Short-chain Basket Handle Porphyrins: Synthesis and Characterisation

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Basket handle porphyrins containing short *p*- or *m*-phenylenedimethylenedioxy chains covalently linked at the *ortho* position of phenyl groups of 5,10,15,20-tetraphenylporphyrin have been synthesised. Isomer **I** of the *para* derivative (H_2L^{Ia}) and isomers **II** and **III** (H_2L^{IIb} and H_2L^{IIIb}) of the *meta* derivative have been characterised by various spectroscopic methods. Electronic and ^1H NMR spectral studies indicate significant distortion of the porphyrin skeleton in these derivatives. Protonation of the free-base derivatives results in a small blue shift of the Q bands, attributed to the lack of conjugation between the phenyl groups and the porphyrin plane because of restricted rotation of the porphyrin–phenyl bond. The bridging phenylenedimethylenedioxy group does not interfere with the axial ligation of metal derivatives (Co^{2+} and Zn^{2+}) of H_2L^{IIb} and H_2L^{IIIb}. Electrochemical studies indicate easier oxidations and more difficult reductions for the free-base derivatives relative to the corresponding unstrapped derivative, attributed in the former case to the loss of coplanarity due to distortion and in the latter to destabilisation of the anions and dianions due to the lack of solvation. Redox potential data for [CoL^{IIb}] indicate that the metal centred molecular orbital $A_1(d_{z^2})$ is situated above the filled A_{2u} orbital of the porphyrin ring.

Structural deformity in the porphyrin skeleton is known significantly to affect the physical properties and chemical reactivities of porphyrins and metalloporphyrins. Thus, a strong antiferromagnetic coupling between the metal centre and the radical centre of an iron porphyrin and the enhanced stability and unusual redox properties of the oxidised products of nickel chlorins and bacteriochlorins have been attributed to the distorted conformations of the tetrapyrrole ring.[1–3] One of the ways of introducing distortion in the porphyrin skeleton is by steric crowding at the porphyrin periphery.[4] This strategy has led to the synthesis and characterisation of several unusual porphyrins such as crown,[5] picket fence,[6] strapped,[7] capped[8] and basket handle porphyrins.[9] However, despite these efforts, significant structural deformation in the porphyrin skeleton is observed only in the 'pyrrole strapped' porphyrins synthesised by Dolphin and co-workers[10] and 'short chain basket handle porphyrins' synthesised by Walker and co-workers.[11] In both cases the presence of a 'short bridging chain' was responsible for the observed distortion.

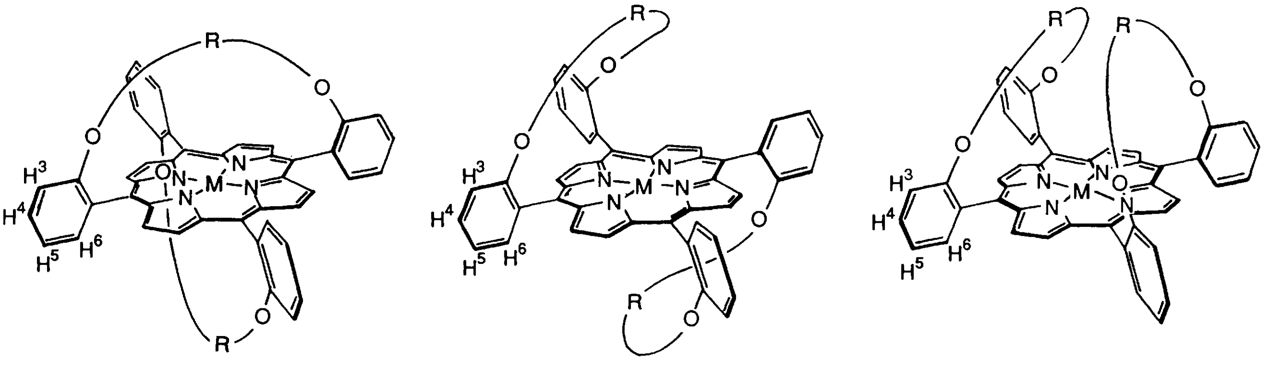
In view of this we have begun a systematic investigation on deformed porphyrin systems with the aim of relating the unusual spectroscopic and redox properties of these systems to the subtle structural changes. In this paper, we report the synthesis and characterisation of basket handle porphyrins and their metal derivatives (Co^{2+} and Zn^{2+}) which are derived from 5,10,15,20-tetraphenylporphyrin (H_2tpp) in which two phenyl groups are bridged by a very short *o*-phenylenedimethylenedioxy chain (Fig. 1). A comparison of the spectral and electrochemical characteristics of these basket handle porphyrins with those reported in the literature allowed the identification of different isomers. The electronic and ^1H NMR spectral features of the porphyrins reveal some unusual features which have been attributed to the significant distortion in the porphyrin skeleton.

Results

The short chain basket handle porphyrins were synthesised according to the method of Momenteau *et al.*[9] by condensation of appropriate dialdehydes with pyrrole in propionic acid. The crude porphyrins which were obtained as mixture of isomers were separated by repeated column chromatography. Only one isomer (H_2L^{Ia}) was separated in pure form when the R group used was *p*-phenylenedimethylene. The other two expected isomers (H_2L^{IIa} and H_2L^{IIIa}) were always found as a mixture and their clear separation has not yet been achieved. Two isomers were separated in pure form (H_2L^{IIb} and H_2L^{IIIb}) when the R was *m*-phenylenedimethylene. The other expected isomer (H_2L^{Ib}) was not formed probably due to the reduced chain length of the R group relative to the *para* derivative.

The ^1H NMR spectra of the free-base basket handle porphyrins are highly characteristic and the integrated intensities of the proton resonances are consistent with the proposed structure (Fig. 2). An inspection of the ^1H NMR data in Table 1 indicates that for isomer H_2L^{Ia} all the eight pyrrole protons resonate as a sharp singlet, the eight protons of the methylene chain are equivalent appearing as a singlet with an upfield shift (0.93 ppm) relative to the corresponding protons in the free dialdehyde, and the eight aromatic protons of the two strapped phenyl rings are equivalent appearing as a singlet shielded (3.53 ppm) compared to the corresponding protons in free dialdehyde by porphyrin anisotropy. The NH protons are highly deshielded (2.32 ppm) relative to 5,10,15,20-tetra(*o*-methoxyphenyl)porphyrin (H_2tmopp).[12,13] The isomers H_2L^{IIb} and H_2L^{IIIb} show two resonances for the pyrrole protons as expected considering the symmetry of the isomers. Also, the methylene chain protons appear as an AB quartet with negligible shielding relative to the free dialdehyde; the phenyl protons of the strapping group are split and experience a small shielding ($\approx$0.45 ppm) relative to the free dialdehyde. The NH protons also experience a small shielding in these two isomers in contrast to the H_2L^{Ia} isomer.

Momenteau *et al.*[9] have pointed out that the chemical shifts of the H^6 proton of the mesophenyl ring and the NH protons are dependent on the chain length of the bridging group and the magnitude of the deshielding of these protons indicates the tension imposed on the porphyrin ring by the bridging group. Fig. 3 shows a plot of this deshielding for various cross-*trans*-linked isomers including H_2L^{Ia} *versus* the number of carbons in the bridging chain. The values for the protons of the strapped phenyl of the H_2L^{Ia} and the corresponding isomers of basket



I
Cross-*trans*-linked

II
Adjacent-*trans*-linked

III
Adjacent-*cis*-linked

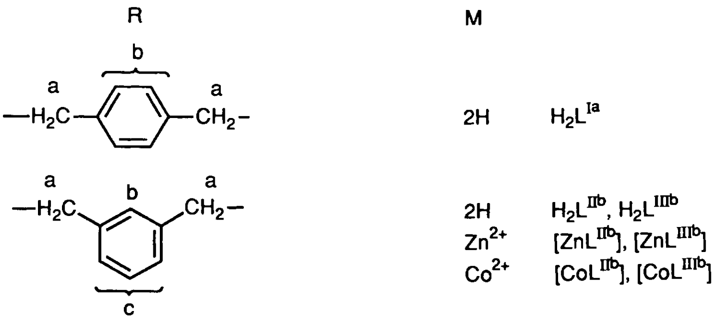


Fig. 1 Structures of the free-base short-chain basket handle porphyrins and their metal derivatives

Table 1 Proton NMR data (δ) for short-chain basket handle porphyrins in $CDCl_3$ at room temperature

		Phenyl (porphyrin)						
Compound	Pyrrole	H^6	H^4	H^3	H^5	Strap CH_2	Phenyl (strap)	NH
H_2tmopp	8.73	8.00	7.75	7.35		—	—	−2.58
H_2L^{Ia}	8.71 (s, 8 H)	8.85 (m, 4 H)	6.86 (m, 4 H)	7.58 (m, 8 H)		4.10 (s, 8 H)	3.89 (s, 8 H)	−0.27
2	—	—	—	—	—	5.03 (s, 4 H)	7.42 (s, 8 H)	—
H_2L^{IIb}	8.92 (s, 4 H) 8.62 (s, 4 H)	8.37 (d, 4 H)	7.49 (t, 4 H)	7.37 (d, 4 H)	7.80 (t, 4 H)	AB Quartet 5.06 (d, 4 H) 4.45 (d, 4 H) J_{AB} = 9.97 Hz	6.55 (s, 6 H) 7.17 (s, 2 H)	−2.77
H_2L^{IIIb}	8.86 (s, 4 H) 8.99 (s, 4 H)	8.34 (d, 4 H)	7.50 (t, 4 H)	7.35 (d, 4 H)	7.80 (t, 4 H)	AB Quartet 5.02 (d, 4 H) 4.53 (d, 4 H) J_{AB} = 9.77 Hz	6.57 (m, 6 H) 7.19 (s, 2 H)	−2.86
1	—	—	—	—	—	5.17 (s, 4 H)	7.33 (m, 8 H)	—

s, d, t and m correspond to singlet, doublet, triplet and multiplet respectively. The numbers in parentheses correspond to the number of protons.

Table 2 Electronic spectral data for short-chain basket handle porphyrins and their dications* in benzene

	Soret band λ_{max}/nm (10^{-4} ε dm^3 mol^{-1} cm^{-1}) B(0,0)	Q bands λ_{max}/nm (10^{-3} ε dm^3 mol^{-1} cm^{-1})			
Porphyrin		Q_y(1.0)	Q_y(0,0)	Q_x(1,0)	Q_x(0,0)
H_2L^{Ia}	433 (22.21)	529 (11.72)	566 (5.16)	605.0 (4.33)	663 (1.24)
$[H_4L^{Ia}]^{2+}$	440 (14.67)		566 (sh) (6.34)	592.0 (8.51)	646 (sh) (3.07)
H_2L^{IIb}	432 (31.72)	526 (12.09)	566 (6.42)	601 (5.14)	657 (3.74)
$[H_4L^{IIb}]^{2+}$	446 (23.8)			599.0 (6.98)	648 (17.62)
H_2L^{IIIb}	428 (34.03)	520 (16.09)	552 (6.88)	602 (4.79)	661 (2.54)
$[H_4L^{IIIb}]^{2+}$	442 (21.54)		544 (sh) (2.87)	586 (9.78)	634 (17.08)
H_2tpp	419 (46.4)	515 (18.7)	548 (8.6)	592 (5.5)	647 (3.9)
$[H_4tpp]^{2+}$	448 (43.6)			608 (9.0)	659 (50.9)

* Generated by addition of a dilute solution of trifluoroacetic acid in benzene.

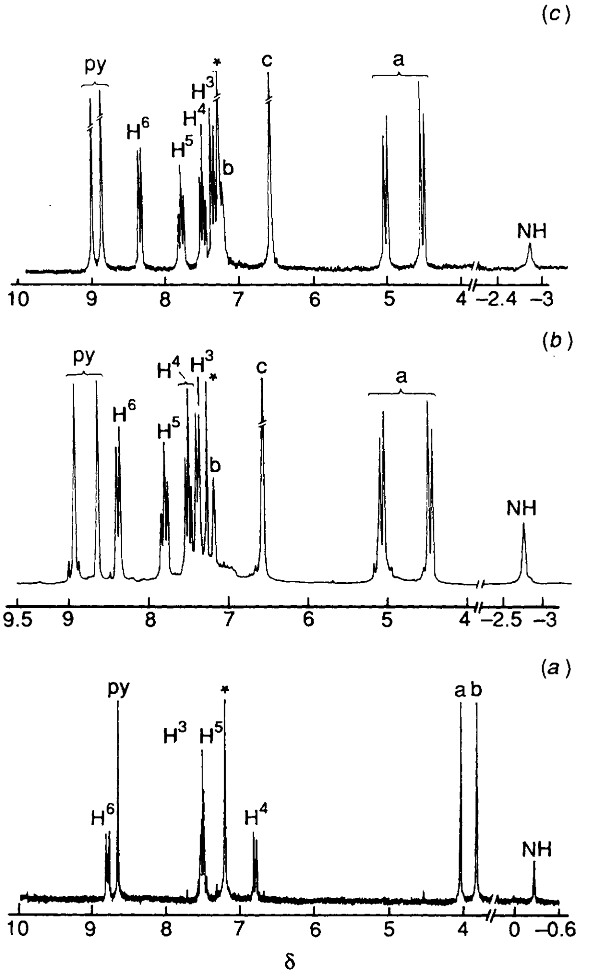


Fig. 2 Proton NMR spectra of H_2L^{Ia} (*a*), H_2L^{IIb} (*b*) and H_2L^{IIIb} (*c*) in $CDCl_3$ (concentration of the porphyrins used = 10^{-3} mol dm^{-3}). The asterisk corresponds to the $CDCl_3$ signal; py = pyrrole protons, see Fig. 1 for labelling

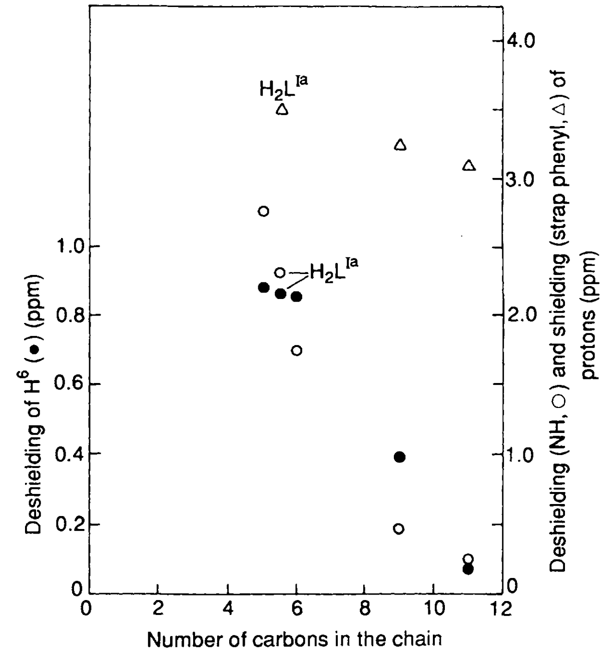


Fig. 3 Plot of the deshielding of the H^6 and NH protons and shielding of the strap phenyl protons *versus* chain length (see text for details) in various cross-*trans*-linked basket handle porphyrins

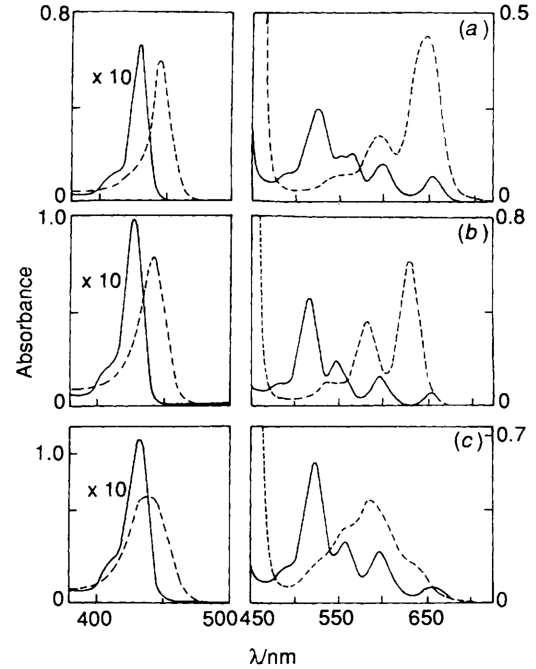


Fig. 4 Electronic absorption spectra of (*a*) H_2L^{IIb}, (*b*) H_2L^{IIIb} and (*c*) H_2L^{Ia} in benzene and their corresponding dications. Concentration for Q bands 10^{-5} mol dm^{-3} and for the Soret band is 10^{-6} mol dm^{-3} (solid line corresponds to neutral form, dotted lines to dications)

handle porphyrins synthesised by Momenteau *et al.*[9] [R = $(CH_2)_4C_6H_4(CH_2)_4$ or $(CH_2)_3C_6H_4(CH_2)_3$] and Simonis *et al.*[11] [R = $(CH_2)_6$ or $(CH_2)_5$] are also included.

The absorption spectral characteristics of the free bases along with the corresponding dications generated by addition of a drop of trifluoroacetic acid in benzene solution are shown in Fig. 4 and listed in Table 2. A comparison with the unstrapped H_2tpp reveals some interesting features; (*a*) a considerable red shift of the Soret and Q bands; (*b*) a drastic reduction in the intensity of both Soret and Q bands; the magnitude of the red shift and intensity decrease depend on the nature of the isomers and the greatest effects are observed for H_2L^{Ia}; (*c*) upon protonation, the Q bands experience a blue shift in contrast to the large red shift observed for protonation of H_2tpp.[14] However, the effects observed parallel those found for *ortho*-substituted tetraphenylporphyrins.[15]

The electronic absorption spectra of the basket handle porphyrins synthesised by Momenteau *et al.*[9] showed very little differences among the different isomers due to the lack of distortion in the porphyrin skeleton because of the longer chain of the bridging group. However, Simonis *et al.*[11] synthesised a series of such porphyrins containing shorter chains and found significant changes relative to the corresponding unstrapped derivative. A comparison of the red shifts and the intensity decreases for the different isomers of the present study with those synthesised by Simonis *et al.* allowed us to distinguish isomer **I** from **II** and **III**. Table 3 lists the magnitude of red shifts of Soret and Q bands of various isomers relative to their unstrapped derivatives.

Metallation of H_2L^{IIb} and H_2L^{IIIb} by the standard literature method[16] afforded the metal derivatives (Co^{2+} and Zn^{2+}). Metallation of H_2L^{Ia} was not achieved even under harsh conditions. It is apparent that the short-chain strapping group causes steric hindrance to the metal, preventing metallation of this isomer. The optical absorption data for the metal derivatives are collected in Table 4. Axial co-ordination of pyridine to the metal induces the expected red shift of the Soret, α and β bands with a change in the last two in intensity.[17] The magnitude of the shifts is comparable to those observed for pyridine binding of [Zn(tpp)]. Axial ligation of [CoL^{IIb}] and [CoL^{IIIb}]

Table 3 Comparison of red shifts (nm) of Soret and Q bands of different isomers relative to H_2tpp

Porphyrin	Soret B(0,0)	Q_y (1,0)	Q_y (0,0)	Q_x (1,0)	Q_x (0,0)	Ref.
* hexyl I	10	12	20	14	10	11
pentyl I	20	22	30	22	20	11
H_2L^{Ia}	14	15	20	16	16	This work
hexyl II	2	2	2	4	−2	11
pentyl II	5	4	2	6	2	11
butyl II	8	6	10	16	14	11
H_2L^{IIb}	14	12	20	13	9	This work
hexyl III	4	2	4	4	−2	11
pentyl III	6	6	6	6	0	11
butyl III	8	6	10	16	14	11
H_2L^{IIIb}	10	6	6	14	13	This work

* The labelling in the original publication has been retained. Hexyl, pentyl and butyl refer to the strapped porphyrins for which R = $(CH_2)_6$, $(CH_2)_5$ and $(CH_2)_4$ respectively.

Table 4 Electronic spectral data for metal derivatives of short-chain basket handle porphyrins in $CHCl_3$

Porphyrin	Soret λ_{max}/nm ($10^{-4}\varepsilon$/dm^3 mol^{-1} cm^{-1})	α λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})	β λ_{max}/nm ($10^{-3}\varepsilon$/dm^3 mol^{-1} cm^{-1})
[ZnL^{IIb}]	427 (25.0)	555 (11.6)	596 (2.4)
[ZnL^{IIb}] + Pyridine	439	572	615
[ZnL^{IIIb}]	430 (19.0)	559 (7.8)	597 (2.97)
[ZnL^{IIIb}] + Pyridine	437	570	612
[Zn(tpp)]	419	548	589
[Zn(tpp)] + Pyridine	430	562	602
[CoL^{IIb}]	417 (14.1)	532.5	—
[CoL^{IIb}] + Pyridine	437	549.5	585
[CoL^{IIIb}]	418 (8.1)	534 (5.05)	—
[CoL^{IIIb}] + Pyridine	438	550	—
[Cotmopp)]	414	529	—
[Co(tmopp)] + Pyridine	440	553	593

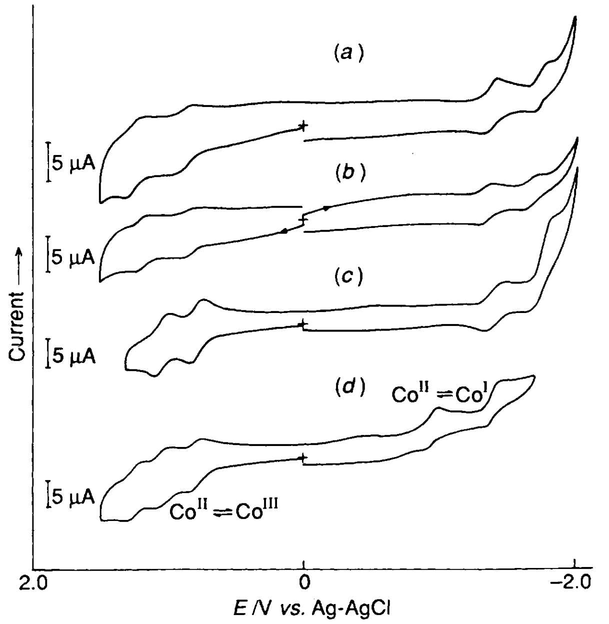


Fig. 5 Cyclic voltammograms of (*a*) H_2L^{Ia} (1.47×10^{-4}), (*b*) H_2L^{IIb} (1.7×10^{-4}), (*c*) [ZnL^{IIb}] (5.2×10^{-4}) and (*d*) [CoL^{IIb}] (5.56×10^{-4} mol dm^{-3}) in CH_2Cl_2 containing 0.1 mol dm^{-3} NBu_4ClO_4 at room temperature. Scan rate 100 mV s^{-1}

results in a six-co-ordinate cobalt(III) porphyrin with two axial pyridine ligands, consistent with the oxidation of Co^{2+} to Co^{3+} in presence of pyridine.[18]

Representative cyclic voltammograms of the free bases H_2L^{Ia} and H_2L^{IIb} and [ZnL^{IIb}] and [CoL^{IIb}] are shown in Fig. 5. The free bases and [ZnL^{IIb}] exhibit two oxidation waves and two reduction waves (with the exception of H_2L^{IIIb} which shows only one oxidation wave) with peak separation $\Delta(E_p - E_a)$ in the range 50–80 mV. An analysis of the ratio of the peak currents suggests one-electron processes for these waves. The complex [CoL^{IIb}] shows three one-electron reversible oxidations and two one-electron reductions [$\Delta(E_p - E_a)$ = 90 and 101 mV]. The first oxidation and reduction process originate from the metal centre corresponding to the formation of cobalt-(III) and -(I) porphyrin derivatives respectively.[19] The second and third oxidation steps are assigned to the formation of cobalt(III) porphyrin cation radical and dication respectively and the potentials for these species compare well with those for similar reactions observed for [Co(tpp)] in CH_2Cl_2.[20]

Discussion

(*a*) ^1H *NMR*.—The three isomers shown in Fig. 1 were identified by (*i*) using the symmetry concept proposed by Momenteau *et al.*[9] and (*ii*) comparing the NMR characteristics of the compounds synthesised in the present study with those of hexyl **II** isomer of Simonis *et al.*[11] whose X-ray structure is known. The cross-*trans*-linked isomer is expected to show a relatively simple NMR spectrum because of its symmetry (D_{2d}), the eight pyrrole protons, methylene chain protons and strapped phenyl ring protons resonating as three separate singlets. Also, since the methylene chain and strapped phenyl protons span the porphyrin ring current above and below the plane, they experience a considerable upfield shift relative to the same protons in the free dialdehyde. The NMR data for H_2L^{Ia} are consistent with these observations indicating cross-*trans*-linked isomer.

The isomers H_2L^{IIb} and H_2L^{IIIb} show two pyrrole resonances and the magnitude of the separation between these resonances has been used to distinguish between these two isomers. An analysis of the peak separation for isomers **II** (adjacent-*trans*-linked) and **III** (adjacent-*cis*-linked) for the hexyl, pentyl and butyl bridged porphyrins of Simonis *et al.*[11] indicates that isomer **II** always shows a larger pyrrole peak separation in a given series. The following data support this observation.

Isomer	Separation (ppm)	Isomer	Separation (ppm)
hexyl **II**	0.22	hexyl **III**	0.09
pentyl **II**	0.38	pentyl **III**	0.02
butyl **II**	0.84	butyl **III**	0.44
H_2L^{IIb}	0.30	H_2L^{IIIb}	0.13

The X-ray crystal structure of hexyl **II** isomer indicates that it has the adjacent-*trans* structure. Interestingly, the basket handle porphyrins of Momenteau *et al.*[9] also show a similar trend. All these experimental data suggest that the compounds H_2L^{IIb} and H_2L^{IIIb} have adjacent-*trans* and adjacent-*cis* structures respectively.

The ortho protons (H^6) of the phenyl ring in H_2L^{Ia} experience a significant downfield shift (0.86 ppm) relative to H_2tmopp suggesting a considerable strain on the porphyrin ring. It is obvious from the plot in Fig. 3 that this strain depends on the chain length, increasing with decreasing chain length. The NH protons also show a similar trend. Their deshielding suggests a larger perturbation of the ring current at the central nitrogen atoms. However, the chemical shift of the pyrrole protons in these isomers is little altered suggesting very little disruption of the peripheral ring current. The shifts of the phenyl, pyrrole and NH resonances observed for H_2L^{Ia} are comparable in magnitude to those of the pentyl **I** isomer of Simonis *et al.*,[11] indicating a considerable static distortion of the porphyrin plane in this isomer.

(*b*) *Electronic Absorption Spectra.*—A theoretical account of the Soret and the Q bands in the visible absorption spectrum of a porphyrin molecule is well documented.[21] For the free-base porphyrins, owing to the symmetry and the vibronic mixing, the Q bands are split into $Q_x(0,0)$, $Q_y(0,0)$, $Q_x(1,0)$ and $Q_y(1,0)$. Thus, any change in the absorption maxima of free-base basket handle porphyrins relative to the corresponding unstrapped derivative indicates changes in the energies of the A_{1u}, A_{2u} and E_g orbitals which are involved in the transition. For H_2L^{Ia} both the Soret and Q bands are affected significantly. Also, the magnitude of the shifts of the Soret and of the Q bands is comparable. This indicates that the energy of the $E_g(\pi^*)$ orbital of the porphyrin macrocycle is affected most in this isomer due to the introduction of the strap. The direction of the shift indicates a slight lowering of the energy of the $E_g(\pi^*)$ orbital, thus decreasing the energy of the transition.[11] Between isomers H_2L^{IIb} and H_2L^{IIIb}, the magnitude of the shifts is comparable to those observed for the corresponding isomers of the pentyl and butyl bridged derivatives of Simonis *et al.*[11] suggesting a slight distortion of the porphyrin plane in these isomers. This is attributed to the decreased chain length of the strap in these *meta* isomers relative to the *para* isomer H_2L^{Ia}. This is also supported by the fact that the $Q_y(0,0)$ bands of these isomers are further split by about 6 nm (Fig. 4). Splitting of this band was also observed for the butyl bridged isomers **II** and **III** of Simonis *et al.*[11]

The intensity of the Q bands is determined by the degree of degeneracy of the highest-occupied molecular orbitals A_{2u} and A_{1u}. When these are exactly degenerate the Q(0,0) band should have zero intensity and as the degeneracy is lifted the Q(0,0) band gains intensity.[21b,22] In the free base H_2tpp the A_{2u} orbital is higher in energy. The fact that the intensity of the Q(0,0) bands of H_2L^{Ia} are reduced by more than 50% relative to the unstrapped tetraphenylporphyrin (Table 2) suggests a smaller energy gap between the A_{2u} and A_{1u} orbitals. Thus, among the short-chain strapped porphyrins (less than six-carbons) it appears that the cross-*trans*-linked isomer is expected to show larger red shifts for both Soret and Q bands with a significant decrease in intensity compared to the other two isomers.

Protonation of unsubstituted or *para*-substituted free-base tetraarylporphyrins generally results in a large red shift of the Q bands while the free-base tetraalkylporphyrins show a blue shift. This difference in behaviour is attributed to the increased resonance interaction between the aryl group and porphyrin ring in tetraarylporphyrins due to the coplanarity of the phenyl ring and porphyrin plane. The X-ray crystal structure of the dication of H_2tpp supports this observation.[23] However, in the basket handle porphyrins synthesised in the present study, restricted rotation around the porphyrin–phenyl bond may forbid any extension of conjugation between the phenyl groups and the porphyrin ring, preventing resonance interaction. A similar effect was observed for the *ortho*-substituted tetraphenylporphyrins upon protonation.[15]

The metal (Zn^{2+}, Co^{2+}) derivatives of H_2L^{IIb} and H_2L^{IIIb} show two-banded 'normal' spectra in the visible region typical of a metalloporphyrin. When $M = Zn^{2+}$ the absorption bands show a red shift of 7–11 nm (Table 4) relative to [Zn(tpp)] suggesting a slight distortion in these cases. However, the magnitude of the shifts observed upon axial ligation of pyridine to form a five-co-ordinate complex are comparable to those of [Zn(tpp)]. This observation clearly demonstrates that the strapping groups in these isomers essentially do not interfere with the incoming axial ligand which is in line with the X-ray crystal structure of the zinc derivative of the hexyl bridged isomer.[11] The oxidation of cobalt(II) porphyrin to the cobalt(III) derivative in the presence of pyridine is well documented and the present observations on pyridine binding to $[CoL^{IIb}]$ and $[CoL^{IIIb}]$ are consistent with literature reports.[18,24]

(*c*) *Electrochemistry.*—The shifts in the redox potentials (Table 5) of the basket handle porphyrins are quite significant. Thus, the easier oxidations relative to H_2tpp are interpreted in terms of loss of coplanarity resulting in decreased electron delocalisation. Support for this also comes from the electrochemical behaviour and X-ray crystal structures of the pyrrole-strapped porphyrins.[25] The harder reductions relative to H_2tpp are attributed to the destabilisation of the porphyrin anions and dianions due to the lack of solvation caused by steric hindrance of the strapping group. The fact that the potential shifts for the formation of dianions are significantly larger (230 mV for H_2L^{Ia}, 120 mV for H_2L^{IIb} and H_2L^{IIIb}) than those observed for the formation of monoanions (160 mV for H_2L^{Ia}, 90 mV for H_2L^{IIb} and 110 mV for H_2L^{IIIb}) is in accordance with the increased charge on the dianions. This is also consistent with the shifts observed for reduction of iron(II) derivatives, of ether-linked basket handle porphyrins.[26]

In $[CoL^{IIb}]$ the metal-centred oxidation and reduction peaks occur at potentials less anodic than those of the corresponding porphyrin ring oxidation and reduction. This suggests that the first oxidation and reduction occur from the metal-centred molecular orbital $A_1(d_{z^2})$ which in $[CoL^{IIb}]$ is situated above the filled A_{2u} orbital and below the $E_g(\pi^*)$ orbitals of the porphyrin ring. For $[ZnL^{IIb}]$ no reaction at the central metal is likely and both oxidations and reduction occur at the porphyrin ring in line with the general behaviour of zinc(II) porphyrins.[27]

Conclusion

The short phenylenedimethylenedioxy bridging chain results in considerable distortion in the porphyrin skeleton of basket handle porphyrins as evidenced by their spectroscopic and electrochemical behaviour. This in turn reflects significant changes in the energies of the π-molecular orbitals of the porphyrin ring. The studies of substituent effects on H_2tpp have clearly demonstrated that the substituent on the pyrrole ring influences the electronic structure of the porphyrin ring more significantly than does the substituent on the phenyl ring. It should be pointed out here that the magnitude and direction of the redox potential shifts observed in the present study are comparable to those observed for pyrrole-substituted H_2tpp, suggesting significant changes in the electronic structure of the porphyrin ring in these basket handle porphyrins.[22b] However, these limited studies do not allow any direct correlation between the electronic structure and the degree of distortion in the porphyrin skeleton. We hope to have an understanding of this by synthesising a variety of short-chain basket handle porphyrins in which the nature of the bridging group is changed. Finally, it is of interest that ESR studies of the photoexcited triplet state of the free bases H_2L^{Ia}, H_2L^{IIb} and H_2L^{IIIb} indicate a considerable decrease (4–20%) in zero-field

Table 5 Electrochemical redox data for free-base and metallo derivatives of short-chain basket handle porphyrins in CH_2Cl_2

	Ring Oxidation, $E_{\frac{1}{2}}$			Ring reduction, $E_{\frac{1}{2}}$	
Porphyrin	I	II	Metal redox data	I	II
H_2L^{Ia}	0.85	1.23	—	−1.39	−1.78
H_2L^{IIb}	0.84	1.20	—	−1.32	−1.67
H_2L^{IIIb}	0.90	—	—	−1.34	−1.67
[ZnL^{IIb}]	0.78	1.04	—	−1.39	−1.75
[CoL^{IIb}]	1.05	1.24	0.80 (Co^{II}–Co^{III}) −0.94 (Co^{II}–Co^{I})	−1.37	—
H_2tpp	1.03	—	—	−1.23	−1.55

Potentials in volts *vs.* Ag–AgCl.

splitting parameters (*D* and *E*) relative to H_2tpp and fluorescence studies indicate a decrease (65–90%) in quantum yield relative to H_2tpp, supporting the conclusions of the UV/VIS, NMR and electrochemical studies.

Experimental

Syntheses.—2,2′-(m-*Phenylenedimethylenedioxy)dibenzaldehyde* **1**. α,α′-*m*-Xylene dibromide (15 g, 56.8 mmol) and anhydrous K_2CO_3 (23.5 g, 170.5 mmol) were added to dry dimethylformamide (dmf, 100 cm^3) and the mixture was stirred for 5 min. Salicylaldehyde (13.8 g, 113.6 mmol) was added and stirring was continued for 4 h at room temperature. The reaction mixture was poured into water (200 cm^3) and extracted with chloroform (3 × 100 cm^3). The organic layer was washed with $NaHCO_3$ (3 × 100 cm^3) and water (3 × 100 cm^3), and dried over Na_2SO_4. Addition of diethyl ether (25 cm^3) to a concentrated organic layer afforded compound **1** as a white crystalline solid (15.7 g, 80%), m.p. 115–117 °C. ^1H NMR ($CDCl_3$): δ 5.17 (s, OCH_2), 6.93 and 7.73 (m, phenyl) 7.33 (m, *m*-xylyl) and 10.37 (s, CHO).

2,2′-(p-*Phenylenedimethylenedioxy)dibenzaldehyde* **2**. α,α′-*p*-Xylene dibromide (15 g, 56.8 mmol), anhydrous K_2CO_3 (23.5 g, 170.5 mmol) and salicylaldehyde (13.8 g, 113.6 mmol) were added to dry dmf (100 cm^3). The reaction mixture was stirred for 5 h at room temperature. Work-up of the reaction mixture as above gave compound **2** as a white crystalline solid (14.7 g, 75%), m.p. 180–182 °C. ^1H NMR ($CDCl_3$): δ 5.03 (s, CH_2), 7.0 and 7.72 (m, phenyl), 7.42 (s, *p*-xylyl) and 10.47 (s, CHO).

Strapped porphyrins H_2L^{IIb} and H_2L^{IIIb}. The dibenzaldehyde **1** (12.5 g, 36.27 mmol) and pyrrole (4.86 g, 72.54 mmol) were dissolved in freshly distilled propionic acid (1000 cm^3). The reaction mixture was refluxed for 1 h and left at room temperature for 12 h. The solvent was evaporated under reduced pressure after filtration. The crude product was purified and separated by column chromatography over silica gel (60–120 mesh) using benzene and benzene–diethyl ether (9:1 v/v) as the eluents. A pink fraction which was eluted with benzene was identified as H_2L^{IIIb}. This was rechromatographed again using silica gel (60–120 mesh) and the pure fraction eluted with benzene (0.5 g, 2%). Another red fraction eluted with benzene–diethyl ether (9:1 v/v) was identified as H_2L^{IIb}. This was rechromatographed again using silica gel (60–120 mesh) and the pure fraction eluted with benzene–diethyl ether (9:1 v/v) to give a crystalline solid (0.75 g, 2.4%).

Strapped porphyrin H_2L^{Ia}. The dibenzaldehyde **2** (3 g, 8.7 mmol) and pyrrole (1.18 g, 17.56 mmol) were allowed to react in boiling propionic acid (500 cm^3). The crude product obtained as above was purified by repeated column chromatography using silica gel (60–120 mesh). A violet band eluted by benzene was identified as H_2L^{Ia}. This was rechromatographed again using silica gel (60–120 mesh) and the pure fraction eluted with benzene to give a crystalline solid (0.23 g, 3%). The other red fraction which was eluted with benzene–diethyl ether (19:1 v/v) was identified as a mixture of two isomers (H_2L^{IIa} and H_2L^{IIIa}) (0.15 g, 2%). A clear separation of these two isomers has not yet been achieved. It was surprising that the yield of the cross-*trans*-linked isomer H_2L^{Ia} is considerably higher compared to those of the other isomers.

[CoL^{IIIb}]. The compound H_2L^{IIIb} (46 mg) was added to a mixture of dmf (10 cm^3), CH_2Cl_2 (10 cm^3) and pyridine (1 cm^3) and heated for 15 min. Cobalt(II) acetate (26 mg, dissolved in 5 cm^3 of dmf) was added. The reaction mixture was refluxed for 6 h. Evaporation of the solvent under reduced pressure followed by a water wash gave the crude product. This was purified over silica gel (60–120 mesh) using benzene to give a single orange band of [CoL^{IIIb}] (25 mg, 54%). A minor second fraction which was eluted with $CHCl_3$ was identified as the pyridine-coordinated cobalt(III) porphyrin.

[CoL^{IIb}]. The compound H_2L^{IIb} (30 mg) was dissolved in $CHCl_3$ (75 cm^3). Cobalt(II) acetate (60 mg) dissolved in methanol (25 cm^3) was added to the boiling $CHCl_3$ solution. The reaction mixture was refluxed for 90 min and evaporation of solvent under reduced pressure followed by a water wash afforded crude [CoL^{IIb}]. The pure complex was obtained after recrystallisation from $CHCl_3$–methanol (1:1) (yield 25 mg, 80%).

[ZnL^{IIIb}]. The compound H_2L^{IIIb} (30 mg) and zinc(II) acetate (30 mg) in a mixture of dmf (10 cm^3) and CH_2Cl_2 (10 cm^3) was refluxed for 8 h. Evaporation of the solvent under reduced pressure followed by a water wash gave [ZnL^{IIIb}] (25 mg, 80%). The poor solubility of the product did not allow ^1H NMR and cyclic voltammetric studies.

[ZnL^{IIb}]. The compound H_2L^{IIb} (50 mg) was dissolved in $CHCl_3$ (100 cm^3). Zinc(II) acetate (100 mg) dissolved in methanol (25 cm^3) was added to the boiling $CHCl_3$ solution. The reaction mixture was refluxed for 30 min and evaporation of the solvent under reduced pressure followed by a water wash gave crude [ZnL^{IIb}]. The pure complex was obtained after recrystallisation from $CHCl_3$–methanol (1:1) (yield 30 mg, 60%).

The details of the spectrometers employed are described in our earlier work.[18]

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References

1 W. R. Scheidt and Y. J. Lee, *Struct. Bonding (Berlin)*, 1987, **64**, 1.
2 E. Fujita and J. Fajer, *J. Am. Chem. Soc.*, 1983, **105**, 6743; Y. J. Lee, W. R. Scheidt and G. Lang, *J. Am. Chem. Soc.*, 1982, **104**, 6791.
3 A. M. Stolzenberg and M. T. Stershic, *Inorg. Chem.*, 1988, **27**, 1614.
4 B. Morgan and D. Dolphin, *Struct. Bonding (Berlin)*, 1987, **64**, 115.
5 C. K. Chang, *J. Am. Chem. Soc.*, 1977, **99**, 2819.
6 J. P. Collman, *Acc. Chem. Res.*, 1977, **10**, 265.
7 A. R. Battersby and A. D. Hamilton, *J. Chem. Soc., Chem. Commun.*, 1980, 117.
8 J. E. Baldwin, M. J. Crossley, T. Klose, E. A. O'Rear and M. K. Peters, *Tetrahedron*, 1982, **38**, 27.
9 M. Momenteau, J. Mispelter, B. Loock and E. Bisagni, *J. Chem. Soc., Perkin Trans. 1*, 1983, 189.
10 T. P. Wijesekera, J. B. Paine III, D. Dolphin, F. W. B. Einstein and T. Jones, *J. Am. Chem. Soc.*, 1983, **105**, 6747.
11 U. Simonis, F. A. Walker, P. L. Lee, B. J. Hanguet, D. J. Meyerhoff and W. R. Scheidt, *J. Am. Chem. Soc.*, 1987, **109**, 2659.
12 J. Weiser and H. A. Staab, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 623.
13 J. Weiser and H. A. Staab, *Tetrahedron Lett.*, 1985, **26**, 6059.
14 A. Ulman and J. Manassen, *J. Am. Chem. Soc.*, 1975, **97**, 6540.
15 M. M. Ner and A. D. Alder, *J. Am. Chem. Soc.*, 1975, **97**, 5107.
16 F. A. Walker, D. Beroiz and K. M. Kadish, *J. Am. Chem. Soc.*, 1976, **98**, 3484.

17 M. Nappa and J. S. Valentine, *J. Am. Chem. Soc.*, 1978, **100**, 5075.
18 D. Reddy, N. S. Reddy, T. K. Chandrashekar and H. V. Willigen, *J. Chem. Soc., Dalton Trans.*, 1991, 2097.
19 X. Q. Lin, B. B. Cocolios and K. M. Kadish, *Inorg. Chem.*, 1986, **25**, 3242.
20 X. H. Mu and K. M. Kadish, *Inorg. Chem.*, 1989, **28**, 3743.
21 (*a*) P. J. Spellane, M. Gouterman, A. Antipas, S. Kim and Y. C. Liu, *Inorg. Chem.*, 1980, **19**, 386; (*b*) M. Gouterman, in *The porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol. 3, p. 1.
22 (*a*) D. J. Quimby and F. R. Longo, *J. Am. Chem. Soc.*, 1985, **97**, 5111; (*b*) R. A. Binstead, M. J. Crossley and N. S. Hush, *Inorg. Chem.*, 1991, **30**, 1259.
23 A. Stone and E. B. Fleischer, *J. Am. Chem. Soc.*, 1968, **90**, 2735; J. B. Kim, J. J. Leonard and F. R. Longo, *J. Am. Chem. Soc.*, 1972, **94**, 3986.
24 D. Pavlovic, S. Asperger, Xh. Ahmeti, B. C. Cizmek, B. Jurisic and Z. Vaksh, *Inorg. Chem.*, 1988, **27**, 1515; Z. Dokuzovic, Xh. Ahmeti, D. Pavlovic, I. Murati and S. Asperger, *Inorg. Chem.*, 1982, **21**, 1576.
25 J. Y. Becker, D. Dolphin, J. B. Paine and T. Wijesekera, *J. Electroanal. Chem. Interfacial Electrochem.*, 1984, **164**, 335.
26 D. Lexa, M. Momenteau, P. Rentien, G. Rytz, J. M. Saveant and F. Xu, *J. Am. Chem. Soc.*, 1984, **106**, 4755; M. Momenteau, *Pure Appl. Chem.*, 1986, **58**, 1493; D. Lexa, P. Maillard, M. Momenteau and J. M. Saveant, *J. Am. Chem. Soc.*, 1984, **106**, 6321.
27 K. M. Kadish, *Prog. Inorg. Chem.*, 1986, **34**, 437.

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