Syntheses of 'Strapped' Porphyrins and the Oxygenation of their Iron(II) Complexes

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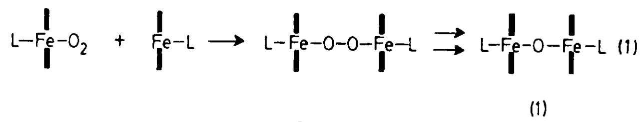
Summary Two 'strapped' porphyrins, containing a chain of atoms linking two opposite *meso*-positions have been synthesized; their iron(II) complexes were oxygenated reversibly at low temperatures (−55 °C) and at 25 °C were converted, irreversibly, into μ-oxo dimers.

Recently it has been demonstrated that suitably hindered porphyrin iron(II) species may be reversibly oxygenated in solution to a relatively stable (1:1) complex at ambient temperature (*ca.* 25 °C). In these cases the bimolecular process, equation (1), which leads by irreversible oxidation to the μ-oxo dimer (1), is slowed by steric hindrance.[1] The same result may be achieved for unhindered iron(II) porphyrins by using low temperatures (*ca.* −50 °C) and low dilution (*ca.* 10^{-4}M) when these substances also exhibit reversible binding of oxygen.[2] At present two different approaches have been developed for provision of steric hindrance above the porphyrin plane, the 'picket fence' model[1(b)] (2) and the 'capped' model[1(c)] (3). We now describe the syntheses of examples of a third alternative hindered structure, the 'strapped' model (**4**).



(1)

[L = Ligand, Fe = porphyrin iron(III) complex]

The syntheses of the substances followed the dipyrrylmethane route developed by Kenner and his collaborators.[3] Thus condensation of benzyl 3,4-dimethylpyrrole-2-carboxylate in ethanolic HCl at 80 °C with the dialdehydes (**5**) and (**6**) gave the bis-dipyrrylmethanes (**7**) and (**8**) in 77 and 80% yield respectively.† The dialdehyde (**5**) was obtained by condensation of salicylaldehyde with 1,12-dibromododecane (75%) and (**6**) was prepared from *o*-formylphenyl 2-hydroxyethyl ether[4] with terephthaloyl chloride (78%). Closure to the porphyrin was achieved by catalytic debenzylation [10% Pd–C, tetrahydrofuran (THF), NEt_3] and reaction with trimethyl orthoformate in dichloromethane with trichloroacetic acid, yielding (**9**) and (**10**) in 23 and 10% yields, respectively.

The spectral data were in complete accord with the suggested structures. Thus the visible spectrum of (**9**) showed λ_{max} (CH_2Cl_2) (log ϵ): 628 (3·08), 576 (3·76), 541 (3·64), 5·07 (4·12), and 409 nm (5·26), shifted with trichloroacetic acid to 610, 568, and 430 nm. Furthermore, the n.m.r. spectrum of (**9**) (CF_3CO_2H), as well as showing the characteristic signals of the NH, methyl, and aromatic protons, showed that 16 of the 24 in-chain C–CH_2–C protons of the 'strap' fell in the region δ +0·50 to −0·90, a characteristic shift only in accord with these protons lying above the porphyrin plane, thereby exposed to the powerful diamagnetic anisotropy of this nucleus.

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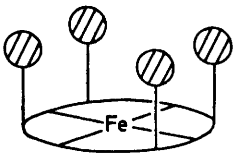
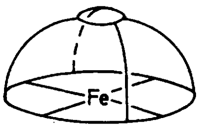
† All new air-stable substances gave suitable combustion and spectroscopic data.

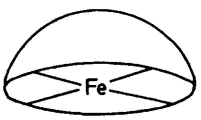
A similar observation was made on (**10**), in which the aromatic protons of the terephthalolyl residue appear at δ 4·40, shifted upfield by 3·30 p.p.m. from their position in the open precursor (**8**).



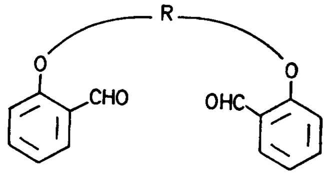
(2)



(3)

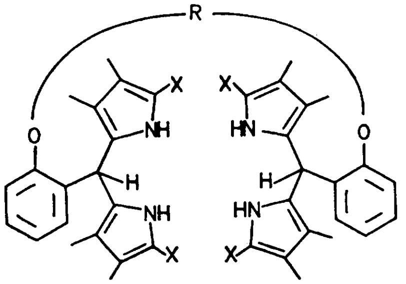


(4)



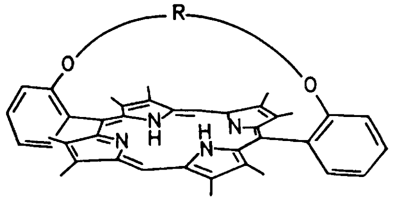
(5) $R = -[CH_2]_{12}-$

(6) $R = -[CH_2]_2-O_2C-C_6H_4-CO_2-[CH_2]_2-$



(7) $R = -[CH_2]_{12}-$

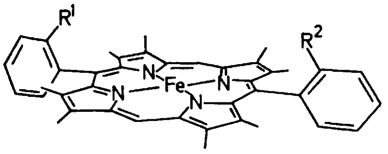
(8) $R = -[CH_2]_2-O_2C-C_6H_4-CO_2-[CH_2]_2-$



(9) $R = -[CH_2]_{12}-$

(10) $R = -[CH_2]_2-O_2C-C_6H_4-CO_2-[CH_2]_2-$

The iron(II) complexes of these porphyrins (**11**) and (**12**), as well as the derivative (**13**), without the 'strap,' were prepared by reaction with $FeCl_2$ in THF to yield the iron(III) chloro-derivatives which were reduced with chromium(II) bis(acetylacetonate) in benzene to the iron(II) complexes.‡



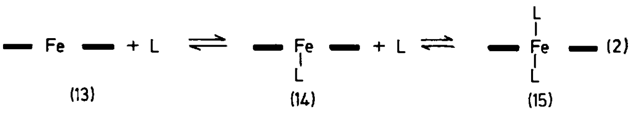
(11) $R^1,R^2 = -O[CH_2]_{12}O-$

(12) $R^1,R^2 = -O[CH_2]_2-O_2C-C_6H_4-CO_2[CH_2]_2-O-$

(13) $R^1,R^2 = H$

When the unhindered iron(II) derivative (**13**) was dissolved in pyridine at −45 °C, it formed the hexaco-ordinate haemochrome, as (**15**), equation (2), which is stable to oxygen. Dissolution of this haemochrome (**15**) in THF at −45 °C provided a sufficient amount of the pentaco-ordinate material (**14**) to enable reversible oxygenation to occur, and upon warming to 25 °C the system was converted irreversibly into the μ-oxo dimer, λ_{max} (THF) 565 nm. This behaviour is typical of an unhindered iron(II) porphyrin.[2]

It was surprising to find, however, that the strapped species (**11**) and (**12**) behaved in an exactly similar manner, as is exemplified by (**11**). Thus dissolution of (**11**), λ_{max} (C_6H_6) 566 and 540 nm, in benzene containing 5% *N*-methylimidazole at 25 °C gave the spectrum of the hexaco-ordinate species, λ_{max} 557, 529, 520 (sh), and 420 nm, which was, as expected, stable to oxygen, but reacted with carbon monoxide to form a complex having λ_{max} 564 (sh), 539, 419, and 397 nm. Preparation of the pyridine haemochrome λ_{max} 553, 524, 516, and 490 nm, at −40 °C in THF with 2 equiv. of pyridine allowed reversible oxygenation at −50 °C over many cycles, to a complex having λ_{max} 570 (sh), 552 (sh), and 538 nm. Warming the solution under oxygen to 25 °C gave rapidly the μ-oxo dimer, λ_{max} 572 nm.



$$\underset{(13)}{-\mathrm{Fe}-} + L \rightleftharpoons \underset{(14)}{\underset{L}{\underset{|}{-\mathrm{Fe}-}}} + L \rightleftharpoons \underset{(15)}{\underset{L}{\underset{|}{\overset{L}{\overset{|}{-\mathrm{Fe}-}}}}} \quad (2)$$

It is apparent from these results that both (**11**) and (**12**) behave as unhindered porphyrins, which suggests that the strap, intended to hinder the attachment of the sixth ligand,

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‡ All manipulations of the iron(II) complexes were conducted in a Schlenk apparatus under argon.

does not provide sufficient steric encumbrance, at least towards pyridine and *N*-methylimidazole. We feel that at low ligand concentration and ambient temperature, sufficient tetraco-ordinate iron(II) complex exists to provide an irreversible route to the μ-oxo dimer, whereas at high ligand concentration mainly the hexaco-ordinate species exists, which is stable to oxygen. Apparently the stereochemical requirements for inhibition of the formation of the unwanted hexaco-ordinated species are quite substantial.

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