Synthesis and Molecular Structure of Formylporphyrin. Intrinsic Properties of Porphyrin *a* [1]

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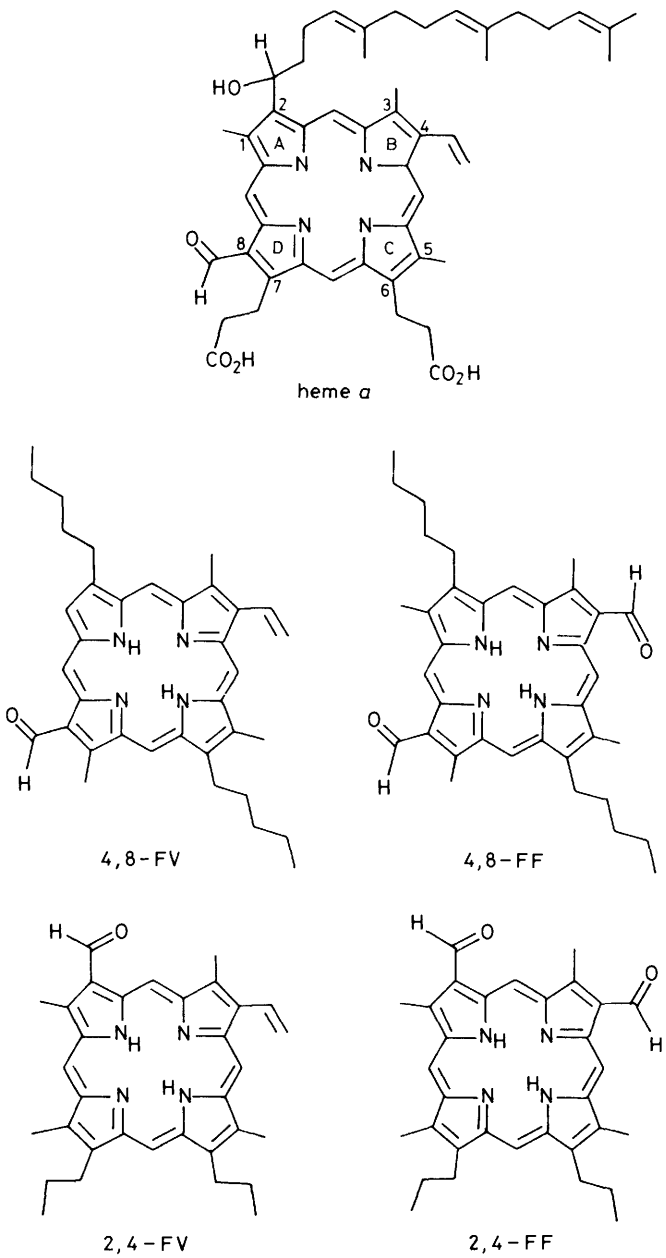
Porphyrins having two electron negative formyl groups or one formyl and one vinyl group substituted on the diagonal pyrrole rings similar to that found in heme *a* have been synthesized and studied. The unique electronic spectra and redox potentials of the 4,8-substituted porphyrins were attributable to the strong π-interactions between the formyl group and the porphyrin ring. A detailed *X*-ray crystal structure of 4,8-diformyl-2,6-di-n-pentyl-1,3,5,7-tetramethylporphin is also reported. The inner nitrogen protons were found localized on the two opposite pyrrole rings not carrying the formyl groups.

Cyctochrome *c* oxidase is the terminal component of the mitochondrial respiratory chain linking electron transport to oxygen reduction. The enzyme is equipped with two heme *a* prosthetic groups and two copper ions. Substantial evidence has shown that dioxygen interacts with only one pair of heme and copper while the other two metal complexes function as electron shuttles; together they provide the four electrons needed for oxygen reduction to water.[2,3] The structure of the heme *a* group is unique in that the porphyrin has a formyl group on pyrrole ring D.[4] In contrast, most known examples of naturally occurring hemes and porphyrins carry substituents at adjacent rings A and B (2,4-positions, *e.g.* chlorocruoroporphyrin or spirographis porphyrin [5]). The diagonal placement of the two electron-withdrawing formyl and vinyl substituents on the porphyrin ring should create a very unique polarization of the heme group. Such properties may be significant for the oxidase functioning. To explore the intrinsic properties of porphyrin *a* as well as to examine the substituent effects with regard to their positions on the ring we have studied a series of formylporphyrins. This paper describes the synthesis and properties of two types of monoformyl-monovinyl- and diformyl-porphyrins. The *X*-ray crystal structure of a diagonally substituted diformylporphyrin is also reported. Other studies using these porphyrin derivatives including oxygen binding,[6] e.s.r. spectra of the iron complexes,[1] m.c.d. spectra, and MO calculations [7] of heme *a* models have been published elsewhere. Deuteroporphyrins bearing diformyl groups at opposite pyrrole rings have been synthesized independently by Clezy and Fookes.[8,9]

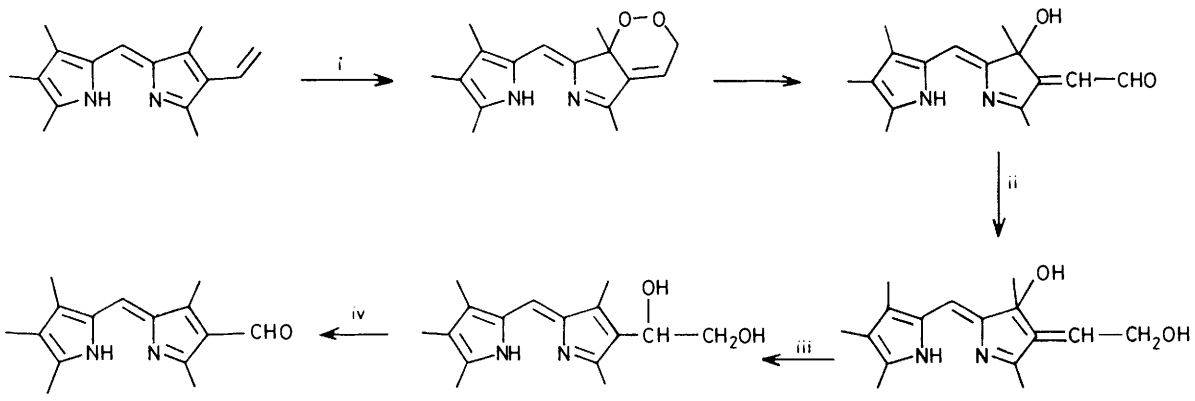
The structures of porphyrin *a* and the synthetic models are shown in Scheme 1. In naming the compounds, we adopted the Fischer school system designating the β-pyrrole positions by the numbers 1—8 starting from the top left corner of ring A.[10] The two electron-withdrawing substituents are therefore numbered as either 2,4- or 4,8-groups in conformity with the porphyrin *a* orientation.



Scheme 1

Results and Discussion

In designing model compounds for porphyrin *a*, it was decided that solubility in nonpolar organic solvents was important and should be maximized. We therefore chose to incorporate long alkyl side chains to the porphyrin. The synthesis of 4,8-FV and 4,8-FF were accomplished by oxidation of divinylporphyrin using the osmium tetraoxide [11] or photo-oxidation methods [12] (Scheme 2). The 4,8-divinylporphyrin was obtained readily from the porphyrin diacetate by LAH reduction, chlorination, followed by elimination using Clezy's NaOH–pyridine procedure.[13] The OsO_4 oxidation was found best when carried out in pyridine using one equivalent of OsO_4 (per porphyrin). The osmate ester was



Scheme 2. *Reagents:* i, O_2, *hν*; ii, $NaBH_4$; iii, H_3O^+; iv, $NaIO_4$

formed within 10 min to yield equal amounts of unchanged material, monoester, and diester. The products were then treated with sulphite solution followed by periodate oxidation. The three porphyrins can be separated easily by chromatography. The formyl-vinylporphyrin can also be prepared in higher yield *via* the hydroxychlorin following Inhoffen's procedure.[12] However, unlike protoporphyrin which exclusively formed the monoadduct with singlet oxygen, the 4,8-divinylporphyrin gave a small amount of the diadduct during photolysis. Judging from the time and effort required, the osmium tetraoxide method is clearly superior.

The 2,4-divinylporphyrin was derived from protoporphyrin. The reduction of the ester groups has previously been carried out with mesoporphyrin.[14] The LAH reaction with mesylate should be monitored carefully; prolonged reaction time could cause insertion of aluminium. The oxidation of the vinyl groups was done conveniently by $KMnO_4$ in refluxing acetone.[15] Curiously, this method did not work well with the 4,8-divinylporphyrin. The resultant 2,4-FV may contain two structural isomers; attempts to separate them using chromatography have not been successful. However, parallel studies using spirographis and isospirographis porphyrin indicated that there is no appreciable difference in absorption spectra or redox potentials between the two isomers.

The visible spectra of porphyrins are strongly dependent on the nature of the peripheral substituents at the ring. It is known that electron negative groups would not only shift the absorption bands to longer wavelength but produce large variations in the pattern of the four visible bands. The presence of one electron negative group, for example, would change the familiar etio-type spectrum (band IV > III > II > I) of all-alkyl porphyrins into a rhodo-type spectrum (III > IV > II > I). The presence of a second electron negative group can either cancel the 'rhodofying' effect of the first group or convert the spectrum into one of the oxorhodo-type (III > II > IV > I) depending on whether the two groups have equal electron-withdrawing strength and whether they occupy the adjacent or the opposite pyrrole rings. These changes can be seen vividly with the spectra of the four synthetic porphyrins (Figures 1A, B). In adjacent substituted porphyrins, the presence of a weak electron negative vinyl group in 2,4-FV does not alter the rhodo spectrum caused by the formyl group whereas in 2,4-FF, the second formyl group cancels the first and restores the spectrum to the etio-type. In oppositely substituted cases, the second group, despite its strength, brings about the oxorhodo spectrum. The spectrum of 4,8-FV is nearly identical to that of porphyrin *a* suggesting that the uniqueness of the latter is caused solely by the presence of the diagonally positioned formyl and vinyl groups and that the synthetic compound should indeed be a good model for the natural chromophore. Spectral data of the synthetic formyl porphyrins and porphyrin *a* are tabulated in Table 1.

Table 1. Absorption spectra of formylporphyrins in CH_2Cl_2

	$\lambda_{max.}$/nm ($10^{-3}\varepsilon_M$)					
Porphyrin	Soret	IV	III	II	I	III/IV
2,4-FV	417	517	557	583	642	
	(160)	(11.1)	(14.8)	(9.6)	(3.0)	1.34
2,4-FF	435	524	560	592	647	
	(142)	(13.5)	(7.8)	(6.6)	(3.6)	0.60
4,8-FV	413	519	562	580	634	
	(170)	(8.0)	(20)	(14)	(1.9)	2.46
4,8-FF	416	526	573	594	646	
	(245)	(6.5)	(23.2)	(17.4)	(5.0)	3.58
Porphyrin *a*	414	518	560	582	645	
						2.36

Substitution effects in porphyrin absorption spectra have been interpreted theoretically by Gouterman,[16] however, specific interactions between formyl groups and the porphin π system have not been extensively studied. It has recently been observed[7] that these formylporphyrins exhibit minus apparent Faraday *A* terms of the Soret band in m.c.d. spectra, in contrast to regular porphyrins which show positive apparent Faraday *A* terms. This inversion of sign cannot be attributable to a pure σ-electron-withdrawing effect (inductive effect) since β-substituted bromoporphyrins do not exhibit minus apparent Faraday *A* terms; it must be derived from the π-interactions (resonance effect). The influence of the formyl group on porphyrin properties can also be observed in redox potentials. The cyclic voltamogram of 4,8-FF is shown in Figure 2 with the four redox couples assigned to the $E_{\frac{1}{2}}$ values of, from left to right, (*P*) dication radical–(P) cation radical; (P) cation radical–(P); (P)–(P) anion radical; and (P) anion radical–(P) dianion radical, respectively. These $E_{\frac{1}{2}}$ value along with those of the other formylporphyrins are compared with meso-, deutero-, and 2,4-dibromodeuteroporphyrin (all dimethyl esters) in Figure 3.

To a first approximation, the polarographic redox span for formation of the monocation and monoanion radicals corresponds to the HOMO – LUMO energy gap which can be related further to the first porphyrin absorption band (neglecting solvation terms).[17] Since the inductive substituent effect is expected to shift the whole stack of π and π* orbital energies up or down without altering the HOMO – LUMO gap while the resonance effect should narrow the gap with increasing delocalization, it is obvious from the electrochemical data

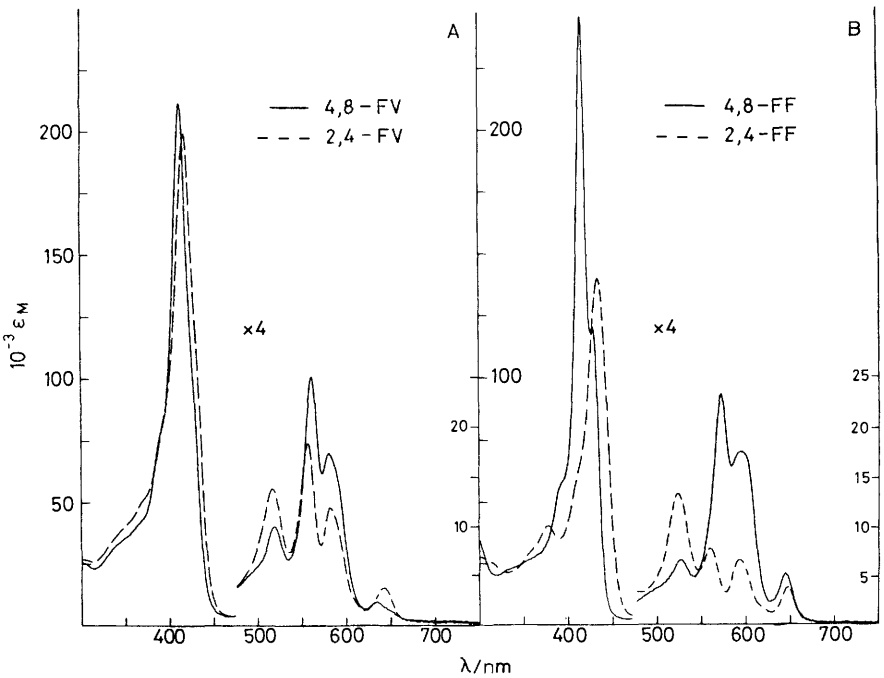


Figure 1. Visible absorption spectra of formylporphyrins, in CH_2Cl_2. A, Monoformyl, 4,8-FV and 2,4-FV; B, diformyl 4,8-FF and 2,4-FF

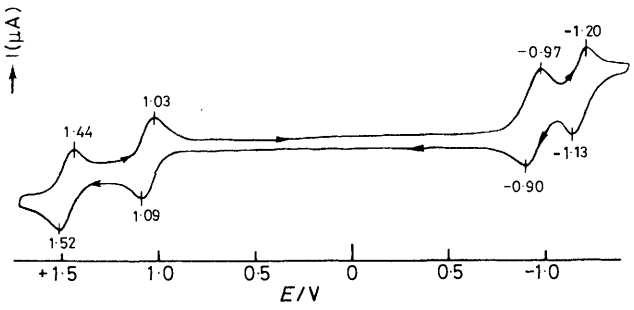


Figure 2. Cyclic voltamogram of (from left) 2^+–1^+, 1^+–0, 0–1 , and 1^-–2^- processes of 4,8-FF, recorded at 100 mV s^{-1} in CH_2Cl_2, 0.1M-Bu_4NClO_4 supporting electrolyte

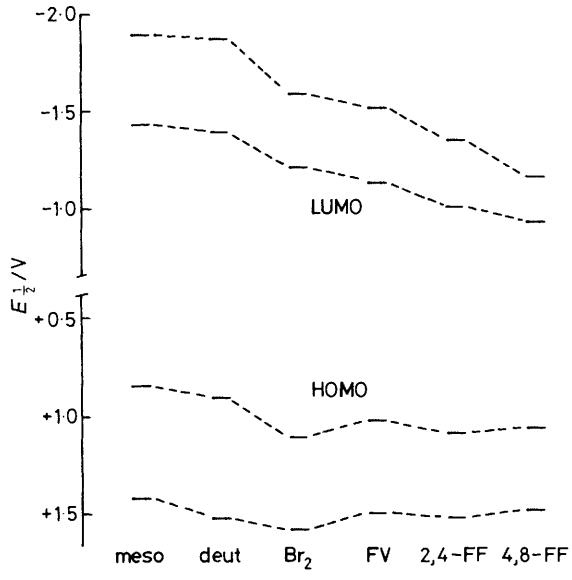


Figure 3. Half-wave redox potentials of mesoporphyrin IX dimethyl ester (meso), deuteroporphyrin IX dimethyl ester (deut), 2,4-dibromodeuteroporphyrin IX dimethyl ester (Br_2), 2,4-FV and 4,8-FV (FV), 2,4-FF, and 4,8-FF; measured in CH_2Cl_2 with 0.1M-Bu_4NClO_4

that the formyl groups have strong π-interactions with porphyrin. We believe that the formyl lowest vacant π* orbital resides very close to the lowest porphyrin π* orbitals and the interaction between them would split the degeneracy of the porphyrin excited states, and lower the energies. An intriguing point from the redox data is that the polarographic span is also sensitive to the substitution pattern at the porphyrin ring, *e.g.* 4,8-FF is not only easier to oxidize but easier to reduce than 2,4-FF, showing the importance of the symmetry element in orbital interactions. A relevant question can be raised as to whether there should be a preferred π electron delocalization pathway in such diagonally substituted formylporphyrins possessing C_{2h} symmetry. The two most plausible valence tautomers of a porphyrin core shown in Figure 4, each with 18π electrons, differ from one another in the relative positions of the protons on nitrogen. While these two forms are degenerate under normal circumstances, it is expected that the introduction of two formyl groups in the opposite pyrrole rings may lift this degeneracy and lock the delocalization pathway in one particular manner. An *X*-ray structure determination of a 4,8-FF single crystal was carried out to

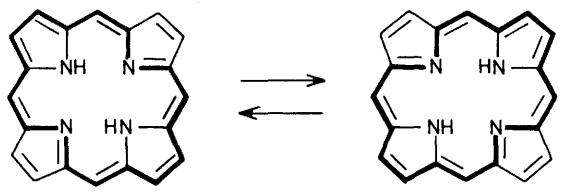


Figure 4. Tautomeric forms of porphin

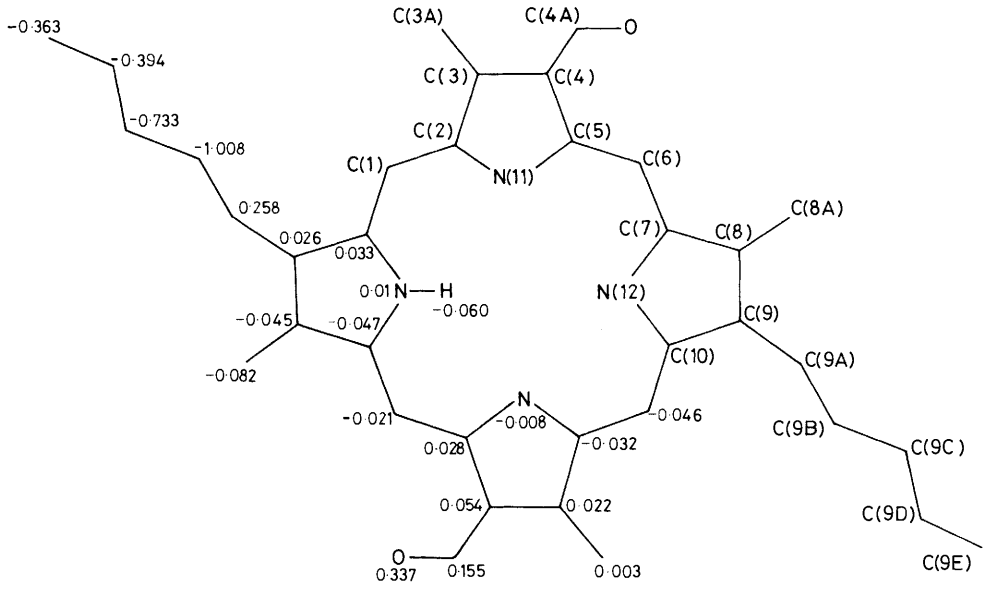


Figure 5. Numbering scheme of 4,8-FF and deviations (in Å) of atoms from the best least squares plane

Table 2. Final atomic parameters of 4,8-FF *

Atom	x	y	z	B_1	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	0.183 1(4)	0.610 1(8)	0.010 0(2)	4.4(3)	4.5(3)	4.2(3)	1.5(3)	−0.9(2)	−0.2(3)
O	0.381 0(3)	1.152 9(7)	0.239 5(2)	6.0(2)	7.1(3)	6.7(2)	1.0(2)	−2.2(2)	−1.8(2)
C(2)	0.205 2(4)	0.756 7(8)	0.060 3(3)	2.9(2)	4.0(3)	4.4(3)	0.9(3)	−0.1(2)	0.5(3)
C(3)	0.302 6(4)	0.759 0(8)	0.114 3(3)	3.4(3)	4.1(3)	4.7(3)	1.2(3)	−0.8(2)	0.6(3)
C(3A)	0.388 6(4)	0.594 9(9)	0.123 8(3)	3.9(2)	4.7(3)	8.1(4)	1.3(3)	−1.7(3)	−0.1(3)
C(4)	0.296 6(4)	0.926 6(8)	0.152 2(2)	3.0(2)	3.5(3)	4.2(3)	0.5(2)	−0.5(2)	0.2(2)
C(4A)	0.378 3(5)	0.994 1(10)	0.210 4(3)	4.1(3)	6.4(4)	5.4(3)	0.8(3)	−1.3(3)	0.2(3)
C(5)	0.194 4(4)	1.029 3(8)	0.120 5(2)	3.4(2)	3.4(3)	3.9(3)	0.4(2)	0.1(2)	0.1(2)
C(6)	0.153 7(4)	1.205 9(9)	0.146 2(2)	3.1(2)	4.4(3)	3.8(2)	−0.0(2)	−0.3(2)	0.1(2)
C(7)	0.057 7(4)	1.312 4(8)	0.119 3(2)	3.7(3)	3.7(3)	3.6(3)	0.1(2)	0.0(2)	0.3(2)
C(8)	0.018 5(4)	1.494 3(8)	0.143 5(3)	4.4(3)	3.3(3)	4.3(3)	0.8(2)	0.3(2)	−0.5(2)
C(8A)	0.071 7(4)	1.607 6(8)	0.207 3(2)	6.0(3)	4.6(3)	4.5(2)	0.8(3)	−0.3(2)	−1.1(3)
C(9)	−0.074 8(4)	1.550 9(9)	0.097 7(3)	5.3(3)	4.4(4)	5.5(3)	1.0(3)	−0.0(3)	−1.2(3)
C(9A)	−0.138 7(5)	1.754 3(10)	0.095 2(3)	5.1(3)	6.7(4)	6.2(3)	−0.5(3)	0.6(3)	−1.7(3)
C(9B)	−0.232 6(6)	1.735 3(12)	0.131 5(4)	9.0(5)	9.2(6)	10.2(5)	0.8(5)	3.1(4)	0.8(5)
C(9C)	−0.290 4(7)	1.957 8(16)	0.134 5(4)	12.4(7)	14.0(9)	11.7(7)	6.6(6)	−1.6(5)	0.5(6)
C(9D)	−0.359 8(7)	1.994 0(15)	0.076 9(5)	9.9(6)	12.0(8)	15.5(8)	−0.2(6)	1.1(6)	0.5(7)
C(9E)	−0.425 8(5)	2.198 2(11)	0.088 8(4)	8.2(5)	7.2(5)	20.8(8)	4.2(4)	3.4(5)	2.8(6)
C(10)	0.096 3(4)	0.600 9(8)	−0.044 8(3)	4.1(3)	3.6(3)	4.8(3)	0.8(3)	0.1(2)	−0.7(3)
N(11)	0.141 8(3)	0.924 8(6)	0.064 8(2)	3.2(2)	3.4(2)	4.0(2)	0.5(2)	−0.4(2)	−0.3(2)
N(12)	−0.013 4(3)	1.258 5(6)	0.060 4(2)	4.3(2)	2.8(2)	4.2(2)	0.6(2)	−0.5(2)	−0.4(2)

* Anisotropic temperature factors are of the form $-[\Sigma_i\Sigma_j(a^*_i a^*_j h_i h_j B_{ij})]/4$ where a^*_i is a reciprocal cell edge and h_i is a reciprocal lattice point index. Standard deviations in parentheses.

seek out special structural features of such a porphyrin and to locate the positions of the nitrogen protons.

Structure Determination.—The crystal structure of 4,8-FF was solved by direct methods using the program MULTAN. The observed reflections with $|F| > 3\sigma(|F|)$ were used in the ensuing refinement. Three cycles of full matrix least squares refinement with isotropic thermal parameters gave $R = 0.14$ ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). Two more cycles with anisotropic thermal parameters for 17 of the atoms reduced R to 0.12. A difference electron density map at this stage revealed residual density around the last three carbon atoms in the pentyl side chain (Figure 5). Slightly different positions for these atoms were obtained from an electron density map and several more cycles of isotropic and anisotropic refinement only lowered R to 0.11. The bond distances of C(9B)–C(9C) 1.69, C(9C)–C(9D) 1.25, and C(9D)–C(9E) 1.66 Å, the residual difference density around these atoms, and their inordinately large thermal parameters suggested that they were probably disordered. Several models for these with partially occupied atoms were attempted but all failed to refine satisfactorily. The positions of 11 hydrogen atoms located from a difference electron density map were then included in the refinement. Two additional cycles with anisotropic parameters for non-hydrogen atoms gave R 0.097. The remaining hydrogen atoms were included at theoretical positions. Several more cycles of refinement varying non-hydrogen atom parameters with hydrogens at theoretical positions calculated from the previous cycle resulted in an R value of 0.072. The weighting scheme used in the least

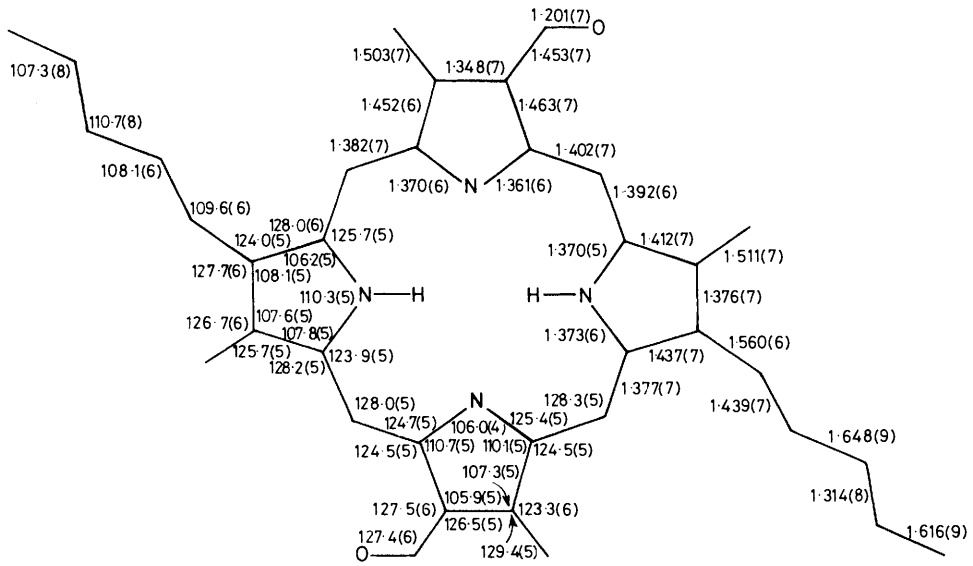


Figure 6. Interatomic bond distances (in Å) and angles (°) of 4,8-FF

Table 3. Final hydrogen atom parameters

Atom	*x*	*y*	*z*	B_{iso} (Å^2)
H(1)	0.2360	0.4866	0.0173	5.5
H(3A1)	0.3521	0.4648	0.1331	6.3
H(3A2)	0.4231	0.5810	0.0807	6.3
H(3A3)	0.4482	0.6269	0.1640	6.3
H(4A1)	0.4378	0.9080	0.2236	6.7
H(6)	0.2015	1.2662	0.1829	4.7
H(8A1)	0.0735	1.5212	0.2494	6.7
H(8A2)	0.1499	1.6462	0.2024	6.7
H(8A3)	0.0273	1.7313	0.2127	6.7
H(9A1)	−0.1660	1.7936	0.0460	7.1
H(9A2)	−0.0874	1.8613	0.1183	7.1
H(9B1)	−0.2059	1.6841	0.1799	11.8
H(9B2)	−0.2872	1.6374	0.1064	11.8
H(9C1)	−0.2317	2.0654	0.1400	15.0
H(9C2)	−0.3328	1.9658	0.1747	15.0
H(9D1)	−0.4124	1.8746	0.0688	15.8
H(9D2)	−0.3162	2.0019	0.0380	15.8
H(9E1)	−0.4669	2.1821	0.1281	19.7
H(9E2)	−0.3707	2.3094	0.0973	19.7
H(9E3)	−0.4795	2.2259	0.0448	19.7
H(12)	−0.0020	1.1400	0.0400	4.7

squares analysis was $w = 1/\sigma^2(|F|)$. At this point, the bond distances between the last three carbon atoms of the pentyl side chain were restrained to be 1.54 ± 0.02 Å and refinement was terminated when the individual parameter shifts of all the atoms were on the average of 0.05 of their standard deviations. The final *R* value was 0.069.

The final atomic co-ordinates and anisotropic thermal parameters of 4,8-FF are given in Table 2 as are the co-ordinates of hydrogen atoms and their isotropic temperature factors (Table 3). The numbering system used for the hydrogen atoms is after the carbon or nitrogen atom to which they are bonded (Figure 5). Structure factors are in Supplementary Publication No. SUP 23507 (14 pp.).*

The atomic positions of the porphin nucleus of the 4,8-FF molecule were fitted to a least squares plane. The deviations of the atoms from this plane are given in Figure 5. The individual pyrrole rings are planar within error (±0.005 Å). The interatomic distances and bond angles of 4,8-FF are given in Figure 6 along with the errors in these quantities based on the standard deviations of the atomic co-ordinates from the least squares refinement.

The structure of the porphin core of 4,8-FF is very similar to other free base porphyrins [18–20] and resembles remarkably the average structure of the porphin skeleton proposed by Codding and Tulinsky.[18] The differences between the two independent pyrrole rings of 4,8-FF are small but like those of the other free base porphyrins, they are significant. In addition, the hydrogen atoms of the central core of 4,8-FF are localized on the same opposing pyrrole rings as other free base porphyrins.

The porphyrin core is practically planar (Figure 5) but shows deviations ranging up to 0.054 Å. The standard deviation of the nucleus from planarity is 0.03 Å with adjacent pyrrole rings tilted by *ca.* 4.1° with respect to each other.

The transannular separation of the imino hydrogen atoms is 2.44 Å in 4,8-FF, slightly longer than the 2.36 Å found in octaethylporphyrin (OEP), but comparing very well with the corresponding distance in porphin (2.45 Å). The imino hydrogen atoms of 4,8-FF are localized on the pyrrole with the pentyl substituent, probably because the presence of the electron-withdrawing formyl group in the other pyrrole renders its nitrogen electrophilic. The deviations from the planarity of OEP indicate that the nitrogen atoms of the pyrrole rings alternate above and below the plane, while in porphin the distribution of the deviations from planarity approximate C_{2v} symmetry, with the mirror planes passing through the methine carbons. In 4,8-FF the nitrogen atoms of the core are practically in the plane of the molecule but the pyrroles are tilted in the methine-C_α direction in such a way that two adjacent methine carbons are down while the centrosymmetrically related ones are tilted upward. In these three free base porphyrins the angles that the pyrrole rings form with the least squares plane of the molecule are all small, ranging 2—4°, and are probably the result of crystal packing arrangement.

The presence of different substituents on the pyrrole rings in 4,8-FF does not seem to drastically influence the average

* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1981, Index Issue.

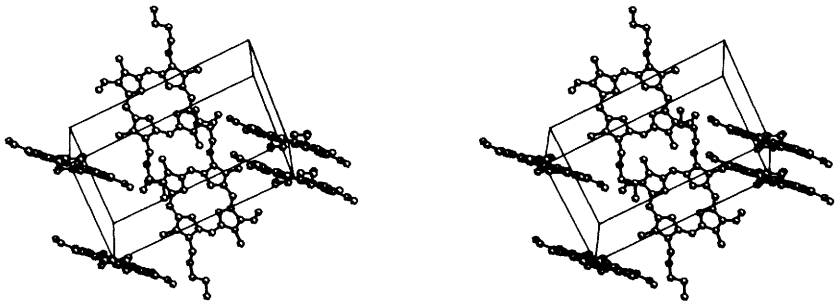


Figure 7. Stereodiagram of crystal packing of 4,8-FF

bond distances and angles in the porphyrin macrocycle. However, the formyl group has a significant effect on bond distances and angles at or near the point of substitution (Figure 6). The C(3)–C(4)–C(5) angle of 105.9 (5)° is *ca.* 1° less than expected (the corresponding angle in the average structure of porphin is 107.1°) while the C(3A)–C(3)–C(4) and C(2)–C(3)–C(3A) angles of 129.4 (5) and 123.3 (6)°, respectively, suggest a steric repulsion of the methyl group located adjacent to the formyl moiety. The carbonyl carbon and oxygen atoms of the formyl are 0.153 and 0.337 Å out of the plane of the porphyrin respectively, so that the formyl group is rotated by only 4.8° out of the plane of the pyrrole to which it is attached. The C(4)–O bond length of 1.201(7) Å is shorter than most C–O double bonds found in organic crystals [C(7)–O 1.216(2),[21] C(3)–O(3) 1.229(7),[22] C(3)–O(3) 1.222(4) Å [23]]. The C(4)–C(4A) length of 1.453(7) Å is very short but compares well with the corresponding values found in substituted pyrrole molecules where there is strong evidence for delocalization of the C–O double bond.[24–26] Since delocalization of the carbonyl electrons in 4,8-FF is through the entire π system of the porphyrin ring, the distortion of the molecule should be minimal and generally within experimental error.

The large values of the C(6)–C(7)–C(8) and C(9)–C(10)–C(1)′ angles of 128.2(5) and 128.0(6)°, respectively, are probably the result of packing effects arising from the presence of the pentyl substituent at the C_β position (Figure 7). Average values for the corresponding angles are 126.6(2)° in porphin and 127.3(1)° in OEP. The pentyl side chain is in an extended conformation and produces some fairly close intermolecular contracts such as O–C(9B), 3.362 (8) Å, and C(3A)–C(9E), 3.610(8) Å.

4,8-FF stacks in layers along the *b* axis in the unit cell and when the arrangement is viewed perpendicular to the molecular planes, one molecule is displaced in the methine–methine direction with respect to the molecule below (Figure 7). The distance between the least squares plane of the adjacent porphyrin rings is 3.42(3) Å corresponding to a normal van der Waals contact.

Conclusions.—Excellent evidence has been obtained that the formyl group in porphyrin *a*-like molecules can strongly perturb the properties of the porphin core by means of π-interactions especially in the vicinity of the substitution. The formyl substituent also renders the porphyrin easier to reduce but harder to oxidize. This shift in redox potentials is also seen in heme *a*, whose $E_{\frac{1}{2}}$ for the Fe^{III}–Fe^{II} couple is more positive than protoheme.[1] Therefore, intrinsically heme *a* may not be the best catalyst for dioxygen reduction since it binds oxygen less well and auto-oxidizes more slowly than protoheme.[6] Nevertheless, the presence of the formyl group would offer an opportunity for modulation of the physical and chemical properties of the heme system by interactions between this dominant substituent and nearby protein residues. For example, a Schiff's base linkage between the formyl group and an amino-group would be attractive in that both formations of the linkage and its subsequent protonation may be subject to functional control.

The present study further showed that the overall molecular structure of the diagonally substituted 4,8-FF does not differ significantly from other free base alkylporphyrins. The inner nitrogen protons are localized on the two opposite pyrrole rings which do not carry the electron negative formyl groups, indicating that the inductive substituent effect is also important in this system.

Experimental

Spectra and Redox Measurements.—Porphyrin solutions were made in anhydrous dichloromethane (distilled from CaH_2). Visible spectra were recorded on a Cary 219 spectrophotometer. Cyclic voltammetry was performed using a Bioanalytical Systems CV-1A unit in a specially constructed glass cell which has two platinum bead electrodes sealed through the cell wall and a total volume of 0.2 ml. All measurements were carried out in 0.1M-tetra-n-butylammonium perchlorate–dichloromethane solution under argon, scan rate 100 mV s^{-1}.

Crystallography.—Single crystals of 4,8-FF were grown by slow evaporation of a toluene solution. Pertinent crystal and associated data are summarized in Table 4. The intensities of the reflections were corrected for background, Lorentz, and polarization effects, but not for absorption, in converting them into structure amplitudes. The standard deviations of the latter were approximated according to Wei and Ward [27] using an instrumental instability factor of 0.02.

4,8-*Divinyl*-2,6-*di*-*n*-*pentyl*-1,3,5,7-*tetramethylporphin.*—4,8-Bismethoxycarbonylmethyl-2,6-di-n-pentyl-1,3,5,7-tetramethylporphin [28] (2.5 g) was dissolved in hot anhydrous tetrahydrofuran (THF) (800 ml). The solution was cooled to room temperature and a small amount of lithium aluminium hydride (LAH) (1 g) in THF (10 ml) was added dropwise with the aid of a pipette. The progress of the reduction was monitored by t.l.c. (silica gel–CH_2Cl_2) until no diester was detected. Water (100 ml) and acetic acid (10 ml) were carefully added to the mixture, precipitated porphyrin was redissolved, and the solvent was removed until *ca.* 200 ml were left. The bishydroxymethylporphyrin crystallized as needles and was collected by filtration (yield 90—95%). The diol was dried and dissolved in DMF (150 ml)–benzoyl chloride (20 ml). The solution was heated on a steam-bath for 30 min and water (500 ml) plus triethylamine (50 ml) were then added. The precipitates of essentially pure porphyrin dichloride were collected by filtration and washed with water. T.l.c. (silica

Table 4. Crystal and intensity collection data

Crystal size	0.12 × 0.12 × 0.96 mm
λ	graphite monochromated Mo
a (Å)	12.120(6)
b (Å)	6.677(3)
c (Å)	19.490(10)
β (°)	99.1(1)
Space group	$P2_1/c$
Molecules/cell	2 (implying centrosymmetric molecules)
Data collection	θ/2θ scan
Range (°)	$2\theta < 50$
Number of reflections	2 766
Number observed with $\|F\| > 3\sigma(\|F\|)$	1 219
μ (cm^{-1})	0.410

gel–CH_2Cl_2) indicated that all diol was converted to the fast moving dichloride, δ($CDCl_3$) 3.85(t) and 4.24(t) (CH_2CH_2Cl). The dichloride was dissolved in pyridine (500 ml) and the solution was heated to reflux. NaOH (5 g) in water (100 ml) was added and heating was continued for 1.5 h. Water (500 ml) and acetic acid (10 ml) were added and the mixture was concentrated. The solid divinyl compound was filtered and recrystallized from the minimum amounts of CH_2Cl_2–methanol (1.8 g); δ(250 MHz; $CDCl_3$) 0.95 (6 H, t), 1.53 (4 H, quin), 1.70 (4 H, quin), 2.26 (4 H, quin), and 4.05 (4 H, t) (pentyl), 3.60 (6 H, s, ring Me), 3.64 (6 H, s, ring Me), 6.2 (4 H, m, vinyl), 8.3 (2 H, m, vinyl), 10.02 (2 H, s, meso H), 10.15 (2 H, s, meso H), and −3.8br (2 H, NH); $\lambda_{max.}$ (CH_2Cl_2) 408, 509, 546, 577, and 633 nm; *m/e* 558 (M^+, $C_{38}H_{46}N_4$).

4-Formyl-8-vinyl- and 4,8-Diformyl-2,6-di-n-pentyl-1,3,5,7-tetramethylporphin.—To a solution of the divinylporphyrin (560 mg, 1 mM) in pyridine (100 ml) was added a solution of osmium tetraoxide (520 mg, 2 mM) in pyridine (10 ml). The mixture was stirred for 20 min at room temperature before an aqueous sodium sulphite solution (15%, 30 ml) was added. The mixture was heated on a steam-bath for 30 min, the cooled solution was then neutralized with dilute HCl. The porphyrin glycol, after isolation by filtration, was redissolved in pyridine (80 ml). Aqueous sodium periodate (5%, 30 ml) was added and the mixture heated on a steam-bath for 30 min, cooled, and then neutralized with dilute HCl. The precipitated porphyrins were collected by filtration and subsequently purified by column chromatography on silica gel. The unchanged divinylporphyrin was eluted first using CH_2Cl_2–20% hexane. The monovinyl-monoformylporphyrin was eluted with pure CH_2Cl_2 and the diformylporphyrin eluted last using CH_2Cl_2–5% MeOH. Yields were divinylporphyrin (70 mg), 4,8-FV (70 mg), and 4,8-FF (250 mg). 4,8-FV had δ($CDCl_3$) 0.93 (6 H, t), 1.5 (8 H, m), 2.1 (4 H, m), 3.68 (2 H, t), and 3.82 (2 H, t) (pentyl), 3.42 (3 H, 2), 3.46 (3 H, s), 3.50 (3 H, s), and 3.55 (3 H, s) (ring Me), 6.2 (2 H, m, vinyl), 8.15 (1 H, m, vinyl), and 10.48 (1 H, s, CHO), 9.60 (1 H, s, meso H), 9.85 (1 H, s, meso H), 10.38 (1 H, s, meso H), 9.40 (1 H, s, meso H), and −1.8br (2 H, NH), $\lambda_{max.}$ (CH_2Cl_2) 413 (ε 170 000), 519 (8 000), 562 (20 000), 580 (14 000), and 634 nm (1 900); *m/e* 560 (M^+, $C_{37}H_{44}N_4O$). 4,8-FF had δ($CDCl_3$) 0.93 (6 H, t), 1.5 (8 H, m), 2.1 (4 H, q), and 3.85 (4 H, t) (all pentyl), 3.52 (3 H, s, ring Me), 10.47 (2 H, s, CHO), 9.48 (2 H, s, meso H), 10.34 (2 H, s, meso), and 1.4br (2 H); $\lambda_{max.}$ (CH_2Cl_2) 416 (ε 245 000), 526 (6 500), 573 (23 200), 594 (17 400), and 646 nm (5 000); *m/e* 562 (M^+, $C_{36}H_{42}N_4O_2$).

2,4-Divinyl-6,7-dipropyl-1,3,5,8-tetramethylporphin.—Protoporphyrin IX dimethyl ester (2 g) was dissolved in anhydrous THF (800 ml) and reduced with LAH in the manner described above to yield the bishydroxypropylporphyrin. The diol was dried and dissolved in hot pyridine (300 ml). To this solution, after it was cooled in an ice-bath, methanesulphonyl chloride (4 ml) was added dropwise followed by triethylamine (5 ml). The mixture was stirred at 0 °C for 30 min and then quenched with ice–water (1 000 ml) and HCl (10 ml). The porphyrin mesylate was separated by filtration, washed with water and a small amount of ether, and then dried. T.l.c. (silica gel–CH_2Cl_2) indicated that the conversion is 100%. The dimesylate (*ca.* 1.5 g) was dissolved in hot anhydrous THF (1 500 ml), the solution was cooled to room temperature, and LAH (0.5 g) was added. The reaction was very slow (monitored by t.l.c.). After 5 h of stirring at room temperature, the reaction was quenched by careful addition of water (10 ml). The solvent was evaporated and the residue extracted with CH_2Cl_2 (300 ml). The organic solution was concentrated and chromatographed on silica gel using CH_2Cl_2–benzene (3 : 1) as eluant. The desired alkylporphyrin (0.8 g) was eluted first, followed by small amounts of monomesylate as well as some unchanged dimesylate. The alkylporphyrin had δ($CDCl_3$) 1.26 (6 H, t), 2.31 (4 H, q), and 4.02 (4 H, q) (propyl), 3.58 (6 H, d) and 3.68 (6 H, d) (ring Me), 6.25 (4 H, m) and 7.28 (2 H, m) (vinyl), 9.96 (1 H, s), 10.02 (1 H, s), 10.12 (1 H, s), and 10.16 (1 H, s) (all meso H), and −3.7br (2 H, NH); $\lambda_{max.}$ (CH_2Cl_2) 407, 505, 541, 575, and 630 nm; *m/e* 502 (M^+, $C_{34}H_{38}N_4$).

2-Formyl-4-vinyl- (and 2-Vinyl-4-formyl)- and 2,4-Diformyl-6,7-dipropyl-1,3,5,8-tetramethylporphin.—The divinylporphyrin above (502 mg, 1 mM) was dissolved in acetone (1 500 ml) and refluxed on a steam-bath. An acetone solution containing finely powdered $KMnO_4$ (300 mg) was added dropwise during 30 min. Reflux was continued for another 15 min. After the reaction, the solution was filtered and concentrated to *ca.* 200 ml. Water (500 ml) and CH_2Cl_2 (500 ml) was added and the extract was removed and evaporated to give a mixture of the crude products. The porphyrins were purified on a silica gel column: the unchanged divinylporphyrin was eluted first with 10% hexane in CH_2Cl_2, followed by the 2,4-FV isomers (120 mg) (CH_2Cl_2 alone), and the diformylporphyrin (70 mg) was eluted last with 10% methanol in CH_2Cl_2.

2,4-FV (2 isomers) had δ($CDCl_3$) 1.26 (6 H, m), 2.25 (4 H, m), and 3.9 (4 H, m) (propyl), 3.46 (3 H, s) and 3.6 (9 H, m) (ring Me), 6.3 (2 H, m) and 8.06 (1 H, m) (vinyl), 11.2 (1 H, s, CHO), 10.5 (1 H, d), 9.83 (1 H, s), 9.70 (1 H, s), and (meso H) 9.56 (1 H, s), and −4br (2 H, NH); $\lambda_{max.}$ (CH_2Cl_2) 417 (ε 160 000), 517 (11 100), 557 (14 800), 583 (9 600), and 642 nm (3 000); *m/e* 504 (M^+, $C_{33}H_{36}N_4O$). 2,4-FF had δ($CDCl_3$) 1.26 (6 H, m), 2.3 (4 H, m), and 3.9 (4 H, m) (propyl), 3.5 (9 H, m) and 3.22 (3 H, s) (ring Me), 10.84 (1 H, s, CHO), 11.0 (1 H, s, CHO), 9.21 (1 H, s), 9.26 (1 H, s), 9.5 (1 H, s), and 9.8 (1 H, s) (meso H), and −4br (2 H, NH); $\nu_{max.}$ (CH_2-

Cl_2) 435 (ε 142 000), 524 (13 500), 560 (7 800), 592 (6 600), and 647 nm (3 600); *m/e* 506 (M^+, $C_{32}H_{34}N_4O_2$).

4,8-*FV by Photolysis of Divinylporphyrin.*—A solution of 4,8-divinyl-2,6-di-n-pentyl-1,3,5,7-tetramethylporphin (250 mg) in CH_2Cl_2 (400 ml) was photolysed in a water-cooled photochemical reaction vessel with a tungsten–halogen lamp (250 W) while it was aerated. The progress of the reaction was monitored by t.l.c. The photolysis was discontinued when *ca.* 70% of the porphyrin had converted into the green chlorins (*ca.* 40 min). The reaction mixture was then chromatographed on silica gel. The unchanged porphyrin was eluted first by 20% hexane in CH_2Cl_2, the major green band of the mono-adduct was eluted with CH_2Cl_2. Two additional green bands (the two isomeric bis-adducts) were obtained when eluted with 10% MeOH in CH_2Cl_2. The major chlorin (120 mg) exhibits δ($CDCl_3$) 0.96 (6 H, t), 1.5 (8 H, m), 1.98 (2 H, q), 2.12 (2 H, q), and 3.7 (4 H, m) (pentyl), 1.60 (3 H, s), 3.22 (3 H, s), 3.45 (3 H, s), and 3.51 (3 H, s) (ring Me), 2.9 (1 H, s, OH), 6.18 (2 H, m) and 8.1 (1 H, m) (vinyl), 6.8 (1 H, d) and 10.2 (=CHCHO), 8.17 (1 H, s), 8.56 (1 H, s), 9.60 (1 H, s), and 9.72 (1 H, s) (meso H), and −3.5 (1 H, d, NH); $\lambda_{max.}$ (CH_2Cl_2) 392, 428, 575, 601, and 660 nm. The two bis-adducts (20 mg each) have identical $\lambda_{max.}$ (CH_2Cl_2), 425, 448, 594, 662, and 773 nm, typical of a bacteriochlorin.

The chlorin (100 mg) was dissolved in CH_2Cl_2 (100 ml). Sodium borohydride (50 mg) in dry methanol (2 ml) was added and after 5 min dilute acetic acid (5 ml) in water (100 ml) was added. The CH_2Cl_2 layer was separated and evaporated to dryness. The resultant diol was dissolved in pyridine and oxidized with a solution of sodium periodate in the same manner described before. Purification of the porphyrin by chromatography and crystallization from MeOH–CH_2Cl_2 yielded 4,8-FV (45 mg) which exhibits visible and n.m.r. spectra identical to that obtained by the osmium tetraoxide oxidation.

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Experimental

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