7) as before yielded the dinitro-'strapped'-bis(pyrromethane) (15) in 73% yield, but hydrogenation of (15), followed by treatment of the crude tetraacid with trimethyl orothoformate and trichloroacetic acid afforded the bis(amino)porphyrin (16) in a very low yield (∿1%). The hydrogenation of (15) to remove the benzyl groups and to reduce the nitro groups was slow and very inefficient and was probably the major contributing factor in the lowered porphyrin yield. Another factor which contributed to the poor yield was the difficulty in separation of bis(amino)porphyrin (16) from the polar open chain and polymeric side products.

Reduction of the nitro groups earlier in the reaction sequence led to much better yields of the porphyrin (16). Thus conversion of (14) into the 'strapped'-bis-(trifluoro-acetamidobenzaldehyde) (17) in high yield and condensation of the dialdehyde (17) with pyrrole (7) gave the 'strapped'-bis(pyrro-methane) (18) in 90% yield. Hydrogenation and ring closure as before gave the 'trifluoroacetamido-modified strapped' porphyrin (19) after two days in 48% yield as a dark-red crystalline solid (m.p. >300°). The use of pure bis(pyrromethane) (18) and the addition of zinc acetate were critical for good yields in the condensation. Bis(amino)-porphyrin (16) (m/e 802) was obtained in very good yield by deprotection of (19) with sodium borohydride in methanol and THF, a reductive method developed by Weygand[20] for deprotection of peptides. The visible spectrum was virtually the same as that of the 'strapped' porphyrin (11) and the ^{1}H NMR spectrum again showed the strapping methylene groups to be shifted considerably upfield. The bis(amino)porphyrin (16) decomposed slowly on storage and was best stored in the protected form (19).

The flexible alkyl chain did not provide sufficent hindrance to stabilize a five coordinate ferrous complex. To provide more steric hindrance to impede haemochrome formation and to prevent μ-oxo dimer formation on the protected face of the porphyrin several more-hindered 'strapped' porphyrins were synthesized, the 'terephthalate-strapped' porphyrin (22) and the 'naphthyl-strapped' porphyrin (27).

The terephthalate ester strap was chosen on the basis of its close resemblance to the pyromellitate ester derivative used to form the 'capped' porphyrin (1).[1] Condensation of 2-(2-hydroxyethoxy)benzaldehyde[1] with terephthaloyl chloride gave the dialdehyde (20) in 78% yield. Acid catalysed condensation of pyrrole (7) with (20) gave the 'terephthalate-strapped'-bis(pyrromethane) (21) which was hydrogenolysed and cyclized with trimethyl orthoformate and trichloro-acetic acid to give the extremely insoluble porphyrin (22) as dark violet crystals in 10% yield. Creation of steric strain in the closure may account for the lower yield of porphyrin by comparison with the less-strained systems (11) and (19). The visible spectrum was essentially identical to that obtained for the 'alkyl-strapped' porphyrins (11) (16) and



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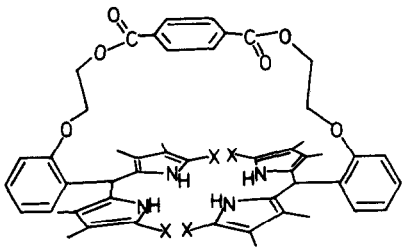
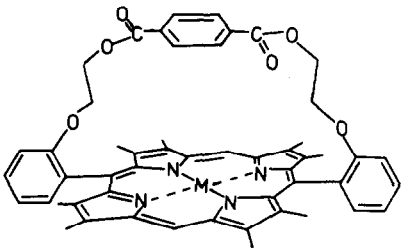


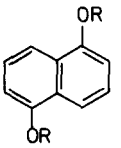
21 X= CO_2CH_2Ph



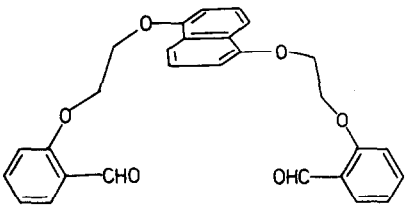
22 M= 2H
33 M= $Fe^{III}Cl$
36 M= Fe^{II}

(19) and the non-strapped diphenylporphyrin (29) reflecting the fact that only substituents on the porphyrin ring or chelated to metalloporphyrins have any significant effect on the visible spectrum since the meso-phenyl substituents are orthogonal to the porphyrin ring because of steric interactions. The ^1H NMR spectrum of (22) showed that the aromatic proton resonance of the terephthalate ester residue (δ 4.40) was shifted upfield by 3.3 ppm by comparison with the 'strapped'-bis(pyrromethane) (21), under the influence of the powerful diamagnetic anisotropy of the ring current. Surprisingly the carbonyl stretching frequency in the infrared spectrum of (22) appeared at 1710 cm^{-1}, indicating that the ester functions were still in conjugation with the aromatic residue in contrast to the 'capped' porphyrin (1) where the ester stretching frequencies occurred at 1735 and 1718 cm^{-1} indicating that the capping aromatic structure is held much more rigidly and that full conjugation of the esters cannot be achieved. This is borne out in the X-ray structure of the 'capped porphyrin' (1)[21] and the difference is discussed again later.

The 'naphthyl-strapped' porphyrin (27) was synthesized by the general route. Treatment of 1,5-naphthalenediol with ethylene oxide in wet THF containing potassium carbonate, at 100° for 30 hours in a sealed bomb gave 1,5-bis(2-hydroxyethoxy)naphthalene (23) in



23 R= CH_2CH_2OH
24 R= CH_2CH_2OTs



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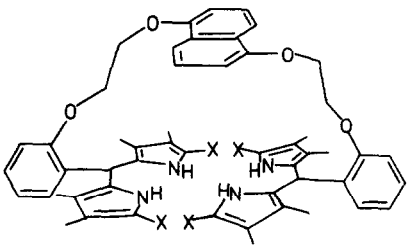
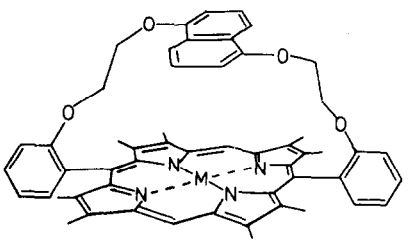


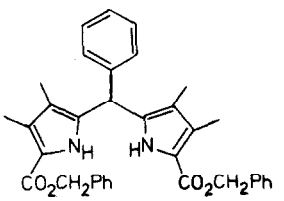
26 X= CO_2CH_2Ph



27 M= 2H
34 M= $Fe^{III}Cl$
37 M= Fe^{II}

43% yield. The diol (23) was readily converted to the bis(tosylate) (24) in pyridine and excess tosyl chloride at 0°. Alkylation of the sodium salt of salicylaldehyde in DMF at 110° gave the 'strapped'-bis(aldehyde) (25) in 76% yield. The bis(pyrromethane) (26) was prepared and closed to the 'naphthyl-strapped' porphyrin (27) in 28% yield as above in a reaction sequence that was highly dependent on the purity of (26).

The corresponding unhindered porphyrin (28) was prepared for comparison of spectral and oxygenation properties of the iron(II) complex. The synthesis followed the general route. Acid-catalysed condensation of benzaldehyde and (7) gave the meso phenylpyrromethane (28) which was converted to 5,15-diphenyloctamethylporphyrin (29) a



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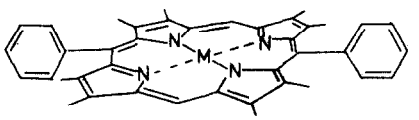


29 M = 2H
35 M = $Fe^{III}Cl$
38 M = Fe^{II}

violet crystalline solid, in 13% yield. No attempt was made to optimize the yield of this extremely insoluble compound.

The closure of the bis(pyrromethane) (10) to the 'alkyl-strapped' porphyrin (11) was studied in some detail. Addition of zinc acetate to the reaction mixture doubled the yield of the porphyrin (11), presumably because pyrrole coordination to the metal acted as a template to better align the pyrromethanes for condensation. The purity of the bis(pyrromethane) (10) and of all the reagents greatly affected the yield of porphyrin. The optimal concentrations of the starting materials for the closure were 0.0025M in the tetraacid, 0.05M in trimethylorthoformate, and 0.15M in trichloroacetic acid. When zinc acetate was not added, the porphyrin was obtained in 20-25% yield. These conditions were similar to those found by Kenner and his co-workers[22,23] to be most effective for the closure of 1,8-b-bilene diacids and 1,8-b-oxobilane diacids; the 1,8-unsubstituted substances can be condensed similarly. Halving the starting concentration of tetraacid did not affect the yield of porphyrin, nor did addition of pyridine to the reaction mixture after 2-4 hours, following the procedure of Kenner.[23] Unlike the case of zinc acetate, addition of cupric acetate did not increase the porphyrin yield but gave the copper chelate of the porphyrin (11), in 22% yield, from which the free-base porphyrin was obtained in quantitative yield by treatment with a mixture of sulphuric acid, water and methylene chloride.

A wide variety of symmetrical pyrromethanes was made by Kenner and his co-workers by the condensation of a 5-unsubstituted pyrrole with an aldehyde under acid catalysis.[23] The only limitation appears to be that when the 2-position of the pyrrole has an electron-withdrawing substituent which decreases the nucleophilicity of the 5-position, the β-pyrrolic positions have to be substituted to prevent formation of α,β and β,β-pyrromethanes.[23]

It is therefore apparent that our route to 'strapped' porphyrins is indeed a general one. Our work concerned with the use of the bis(amino)porphyrin (16) in the synthesis of pentadentate ligands will be reported separately.

Oxygenation of the Iron(II) 'Strapped' Porphyrins

The 'alkyl-strapped' porphyrin (11) was converted to the tetracoordinate iron(II) complex (30) as shown in Scheme 2. Metallation with anhydrous ferrous chloride in anhydrous THF gave the (chloro)iron(III) derivative (31). Purification of (31) by chromatography over alumina yielded the ferric μ-oxo dimer (32), (λ_{max} 573,709 nm), due to facile ligand exchange under the basic conditions of the column. Brief treatment with dilute hydrochloric acid reconverted the ferric μ-oxo dimer (32) to the

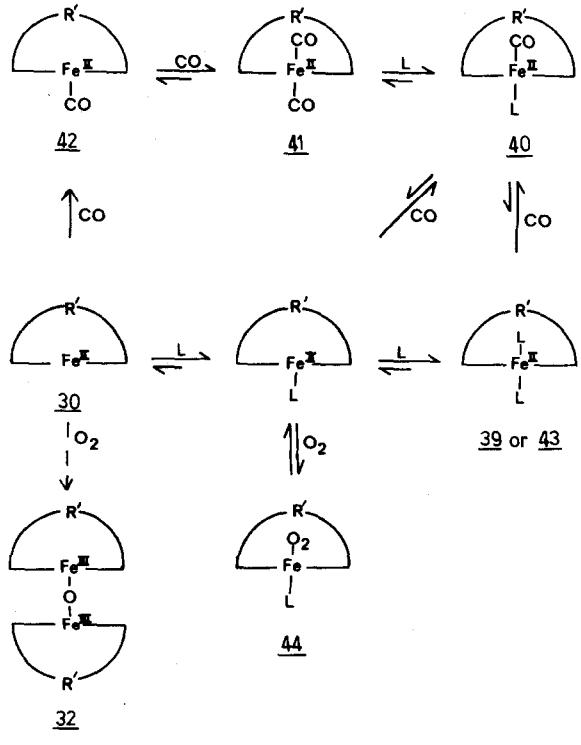
(chloro)iron(III) derivative (31) (λ_{max} 648, 589(sh), 540(sh), 514, 410(sh), 390 nm). Reduction of (31) with excess chromous acetylacetonate using a modification of Collman's method[7] gave the oxygen-sensitive ferrous complex (30) which was isolated under argon as a brick-red crystalline solid, (λ_{max} (benzene, Argon) 566, 538 nm).

Treatment of the free-base porphyrins (22), (27) and (29) with ferrous chloride in the same way afforded the corresponding ferric chloro derivatives (33), (λ_{max} 650, 595(sh), 540(sh), 510, 394 nm), (34) (λ_{max} 647, 545(sh), 511, 408 (sh), 393 nm) and (35), (λ_{max} 645, 545(sh), 506, 389 nm), in good yields. The (chloro)iron(III) derivatives were reduced to the corresponding 4-coordinate iron(II) complexes (36), (37) and (38) with chromous acetylacetonate in benzene. All manipulations of the iron(II) complexes, which were obtained as brick-red solids, were conducted in a Schlenk apparatus under dry oxygen-free argon.

None of the hindered 'strapped' porphyrins complexes showed reversible binding of dioxygen for sufficient time to encourage us that this approach was worth pursuing. The following study on the ('alkyl-strapped' porphyrin)iron(II) complex (30) being typical.

When (30) was dissolved in benzene containing either 5% or 10% 1-methylimidazole the spectrum of the hexacoordinate haemochrome species (39), shown schematically in Scheme 3, was obtained. The visible spectrum of the complex λ_{max} 557, 529, 520(sh), 420 nm was essentially superimposable on the spectrum of the bis(1-methylimidazole) complex of the unhindered porphyrin (38), λ_{max} 554, 526, 519(sh), 420 nm. The bis(1-methylimidazole) haemochrome (39) was stable to oxygen, but purging the solution with carbon monoxide led to the immediate formation of a new species, λ_{max} 564(sh), 539, 419, 397(sh) nm, indicating the formation of (carbonyl) (1-methylimidazole) ('alkyl-strapped' porphyrin)iron(II) (40).[24] Considering the apparent lack of steric encumbrance afforded by the strap, this species is probably a mixture of isomers in which the apical ligands are partly interchanged. Dissolution of (30) in benzene saturated with carbon monoxide yielded a species, λ_{max} 548, 415, 403(sh) nm, which was probably a mixture of biscarbonyl complex (41) along with a small amount of the pentacoordinate monocarbonyl complex (42), by analogy to simple deuterohaem-carbon monoxide complexes which show similar spectral properties.[24] Addition of 1-methylimidazole to the solution of (41) and (42) led again to the formation of (40),

Scheme 3



λ_{max} 564(sh), 539, 419, 397(sh) nm.

The failure of (30) to form an oxygen complex in 5% 1-methylimidazole was unexpected and in sharp contrast to results obtained with the ferrous 'capped porphyrin' (1) which easily formed a stable oxygen complex under similar conditions.[4] Rather, the results were typical of simple unprotected ferrous porphyrins which, in the presence of a large excess of a nitrogen ligand, form a haemochrome which does not react with oxygen but does react with the stronger ligand, carbon monoxide, to form a monocarbonyl adduct. Therefore the method used to obtain oxygenation of simple hemes was applied to (30).

Bispyridine('strapped'-porphyrin)iron(II) (43) was synthesized by dissolving (30) in neat oxygen-free pyridine under argon, followed by removal of all excess pyridine to yield the complex as a brick-red solid. The pyridine complex (43) was dissolved in dry tetrahydrofuran at -55° and the spectrum obtained: λ_{max} 553, 524, 490(sh) nm was very similar to the spectrum of (30) in 5% 1-methylimidazole under argon. Now however, when the solution was exposed to oxygen at -55° a spectral shift was observed: λ_{max} 570(sh), 552(sh), 538 nm as the dioxygen adduct (44), formed. Deoxygenation of the solution by an argon purge restored the spectrum of the original ferrous bispyridine complex (43). The solution was oxygenated and deoxygenated over several more cycles with very little deterioration of (43) or (44). When a solution of the oxygen complex was allowed to warm to room temperature, irreversible oxidation occurred, yielding the ferric μ-oxo dimer (32), λ_{max} 572. In contrast to this, when a solution of (43) in THF at -55° was exposed to carbon monoxide, the resulting monocarbonyl adduct, λ_{max} 615(sh), 565(sh), 537 nm, was stable at room temperature for several hours. The unhindered porphyrin (38) and the terephthalate- and naphthalene-strapped complexes (36) and (37) showed the same behaviour.

The results can be explained and summarized by the equilibria depicted in Scheme 3. The results strongly indicated that the straps were flexible enough to permit pyridine or 1-methylimidazole complexation on both sides of the porphyrin plane, thus in high base concentrations, such as 5% 1-methylimidazole, the equilibrium is shifted strongly toward the formation of the hexacoordinate haemochrome; apparently the presence of the strap does not weaken the binding of a second nitrogen base to an extent that oxygen can begin to effectively compete to form an oxygen adduct. The oxygen adduct can form at low base concentrations when it is probable that there is a relatively higher concentration of the pentacoordinate species with which it can complex. Unfortunately under these conditions there is also a relatively higher concentration of the tetracoordinate species which can oxygenate to form ferric μ-oxo dimers, unless low temperature are employed to slow this autoxidation.

In an attempt to avoid haemochrome formation the bulkiness of the nitrogen ligand was increased, with only modest success. Reversible oxygenation of the ('terephalate-strapped' porphyrin)iron(II) complex (36) in neat 2,4-lutidine was observed at -28° but in 3,5-lutidine a strong haemochrome which was stable to dioxygen was formed. This result is therefore almost certainly due to repulsive interactions between the hydrogens of the 2-methyl group and the electrons of the porphyrin plane which would weaken the ability of the 2-substituted ligand to coordinate twice,[24,25] rather than to the interactions between the ligand and the terephthalate strap.

These results clearly demonstrate that substantial hindrance is necessary to prevent the coordination of a second nitrogen ligand to a ferrous porphyrin. Recent studies by Battersby and his colleagues[12,26] have shown that even doubly-strapped porphyrins do not prevent μ-oxo dimer formation from occurring via a face protected by an anthracene-strap or a pyridine-strap in a case where haemochrome formation can be excluded. These results further expose the inherent difficulty in creating an oxygen-binding cavity with about 4Å clearance over the porphyrin plane to allow free coordination of dioxygen while at the same time having a tight enough strap to prevent the close approach of a second porphyrin complex and hence prohibit irreversible oxidation by μ-oxo dimer

formation. The difficulty in enforcing a rigid structure supported by only two arms is manifest in the difference between the 'C_2-capped' porphyrin (1) complexes and the 'terephthalate-strapped' porphyrin (22) complexes which have the same capping structure but the former has four supports. An approach using even tighter straps will have two limitations; first there will be considerably more energy to be overcome on entropy groups in ring formation, and second it is likely that tighter straps will severely hinder the binding-site and lead to complexes of very low affinity for dioxygen. A recent approach of Traylor to tighten the strap after its formation by a second reaction may offer a solution to these difficulties but even in this case a rather small change in structure seems to have precluded binding of carbon monoxide on the protected face completely.[14]

In view of the apparent mobility of strapping structures with the consequent lack of fine control over the cavity size in 'strapped' porphyrins and the general reactiveness of unsubstituted meso-positions on porphyrins when they are not protected by a protein structure, we are concentrating our efforts towards the synthesis of reversible-oxygen carriers on derivatives of the 'capped' porphyrins which to date have been the only successful models which both prevent haemochrome formations and preclude μ-oxo dimer formation on the protected face.

Acknowledgements

We thank the National Institutes of Health and the National Science Foundation for financial support and Dr R.T. Aplin for mass spectra.

EXPERIMENTAL

The general experimental details were the same as those described previously.[1]

2,2'-(1,12-dodecylenedioxy)dibenzaldehyde (8)

Salicylaldehyde (13.4 g, 0.11 mol) was added to a suspension of sodium hydride (4.5 g, 0.11 mol) in dry THF (200 ml) at room temperature under nitrogen. The mixture was heated at reflux and dry DMF was added until a clear yellow solution was obtained. 1,12-Dibromododecane (16.4 g, 0.05 mol) was added and the resulting mixture was heated at reflux overnight. The reaction mixture was poured into ice water and the resulting precipitate was collected and dissolved in dichloromethane. The organic phase was washed with 1N NaOH and brine, dried (Na_2SO_4) and concentrated to an oil. Trituration with ether gave an amorphous solid (13.1 g, 65%), m.p. 76-79°. Recrystallization from acetone gave the dialdehyde (8) as colourless needles, m.p. 79-80°. IR: ν_{max} (nujol) (cm^{-1}): 1680. MS: (m/e): 410(25), 123(70), 122(50), 121 (60), 69(60), 55(100%). Calc. for $C_{26}H_{34}O_4$: m/e 410.2455. Found: m/e 410.2456. NMR: δ ($CDCl_3$): 1.3-2.1 (m, 20H), 4.1(t, 4H), 6.8-8.0(m, 8H), 10.5(s, 2H).

'Alkyl-strapped'-bis(pyrromethane) (9)

A solution of dialdehyde (8) (3.84 g, 9.4 mol) and benzyl 3,4-dimethylpyrrole-2-carboxylate[27] (7) (8.25 g, 36.0 mmol) in absolute ethanol (50 ml) was heated to reflux under nitrogen. Concentrated hydrochloric acid (0.10 ml) was added and the reaction was heated a further 30 min. The solution was then diluted with dichloromethane and the organic phase washed with aqueous sodium bicarbonate and brine, dried (sodium sulphate), and concentrated in vacuo. The residue was dissolved in ether and filtered through neutral alumina (Woelm grade I, ca. 50 g, ether/ethyl acetate eluant) to yield (9) as a foam (10.50 g, 87%) on workup. IR: ν_{max} (nujol) (cm^{-1}): 3430, 3270, 1670. NMR: δ($CDCl_3$): 1,3(m, 20H), 1.85(s, 12H), 2.35(s, 12H), 3.9(m, 4H), 5.3(s, 8H), 5.8 (s, 2H), 6.8-7.4(m, 28H), 8.7(m, 4H).

('Alkyl-strapped' porphyrin)zinc(II) (12)

A mixture of the 'alkyl-strapped'-bis-(pyrromethane) (9) (1.22 g, 0.94 mmol), dry triethylamine (0.3 g) and 10% Pd/C (0.30 g) in dry THF (150 ml) was shaken for 1 h under hydrogen (1 atmosphere). Filtration through Celite and concentration in vacuo yielded the tetraacid as a foam. The foam was dissolved in dry dichloromethane (250 ml) and trimethyl orthoformate (2.08 ml, 19 mmol) was added followed by a solution of trichloroacetic acid (9.31 g, 57 mmol) in dry dichloromethane (100 ml) and the resulting solution was stirred in the dark under a drying tube ($CaSO_4$) for 5 h. A suspension of zinc acetate dihydrate (0.50 g) in dry methanol (2 ml) was added and the reaction was stirred a further 48 h in the dark. The reaction mixture was washed with 10% sodium carbonate and water, dried (Na_2SO_4), and concentrated to dryness in vacuo. The residue was dissolved in dichloromethane (200 ml) and heated to reflux. A suspension of zinc acetate (0.50 g) in methanol (2 ml) was added and heating continued for 5 min. The mixture was concentrated to dryness in vacuo and chromatographed on silica gel (50 g) (0 to 1% methanol in dichloromethane eluant) to yield ('alkyl-strapped' porphyrin)zinc(II) (12) on workup as a pink-purple solid (333 mg, 42%), m.p. >300°. (Found: C, 74.44; H, 7.04; N, 6.40. Calcd. for $C_{52}H_{58}N_4O_2Zn$: C, 74.67; H, 6.99; N, 6.70%). VIS: λ_{max} (log ε) ($CHCl_3$) (nm): 572(3.94), 538(4.19), 500(3.42), 410(5.46), 390(sh), (4.59). NMR: δ ($CDCl_3$, CD_2Cl_2): -0.5 (m, 8H), -0.2 to +0.1 (m, 8H), 0.7-1.1 (m, 4H), 2.52(s, 12H), 3.51(s, 12H), 4.0 (m, 4H), 7.1-8.0(m, 8H), 10.13(s, 2H).

'Alkyl-strapped' porphyrin (11)

('Alkyl-strapped' porphyrin)zinc(II) (12) (84 mg, 0.10 mmol) was dissolved in dry dichloromethane (100 ml) and a stream of dry hydrogen bromide gas blown through the solution for 5 min. The solution was extracted successively with water (2 × 100 ml), saturated sodium bicarbonate solution (2 × 100 ml), washed with brine, dried (Na_2SO_4), filtered and

concentrated to give the 'strapped' porphyrin (11) as a purple solid (76 mg, 98%): m.p. >300°: IR: ν_{max} (KBr) (cm^{-1}): 3400, 2930, 2860. VIS: λ_{max} (log ε) (CH_2Cl_2) (nm): 628(3.08), 5.76(3.76), 541(3.64), 507(4.12), 409(5.26), λ_{max} (CH_2Cl_2-CF_3COOH) (nm): 610, 568, 430. NMR: δ (CF_3COOH): -3.7(br m, 4H), -0.9 to -0.6 (br m, 4H), -0.4 to -0.1 (br, m, 4H), -0.1 to 0.5 (br m, 4H), 0.9-1.3 (br, m, 4H), 2.70(s, 12H), 3.52(s, 12H), 4.2-4.4(m, 4H), 7.4-8.4(m, 8H).

2,2'-(1,12-dodecylenedioxy)bis(5-nitrobenzaldehyde) (14)

A mixture of the sodium salt of 5-nitrosalicyclaldehyde (7.5 g, 0.04 mol) and 1,12-dibromododecane (6.5 g, 0.02 mmol) was heated at 120-130° under nitrogen for 1½ h. DMF (20 ml) was added and the mixture was heated a further 2 h. The reaction mixture was poured into water (400 ml) and extracted with dichloromethane (3 × 200 ml). The combined organic extracts were washed with 2% sodium hydroxide solution (300 ml) and with water (300 ml) dried ($NaSO_4$) and concentrated in vacuo to yield a yellow oil which crystallized on trituration with ether. The crude product was dissolved in dichloromehtane-ethyl acetate (40:1, 200 ml) and shaken with neutral alumina (40 g). The mixture was filtered and the alumina was washed with 40:1 dichloromethane-ethyl acetate (200 ml) and with 20:1 dichloromethane-ethyl acetate (200 ml). The combined filtrates were concentrated in vacuo to yield (14) as a yellow powder which was used without further purification (7.2 g, 73%): m.p. 97-100°. IR: ν_{max} (nujol) (cm^{-1}): 1680, 1580, 1520, 1340. NMR: δ ($CDCl_3$): 1.2-1.6 (m, 20H), 4.23(t, 4H), 7.07(m, 2H), 8.2-8.6(m, 4H), 10.40(s, 2H).

'Alkyl-strapped'-bis(nitrophenylpyrromethane) (15)

To a solution of benzyl 3,4-dimethylpyrrole-2-carboxylate (7) (3.67 g, 16.0 mmol) and the dialdehyde (14) (2.00 g, 4.0 mmol) in absolute ethanol (25 ml) was added concentrated hydrogen chloride (0.3 g). The solution was heated at reflux under nitrogen for 30 min, then concentrated to dryness in vacuo. The residue was triturated with ether to yield (15) as a yellow amorphous powder (5.00 g, 90%). IR: ν_{max} (nujol) (cm^{-1}): 3280, 1670(br), 1590, 1350. NMR: δ ($CDCl_3$): 1.25(m, 20H); 1.83(s, 12H); 2.30(s, 12H); 3.9(m, 4H); 5.20(s, 8H); 5.77(s br, 2H); 7.28(s, 2H); 6.7-8.2(m, 6H); 8.7(m, 4H).

2,2'-(1,12-Dodecylenedioxy)bis(5-trifluoroacetamidobenzaldehyde) (17)

A solution of the dialdehyde (14) (3.0 g, 6.0 mmol), ethylene glycol (3 ml) and p-toluene sulfonic acid (0.01 g), in benzene (300 ml) was heated at reflux under nitrogen in a Dean-Stark apparatus for 20 h. The cooled reaction mixture was diluted with ether, washed thoroughly with water, and brine, dried (Na_2SO_4), and concentrated to dryness in vacuo to yield 2,2'-(1,12-dodecylenedioxy)bis-(5-nitrobenzaldehyde ethylene acetal) which solidified as colourless crystals (3.40 g, 96%), m.p. 109-111°. IR: ν_{max} (film) (cm^{-1}): 1590, 1340. NMR: δ ($CDCl_3$): 1.2-2.2(m, 20H), 4.0-4.4(m, 12H), 6.2(s, 2H), 6.8-8.5(m, 6H).

A mixture of the foregoing acetal (1.18g, 2.0 mmol) and 10% Pd/C (0.26 g) in 1:1 ethyl acetate/absolute ethanol (100 ml) was shaken under a hydrogen atmosphere (1 atm) overnight. The catalyst was removed by filtration through Celite and was washed well with dichloromethane. The combined filtrates were concentrated in vacuo. Trituration of the resulting oil with ether gave 2,2'-(1,12-dodecylenedioxy)bis(5-aminobenzaldehyde ethylene acetal) as a yellow foam (1.01 g, 95%) which was used immediately without further purification. IR: ν_{max} (film) (cm^{-1}): 3410, 3350. NMR: δ ($CDCl_3$): 1.2-1.8(m, 20H), 3.40(s, 4H, exchangeable with D_2O), 3.9-4.2 (m, 12H), 6.10(s, 2H), 6.6-6.9(m, 6H).

Trifluoroacetic anhydride (15 ml) was slowly added to a mixture of the foregoing bisamino compound (3.70 g, 7.0 mmol) and potassium carbonate (1.0 g) in dichloromethane (25 ml) under nitrogen at room temperature. The resulting mixture was stirred for 1 h and concentrated in vacuo. The residue was dissolved in ethyl acetate (100 ml) and washed with water (100 ml). The wet ethyl acetate solution was made acidic (ca. 3 drops trifluoroacetic acid) and allowed to stand several hours, then it was washed with aqueous sodium bicarbonate and brine, dried (Na_2SO_4) and concentrated in vacuo to give an oil which was triturated with ether to give (17) as a colourless solid (4.24 g, 95.7%). IR: ν_{max} (nujol) (cm^{-1}): 3300, 1710, 1670. NMR: δ ($CDCl_3$/d_6-acetone): 1.3-1.9(m, 20H), 4.2 (t, 4H), 7.1-8.1(m, 6H), 8.4(br m, 2H), 8.75 (s, 2H).

'Trifluoroacetamido-modified-alkyl-strapped'-bis(pyrromethane (18)

A solution of benzyl 3,4-dimethylpyrrole-2-carboxylate (7) (4.59 g, 2.0 mmol) and dialdehyde (17) (3.23 g, 5.1 mmol) in absolute ethanol (80 ml) was heated to reflux under nitrogen. Concentrated hydrochloric acid (0.10 ml, 1.2 mmol) was added and heating was continued for 1 h. The reaction was diluted with dichloromethane (250 ml), washed with aqueous sodium bicarbonate and brine, dried (sodium sulphate), and concentrated to dryness in vacuo to yield 7.6 g of a yellow foam. The foam was dissolved with heating into a minimum amount of dichloromethane and an off-white amorphous solid (6.80 g) was obtained by precipitation with diethyl ether. Further purification was effected by filtration through alumina (40 g, activity I), using dichloromethane containing 1% methanol as eluant. The bis(pyrromethane) (18) was obtained as a colourless solid with indefinite m.p. on workup. (Found: C, 68.27; H, 6.09; N, 5.33. Calcd. for $C_{86}H_{90}F_6N_6O_{12}$: C, 68.24; H, 5.99; N, 5.55%). IR: ν_{max} (nujol) (cm^{-1}): 3260, 1700 1670(br). NMR: δ ($CDCl_3$): 1.2(br s, 16H), 1.4(m, 4H), 2.03(s, 12H), 2.22(s, 12H), 3.8(t, 4H), 5.1 (d, 8H), 5.72(s, 2H), 6.8-7.8(m, 6H), 7.24(s, 20H), 8.2(m, 2H), 8.8(m, 4H).

'Trifluoroacetamido-modified-alkyl-strapped' porphyrin (19)

A mixture of bis(pyrromethane) (18) (3.032 g, 2.00 mmole), 10% Pd/C (0.723 g) and triethylamine (0.8 g) in dry THF (200 ml) was shaken under hydrogen (1 atmosphere) until hydrogen uptake was complete (30 min). The solution was filtered through Celite and concentrated to dryness. The resultant foam was dissolved in dry dichloromethane (800 ml) and trimethyl orthoformate (4.60 ml, 41.9 mmol) and trichloroacetic acid (19.60 g, 120.0 mmol) added. The reaction mixture was stirred in the dark protected from moisture for 3.5 h and zinc acetate (1.0 g) in dry methanol (15 ml) was added. After the

mixture was stirred for 48 h it was washed with 1N hydrochloric acid (2× 100 ml) water (100 ml), aqueous sodium bicarbonate (100 ml) and brine (100 ml), dried (Na_2SO_4) and concentrated to dryness. The residue was chromatographed over silica (100 g). Dichloromethane containing 1% methanol eluted the porphyrin (19) (972 mg, 49%), m.p. >300°. (Found: C, 67.39; H, 6.16; N, 8.17. Calcd. for $C_{56}H_{60}N_6O_4F_6$: C, 67.59; H, 6.08; N, 8.45%). IR: ν_{max} (KBr) (cm^{-1}): 3410, 1710. MS: (FD) (m/e): 994(M^+). VIS: λ_{max} (log ε) (CH_2Cl_2) (nm): 627(3.30), 574(3.60), 540 (3.51), 506(4.04), 408(5.18), phyllo-type spectrum[19]; (CH_2Cl_2 + Cl_3CCO_2H) (nm): 606(sh), 568, 525(sh), 427. NMR: δ (d_6DMSO): -2.5(br 2H, m), -0.5 to -0.2(m, 4H), -0.20 - 0.0(m, 8H), 0.85(m, 4H), 1.2(m, 4H), 2.53(s, 12H), 3.53(s, 12H), 3.98(m, 4H), 7.44(d, J 9 Hz, 2H) 8.10(d, J 3 and 9 Hz, 2H), 8.21 (d, J 3 Hz, 2H) 10.21 (br s, 2H), 11.31(s, 2H).

'Alkyl-strapped' bis(amino)porphyrin (16)

a From the protected porphyrin (19)

Sodium borohydride (60 mg, 1.6 mmol) was added to a stirred suspension of the porphyrin (19) (100 mg, 0.10 mmol) in dry THF (15 ml) under argon in the dark. Absolute ethanol (5 ml) was added and the mixture warmed gently to dissolve the reactants. The solution was stirred under argon for 1.25 h, dry methanol (10 ml) added and the solution stirred a further 20 min. Water (20 ml) was added slowly causing porphyrin to crystallize. The crude porphyrin was collected by filtration and chromatographed over silica (20 g) with dichloromethane containing 0-5% methanol to give 'alkyl-strapped'bis(amino)porphyrin (16) as a purple solid (66 mg, 82%), m.p. >300°. IR: ν_{max} (KBr) (cm^{-1}): 3400, 3300, 1610. MS: (FD) (m/e): 802(M^+). VIS: λ_{max} (CH_2Cl_2) (nm): 629, 576, 542, 508, 410; λ_{max} (CH_2Cl_2 + Cl_3CCO_2H) (nm): 607(sh), 567, 527(sh), 426, 418. NMR: δ ($CDCl_3$): -0.7 to -0.4(m, 4H), -0.3 to +0.1 (m, 8H), 0.6-1.0 (m, 8H), 2.55(s, 12H), 3.55(s, 12H), 3.85(m, 4H), 7.05(br s, 4H), 7.30(s, 2H), 10.20(s, 2H).

b From 'alkyl-strapped'-bis(nitrophenyl-pyrromethane) (15)

A mixture of the bis(pyrromethane) (15) (0.737 g, 0.53 mmol) and 10% Pd/C (0.364 g) in dry THF (50 ml) containing triethylamine (0.2 g) was hydrogenated for 3 days. The mixture was filtered through Celite and concentrated to dryness in vacuo. The resulting dark yellow foam was dissolved in dichloromethane (150 ml), anhydrous trichloroacetic acid (4.90 g, 30.0 mmol) in dichloromethane (50 ml) and trimethyl orthoformate (1.54 ml, 14.0 mmol) was added, and the reaction was stirred in the dark for 4 h and pyridine (4 ml) added. The reaction mixture was stirred overnight and then washed with water, aqueous sodium bicarbonate, and brine, dried (sodium sulphate), and concentrated to dryness in vacuo. Chromatography of the residue on alumina (activity I) gave the porphyrin (16) as a purple solid on workup (5 mg, 1%), m.p. >300°, with identical spectra properties as the material from route (a).

Bis-2-(2-formylphenoxy)ethyl terephthalate (20)

Terephthaloyl chloride (20.3 g, 0.0 mol) and 2-(2-hydroxyethoxy)benzaldehyde[1] (33.5 g, 0.2 mol) were dissolved in anhydrous ether (440 ml). Triethylamine (20.2 g, 0.2 mol) was added slowly and the resulting mixture was stirred at room temperature overnight. The mixture was diluted with dichloromethane (1200 ml), washed with water (500 ml), dilute aqueous hydrochloric acid (500 ml), dilute aqueous sodium bicarbonate (500 ml), and again with water (500 ml). The organic phase was dried (Na_2SO_4) and concentrated in vacuo to a pale yellow oil which crystallized slowly. The crystalline mass was triturated with warm ether (50 ml) and filtered to yield the dialdehyde (20), which was used without further purification (36.0 g, 78%). IR: ν_{max} (nujol) (cm^{-1}): 1720, 1690. NMR: δ ($CDCl_3$): 4.5(m, 4H), 4.8(m, 4H), 6.2-8.2(m, 12H), 10.6(s, 2H).

'Terephthalate-strapped'-bis(pyrromethane) (21)

A solution of the dialdehyde (1.15 g, 2.5 mmol) and benzyl 3,4-dimethylpyrrole-2-carboxylate (2.29 g, 10.0 mmol) in absolute ethanol (15 ml) was heated to reflux under nitrogen and concentrated hydrochloric acid (0.04 ml) was added. The reaction was heated under reflux for 30 min, neutralized with concentrated ammonium hydroxide, and concentrated in vacuo. The crude product was dissolved in dichloromethane and filtered through a short plug of alumina. The eluant was concentrated in vacuo to yield the bis(pyrromethane) (21) as a yellow foam (2.65 g, 79%). IR: ν_{max} (nujol) (cm^{-1}): 3410, 3240, 1710, 1680. NMR: δ ($CDCl_3$): 1.47(s, 12H), 1.93(s, 12H), 4.0(m, 4H), 4.2 (m, 4H), 4.93(s, 8H), 5.52(s, 2H), 6.7-7.2(m, 28H), 7.70(s, 4H), 8.4(m, 4H).

'Terephthalate-strapped' porphyrin (22)

The 'terephthalate-strapped'bis(pyrromethane) (21) (1.078 g, 0.80 mmol), triethylamine (0.3 g), and 10% Pd#C (0.146 g) in dry THF (100 ml) were shaken under hydrogen (1 atmosphere) until hydrogen uptake ceased (4h), filtered through Celite and the filtrate was concentrated in vacuo. The resulting yellow foam was dissolved in dichloromethane (640 ml) and trichloroacetic acid (15.7 g, 96.0 mmol) and trimethyl orthoformate (4.2 ml, 38.4 mmol) added. The mixture was stirred in the dark for 5 h, pyridine (10 ml) was added and the stirring continued a further 12 h. The resultant dark green solution was washed with IN hydrochloric acid (3× 200 ml), water (200 ml) aqueous sodium bicarbonate (2× 200 ml) and brine (200 ml), dried (Na_2SO_4) and concentrated in vacuo to yield a purple-black residue which was chromatographed on alumina(activity I, ca. 75 g). Elution with dichloromethane containing 0.5% methanol gave the 'terephthalate-strapped' porphyrin (22) as a purple solid (94 mg, 10%), m.p. >300°. IR: ν_{max} (nujol) (cm^{-1}): 1710. MS: (FD) (m/e): 824(M^+). VIS: λ_{max} ($CHCl_3$ + trace p-tolyene-sulphonic acid) (nm): 610, 571, 532(sh), 433. NMR: δ (TFA): -4.90(m, 2H), 2.63(s, 12H), 3.47(s, 12H), 4.3(m, 8H), 4.40(s, 4H), 7.4-8.2(m, 8H).

1,5-Bis(2-hydroxyethoxy)naphthalene (23)

1,5-Dihydroxynaphthalene (10.16 g, 63.4 mmol) was added to a stirred solution of potassium carbonate (26.4 g) in water (200 l) and THF (50 ml). The deep violet solution was filtered and cooled in ice and placed in a 1.5 l rocking bomb. Ethylene oxide (12.5 g) was condensed at -78°C and added to the bomb, which was immediately sealed. The solution was shaken and heated at 100°C for 30 h and

allowed to cool over 36 h. The THF was evaporated off and the grey-brown precipitate was collected by filtration, dissolved in THF and filtered through a short pad of alumina. Evaporation of the solvent afforded 1,5-bis(2-hydroxyethoxy)naphthalene (23) (6.81 g, 43.2%). Crystallisation from chloroform/acetone gave (23) as colourless needles, m.p. 180-182° (Found: C, 67.79; H, 6.46. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50%). IR: ν_{max} (KBr) (cm^{-1}): 3350, 1590. MS: (m/e): 248(M^+). NMR: δ (d_6-acetone): 3.6(s, 2H), 3.9-4.3(m, 8H), 6.8-7.9(m, 6H).

Tosylation of 1,5-bis(2-hydroxyethoxy)-naphthalene (23)

The naphthalene (23) (0.90 g, 3.6 mmol) was taken up in dry redistilled pyridine (30 ml) and the solution cooled to 0°C. p-Toluenesulphonyl chloride (2.7 g, 14.2 mmol) was added and the mixture stirred at 0°C for 48 h, poured into ice-water (150 ml). The precipitate was collected by filtration, washed well with cold water, dried in vacuo, and washed with benzene. Recrystallisation from chloroform gave the bistosylate (24) as colourless needles (1.04 g, 52%), m.p. 204-206°. IR: ν_{max} (KBr) (cm^{-1}): 3070, 2930, 1595. MS: (m/e): 556(M^+). NMR: δ ($CDCl_3$): 2.35(s, 6H), 4.1-4.6(m, 8H), 6.5-7.8(m, 14H).

1,5-Bis[2-(2-formylphenoxy)ethoxy]-naphthalene (25)

A solution of the sodium salt of salicylaldehyde (0.70 g, 4.9 mmol) and the bistosylate (24) (0.802 g, 1.4 mmol) in dry DMF (175 ml) was heated at 110°C under nitrogen for 21 h and concentrated in vacuo to a brown residue which was partitioned between chloroform and water. The chloroform layer was retained and the brown aqueous layer extracted several times with chloroform. The combined chloroform layers were evaporated to dryness. Recrystallisation of the product from dichloromethane/methanol gave the naphthalene (25) as colourless crystals (0.502 g, 76%), m.p. 160-163°. (Found: C, 72.69; H, 5.70. Calc. for $C_{28}H_{24}O_6$. CH_3OH: C, 72.44; H, 5.55%). IR: ν_{max} (KBr) (cm^{-1}): 1680, 1590. MS: (m/e): 456(M^+). NMR: δ ($CDCl_3$): 4.5(s, 8H), 6.7-7.8(m, 14H), 10.3(s, 2H).

'Naphthalene-strapped'-bis(pyrromethane) (26)

A solution of the naphthalene (25) (0.871 g, 0.20 mmol) and benzyl 3,4-dimethyl-pyrrolecarboxylate (7) (1.748 g, 0.80 mmol) in chloroform (200 ml) and ethanol (100 ml) was heated to reflux and concentrated hydrochloric acid (2 ml) added. After 1 h the reaction mixture was cooled to room temperature, neutralized with sodium bicarbonate and partitioned between chloroform and water. The organic layer was dried (Na_2SO_4) and concentrated to dryness. Recrystallisation from dichloromethane/methanol (3:1, v/v) gave the bis(pyrromethane) (26) as off-white needles (1.75 g, 66%), m.p. 199-203°. (Found: C, 75.26; H, 6.37; N, 3.85. Calcd for $C_{84}H_{80}N_4O_{12}$: H, 75.43; H, 6.03; N, 4.19%). IR: ν_{max} (KBr) (cm^{-1}): 3420, 1695, 1670. MS: (FD) (m/e): 1336(M^+). NMR: δ ($CDCl_3$): 1.65(s, 12H), 2.1(s, 12H), 4.2(m, 8H), 5.1(s, 8H), 5.7(s, 2H), 7.2(s, 20H), 6.6-7.7(m, 14H), 8.25(s, 4H).

'Naphthyl-strapped' porphyrin (27)

The bis(pyrromethane) (26) (1.34 g, 1.0 mmol), and 10% Pd/C (0.27 g) in dry THF (250 ml) were shaken under hydrogen (1 atmosphere) until uptake ceased (30 min), filtered through Celite and the filtrate was concentrated in vacuo. The residue was dissolved in dichloromethane (500 ml) and trichloroacetic acid (12.25 g, 75 mmol) and trimethyl orthoformate (3.3 ml, 30 mmol) added. Zinc acetate (0.2 g) in methanol (2 ml) was added and the mixture stirred for 20 h in the dark. The reaction solution was washed successively with 1N hydrochloric acid, water, aqueous sodium bicarbonate, and brine, dried (Na_2SO_4) and concentrated in vacuo to yield a purple-black residue which was chromatographed over silica. Elution with dichloromethane containing 3% methanol gave the porphyrin (27) as a purple solid (230 mg, 28%), m.p. >300°. MS: (FD) (m/e): 816(M^+). VIS: λ_{max} (CH_2Cl_2) nm: 629, 577, 542, 508, 412. NMR: δ ($CDCl_3$): 2.4(s, 12H), 3.3(s, 12H), 3.5-4.7(m, 14H), 6.5-8.0(m, 9H), 9.7(s, 2H).

Dibenzyl meso-phenyl-3,3', 4,4'-tetramethyl-pyrromethane-5,5'-dicarboxylate (28)

A solution of benzyl 3,4-dimethylpyrrole-2-carboxylate (7) (3.40 g, 14.85 mmol) and benzaldehyde (1.06 g, 10.0 mmol) in absolute ethanol was heated to reflux under nitrogen and hydrochloric acid (0.05 g) was added. After 30 min the solution was neutralized with ammonium hydroxide and the mixture concentrated to dryness. The residue was dissolved in dichloromethane and washed with aqueous sodium bicarbonate and brine, dried (sodium sulphate) and filtered through a short plug of alumina. Evaporation of the filtrate gave the pyrromethane (28) as a pale yellow foam (3.0 g, 75%). NMR: δ ($CDCl_3$): 1.83(s, 6H), 2.23(s, 6H), 5.11(s, 4H), 5.52 (s, 1H), 7.10(m, 5H), 7.27(s, 10H), 9.10(m, 2H).

5,15-Diphenyl-2,3,7,8,12,13,17,18-octamethyl-porphine (29)

The pyrromethane (28) (1.093 g, 2.0 mmol) was dissolved in dry THF (75 ml) containing dry triethylamine (0.15 g), and 10% Pd/C (0.27 g) was added. The mixture was shaken under 1 atmosphere of hydrogen until uptake had ceased (2½ h). The catalyst was removed by filtration through Celite (super-cel) and the filtrate was concentrated to dryness in vacuo. The resulting foam was dissolved in dichloromethane (600 ml), and anhydrous trichloroacetic acid (19.60 g, 120.0 mmol) in dichloromethane (200 ml), and trimethyl orthoformate (4.4 ml, 40.0 mmol) added. The resulting red solution was stirred in the dark for 4 h. Pyridine (14 ml) was added and stirring continued overnight. The solution was then purged with air for 5 min and stirred in the light for 4 h. The dark green solution was concentrated in vacuo to half volume, washed with 1N hydrochloric acid (3 × 200 ml), water (200 ml), saturated sodium bicarbonate (2 × 200 ml), and brine (200 ml), dried (Na_2SO_4), and concentrated to dryness in vacuo. The purple-black residue was dissolved in dichloromethane and chromatographed on alumina (activity I, 45 g). Elution with dichloromethane containing 0-5% methanol gave the porphyrin (29) as a violet microcrystalline solid on evaporation (75.5 mg, 13%), m.p. >300°. VIS: λ_{max} ($CHCl_3$) (nm): 626, 576, 542, 508, 408 (Phyllo-type spectrum)[19]; ($CHCl_3/CF_3COOH$) 620, 573, 533(sh), 433. NMR: δ ($CDCl_3$, CD_2Cl_2): -1.01(m, 2H), 2.27(s, 12H), 3.29(s, 12H), 7.3-8.4(m, 10H), 10.26(s, 2H).

Synthesis of Metalloporphyrins

The metallation of the porphyrins (11), (22), (27) and (29) followed a standard procedure of which the following synthesis is typical.

Chloro('alkyl-strapped' porphyrin)iron(III) (31)

A solution of 'strapped' porphyrin (11) (59, 0.076 mmol) and anhydrous ferrous chloride (60 mg, 0.47 mmol) in dry THF (20 ml) was heated at reflux under nitrogen for 1.5 h. Evaporation of the solvent under reduced pressure left a residue which was dissolved in hot chloroform (30 ml) and chromatographed on dry alumina (activity IV, 40 g) using hot chloroform to elute the green band of the porphyrin as the ferric μ-oxo dimer (32): λ_{max} ($CHCl_3$) 584, 475(sh), 406, 364(sh). A chloroform solution (200 ml) of the μ-oxo dimer was shaken with 2% aqueous hydrochloric acid (200 ml) to regenerate the (chloro)-iron(III) derivative. The organic layer was washed with water (100 ml), dried ($NaSO_4$), filtered and evaporated to yield chloro('alkyl-strapped'-porphyrin)iron(III) (31) as purple-black crystals (55 mg, 84%), m.p. >300°. MS: (FD) (m/e): 862 (M^+), VIS: λ_{max} ($CHCl_3$) (nm): 648, 589(sh), 540(sh), 514, 410(sh), 390.

Reduction of chloro(porphyrin)iron(III) complexes to (porphyrin)iron(II)

The following general procedure was used.

All of the apparatus and solvents were dry and rigorously oxygen free as described previously.[1] An excess of chromous bis(acetylacetonate) was transferred through a connecting adapter under vacuum to a 50 ml Schlenk flask (previously purged with argon) containing 100 mg of the appropriate (chloro)-iron(III) complex. The flask under argon was then attached to a 15 ml Schlenk filter equipped with a medium frit under argon. Approximately 40-50 ml of deoxygenated dry benzene was added by cannula under argon and the resultant mixture was heated at reflux under argon for 30 min. The reaction mixture was concentrated to approximately 10-20 ml by briefly evacuating the system and then purging with argon. Then approximately 20 ml deoxygenated dry methanol was added via cannula under argon. The oxygen-sensitive, brick-red ferrous porphyrin crystallised from the solution on cooling (ice-bath) for 30 min and was collected by filtration under argon through the Schlenk filter, dried under vacuum, and stored under argon. The complexes were stable enough to allow manipulation in air for short periods.

Oxygenation and Carbonylation studies on (porphyrin)iron(II) complexes

Carbon monoxide and dioxygen binding studies were carried out by the same method as has been described previously.[1,4,5,6,7]

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