Both-faces Hindered Porphyrins. Part 4.[1] Synthesis of Functionalized Basket-handle Porphyrins Designed for a Strict Intramolecular Axial Ligation in Superstructured Complexes

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The concept of basket-handle porphyrins, in a cross-*trans* configuration, is applied to the design of new compounds which possess a chemical group attached to the central carbon of one bridging chain in order to mimic the axial co-ordination of the active site of hemoproteins. The key intermediates used in these syntheses are prepared from 5,10,15,20-tetraphenylporphyrin the two phenyl groups in opposing positions of which are bridged by a ketonic chain, whilst the two other phenyl groups carry a polymethylene chain, (**8b**) and (**24**), or a pyridyl one, (**33**) and (**41**), *via* ether or amide linkages. These compounds are clearly reduced to alcohol derivatives which may be further derivatized under mild conditions to give functionalized porphyrins having pendant O, N, and S donor chemical groups as potential axial ligands. Additional diketonic porphyrins (**8c**) and (**40**) have been obtained during the preceding synthesis to allow the preparation of symmetrical disubstituted compounds. The characterization of these new superstructured porphyrins was established by ^{1}H n.m.r. spectroscopy as well as the relative inner or outer position of the substituted chemical groups.

In considering possible approaches to the development of active site models of hemoproteins we have previously reported the synthesis of compounds having an oxygen-binding ability.[2] These iron(II) hanging-base basket-handle porphyrins in which both the doubly facial protection of the macrocycle and the insertion of a nitrogenous base (imidazole or pyridine) into one of the two handles provide a reversible oxygen-binding ability at room temperature without rapid auto-oxidation of the central iron as commonly observed with flat open hemes.

Such superstructured porphyrins suggested to us that related compounds were possible in which the chemical nature of the handle could be modified in order to mimic the axial ligands bound to the heme iron in natural compounds. Such a functionalization of one or two handles by potential hanging ligands appears to be of considerable interest in determining the factors affecting magnetic properties, redox potentials, and catalytic activities of hemoproteins. Thus, N donor ligands (imidazole from histidine) are known to co-ordinate to at least one of the two axial co-ordination sites of iron (hemoglobin, myoglobin, cytochromes b and c, and some peroxidases),[3–6] whilst O and S donor ligands have also been found.[7–11]

To mimic the functional differentiation of such natural compounds arising from differences in axial ligation to the heme iron, porphyrins containing a variety of potentially ligating sites have been developed.[12–15] While such model compounds eliminate the need for an excess of free ligand in solution, there was no control of intramolecular co-ordination, as shown by the intermolecular association observed with chelated or tailed hemes in which the covalent axial ligand was imidazole.[16–18]

The present paper reports the full synthesis and ^{1}H n.m.r. characterization of new, functionalized basket-handle porphyrins incorporating N, O, or S donor groups attached to the central position of one or both handles. In such an approach, the covalent linkage to the superstructure(s) should permit strict control of the intramolecular co-ordination number of the iron atom. Two series of functionalized porphyrins which differ by the anchoring mode of the handles to the macrocycle (ether or amide functions) have been prepared. In fact, the nature of the anchoring groups exerts a strong influence on the redox and co-ordination properties of metalloporphyrin complexes. Of particular relevance to the present syntheses is the observation that amide-linked chains give greater stabilization by dipolar interactions of the negatively charged complexes[19,20] but also of the axial co-ordination of neutral ligands[21,22] in comparison with compounds having ether-linked chains. These new integrated molecular systems appear ideally suited to studies of the physicochemical properties arising both from differences in axial ligation to the heme iron and from differences in the environment surrounding the heme as observed in hemoproteins.

Results and Discussion

Synthesis.—We ensured a convenient anchorage position for the chemical group required for strict co-ordination of the central metallic ion trapped in the porphyrin ring, by preparing first basket-handle porphyrins in which the functional group is a ketone function at the central carbon of one (or two) handle(s). The general strategy for preparing these key intermediate compounds was similar to that described previously for the preparation of hanging-base basket-handle porphyrins in the ether series[23] as well as in the amide series.[1] As shown in Schemes 1 and 2, these compounds are derived from *ortho* substituted 5,10,15,20-tetraphenylporphyrin in which two phenyl rings in opposing positions are linked by chains through each side of the macrocycle ring (compounds in a cross-*trans* configuration) using ether or amide anchoring groups: the latter introduce a variation of the polarity in the vicinity of the active centre.

Monofunctionalized Porphyrins.—The preparation of the keto porphyrin in the ether series required coupling of 5,10,15,20-tetrakis(*o*-hydroxyphenyl)porphyrin (**7**) with the dibromo ketone (**6**) (see Scheme 1), the latter being prepared as follows. Diethyl 5-oxononane-1,9-dicarboxylate (**2**) obtained from the diacid (**1**)[24] was treated with ethylene glycol to give the dioxolane derivative (**3**). This on $LiAlH_4$ reduction gave the diol (**4**) which was deprotected by acidic cleavage of the dioxolane group in the presence of acetone to afford compound (**5**). Treatment of this with 66% HBr afforded the desired dibromo ketone (**6**).

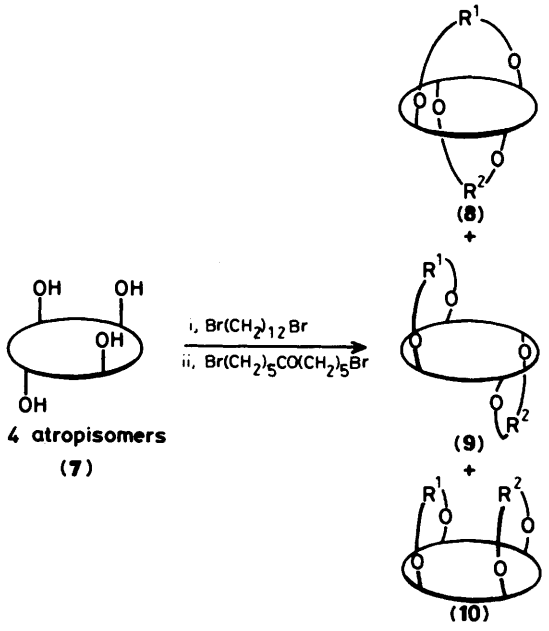
The key intermediate, the keto porphyrin (**8b**) was obtained

$RO_2C(CH_2)_4\underset{\underset{X}{\|}}{C}(CH_2)_4CO_2R$

(1) R = H, X = O
(2) R = Et, X = O
(3) R = Et, X = $O(CH_2)_2O$

$R(CH_2)_5\underset{\underset{X}{\|}}{C}(CH_2)_5R$

(4) R = OH, X = $O(CH_2)_2O$
(5) R = OH, X = O
(6) R = Br, X = O

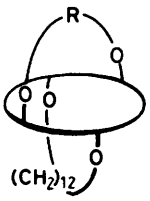


a; $R^1 = R^2 = -(CH_2)_{12}-$
b; $R^1 = -(CH_2)_{12}-$, $R^2 = (CH_2)_5CO(CH_2)_5-$
c; $R^1 = R^2 = -(CH_2)_5CO(CH_2)_5-$

Scheme 1.

by a one-pot high-dilution coupling reaction of 5,10,15,20-tetrakis(*o*-hydroxyphenyl)porphyrin (**7**) (four atropisomers)[25] with 1,12-dibromododecane and 1,11-dibromoundecane-6-one (**6**) successively added in dimethylformamide at 100 °C in the presence of an excess of anhydrous potassium carbonate. Chromatography on silica gel column (66—230 μm) of the reaction mixture gave three major fractions. Initial elution with toluene–methylene dichloride (1:1, v/v) gave a mixture of the cross-*trans*-linked, adjacent-*trans*-linked, and adjacent-*cis*-linked isomers (**8a**), (**9a**), and (**10a**) bearing two identical polymethylene chains.[25] Subsequent elution with methylene dichloride–ether (100:1, v/v) gave a second fraction corresponding to a mixture of the three isomers of dissymetric porphyrins (**8b**), (**9b**), and (**10b**). A more polar fraction was eluted with methylene dichloride–acetone (100:5, v/v) which was identified as a mixture of the di-bridged porphyrins (**8c**), (**9c**), and (**10c**). In order to isolate the expected compound (**8b**), the second fraction was rechromatographed on a silica gel column (40—60 μm) with methylene dichloride as eluant. The less polar porphyrin corresponding to the first band was identified (^1H n.m.r.) as compound (**8b**) (13%) in which the handles bind two opposite *meso*-phenyl groups (cross-*trans*-linked isomer).

Compound (**8b**) was used to prepare the functionalized porphyrins (**11**)—(**21**) in the following way. With sodium borohydride in tetrahydrofuran–ethanol (**8b**) gave (**11**) and this with triphenylphosphine–carbon tetrabromide in the presence of pyridine in tetrahydrofuran under mild conditions gave compound (**12**) in an almost quantitative yield (96% after chromatography).[26] This compound was then the precursor of several porphyrins. Thus, on reaction with sodium methyl sulphide it gave compound (**13**). Whilst on treatment with potassium thioacetate in dimethylformamide at 100 °C followed by saponification with 5% aqueous potassium hydroxide under argon and acidification, it afforded the thiol (**15**).



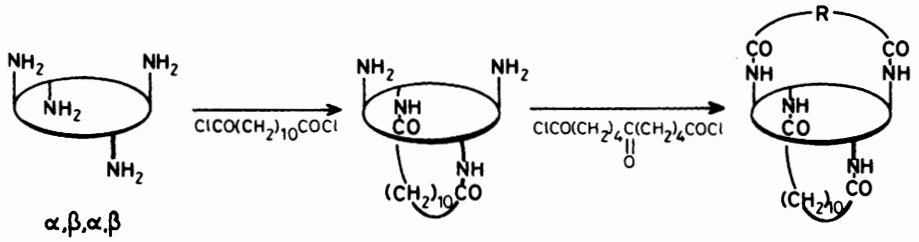
(**8b**) R = $-(CH_2)_5-\underset{\underset{O}{\|}}{C}-(CH_2)_5-$
(**11**) R = $-(CH_2)_5-\underset{\underset{OH}{|}}{CH}-(CH_2)_5-$
(**12**) R = $-(CH_2)_5-\underset{\underset{Br}{|}}{CH}-(CH_2)_5-$
(**13**) R = $-(CH_2)_5-\underset{\underset{SMe}{|}}{CH}-(CH_2)_5-$
(**14**) R = $-(CH_2)_5-\underset{\underset{SAc}{|}}{CH}-(CH_2)_5-$
(**15**) R = $-(CH_2)_5-\underset{\underset{SH}{|}}{CH}-(CH_2)_5-$

(**16**) R = $-(CH_2)_5-\underset{\underset{\text{imidazol-1-yl}}{|}}{CH}-(CH_2)_5-$
(**17**) R = $-(CH_2)_5-CH{=}CH-(CH_2)_4-$
(**18**) R = $-(CH_2)_5-\underset{\underset{OMe}{|}}{CH}-(CH_2)_5-$
(**19**) R = $-(CH_2)_5-\underset{\underset{NOH}{\|}}{C}-(CH_2)_5-$
(**20**) R = $-(CH_2)_5-\underset{\underset{N\,OAc}{\|}}{C}-(CH_2)_5-$
(**21**) R = $-(CH_2)_5-\underset{\underset{NH_2}{|}}{CH}-(CH_2)_5-$

Imidazole is known to be a potential axial ligand of some metalloporphyrins and one of its derivatives, (**16**), was easily obtained by reaction of (**12**) with an excess of imidazole in dimethylformamide at 100 °C for 3 days (62% yield). A second porphyrin was present in the reaction mixture, its ^1H n.m.r. spectrum containing, in addition to the expected porphyrinic and polymethylene proton resonances, two new resonances as AB multiplets at 2.90 and 2.32 p.p.m. (*J* 15 Hz corresponding to ^1H each); these signals were assigned to the ethylenic protons of compound (**17**). The transdehydrohalogenation of (**12**) to give this ethylenic derivative was not prevented by changing the solvent and temperature or by using the sodium or silver salts of imidazole.[27] A similar elimination was observed during attempts to prepare the methoxy derivative (**18**) from (**12**) in the presence of sodium methoxide. In contrast, coupling of the porphyrin (**11**), as its sodium salt, with methyl iodide offered a readily accessible route to methoxy compound (**18**) which was obtained in a good yield (73%).

The keto porphyrin (**8b**) also provided other functionalized porphyrins. Thus, it was readily converted into the oxime (**19**) by treatment with hydroxylamine hydrochloride. Since the hydroxyamino group was unaffected by $AlLiH_4$, the corresponding amino compound (**21**) was obtained by reduction with commercially available BH_3–THF of the *o*-acetyl compound (**20**).

Functionalized amide basket-handle porphyrins obtained in this work are presented in Scheme 2. The alternating αβαβ atropisomer of 5,10,15,20-tetrakis(*o*-aminophenyl) porphyrin (**22**)[1] was used as starting material. The monohandle porphyrin (**23**) was prepared and isolated as previously described.[1] The



α,β,α,β

(22)

(23)

R

(24) $-(CH_2)_4-C(=O)-(CH_2)_4-$

(25) $-(CH_2)_4-CH(OH)-(CH_2)_4-$

(26) $-(CH_2)_4-CH(Br)-(CH_2)_4-$

(27) $-(CH_2)_4CH=CH(CH_2)_3-$

(28) $-(CH_2)_4-CH(SAc)-(CH_2)_4-$

(29) $-(CH_2)_4-CH(SH)-(CH_2)_4-$

(30) $-(CH_2)_4-CH(\text{imidazoyl-1-yl})-(CH_2)_4-$

Scheme 2.

diacid (**1**) was converted into the corresponding diacid chloride using the standard oxalyl chloride method. It was then condensed with an equivalent amount of the porphyrin (**23**) under highly dilute conditions in tetrahydrofuran at room temperature to give the monoketo porphyrin (**24**) which was then converted into the hydroxy derivative (**25**) by $NaBH_4$ reduction. Subsequent bromination with CBr_4–Ph_3P gave (**26**) (77% yield).

The reactions of the bromoporphyrin (**26**) both with sodium methyl sulphide and potassium thioacetate under conditions similar to those described for the preparation of compounds (**13**) and (**14**) in the ether series were unsuccessful and gave almost exclusively the ethylenic porphyrin (**27**). This reactivity may be attributed to the great polarity of the cavity due to the presence of anchoring amide groups.[19] Another procedure was attempted to obtain the desired acetylthio derivative (**28**). Thus, in toluene solution, reaction of (**26**) with KSAc in the presence of dicyclohexyl 18 crown 6 as catalyst was employed. This procedure furnished the porphyrin (**28**) as the major product (76% yield). The ethylenic porphyrin was not completely eliminated, but its amount was considerably decreased (18%). Hydrolysis of (**28**) with potassium hydroxide in THF followed by acidification gave the mercapto porphyrin (**29**).

Coupling of imidazole with (**26**) under reaction conditions similar to those described above for the preparation of (**16**) afforded the hanging imidazole porphyrin (**30**) (53% yield) accompanied by the monethylenic derivative (**27**).

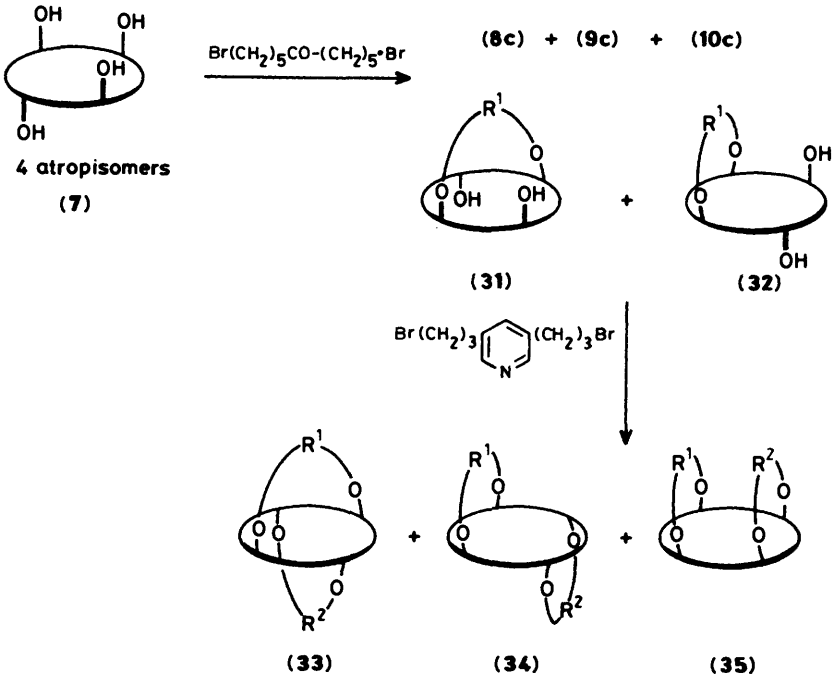
Unsymmetrical Difunctionalized Porphyrins.—Simulation of the co-ordination sphere of iron in hemoproteins can be achieved by the presence of two different axial ligands one of which at least is a N donor residue and both of which are covalently attached to the porphyrin ring. For this purpose we turned out attention to the synthesis of a further family of difunctionalized basket-handle porphyrins in which pyridine is inserted into one handle and one of the neutral or anionic chemical groups described above is in the other.

To obtain these compounds in the ether series we prepared the key intermediate (**33**) from the porphyrin (**7**) *via* the single-face hindered porphyrin (**31**) having a ketone handle. First, the reaction was carried out (Scheme 3) by mixing the four atropisomers of 5,10,15,20-tetrakis(*o*-hydroxyphenyl)porphyrin (**7**) with the dibromo compound (**6**) according to the method previously described in Part 2 of this series of papers.[23]

Chromatography of the reaction mixture showed three main bands which corresponded respectively to the both-faces hindered prophyrin isomers (**8c**), (**9c**), and (**10c**), the single-face hindered porphyrin isomers (**31**) and (**32**), and the unchanged starting material. Then, the second fraction was directly treated with dibromopropylpyridine–HBr[25] in dimethyformamide. After work-up, the crude product was chromatographed on a silica gel column. Elution with methylene dichloride–ether (1:1, v/v) gave first a minor fraction which was assigned to unchanged symmetrical both-faces hindered porphyrins. The second fraction eluted with methylene dichloride–acetone corresponded to the unsymmetrical basket-handle porphyrins (**33**), (**34**), and (**35**). They were separated by t.l.c. on silica gel plates using methylene dichloride–acetone (10:2, v/v). Reduction of the keto pyridine compound (**33**) was achieved by reaction with $NaBH_4$ as described above to give (**36**) which was subsequently brominated with CBr_4–Ph_3P to afford (**37**). Treatment of the latter with an excess of NaSMe and chromatographic purification provided the methylthio porphyrin (**38**) (60% yield).

A two-step procedure was also used in order to prepare analogues in the amide series (Scheme 4). Reaction of the porphyrin (**22**) with 1 equiv. of the diacid chloride of (**1**), followed by separation on silica gel yielded, successively, the single-face porphyrin (**39**) and the symmetrical both-faces porphyrin (**40**) in 47 and 21% yield respectively. Compound (**39**) can be easily substituted on the second face with the appropriate pyridine handle. Thus pyridine-3,5-diylbis(propionic acid) as its diacid chloride[1] was coupled by the procedure analogous to that used in the first step. This afforded the pyridine ketone compound (**41**) (59% yield). Reduction of (**41**) with $NaBH_4$ in methanol gave (**42**) which was transformed into the bromo derivative (**43**) as for the other bromo compounds described above. The monoimidazole porphyrin (**44**) was prepared by treatment of (**43**) with an excess of imidazole in dimethylformamide. Purification of this compound showed the presence of a less-polar porphyrin which was identified, on the basis of ^1H n.m.r. evidence, as the monoethylenic monopyridine porphyrin (**45**). When (**43**) was heated with KSAc two compounds were obtained which could not be separated by chromatography in their free-base form. Treatment of the total material with an excess of $Zn(OAc)_2$–$2H_2O$ in acetic acid furnished the zinc(II) complexes. After work-up and slow removal of the solvent, a pure crystalline compound separated. Subsequent demetallation of this with trifluoroacetic acid gave a free-base porphyrin which was identified as the expected porphyrin (**46**) (60% yield).

Symmetrical Difunctionalized Porphyrins.—Since porphyrins (**8c**) and (**40**) bearing two ketone handles as superstructures have been obtained during the preparation of monoketo



	R^1	R^2
(33), (34), (35)	$-(CH_2)_5-\underset{\underset{O}{\|}}{C}-(CH_2)_5-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$
(36)	$-(CH_2)_5-\underset{\underset{OH}{\|}}{CH}-(CH_2)_5-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$
(37)	$-(CH_2)_5-\underset{\underset{Br}{\|}}{CH}-(CH_2)_5-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$
(38)	$-(CH_2)_5-\underset{\underset{SMe}{\|}}{CH}-(CH_2)_5-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$

Scheme 3.

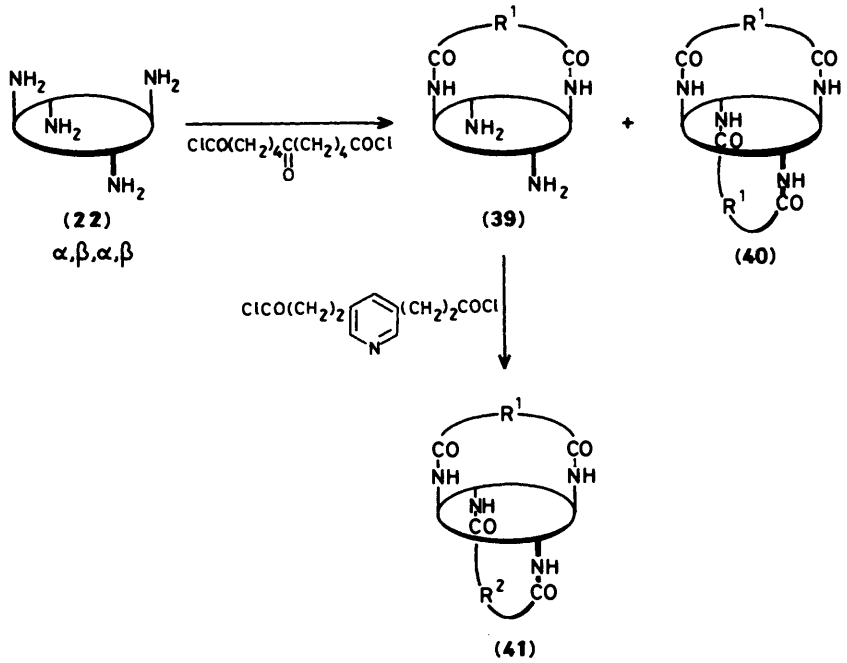
porphyrins, we decided to synthesize difunctionalized basket-handle porphyrins also in order to obtain potential models of cytochromes b known to contain two imidazole rings as axial ligands.

Thus, the fraction containing the mixture of (**8c**), (**9c**), and (**10c**) was re-chromatographed on silica gel plates. Elution with methylene dichloride–ether (100:5, v/v) afforded three bands. The first one was assigned, on the basis of ^{1}H n.m.r. evidence, the structure of the expected cross-*trans*-linked isomer (**8c**). The reduction of the diketo porphyrin (**8c**) with $NaBH_4$ in methanol–tetrahydrofuran gave the dihydroxyporphyrin (**47**) (70% yield) after chromatography. It was then transformed into the corresponding dibromo derivative (**48**) by treatment with CBr_4–Ph_3P. Imidazole substitution in dimethylformamide and subsequent chromatography on silica gel gave three main bands. The structure of each compound was established by ^{1}H n.m.r. spectroscopy. The bis-hanging-imidazole basket-handle porphyrin (**49**) corresponding to the more polar fraction was isolated in 57% yield. The ^{1}H n.m.r. spectrum of the compound present in the second fastest band showed three signals due to the imidazole protons (singlets at 6.36, 6, and 5 p.p.m.) and two signals assigned to ethylenic protons (multiplets at 2.9 and 2.3 p.p.m.). This compound was referred to the unsymmetrical bifunctionalized porphyrin (**51**) (14% yield) . Only these latter signals were present in the spectrum of the less polar compound consistent with the formulation of the diethylenic basket-handle porphyrin (**50**) obtained in 5% yield.

The preparation of a bis-hanging-imidazole basket-handle porphyrin in the amide series was performed using similar chemical sequences. Thus the diketone porphyrin (**40**) obtained during the preparation of (**39**) was easily converted into the dihydroxy compound (**52**). Subsequent bromination gave the porphyrin (**53**) which was treated with an excess of imidazole to give the bis imidazole compound (**54**) (18% yield) after chromatography. In fact this low yield was due to dehydrobromination side-reactions which generated compounds (**55**) and (**56**) isolated in 36 and 20% yields respectively.

^{1}H *N.m.r. Spectra.*—^{1}H N.m.r. spectra recorded at 100 MHz were used for the characterization of the synthesized compounds and the conformation of the functionalized handles. The main chemical shifts are listed in Tables 1 and 2. Assignments of the resonances to individual protons are based on integration and selective homonuclear decoupling experiments. These spectra are very similar to those of ether and amide hanging-base basket-handle porphyrins in a cross-*trans* configuration previously described[1,23] for which the proton shifts may be regarded as dominated by the porphyrin ring current.

Except for the spectra of the symmetric compounds (**8c**) and



	R^1	R^2
(41)	$-(CH_2)_4-C(=O)-(CH_2)_4-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$
(42)	$-(CH_2)_4-CH(OH)-(CH_2)_4-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$
(43)	$-(CH_2)_4-CH(Br)-(CH_2)_4-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$
(44)	$-(CH_2)_4-CH$(imidazoyl-1-yl)$-(CH_2)_4-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$
(45)	$-(CH_2)_4-CH=CH-(CH_2)_3-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$
(46)	$-(CH_2)_4-CH(SAc)-(CH_2)_4-$	$-(CH_2)_3-$(pyridine-3,5-diyl)$-(CH_2)_3$

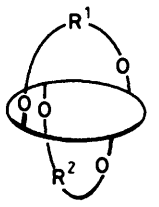
Scheme 4.

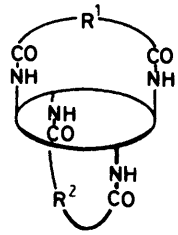
(**40**) bearing two ketone handles for which the eight pyrrolic protons are expected to be equivalent, the most important feature is that the resonances of these protons appear as one or two AB patterns indicating an effective dissymetry of the molecule.

In the ether series, the methylene proton resonances of the handles appear in the 4 to −1.5 p.p.m. range. The α methylene protons resonances are always well separated from the other methylenes and are shifted downfield. Furthermore, the two geminal protons on the ε carbons of the functionalized chain are non equivalent and appear as two sets of resonance: those indicate the rigidity of the central part of the bridged chain, the inner protons absorbing at high field and the outer protons at low field.

The compounds in the amide series exhibit spectra similar to those of the corresponding compounds in the ether series. The most significant feature of these spectra is the upfield shift of the proton of the amide groups linking the handles to the macrocycle. They are easily assigned by deuterium exchange. The shift of these protons is closely correlated with the length of the chains, the shorter chain leading to the larger upfield shift arising from the ring current of the porphyrin. The spectrum of compound (**24**) exhibits two amide resonances each integrating as two protons. In contrast, the spectra of compounds (**25**)—(**30**) exhibit three amide proton resonances. The two lowfield resonances (1 H each) correspond to the amide protons of the polymethylene chain. This non equivalence is due to the dissymmetry of the functionalized chain on the other side of the porphyrin plane. Such behaviour is not observed in the spectrum of the ethylenic compound (**27**) in which the splitting is observed for the amide protons of the functionalized chain. The spectra of compounds (**41**)—(**46**) which incorporate a pyridine into one of the two handles show a non equivalence of the amide protons of the pyridine chain for the same reason.

A comparison of the chemical shifts of the protons of the appended chemical groups with those of the single proton borne by the central carbon of the functionalized chain gives a direct indication of their respective inner or outer localization. Thus, the large shift difference between the hydroxy proton in compound (**11**) (−2.12 p.p.m.) and the same proton in a free analogous chain (4.26 p.p.m.) taken as the reference product shows that the former is strongly affected by the ring current of the porphyrin due to its pointing towards the porphyrin centre. The alcohol proton signal of the analogue amide porphyrin (**25**)





$R^1 = R^2$

(8c) $-(CH_2)_5-C(=O)-(CH_2)_5-$

(47) $-(CH_2)_5-CH(OH)-(CH_2)_5-$

(48) $-(CH_2)_5-CH(Br)-(CH_2)_5-$

(49) $-(CH_2)_5-CH(\text{imidazol-1-yl})-(CH_2)_5-$

(50) $-(CH_2)_5-CH=CH-(CH_2)_4-$

(51) R^1 $-(CH_2)_5-CH(\text{imidazol-1-yl})-(CH_2)_5-$; R^2 $-(CH_2)_5-CH=CH-(CH_2)_4-$

$R^1 = R^2$

(40) $-(CH_2)_4-C(=O)-(CH_2)_4-$

(52) $-(CH_2)_4-CH(OH)-(CH_2)_4-$

(53) $-(CH_2)_4-CH(Br)-(CH_2)_4-$

(54) $-(CH_2)_4-CH(\text{imidazol-1-yl})-(CH_2)_4-$

(55) $-(CH_2)_4-CH=CH-(CH_2)_3-$

(56) R^1 $-(CH_2)_4-CH(\text{imidazol-1-yl})-(CH_2)_4-$; R^2 $-(CH_2)_4-CH=CH-(CH_2)_3-$

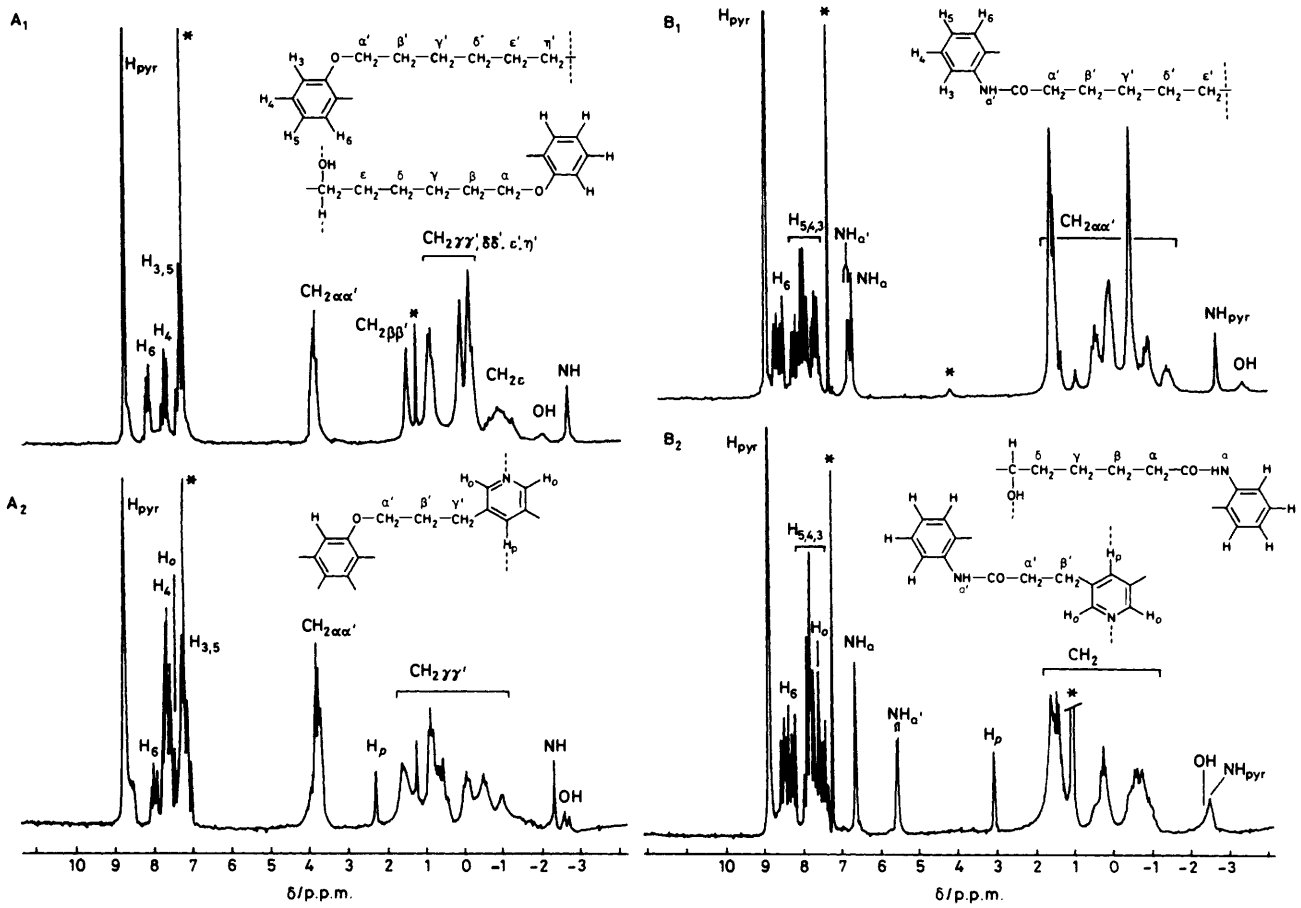


Figure. ^1H N.m.r. spectra of hydroxy basket-handle porphyrins in $CDCl_3$. Ether series. A1: porphyrin (**11**) and A2 porphyrin (**33**); amide series. B1: porphyrin (**25**) and B2 porphyrin (**42**). The assignments are shown in the Figure

Table 1. ^{1}H N.m.r. spectra of functionalized basket-handle porphyrins (ether series) in $CDCl_3$ at 34 C (δ in p.p.m. from TMS)

	meso-Phenyl[a]			H-Methylene[a]						CHX		
H_{pyr}[a]	6-H	4-H	3-H/5-H	α—α′	β—β′	Other	out	ε	in	H	X	NH_{pyr}
(**8b**) 8.77	8.18—8.09	7.75	7.38 to 7.17	3.89	0.84	0.04 to −0.28			−0.54			−2.59
(**11**) 8.78—8.76	8.16	7.87	7.49	3.93	1.51 to	−0.21		−0.88		1.71[b]	−2.12 (OH)	−2.64
(**12**) 8.77—8.73	8.15	7.75	7.36	3.90	0.89	0.12 to −0.27			−1.36	1.89		−2.61
(**13**) 8.78—8.74	8.23—8.16	7.75	7.34	3.90	0.87	0.14 to −0.10	0.54		−0.70	−0.90	1.11 (SCH_3)	−2.57
(**14**) 8.77—8.74	8.18	7.75	7.32	3.82	0.90	0.20 to −0.20			−1.20		2.00 ($SCOCH_3$)	−2.58
(**15**) 8.72—8.66	8.19—8.17	7.70	7.30	3.88	0.85	0.16 to −0.57			−1.20			−2.68
(**16**) 8.79—8.76	8.12—8.05	7.76	7.30	3.90	0.90 to	−0.73			−1.72	1.84	6.32 5.91 (Im) 4.95	−2.54
(**17**) 8.75	8.16	7.76	7.35	3.90	0.89	0.17		to −0.90			2.90 (ethylenic) 2.32	−2.58
(**18**) 8.77—8.74	8.23—8.16	7.75 to 7.25		3.83	0.91	0.15 to −0.30	−0.78		−1.16		2.13 (OCH_3)	−2.37
(**19**) 8.76	8.23—8.10	7.74	7.47 to 7.22	3.87	0.91			to −0.29				−2.56
(**20**) 8.76	8.24—8.07	7.75	7.47 to 7.24	3.87	0.85	0.12		to −0.28			1.85 ($OCOCH_3$)	−2.53
(**21**) 8.80—8.76	8.21—8.14	7.75	7.45 to 7.26	3.71	0.90 to	−0.20	−0.6		−1.46	−1(?)	4.17 (NH_2)	−2.19
(**33**) 8.78—8.87	8.57—8.29	7.77	7.53 to 7.12	3.80		1		to −1.2			7.65 (H_o)[a] 2.35 (H_p)	−2.22
(**36**) 8.81	8.72	7.93 to 7.20		3.88	1.20			to −1.1			7.71 (H_o)[a] 2.41 (H_p) −2.64(OH)	−2.20
(**37**) 8.80	8.62	7.84 to 7.11		3.79	0.90 to	−0.14			−0.90	2.25	7.64 (H_o)[a] 2.35 (H_p)	−2.28
(**38**) 8.82	8.61	7.89 to 7.08		3.77	0.95			to −0.45		−0.95	7.68 (H_o)[a] 2.40 (H_p) 1.93 (SCH_3)	−2.23
(**8c**) 8.79	8.23—8.15	7.76	7.37	3.84	0.83	0.83		to −0.57				−2.52
(**47**) 8.79	8.29—8.22	7.74	7.36	3.84	0.87	0		to −1.2		0.43	−1.74 (OH)	−2.67
(**48**) 8.77	8.25	7.76	7.35	3.84	0.84	0.15 to −0.25	0.05		−1.23	1.99		−2.60
(**49**) 8.81	8.05—7.99	7.78	7.40	3.86	0.85	0.20		to −1.77		0.46	6.12 5.84 (Im) 3.95	−2.50
(**51**) 8.79	8.15	7.75	7.35	3.86	0.83			to −1.69		0.47	6.36 6.00 (Im) 5.00 2.92 (ethylenic) 2.32	−2.52

[a] The assignment is shown on the Figure. [b] In $(CD_3)_2SO$.

is found at −3.10 p.p.m.; *i.e.* with an upfield shift of $\Delta\delta = 0.98$ p.p.m. relative to (**11**). The larger flexibility of the polymethylene chains in the ether series can explain this difference, the larger upfield shift for the appended chemical group in the amide series corresponding to a more axial position. However, an additional hydrophobic field effect (micro polar effect) due to the amide groups could also contribute to this large upfield shift. A multiplet (1 H) resonance in the ether compounds near 2 p.p.m. which is distinctly downfield from the methylene region is assigned to C*H*–OH because of its outer position. In the amide series this proton resonance was never detected at 100 MHz because it is located in the range of the methylene resonances. The chemical shift of the central methylene proton, at 1.89 and 1.84 p.p.m. for the bromoporphyrin (**12**) and the imidazole porphyrin (**16**) respectively, clearly indicates that the hanging chemical groups are in the cavity.

For other compounds bearing sterically hindered chemical groups, the situation seems different. Thus, the methyl proton resonance of the methylthio porphyrins (**13**) which appears at 1.11 p.p.m. is less affected by the ring current than the geminal proton (C*H*SCH_3) whose resonance is at −0.90 p.p.m. Furthermore, this latter resonance is shifted 3.38 p.p.m. upfield relative to that for the free chain. The most striking explanation is that the methylthio group should, therefore, be in the outer position whereas the CH proton points to the porphyrin ring. Similar conformations are expected for compounds bearing acetylthio, methoxy, acetyl, and amino groups regarding their chemical shifts.

Finally, the pyridine H_p proton resonance of all the unsymmetrical difunctionalized porphyrins appears as a characteristic triplet largely shifted to highfield whereas the resonance of the two equivalent pyridine H_o protons assigned by selective decoupling experiments to a doublet are located within the phenyl proton resonances. The large upfield shift of the former resonance implies an orientation in which the nitrogen atom of the pyridine points outwards. It is apparent in these spectra that the resonances of almost all the protons of the appended chemical groups are not affected by the presence of the pyridine chain bridging the opposite face of the porphyrin: this suggests that the configuration of the functionalized handles in mono- and di-functionalized basket handle porphyrins may be the same.

This structural behaviour has been considered for an interpretation of the paramagnetic properties of the iron(III) complexes of compounds in which oxygen or nitrogen ligand donors are incorporated into one or two handles.[28]

Table 2. ^{1}H N.m.r. of functionalized basket-handle porphyrins (amide series) in $CDCl_3$ at 34 °C (δ in p.p.m. from TMS)

		meso-Phenyl[a]		NH-amide					
	H_{pyr}[a]	6-H	3-H/4-H/5-H	Polymethylene chain	Functionalized chain	Pyridine chain	CHX X	Pyridine	NH_{pyr}
(**24**)	8.85	8.64—8.47	8.20 to 7	6.7	6.58				−2.65
(**25**)	8.90—8.86	8.62—8.44	8.20 to 7.48	6.81—6.77	6.72		−3.10 (OH)		−2.64
(**26**)	8.86—8.85	8.59	8.18 to 7.53	6.75—6.65	6.52				−2.62
(**27**)	8.86	8.66 to	7.50	6.78	6.44—6.33		3.06 (ethylenic) 2.61		−2.61
(**28**)	8.88—8.85	8.58	8.25 to 7.51	6.76—6.66	6.53		1.92 ($SCOCH_3$)		−2.61
(**29**)	8.80	8.59—8.42	8.24 to 7.37	6.68—6.58	6.38				−2.68
(**30**)	8.88	8.63—8.40	8.20 to 7.50	6.85—6.76	6.67		6.95 5.03 (Im) 4.54		−2.56
(**39**)	8.97—8.81	8.47—8.17	8.04 to 7.08	3.41 (NH_2)	6.16				−2.64
(**41**)	8.93—8.87	8.54	8.33 to 7.42		6.55	5.54		7.64 (H_o)[a] 3.11 (H_p)	−2.42
(**42**)	8.91	8.53—8.41	8.28 to 7.45		6.70	5.56—5.50	−2.46 (OH)	7.60 (H_o)[a] 3.05 (H_p)	−2.51
(**43**)	8.92	8.56	8.30 to 7.60		6.40	5.58—5.49		7.60 (H_o)[a] 3.20 (H_p)	−2.36
(**44**)	8.92	8.58—8.47	8.32 to 7.49		6.50	5.51	6.64 6.43 (Im) 5.62	7.60 (H_o)[a] 3.11 (H_p)	−2.38
(**46**)	8.90	8.55	8.47 to 7.43		6.37	5.60—5.51	2.05 ($SCOCH_3$)	7.69 (H_o)[a] 3.23 (H_p)	−2.34
(**40**)	8.85	8.50—8.42	8.25 to 7.55		6.57				−2.70
(**52**)	8.90	8.48—8.40	8.25 to 7.58		6.67—6.63		−2.64 (OH)		−2.84
(**53**)	8.85	8.54—8.47	8.45 to 7.35		6.67—6.57				−2.84
(**54**)	8.91—8.88	8.37—8.29	8.13 to 7.53		6.70—6.64		5.99 5.12 (Im) 4.58		−2.49

[a] The assignment is shown on the Figure.

Experimental

All chemicals used were of reagent grade and were purchased from Aldrich. Reaction solvents (Prolabo) for the synthesis were purified before use. Dimethylformamide (DMF) was distilled and kept over 4 Å molecular seive. Tetrahydrofuran (THF) was purified by distillation from benzophenone–sodium. Merck silica gel 60 (40—60 μm) was used for column chromatography. Merck pre-coated preparative plates (silica gel 60, 2 mm) were used for t.l.c. Elemental analysis were carried out by the Service Central de Microanalyse du C.N.R.S. ^{1}H N.m.r. spectra of free-base porphyrins in deuteriochloroform (C.E.A. France) were measured using a Varian XL 100 spectrometer in the Fourier Transform mode using 4 K data points in the frequency domain. Chemical shifts were referenced to internal tetramethylsilane.

Diethyl 6,6-*Ethylenedioxyundecanedioate* (**3**).—A solution of the keto diester (**2**) (8.89 g, 31 mmol), obtained by esterification of the corresponding diacid (**1**),[24] in a mixture of ethylene glycol (8 ml), triethyl orthoformate (16 ml), and a catalytic amount of toluene-*p*-sulphonic acid (480 mg) was refluxed for 20 min. Excess of ethyl formate and ethanol were distilled off and the residue was cooled and poured into saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ether and the combined organic layers were washed with 10% aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated. Distillation of the residue under reduced pressure (b.p. 175 °C, 2.5 mmHg) afforded the title compound (8.04 g, 78%) (Found: C, 61.9; H, 9.25. $C_{17}H_{30}O_6$ requires C, 61.79; H, 9.15%); δ 4.13 (quad, 2 × CH_3H_2), 3.92 (s, 2 × OCH_2), 2.30 (t, 2 × CH_2CO), 1.56 (m, 6 × CH_2), and 1.26 (t, 2 × OCH_2CH_3).

1,11-*Dihydroxyundecan*-6-*one Ethylene Acetal* (**4**).—A solution of the diester (**3**) (9.14 g, 27.7 mmol) in anhydrous ether (70 ml) was added dropwise over 1 h to a stirred suspension of $LiAlH_4$ (1.5 g) in the same solvent (100 ml). The reaction mixture was stirred at room temperature for 2 h and the excess of $LiAlH_4$ was decomposed with water (30 ml). The ether layer was decanted and the remaining solid was washed with ether. The combined organic layers were dried (Na_2SO_4) and evaporated to afford the diol as a colourless oil (6.15 g, 90%) which was used without purification; δ 3.19 (s, 2 × OCH_2), 3.61 (t, 2 × CH_2OH), 1.77 (t, 2 × CH_2C), and 1.48 (6 × CH_2).

1,11-*Dihydroxyundecan*-6-*one* (**5**).—To a solution of the acetal (**4**) (6.15 g, 25 mmol) in water (100 ml), 6M sulphuric acid (15 ml) and acetone (10 ml) were added. The mixture was refluxed for 1.5 h and then concentrated (30 ml). The aqueous layer was extracted with methylene dichloride (× 3) and the extract dried (Na_2SO_4) and slowly evaporated to give the ketone as a white solid (4.76 g, 94%), m.p. 58.5 °C (Found: C, 65.3; H, 11.0. $C_{11}H_{12}O_3$ requires C, 65.31; H, 10.96%); δ 3.62 (t, 2 × CH_2OH), 2.41 (t, 2 × CH_2CO), and 1.54 (6 × CH_2).

1,11-*Dibromoundecan*-6-*one* (**6**).—A mixture of the diol (**5**) (4.5 g, 14 mmol) and 66% aqueous hydrobromide acid (20 ml) was refluxed for 4 h. The oily compound formed was separated from the aqueous solution and dissolved in methylene dichloride. The organic layer was washed with 5% aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated and the oily residue was distilled under reduced pressure (b.p. 153 °C, 2 mmHg) to afford the title compound (6.28 g, 86%) (Found: C, 40.5; H, 6.0;

Br, 49.0. $C_{11}H_{20}Br_2$ requires C, 40.27; H, 6.14; Br, 48.71%); δ, 3.41 (t, 2 × CH_2Br), 2.43 (t, 2 × CH_2CO), 1.88 (quint, 2 × CH_2CH_2Br), and 1.52 (m, 4 × CH_2).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*oxoundecane*-1,11-*dioxy*)*diphenyl*]*porphyrin* (**8b**).—A solution of 1,12-dibromododecane (1.640 g, 5 mmol) in dry DMF was added dropwise during 2 h to a mixture of 5,10,15,20-tetrakis(*o*-hydroxyphenyl)porphyrin (**7**) (3.39 g, 5 mmol) and an excess of anhydrous potassium carbonate (10 g) in the same solvent (500 ml) at 100 °C under argon. After addition was complete, stirring was continued for 1.5 h. 1,11-Dibromoundecan-6-one (**6**) (1.64 g, 5 mmol) in dry DMF was added dropwise to the reaction mixture during 2 h after which it was set aside overnight. The reaction mixture was then cooled and filtered and the filtrate was evaporated to dryness. The residue was taken up in chloroform and the organic solution was washed with water (× 3), dried (Na_2SO_4), and evaporated. The mixture of porphyrins in toluene was loaded onto a silica gel column (4.5 × 35 cm). Elution with toluene–methylene dichloride (1:1, v/v) gave the symmetric polymethylene basket-handle porphyrins (**8a**), (**9a**), and (**10a**) (494 mg, 10%). A more polar fraction eluted with methylene dichloride–ether (100:1, v/v) was thought to contain the dissymetric basket-handle porphyrins (**8b**), (**9b**), and (**10b**) (1.313 g, 26%). A third fraction obtained by elution with methylene dichloride–ether (100:5, v/v) was identified as a mixture of the three isomeric symmetric ketone basket-handle porphyrins (**8c**), (**9c**), and (**10c**) (489 mg, 9.7%).

In order to separate the three isomers (**8b**), (**9b**), and (**10b**), the second fraction was loaded onto a silica gel column (4 × 100 cm). The fastest moving band obtained by elution with methylene dichloride corresponded to the cross-*trans* linked isomer (**8b**) which crystallized from methylene dichloride–methanol as a purple solid (656 mg, 13%) (Found: C, 79.0; H, 7.1; N, 5.65. $C_{67}H_{70}N_4O_5$ requires C, 79.57; H, 6.98; N, 5.54%).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*hydroxyundecylenedioxy*)*diphenyl*]*porphyrin* (**11**).—To a solution of (**8b**) (0.61 g, 0.6 mmol) in a mixture of THF (50 ml) and ethanol (50 ml) a large excess of sodium borohydride (400 mg) was added portionwise. After being stirred at room temperature for 3 h the mixture was poured into water (150 ml) and acidified to destroy the excess of hydride. The resulting solution was extracted with toluene and the extract washed with water and dried (Na_2SO_4). The organic layer was concentrated to a small volume and purified by silica gel column chromatography (3 × 2 cm). Elution with methylene dichloride–ether (100:2 to 100:5, v/v) gave (**11**) (503 mg, 83%) which was crystallized from methylene dichloride–methanol (Found: C, 78.45; H, 7.25; N, 5.55. $C_{67}H_{72}N_4O_5$ requires C, 79.41; H, 7.16; N, 5.53%).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*bromoundecylenedioxyl*)*diphenyl*]*porphyrin* (**12**).—To a mixture of (**11**) (0.3 g, 0.3 mmol), pyridine (200 ml), and carbon tetrabromide (750 mg, 2.26 mmol) in THF (15 ml) was added small portions of triphenylphosphine (3 × 260 mg). The reaction was monitored by t.l.c. on analytical silica gel plates and shown to be complete after the three additions. The reaction mixture was stirred for a further 30 min and then poured into toluene. The organic layer was washed with water (× 4), dried (Na_2SO_4), and concentrated to a small volume. The product was purified by silica gel column chromatography (3 × 20 cm) eluting first with toluene and then with toluene–methylene dichloride (1:1, v/v) to yield compound (**12**) as a purple solid (306 mg, 96%) (Found: C, 72.0; H, 6.35; Br, 11.05; N, 5.35. $C_{67}H_{71}BrN_4O_4$ requires C, 74.77; H, 6.65; Br, 7.42; N, 5.21%).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*methylthioundecylenedioxy*)*diphenyl*]*porphyrin* (**13**).—A solution of sodium (100 mg) in absolute ethanol (5 ml) was saturated with methyl sulphide at room temperature. To the resulting mixture was added compound (**12**) (80 mg, 0.07 mmol) in a mixture of tetrahydrofuran (5 ml) and ethanol (5 ml). The solution was then heated at 100 °C for 4 h under argon and then evaporated to dryness. The solid residue was dissolved in toluene, and the solution washed with water (× 4), dried (Na_2SO_4), and concentrated. Chromatography of the residue on a silica gel column (2 × 20 cm) with toluene as eluant afforded the title compound (**13**) which was crystallized from methylene dichloride–methanol (52 mg, 67%) (Found: C, 76.95; H 6.75; N, 5.45; S, 3.0. $C_{68}H_{74}N_4O_4S$ requires C, 77.06; H, 7.31; N, 5.21; S, 2.98%).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*acetylthioundecylenedioxy*)*diphenyl*]*porphyrin* (**14**).—The bromoporphyrin (**12**) (100 mg, 0.1 mmol) was dissolved in dimethylformamide (5 ml) and potassium thioacetate (100 mg, 0.9 mmol) was added under argon. The resulting solution was heated at 100 °C for 30 min and then evaporated to dryness under reduced pressure. The residue was redissolved in toluene and the solution washed with water, aqueous hydrogen carbonate, and water and then dried (Na_2SO_4), and evaporated. Chromatography of the residue on silica gel column (2 × 15 cm) eluting with toluene gave some minor fractions. The desired product was recovered with toluene–methylene dichloride (3:2, v/v) and recrystallized from methylene dichloride–methanol (59 mg, 60%) (Found: C, 76.9; H, 6.95; N, 5.2; S, 3.3. $C_{69}H_{74}N_4O_5S$ requires C, 77.35; H, 6.96; N, 5.23; S, 2.99%).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*mercaptoundecylenedioxy*)*diphenyl*]*porphyrin* (**15**).—A mixture of compound (**14**) (35 mg, 0.033 mmol) and KOH (1M KOH in ethanol–water solution, 4:1 v/v; 3 ml) in THF (3 ml) was stirred at room temperature under argon for 3 h. The reaction mixture was acidified with 1M H_2SO_4 (3 ml) and extracted with toluene, and the extract washed with water (× 4) and dried (Na_2SO_4). After concentration, the solution was submitted to silica gel t.l.c. Elution with toluene–cyclohexane (2:1, v/v) gave one major band corresponding to the more polar compound which was identified as the title porphyrin (25 mg, 73%) (Found: C, 78.20; H, 6.9; N, 5.4; S, 3.1. $C_{67}H_{72}N_4O_4S$ requires C, 78.17; H, 7.05; N, 5.44; S, 3.11).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*imidazol*-1-*ylundecylenedioxy*)*diphenyl*]*porphyrin* (**16**).—A solution of the porphyrin (**12**) (300 mg, 0.28 mmol) and the imidazole (1.02 g, 14.7 mmol) in dimethylformamide (30 ml) was stirred and heated at 100 °C for 72 h. The solvent was then evaporated under reduced pressure and the residue taken up with toluene. The organic phase was washed with water (× 4), dried (Na_2SO_4), and concentrated. The resulting solution was chromatographed on silica gel column (2 × 20 cm). Elution with toluene gave a first fraction which was identified as the starting material (20 mg, 6.7%). A second fraction was recovered by elution with toluene–acetone (9:1, v/v) corresponding to the ethylenic handle porphyrin (**17**) (85 mg, 30.6%). The title compound, the more polar product, was eluted with toluene–acetone (1:1, v/v) and recrystallized from methylene dichloride–hexane (184 mg, 62%) (Found: C, 78.95; H, 7.2; N, 8.0. $C_{70}H_{73}N_6O_4$ requires C, 79.14; H, 6.93; N, 7.91%).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*methoxyundecylenedioxy*)*diphenyl*]*porphyrin* (**18**).—The hydroxyporphyrin (**11**) (50 mg, 0.04 mmol) in dry DMF (8 ml) was added to sodium hydride (50% in oil; 100 mg, 2.1 mmol) and

this was followed by methyl iodide (150 μl, 2.41 mmol). The reaction mixture was stirred at 50—60 °C for 1 h. After cooling, the excess of reducing agent was decomposed by addition of water and the solvent was evaporated to dryness. The residue was dissolved in methylene dichloride and the solution washed with water (×4), dried (Na_2SO_4), and evaporated. Subsequent silica gel column chromatography (2 × 15 cm) of the residue developed with methylene dichloride–ether (10:1, v/v) gave the desired compound (**18**) which was crystallized from methylene dichloride–methanol (37 mg, 73%) (Found: C, 79.3; H, 7.25; N, 5.48. $C_{68}H_{74}N_4O_5$ requires C, 79.50; N, 7.26; N, 5.45%).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*hydroxyminoundecylenedioxy*)*diphenyl*]*porphyrin* (**19**).—To a solution of (**8b**) (200 mg, 0.2 mmol) in tetrahydrofuran (20 ml) were added hydroxylamine hydrochloride (1 g) and ethanolic KOH (2M; 4 ml). The mixture was stirred at room temperature for 2.5 h and evaporated to dryness. The residue was taken up with water, acidified with 1M hydrochloric acid, and extracted with toluene. The organic layer was washed with water (×2), dried (Na_2SO_4), and evaporated to a small volume which was applied to a column of silica gel (2 × 20 cm). Elution with methylene dichloride–ether (100:7, v/v) gave a major fraction which was crystallized from methylene dichloride–methanol to yield compound (**19**) (177 mg, 87%) (Found: C, 77.55; H, 6.85; N, 6.65. $C_{67}H_{71}N_5O_5$ requires C, 78.41; H, 6.97; N, 6.82%).

α-5,15-[2,2′-(*Dodecamethylenedioxy*)*diphenyl*]:β-10,20-[2,2′-(6-*aminoundecylenedioxy*)*diphenyl*]*porphyrin* (**21**).—The oxime (**19**) (80 mg, 0.078 mmol) in toluene (8 ml) was treated with acetyl chloride (15 μl) in the presence of sodium hydrogen carbonate (250 mg). The mixture was washed with water, dried (Na_2SO_4), and evaporated to give the acetyl derivative (**20**) which was crystallized from methylene dichloride–methanol (66 mg, 79%) (Found: C, 77.35; H, 6.95; N, 6.4. $C_{69}H_{73}N_5O_6$ requires C, 77.57; H, 6.89; N, 6.55%). This was dissolved in THF (2 ml) and treated with a solution of 1M BH_3–THF (2 ml) under argon. The resulting solution was kept at room temperature for 48 h after which it was cooled to 0 °C and treated with water (2 ml) and 4M HCl (2 ml). It was then heated under reflux for 1.5 h after which it was treated with aqueous NaOH to neutralize the HCl. The resulting solution was extracted with toluene and the extract washed with water and dried (Na_2SO_4). Evaporation of the extract gave the product which was purified by preparative t.l.c. on alumina plates with toluene–methanol (100:1.5, v/v) to afford the title compound (**21**) [50 mg, 63% from the hydroxyimine (**19**) and 79% from acetylporphyrin (**20**)] (Found: C, 79.25; H, 7.35; N, 6.9. $C_{67}H_{73}N_5O_4$ requires C, 79.49; H, 7.27; N, 6.92%).

α-5,15-[2,2′-(*Dodecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-[2,2′-(6-*oxoundecamethylenedicarbonylamino*)*diphenyl*]*porphyrin* (**24**).—5-Oxononane-1,9-dicarboxylic acid (**1**) (0.253 g, 1.1 mmol) and oxalyl chloride (1.5 ml) in toluene (5 ml) were heated at 50 °C for 3 h. The solvent and excess of reagent were then evaporated and the residue was dissolved in dry toluene (5 ml). The solvent was evaporated and the residual diacid chloride was taken up in the dry THF (50 ml) and then added dropwise under argon to a solution of α-5,15-[2,2′-(dodecamethylenedicarboxylamino)diphenyl]:β,β-10,20-bis-(*o*-aminophenyl)porphyrin (**23**) prepared from 5,10,15,20-tetrakis-(*o*-aminophenyl)prophyrin, the α,β,α,β-atropisomer (**22**), following the previously described procedure[1] at room temperature. After 2 h, the solvent was evaporated and the resulting crude porphyrin was dissolved in methylene dichloride, and the solution washed with water (×3), dried (Na_2SO_4), and concentrated. Chromatography of this concentrate on a silica gel column with methylene dichloride–acetone (3:1, v/v) gave the title compound (**24**) which was crystallized from methylene dichloride–hexane (0.765 g, 72%) (Found: C, 73.7; H, 6.45; N, 9.7. $C_{67}H_{66}N_8O_5 \cdot 2H_2O$ requires C, 73.2; H, 6.42; N, 10.19%).

α-5,15-[2,2′-(*Dodecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-[2,2′-(6-*hydroxyundecamethylenedicarbonylamino*)*diphenyl*]*porphyrin* (**25**).—The foregoing compound (**24**) (531 mg, 0.5 mmol) was reduced in methanol (200 ml) by treatment with an excess of sodium borohydride (95 mg, 2.5 mmol). After complete reaction (monitored by analytical t.l.c. on silica gel) the solution was treated with water and diluted sulphuric acid. The porphyrin (**25**) was extracted with methylene dichloride, and the extract washed with water and aqueous hydrogen carbonate, dried (Na_2SO_4); after evaporation the product was immediately crystallized from methylene dichloride–hexane (521 mg, 98%) (Found: C, 74.45; H, 6.65; N, 10.0. $C_{67}H_{68}N_8O_5 \cdot H_2O$ requires C, 74.28; H, 6.51; N, 10.34%).

α-5,15-[2,2′-(*Dodecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-[2,2′-(6-*bromoundecamethylenedicarbonylamino*)*diphenyl*]*porphyrin* (**26**).—This compound was obtained by the same method used for the preparation of compound (**12**) from compound (**25**) (532 mg, 0.5 mmol). The crude product in toluene was chromatographed on silica gel column (2 × 25 cm). The excess of CBr_4 was removed by elution with methylene dichloride–acetone (100:5, v/v). Subsequent elution with methylene dichloride–acetone (100:20, v/v) gave the porphyrin (**26**) which contained $Ph_3P{=}O$. To eliminate the latter, the porphyrin was crystallized from toluene–hexane (1:1, v/v) (434 mg, 77%) (Found: C, 71.5; H, 6.15; Br, 6.81; N, 9.95. $C_{67}H_{67}BrN_8O_4$ requires C, 71.33; H, 5.99; Br, 7.08; N, 9.93%).

α-5,15-[2,2′-(*Dodecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-[2,2′-(6-*acetylthioundecamethylenedicarbonylamino*)*diphenyl*]*porphyrin* (**28**).—To a solution of dicyclohexyl-18-crown 6 (372 mg, 1 mmol) and potassium thioacetate (114 mg, 1 mmol) in toluene (15 ml) under argon was added the bromoporphyrin (**26**) (225 mg, 0.2 mmol). The solution was heated at 60 °C for 6 h and then evaporated to dryness. The residue was dissolved in methylene dichloride and the solution washed with water (×3) and dried (Na_2SO_4). The crude product was first crystallized from methylene dichloride–hexane in order to eliminate the crown-ether. The solid material was chromatographed on silica gel plates using methylene dichloride–ether (5:1, v/v) as eluant. Two major bands were obtained which were separately recovered and crystallized from methylene dichloride–hexane. The first band corresponding to the least polar compound yielded the ethylenic porphyrin (**27**) (37 mg, 18%) (Found: C, 78.2; H, 6.5; N, 10.12. $C_{67}H_{66}N_8O_4$ requires C, 76.84; H, 6.35; N, 10.70%). The second band to be eluted was shown to contain the title compound (**28**) (170 mg, 76%) (Found: C, 73.4; H, 6.5; N, 9.7; S, 2.65. $C_{69}H_{70}N_8O_5S$ requires C, 73.70; H, 6.28; N, 9.97; S, 2.85%).

α-5,15-[2,2′-(*Dodecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-[2,2′-(6-*mercaptoundecamethylenedicarbonylamino*)*diphenyl*]*porphyrin* (**29**).—In the same manner as for (**15**), the title compound was prepared using (**28**) (112 mg, 0.1 mmol). The product was chromatographed on a silica gel plate with methylene dichloride–acetone (2:1, v/v) as eluant. The major band was collected and the crude product crystallized from methylene dichloride–hexane to give the title compound (**29**) (75 mg, 70%) (Found: C, 71.1; H, 6.25; N, 9.3; S, 2.7. $C_{67}H_{68}N_8O_4S \cdot 3H_2O$ requires C, 70.87; H, 6.57; N, 9.87; S, 2.82%).

α-5,15-[2,2′-(*Dodecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-[2,2′-(6-*imidazol*-1-*yl-undecamethylenedicarbonylamino*)-*diphenyl*]*porphyrin* (**30**).—This compound was prepared in an

analogous manner to that described above for the preparation of (**16**) using compound (**26**) (225 mg, 0.2 mmol) and imidazole (680 mg, 10 mmol) in dry DMF. The porphyrin mixture was chromatographed on silica gel plates. Elution with methylene dichloride–acetone (1:1, v/v) gave two bands. The most polar fraction (2nd band) was fully characterized, after crystallization from methylene dichloride–hexane, by its n.m.r. spectrum as the desired compound (**30**) (118 mg, 53%) (Found: C, 72.1; H, 6.5; N, 12.1. $C_{70}H_{70}N_{10}O_4 \cdot 2H_2O$ requires C, 73.0; H, 6.50; N, 12.20%).

The first fraction was rechromatographed on silica gel plates, eluting with methylene dichloride–acetone (9:1, v/v) to give two fractions which were characterized as the starting material (**26**) (36 mg, 18%) and the ethylenic porphyrin (**27**) (50 mg, 27%) (Found: C, 76.05; H, 6.5; N, 10.1. $C_{67}H_{66}N_8O_4 \cdot H_2O$ requires C, 75.54; H, 6.43; N, 10.52%).

α-5,15-[2,2′-(6-*Oxoundecane*-1,11-*dioxydipropoxy*)*diphenyl*]:β10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*diproxy*]*diphenyl*}-*porphyrin* (**33**).—A solution of 1,11-dibromoundecan-6-one (**6**) (1.312 g, 4 mmol) in dry dimethylformamide (150 ml) was added dropwise during 4 h to a mixture of 5,10,15,20 tetrakis-(*o*-hydroxyphenyl)porphyrin (**7**) (2.71 g, 4 mmol) and an excess of anhydrous potassium carbonate (8 g) in the same solvent (400 ml) at 100 °C under argon. After the addition was complete stirring was continued for 4 h at the same temperature; the mixture was then filtered and the filtrate evaporated to dryness. The residue was dissolved in methylene dichloride and directly subjected to column chromatography (silica gel, 4 × 30 cm). Elution with methylene dichloride–ether (100:2, v/v) afforded a first fraction which was identified by analytical t.l.c. as a mixture of three isomers of dibridged basket-handle porphyrins (**8c**), (**9c**), and (**10c**) (692 mg, 17%). A more polar fraction eluted with methylene dichloride–ether (100:5, v/v) was thought to be monobridged porphyrins (**31**) and (**32**) (1.072 g, 31%). Unchanged starting material (**7**) could be recovered with methylene dichloride–acetone (1:1, v/v) (565 mg, 20%).

The two isomers, cross-linked (**31**) and adjacent linked (**32**), were not separated and used without further purification for the second step. 3,5-Bis(3-bromopropyl)pyridine[23] (525 mg, 1.3 mmol) in dry DMF (40 ml) was added dropwise under argon during 4 h at 100 °C to a solution of the porphyrins (**31**) and (**32**) and an excess of anhydrous potassium carbonate (2.5 g) in DMF (125 ml). After being stirred for 4 h, the reaction mixture was filtered and the filtrate was evaporated. The residue was dissolved in a small volume of toluene (10 ml) and the resulting solution was loaded onto a silica gel column (3 × 30 cm). Elution with methylene dichloride–ether (1:1, v/v) gave a very small fraction which was identified as a mixture of (**8c**), (**9c**) and (**10c**). Compounds (**33**), (**34**) and (**35**) were eluted with methylene dichloride–acetone (10:2, v/v) to (1:1, v/v). These three isomers were separated by preparative silica gel t.l.c. Development with methylene dichloride–acetone (10:2, v/v) gave three bands. The first corresponded to the expected compound (**33**) which crystallized from methylene dichloride–methanol as purple crystals (230 mg, 18%) (Found: C, 77.45; H, 6.05; H, 6.95. $C_{66}H_{61}N_5O_5 \cdot CH_3OH$ requires C, 77.65; H, 6.32; N, 6.76%).

α-5,15-[2,2′-(6-*Hydroxyundecamethylenedioxy*)*diphenyl*]:β-10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*dipropoxy*]*diphenyl*}*porphyrin* (**36**).—This compound was prepared in an analogous manner to the above compound (**11**) from (**33**) in 93% yield after crystallization from methylene dichloride–methanol (Found: C, 77.35; H, 6.3; N, 6.8. $C_{66}H_{63}N_5O_5 \cdot CH_3OH$ requires C, 77.50; H, 6.50; N, 6.74%).

α-5,15-[2,2′-(6-*Bromoundecamethylenedioxy*)*diphenyl*]:β-10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*dipropoxy*]*diphenyl*}*porphyrin* (**37**).—The foregoing compound (**36**) was brominated following the method described above for the preparation of (**12**). It was purified by chromatography on silica gel column using methylene dichloride–acetone (5:1, v/v) as eluant and then crystallized from methylene dichloride–methanol in 78% yield (Found: C, 73.55; H, 5.85; Br, 7.5; N, 6.55. $C_{66}H_{62}BrN_5O_4 \cdot CH_3OH$ requires C, 73.08; H, 6.04; N, 6.36; Br, 7.25%).

α-5,15-[2,2′-(6-*Methylthioundecamethylenedioxy*)*diphenyl*]:β-10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*dipropoxy*]*diphenyl*}*porphyrin* (**38**).—This compound was prepared according to the procedure described for the preparation of (**13**) using the foregoing compound (**37**) (100 mg, 0.94 mmol) in a mixture of DMF–ethanol (1:3, v/v). The crude product was purified by t.l.c. on silica gel plates with methylene dichloride–acetone (5:1, v/v) as eluant. The major band was collected and the product crystallized from methylene dichloride–methanol to give purple crystals of (**38**) (58 mg, 60%) (Found: C, 76.85; H, 6.2; N, 6.8; S, 3.05. $C_{67}H_{65}N_5O_4S \cdot CH_3OH$ requires C, 76.44; H, 6.51; N, 6.55; S, 3.0%).

α-5,15-[2,2′-(6-*Oxoundecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*dipropionamido*]-*diphenyl*}*porphyrin* (**41**).—5-Oxononane-1,9-dicarbonyl chloride (460 mg, 2 mmol) (see above) in dry THF (100 ml) was added dropwise during 2 h to a mixture of 5,10,15,20-tetrakis-(*o*-aminophenyl)porphyrin (**22**) (1.348 g, 2 mmol) and triethylamine (600 μl, 5 mmol) in the same solvent (300 ml) at room temperature under argon. Solvent was then evaporated and the residue was dissolved in methylene dichloride. The solution was washed with water (× 3), dried (Na_2SO_4), concentrated, and then chromatographed on silica gel column (2 × 30 cm). Elution with methylene dichloride–ether (10:1, v/v) gave the unchanged starting material (**22**) (272 mg, 20%). A second band to be eluted with methylene dichloride–acetone (2:1, v/v) was shown to contain the monohandle porphyrin, α-5,15-[2,2′-(6-*oxoundecamethylenedicarbonylamino*)*diphenyl*]:β,β-10,20-*bis*(o-*aminophenyl*)*porphyrin* (**39**) which crystallized from methylene dichloride–hexane (805 mg, 46.5%) (Found: C, 73.55; H, 5.8; N, 12.3. $C_{55}H_{48}N_8O_3 \cdot 2H_2O$ requires C, 72.99; H, 5.79; N, 12.38%). Further elution with methylene dichloride–acetone (1:1, v/v) afforded a third band which yielded the symmetrical basket handle porphyrin α-5,15:β-10,20-*bis*[2,2′-(6-*oxoundecamethylenedicarbonylaminodiphenyl*]*porphyrin* (**40**) (443 mg, 21%) (Found: C, 73.3; H, 5.95; N, 10.75. $C_{66}H_{62}N_8O_6 \cdot H_2O$ requires C, 73.31; H, 5.97; N, 10.36%). Pyridine-3,5-diyldi(propionic acid) hydrochloride (360 mg, 1.4 mmol) was converted into its diacid chloride following the procedure previously described.[1] It was dissolved in dry methylene dichloride (100 ml) and the resulting solution was added dropwise to a solution of compound (**39**) (600 mg, 0.7 mmol) and pyridine (0.5 ml) in the same solvent (300 ml). After addition, the reaction mixture was stirred for a further 1 h, and then washed with water (× 3) and dried (Na_2SO_4). After evaporation of the organic solvent, the crude porphyrin was chromatographed on a silica gel column. Elution with methylene dichloride–acetone (1:1, v/v) first removed a fraction corresponding to unchanged starting porphyrin (**39**) (75 mg, 13%). Methylene dichloride–methanol (10:1, v/v) used as eluant gave the title porphyrin (**41**) which was crystallized from methylene dichloride–hexane (434 mg, 59%) (Found: C, 71.45; H, 5.65; H, 11.35. $C_{66}H_{57}N_9O_5 \cdot 3H_2O$ requires C, 71.39; H, 5.72; N, 11.35%).

α-5,15-[2,2′-(6-*Hydroxyundecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*dipropionamido*]-*diphenyl*}*porphyrin* (**42**).—This compound was obtained from (**41**) (138 mg, 0.13 mmol) by the foregoing reductive procedure

used for the preparation of (**25**) (116 mg, 84%) (Found: C, 70.9; H, 5.8; N, 11.1. $C_{66}H_{59}N_9O_5 \cdot 4H_2O$ requires C, 70.13; H, 5.97; N, 11.15%).

α-5,15-[2,2′-(6-*Bromoundecamethylenedicarbonylamino)diphenyl*]:β-10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*dipropionamido*]-*diphenyl*}*porphyrin* (**43**).—An analogous reaction to that described above for the preparation of (**26**) was used from (**42**) (100 mg, 0.1 mmol) to give the title compound (**43**) (90.5 mg, 86%) (Found: C, 70.15; H, 5.45; Br, 7.1; N, 11.5. $C_{66}H_{58}BrN_9O_4$ requires C, 70.71; H, 5.21; Br, 7.13; N, 11.24%).

α-5,15-[2,2′-(6-*Imidazol*-1-*yl-undecamethylenedicarbonylamino*)*diphenyl*]:β-10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*dipropionamido*]*diphenyl*}*porphyrin* (**44**).—This compound was obtained from (**43**) (100 mg, 0.09 mmol) by reaction with imidazole using the method described for the preparation of (**16**). It was submitted to preparative silica gel t.l.c. and developed with methylene dichloride–acetone (1:2, v/v). Two bands were obtained. The compounds were individually isolated with methylene dichloride–methanol (100:5, v/v) and characterized by their ^{1}H n.m.r. The compound in the first band was assigned to the ethylenic derivative (**45**) (34 mg, 37%). The slower moving band corresponded to the desired compound (**44**) and was crystallized from methylene dichloride–hexane (29 mg, 30%) (Found: C, 69.9; H, 5.85; N, 13.0. $C_{69}H_{61}N_{11}O_4 \cdot 4H_2O$ requires C, 70.21; H, 5.89; N, 13.05%).

α-5,15-[2,2′-(6-*Acetylthioundecamethylenedicarbonylamino*)-*diphenyl*]:β-10,20-{2,2′-[3,3′-(*pyridine*-3,5-*diyl*)*dipropio-amido*]*diphenyl*}*porphyrin* (**46**).—In the same manner as described for (**28**), the title compound was prepared using (**43**) (57 mg, 0.5 mmol). The crude product was submitted to t.l.c. on silica gel plates with methylene dichloride–acetone (1:1, v/v) as eluant. Only one band was obtained which was collected to give purple crystals after crystallization from methylene dichloride–hexane (80 mg). N.m.r. spectroscopy revealed two compounds. In order to separate them, $Zn(OAc)_2 \cdot 2H_2O$ in acetic acid was added to the porphyrins in methylene dichloride and the mixture was stirred under reflux for 5 min. The solvent was evaporated and the crude product was taken up in methylene dichloride and washed successively with water, aqueous potassium hydrogen carbonate, and water, and then dried (Na_2SO_4). The solvent was slowly removed under reduced pressure to give purple crystals during the concentration. They were dissolved in methylene dichloride and the soluton was washed with aqueous trifluoroacetic acid, water, aqueous potassium hydrogen carbonate, and water and then dried (Na_2SO_4). Evaporation to dryness gave the title compound (**46**) which recrystallized from methylene dichloride–hexane (45 mg, 60%) (Found: C, 71.45; H, 5.65; N, 11.4; S, 2.5. $C_{68}H_{61}H_9N_9O_5S \cdot 2H_2O$ requires C, 70.87; H, 5.69; N, 10.93; S, 2.78%).

α-5,15:β-10,20-*Bis*[2,2′-(6-*Oxoundecamethylenedioxy*)-*diphenyl*]*porphyrin* (**8c**).—This compound was separated from the mixture of the three isomers (**8c**), (**9c**), and (**10c**) by preparative t.l.c. with methylene dichloride–ether as eluant (100:5, v/v). The least polar compound (band 1) was identified by n.m.r. as the cross-*trans*-linked isomer (**8c**) (Found: C, 77.9; H, 6.5; N, 5.7. $C_{66}H_{66}N_4O_6$ requires C, 78.4; H, 6.6; N, 5.5%).

α-5,15:β-10,20-*Bis*[2,2′-(6-*Hydroxyundecamethylenedioxy*)-*diphenyl*]*porphyrin* (**47**).—Reduction of the diketone porphyrin (**8c**) (600 mg, 0.59 mmol) was accomplished using the method described for the preparation of (**11**). Chromatography on silica gel plates with methylene dichloride–ether (100:7, v/v) gave a major band which corresponded to the desired compound which was crystallized from methylene dichloride–methanol (426 mg, 70%) (Found: C, 77.65; H, 6.95; N, 5.45. $C_{66}H_{70}N_4O_6$ requires C, 78.08; H, 6.95; H, 5.52%).

α-5,15:β-10,20-*Bis*[2,2′-(6-*Bromoundecamethylenedioxy*)-*diphenyl*]*porphyrin* (**48**).—The foregoing compound (**47**) was treated in THF in the same manner to that used for the preparation of (**12**). The porphyrin was purified by chromatography on a silica gel column. A first elution with toluene–hexane removed $Ph_3P{=}O$. The expected porphyrin was then eluted with toluene and crystallized from methylene dichloride–methanol (90%) (Found: C, 69.75; H, 5.85; Br, 13.9; N, 5.15. $C_{66}H_{68}Br_2N_4O_4$ requires C, 69.47; H, 6.01; Br, 14.01; N, 4.91%).

α-5,15:β-10,20-*Bis*[2,2′-(6-*Imidazoyl*-1-*ylundecamethylene-dioxy*)*diphenyl*]*porphyrin* (**49**).—This compound was obtained from (**48**) (300 mg, 0.26 mmol) according to the method used for the preparation of (**16**). Chromatography of the crude porphyrin on silica gel plates with toluene–acetone (1.5:1, v/v) as eluant gave three major fractions. The fastest moving bands corresponded to the diethylenic basket-handle porphyrin (**50**) (13 mg, 5%). The second moving band was identified as the monoethylenic-monoimidazole basket-handle porphyrin (**51**) (41 mg, 14%). The slower moving band corresponded to the desired bis-imidazole basket-handle porphyrin (**49**) (168 mg, 57%) (Found: C, 76.6; H, 6.6; N, 9.5. $C_{72}H_{74}N_8O_4$ requires C, 77.53; H, 6.69; N, 10.05%).

α-5,15:β-10,20-*Bis*[2,2′-(6-*Hydroxyundecamethylenedicarbonylamino*)*diphenyl*]*porphyrin* (**52**).—Reduction of the diketo porphyrin (**40**) (1.064 g, 1 mmol) was performed in a mixture of methanol–methylene dichloride (2:1, v/v) using the procedure described for the preparation of (**25**). The title compound was purified by chromatography on silica gel column, eluted with methylene dichloride–acetone (1:2, v/v), and crystallized from methylene dichloride–ethanol–hexane (865 mg, 86%) (Found: C, 73.05; H, 6.3; N, 10.3. $C_{66}H_{66}N_8O_6 \cdot H_2O$ requires C, 73.04; H, 6.32; N, 10.32%).

α-5,15:β-10,20-*Bis*[2,2′-(6-*Bromoundecamethylenedicarbonylamino*)*diphenyl*]*porphyrin* (**53**).—Bromination of the above porphyrindiol (700 mg, 0.66 mmol) was accomplished in the usual way [see the preparation of (**12**)]. The reaction mixture was chromatographed on silica gel column. Elution with methylene dichloride–acetone (10:1, v/v) gave a minor fraction. The expected porphyrin was obtained during a second elution with methylene dichloride–acetone (5:1, v/v) which was crystallized from toluene–cyclohexane (1:1, v/v) (650 mg, 81%) (Found: C, 66.9; H, 5.73; Br, 13.55; N, 9.5. $C_{66}H_{64}Br_2N_8O_4$ requires C, 66.44; H, 5.41; Br, 13.39; N, 9.39%).

α-5,15:β-10,20-*Bis*[2,2′-(6-*Imidazol*-1-*ylundecamethylenedicarbonylamino*)*diphenyl*]*porphyrin* (**54**).—The foregoing compound (**53**) (612 mg, 0.5 mmol) was converted into the bis(imidazole) derivative as described for the similar conversion leading to (**16**). The crude product was submitted to preparative silica gel t.l.c. and developed with methylene dichloride–acetone (1:3, v/v). Three major bands were obtained which were individually isolated. The two fastest moving bands corresponded to the diethylenic and the monoethylenic, monoimidazole basket-handle porphyrins, respectively (**55**) (220 mg, 36%) and (**56**) (228 mg, 20%). The third band which corresponded to the more polar compound was identified as the expected bis-(imidazole) basket-handle porphyrin (**54**) (108 mg, 18%) (Found: C, 69.55; H, 6.25; N, 13.4. $C_{72}H_{70}N_{12}O_4 \cdot 4H_2O$ requires C, 69.77; H, 6.34; N, 13.56%).

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