

Structure of the Free-Base "Capped" Porphyrin, 5,10,15,20-[Pyrromellitoyl(tetrakis-*o*-oxyethoxyphenyl)]porphyrin

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Abstract: The structure of the free-base, "capped" porphyrin 5,10,15,20-[pyrromellitoyl(tetrakis-*o*-oxyethoxyphenyl)]porphyrin (H₂Cap) has been determined by three-dimensional, single-crystal, X-ray diffraction methods using diffractometer data collected with Mo K α radiation. The material crystallizes as the pentachloroform, monomethanol solvate, H₂Cap·5CHCl₃·CH₃OH, in space group $C_{2h}^5 - P2_1/n$ with four formula units in a cell of dimensions (at -150° C) $a = 19.947$ (6) Å, $b = 16.569$ (5) Å, $c = 22.602$ (7) Å, $\beta = 104.57$ (1)°, $V = 7230$ Å³. The structure was described by 495 variable parameters and at convergence the values for R and R_w (on F , 8552 data having $F_o^2 > 3\sigma(F_o^2)$) were 0.073 and 0.094. In contrast to most other free-base porphyrins, the 24-atom porphyrin skeleton is markedly nonplanar (mean displacement from the least-squares plane 0.135 Å; maximum displacement 0.354 Å), but conforms closely to idealized D_{2d} symmetry. The considerable steric strain involved in attaching a pyrromellitoyl(tetrakisoxoethoxy) "cap" to the ortho positions of the tetraphenylporphyrin core is released most obviously through buckling of the porphyrin skeleton. The transannular separation between aminopyrrole nitrogen atoms is 4.182 (6) Å; between imino nitrogen atoms it is 4.038 (5) Å. The separations between the centroids of the phenyl "cap" and respectively those of the four pyrrole nitrogen atoms and the 24-atom porphyrin skeleton are 3.86 and 3.96 Å—results of considerable interest in relation to the ligand binding properties of iron(II) and cobalt(II) derivatives of H₂Cap.

Introduction

Model systems have been widely studied in attempts to understand better the structure-function relationships of oxygen-binding hemoproteins, such as myoglobin and hemoglobin.¹⁻⁶ Of the well-characterized model systems used, only the iron(II) derivatives of the "picket-fence" porphyrin,³ H₂TpivPP,⁷ and of the "capped" porphyrin⁸⁻¹⁰ (see Figure 1) exhibit reversible uptake of dioxygen to give dioxygen complexes stable at ambient temperatures.¹¹ Both these porphyrins, derivatives of 5,10,15,20-tetraphenylporphyrin (H₂TPP), have bulky ortho substituents which create a protected site, analogous to that provided by the protein, where small molecules such as O₂, CO, and NO may bind to the metal center. The "capped" porphyrin system possesses several inherent advantages over the much more extensively studied "picket-fence" porphyrin, chief of which is that binding of a second axial base, such as 1-methylimidazole, the usual synthetic analogue for histidine of the hemoglobins, is either prevented completely in the case of Fe(Cap)(1-MeIm) or severely hindered in the case of Fe(HmCap)(1-MeIm).¹⁰ Whereas the stereochemistries of a number of "picket-fence" porphyrin derivatives have been defined,^{1,12-14} no precise structural data have yet been obtained for the "capped" porphyrin.

The cap of the "capped" porphyrin is conformationally more rigid in contrast to the rather flexible "pickets" of the "picket-fence" porphyrin—crystallographically a highly desirable feature. Furthermore the 24-atom porphyrinato skeleton generally is essentially planar (mean displacement typically less than 0.03 Å) for the conformationally flexible porphyrins, not only in the free-base form (for example, H₂TPrP,¹⁵ porphine,¹⁶ H₂OEP,¹⁷ H₂MPIXDME,¹⁸ and H₂PPIXDME¹⁹) but also in their metallo derivatives.¹ Some notable exceptions are Ni(OEP) in the tetragonal form,²⁰ where marked ruffling of the porphyrinato skeleton is associated with unusually short M-N_{porph} bond lengths, H₂TPP in both the triclinic^{21a} and tetragonal forms,^{21b} and Fe(TPP)-(2-MeIm), where unusually large doming of the porphyrinato skeleton is attributed to crystal packing forces.¹ Other metallo derivatives of H₂TPP have essentially planar porphyrinato cores. These porphyrins all lack substituents which could supply internal constraints to force the porphyrin to adopt a nonplanar configuration seen in the highly substituted meso-substituted octaethylporphyrins.²²

For deoxyhemoglobin it has been calculated²³ that the protein envelope enforces a nonplanar conformation upon the heme group. Consequently, studies of the ligand affinities of the "capped" porphyrin model system, where internal constraints may prevent a planar porphyrin geometry, coupled with comparison of such a system with the less constrained model systems based upon TPP or TpivPP, may shed light on the interaction of hemoglobin with small molecules. The first base binding and the dioxygen binding properties of iron(II) and cobalt(II) derivatives of "capped" porphyrins¹⁰ are very different from those of analogous complexes of TPP and TpivPP.^{2,3} To understand better these differences provides a compelling reason for determining the crystal and molecular structure of the free-base porphyrin, H₂Cap·5CHCl₃·CH₃OH, the first "capped" porphyrin compound that we have thus far been able to crystallize.

Experimental Section

Preparation of H₂Cap·5CHCl₃·CH₃OH. The free-base porphyrin in powder form was kindly supplied by Professor J. E. Baldwin. Over the period of 1 year very large crystals were obtained by solvent diffusion at 5° C of methanol into a chloroform solution of H₂Cap. On the basis of density measurements (see below) and thermogravimetric analysis for loss of solvent the formulation of these crystals is H₂Cap·5CHCl₃·CH₃OH.

Crystallographic Study of H₂Cap·5CHCl₃·CH₃OH. Solvate loss occurs rapidly when crystals are exposed to air at room temperature. Symmetry and systematic absences consistent with the monoclinic space groups $C_{2h}^6 - C2/c$ or $C_s^4 - Cc$ were observed by precession and Weissenberg photography of a crystal sealed in a capillary. Cell constants at room temperature are $a = 20.18$ Å, $b = 16.81$ Å, $c = 22.92$ Å, $\beta = 105.2^\circ$, $V = 7511$ Å³. The calculated and observed densities were 1.472 and 1.47 (1) g cm⁻³, respectively. The crystal selected for data collection upon a Picker FACS-I automatic diffractometer was chipped from a large crystal. During the cooling to approximately -150° C for data collection, the crystal underwent a phase change to space group $C_{2h}^5 - P2_1/n$, presumably a consequence of an increased ordering of the solvate molecules. Reflections of the type hkl where $h + k$ is odd were still systematically weak but were observable. Crystal quality was apparently unaffected by the phase change since crystal mosaicities (peak width at half peak height as determined using ω scans) were typically in the range 0.12-0.19°. Lattice parameters at -150° C were obtained, as previously described,²⁴ by the hand centering of 19 reflections in the range $0.4030 < \lambda^{-1} \sin \theta < 0.4468$ Å⁻¹ ($33.22^\circ < 2\theta < 36.95^\circ$) using Mo K α

Table I. Crystal Data and Data Collection Procedures for H₂Cap·5CHCl₃·CH₃OH

formula	C ₆₈ H ₅₃ Cl ₁₅ N ₄ O ₁₃
formula weight, amu	1665.99
space group	C _{2h} ⁵ - P2 ₁ /n
a, Å	19.947(6)
b, Å	16.569(5)
c, Å	22.602(7)
β, deg	104.57(1)
V, Å ³	7230
Z	4
temp	~ -150 °C ^a
crystal shape	ten-sided lump, ~0.90 × 0.57 × 0.50 Å; principal bounding faces, {111}, {100}
crystal volume, mm ³	0.206
radiation	graphite-monochromated Mo Kα, λ(Kα ₁) 0.7093 Å
linear abs coeff, cm ⁻¹	6.10
transmission factors	0.74-0.76 (no correction made)
detector aperture	5.3 mm wide, 5.0 mm high, 32 cm from crystal
take-off angle, deg	3.0
scan speed	2.0° in 2θ per min
λ ⁻¹ sin θ limits, Å ⁻¹	0.0431-0.5790 (3.5° < 2θ (Mo Kα ₁) < 48.5°)
background counts	10 s at each end of scan, with rescan option ^b
scan range	1.1° below Kα ₁ to 1.0° above Kα ₂
data collected	±h,k,l
p	0.05
unique data, including systematic absences	11 565
unique data with F _o ² > 3σ(F _o ²)	8552

^a The low-temperature system is based on a design by Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. ^b Lenhart, P. G. *J. Appl. Crystallogr.* **1975**, *8*, 568-570.

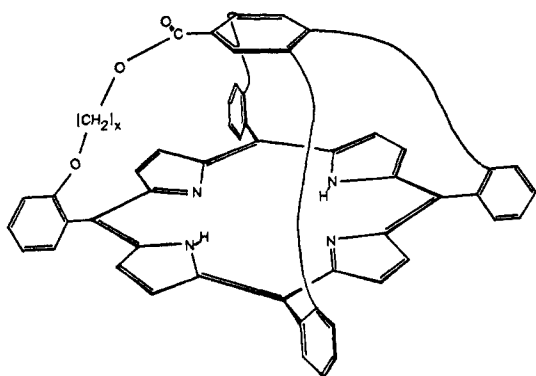


Figure 1. "Capped" porphyrin molecules: (a) $x = 2$, H₂Cap; (b) $x = 3$, H₂HmCap. The four chains linking the phenyl "cap" to the tetraphenylporphyrin moiety are identical.

radiation ($\lambda = 0.7093$ Å). Other important features of data collection are summarized in Table I.

The structure was solved using the MULTAN78 program. In the resultant *E* map, 100 atoms (i.e., almost all atoms) of the porphyrin and solvate species appeared. Standard procedures and programs²⁴ were used to develop and refine this structure, with the Northwestern University CDC6600 computer being used initially and the Lawrence Berkeley Laboratory CDC7600 computer for the final stages. Atoms in phenyl groups were constrained to *D*_{6h} geometry (C-C = 1.395 Å), although in the final stages of refinement the constraints on the phenyl "cap" were removed. Isotropic refinement of the model led to values for *R* and *R*_w on *F*_o of 0.180 and 0.236, respectively. The thermal parameters of the solvate molecules were now allowed to vary anisotropically, and further refinement of the model lowered the values for *R* and *R*_w to 0.105 and 0.139. In the difference Fourier synthesis which followed, despite large peaks around two of the five chloroform

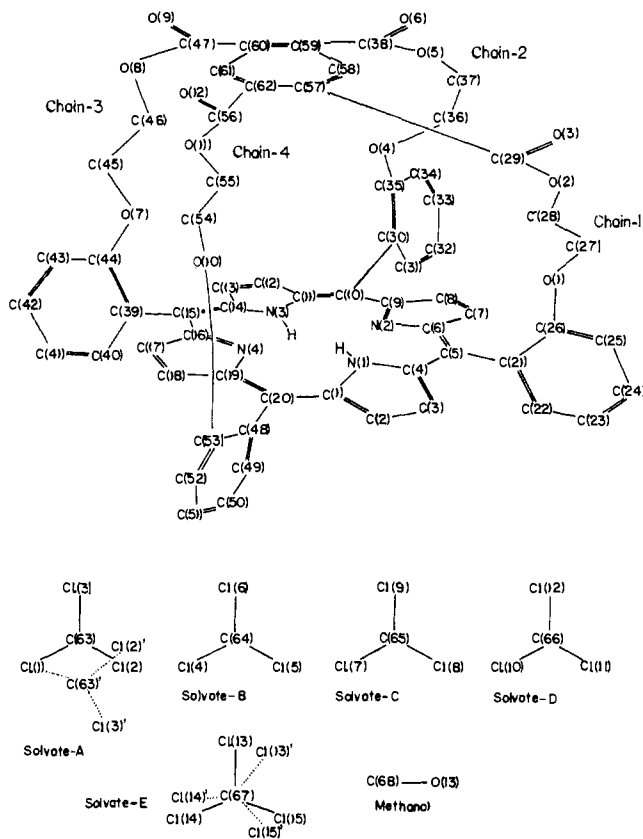


Figure 2. Atom labeling scheme for H₂Cap·5CHCl₃·CH₃OH.

solvate molecules, all hydrogen atoms, except for the hydroxyl hydrogen atom of the methanol molecule, were observed and included at their idealized positions in subsequent structure-factor calculations as a fixed contribution to *F*_c. One disordered chloroform molecule (chloroform E) suffered a rotational disorder about the C-H bond. For another, chloroform A, alternative sites existed such that one Cl atom was common to both sites. Figure 2 illustrates the disorder and defines the atom labeling scheme for the porphyrin and solvate molecules. The minor components were granted only isotropic thermal parameters. The final model was described by 495 variable parameters, including parameters describing the occupancies of the solvate molecules. Upon refinement the final values for *R* and *R*_w were 0.073 and 0.094. The standard error in an observation of unit weight is 2.51 e. For chloroform A the total occupancy is 0.931 (4), apportioned 0.730:0.201 (4) between the major and minor components. For solvate E the occupancy of the major component is 0.772 (7) and of the minor 0.148 (7). For this solvate molecule, because of near superposition of chlorine positions and because of probable disorder in the carbon atom position, which is inferred from its abnormally high thermal parameters, the estimated standard deviations in bond distances and angles derived from the inverse of the least-squares matrix are grossly underestimated. The occupancies of chloroform solvate molecules B, C, and D are 0.853 (3), 0.899 (3), and 0.926 (3), respectively. The occupancy for the methanol solvate molecule is 0.906 (10). The apparent departures of the chloroform solvate molecules from the full occupancies of 1.0 expected from density and thermogravimetric measurements may arise from the inadequacies of the anisotropic model, or any other model, to cater adequately for unresolved disorder. These inadequacies are reflected in the residual electron density which is concentrated around the chloroform solvate molecules with a highest peak of 0.93 (10) e Å⁻³. Values for the minimized function are independent of the magnitude of *F*_o; there is a slight dependence on the magnitude of λ⁻¹ sin θ with very low angle data (λ⁻¹ sin θ < 0.269 Å⁻¹) returning a higher value. In view of the phase transition from *C*2/*c* or *C*c to *P*2₁/*n* it is comforting that no dependency upon any combination of Miller indices could be found.

Full anisotropic refinement was not carried out because of the expense involved with minimal expectation of dramatic changes in porphyrin parameters from these low-temperature data. Final nonhydrogen parameters are listed in Tables II and III. Hydrogen

Table II. Positional and Thermal Parameters for H₂Cap·5CHCl₃·CH₃OH

ATOM	X ^a	Y	Z	R11 OR B ₁₁ ^c	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
CL (1)	0.348231 (94)	0.50513 (10)	0.197248 (76)	38.69 (69)	29.47 (74)	16.92 (42)	2.26 (53)	6.90 (40)	-1.00 (41)
CL (2)	-0.342884 (12)	0.59811 (12)	0.28015 (13)	14.35 (61)	22.49 (85)	30.72 (77)	-2.28 (57)	10.08 (56)	7.26 (61)
CL (3)	0.10510 (11)	0.59919 (12)	0.325397 (92)	26.01 (70)	27.07 (90)	16.39 (51)	-3.81 (60)	2.58 (44)	1.00 (50)
CL (4)	0.316698 (84)	0.20417 (11)	0.660750 (75)	15.82 (48)	40.93 (85)	15.20 (40)	0.22 (50)	5.80 (34)	-4.18 (45)
CL (5)	0.25490 (10)	0.07339 (10)	0.580982 (79)	35.79 (69)	20.53 (68)	17.30 (43)	0.06 (53)	10.41 (42)	-1.47 (42)
CL (6)	0.240018 (79)	0.23751 (10)	0.536478 (78)	14.16 (47)	29.78 (75)	19.91 (45)	-1.56 (45)	5.49 (35)	6.25 (44)
CL (7)	0.873795 (88)	0.50699 (12)	0.476112 (92)	16.38 (52)	49.62 (99)	28.26 (56)	1.24 (55)	1.01 (40)	-1.51 (56)
CL (8)	0.70376 (12)	0.46219 (12)	0.453109 (96)	42.51 (81)	38.63 (92)	25.97 (56)	-15.78 (67)	-12.99 (51)	11.08 (55)
CL (9)	0.689769 (99)	0.56711 (11)	0.414902 (98)	27.11 (63)	27.38 (79)	34.32 (61)	4.50 (54)	-5.21 (47)	-3.50 (53)
CL (10)	0.17029 (92)	0.49578 (14)	0.043758 (96)	15.05 (50)	67.5 (12)	30.79 (50)	1.15 (61)	-0.02 (41)	-2.78 (64)
CL (11)	0.301070 (89)	0.56544 (11)	0.091171 (76)	28.61 (59)	33.83 (79)	17.91 (43)	-5.88 (53)	-3.14 (38)	-0.46 (44)
CL (12)	0.28887 (11)	0.51698 (11)	0.024414 (92)	41.42 (76)	28.68 (77)	29.18 (56)	10.07 (59)	11.07 (50)	-1.12 (50)
CL (13)	0.50705 (22)	0.19916 (18)	0.74537 (15)	96.3 (18)	13.9 (10)	15.50 (71)	-8.1 (10)	-9.17 (76)	1.90 (67)
CL (14)	0.44753 (21)	0.35388 (20)	0.73654 (39)	41.8 (15)	32.4 (13)	116.2 (38)	-0.2 (11)	38.5 (10)	-11.7 (18)
CL (15)	0.59288 (22)	0.34626 (18)	0.78965 (15)	36.9 (18)	40.8 (14)	37.24 (95)	-4.1 (11)	-9.00 (93)	-12.48 (86)
C (63)	0.03495 (39)	0.53522 (42)	0.26722 (37)	17.1 (23)	12.6 (28)	23.3 (22)	-2.2 (20)	8.8 (19)	-2.0 (19)
C (64)	0.24707 (32)	0.17341 (37)	0.59991 (30)	13.8 (19)	19.3 (25)	16.4 (17)	-3.7 (18)	5.1 (14)	-1.4 (16)
C (65)	0.73504 (35)	0.49974 (43)	0.47111 (30)	21.1 (21)	42.2 (33)	14.8 (16)	-9.4 (21)	-1.0 (15)	-5.2 (19)
C (66)	0.25518 (32)	0.47422 (40)	0.07416 (29)	18.2 (20)	34.1 (29)	16.1 (16)	0.2 (19)	1.3 (14)	5.4 (17)
C (67)	0.51383 (61)	0.30636 (59)	0.74493 (58)	73.0 (55)	39.7 (42)	69.7 (53)	-0.5 (38)	-44.3 (44)	-15.6 (36)
O (13)	-0.24118 (23)	0.07393 (31)	-0.10261 (20)	21.4 (16)	50.7 (26)	17.1 (12)	5.0 (16)	6.8 (10)	1.0 (14)
C (68)	-0.27111 (40)	0.15036 (48)	-0.09741 (33)	28.9 (27)	45.5 (39)	20.4 (20)	0.7 (25)	10.5 (18)	-0.1 (21)
CL (2) ^b	-0.09702 (46)	0.49502 (53)	0.17399 (40)	4.34 (23)	ATOM	X	Y	Z	B
CL (3) ^b	-0.01614 (96)	0.5051 (10)	0.29619 (77)	6.89 (42)	C (27)	-0.27781 (28)	0.11752 (33)	0.73275 (24)	2.76 (10)
CL (13) ^b	0.46415 (67)	0.35750 (78)	0.69581 (50)	1.03 (28)	C (28)	-0.25053 (26)	0.03306 (30)	0.74054 (22)	1.94 (9)
CL (14) ^b	0.54549 (64)	0.35417 (63)	0.79936 (46)	6.68 (30)	O (2)	-0.18038 (17)	0.03063 (20)	0.73279 (15)	2.03 (6)
CL (15) ^b	0.51606 (77)	0.2097 (10)	0.73374 (75)	3.18 (32)	C (29)	-0.12969 (24)	0.05387 (29)	0.77996 (21)	1.71 (9)
C (63)	-0.0226 (16)	0.5313 (19)	0.2243 (16)	2.85 (58)	O (3)	-0.13755 (17)	0.07039 (21)	0.83020 (15)	2.37 (7)
N (1)	-0.09152 (19)	0.28708 (23)	0.78513 (17)	1.48 (7)	O (4)	0.08351 (17)	0.19795 (19)	0.54045 (15)	1.91 (6)
C (1)	-0.08857 (25)	0.29974 (29)	0.84575 (22)	1.64 (9)	C (36)	0.05356 (26)	0.12195 (30)	0.51704 (22)	1.96 (9)
C (2)	-0.15772 (24)	0.31199 (29)	0.85006 (21)	1.77 (9)	C (37)	-0.01839 (25)	0.11214 (30)	0.52681 (22)	1.88 (9)
C (3)	-0.20006 (25)	0.30688 (29)	0.79309 (22)	1.95 (9)	O (5)	-0.01676 (16)	0.11608 (19)	0.59093 (14)	1.73 (6)
C (4)	-0.15859 (24)	0.29154 (28)	0.75112 (21)	1.51 (8)	C (38)	0.00527 (24)	0.05014 (28)	0.62321 (21)	1.62 (9)
C (5)	-0.18235 (24)	0.28563 (28)	0.68753 (21)	1.65 (8)	O (6)	0.01971 (17)	-0.01250 (21)	0.60264 (15)	2.20 (7)
N (2)	-0.07109 (19)	0.29203 (23)	0.65967 (17)	1.61 (7)	O (7)	0.25688 (18)	0.17057 (21)	0.79413 (15)	2.28 (7)
C (6)	-0.14136 (24)	0.28474 (28)	0.64555 (21)	1.59 (8)	C (45)	0.29436 (27)	0.09685 (32)	0.80210 (23)	2.29 (10)
C (7)	-0.16984 (25)	0.28398 (29)	0.57997 (22)	1.85 (9)	C (46)	0.25351 (26)	0.03891 (30)	0.75563 (23)	2.10 (9)
C (8)	-0.11624 (25)	0.29292 (29)	0.55495 (22)	1.76 (9)	O (8)	0.1839 (17)	0.03234 (20)	0.76310 (15)	2.00 (6)
C (9)	-0.05454 (24)	0.29853 (28)	0.60463 (21)	1.61 (8)	C (47)	0.13348 (24)	0.06493 (28)	0.71924 (21)	1.71 (9)
C (10)	0.01230 (24)	0.30890 (28)	0.59695 (21)	1.61 (9)	O (9)	0.14090 (18)	0.09262 (21)	0.67197 (15)	2.40 (7)
N (3)	0.07590 (19)	0.29594 (22)	0.70507 (17)	1.48 (7)	O (10)	-0.09782 (17)	0.19040 (20)	0.95274 (15)	2.12 (7)
C (11)	0.07218 (23)	0.30982 (28)	0.64439 (21)	1.53 (8)	C (54)	-0.06261 (26)	0.11770 (30)	0.97821 (23)	2.18 (10)
C (12)	0.14171 (25)	0.32552 (29)	0.64005 (22)	1.85 (9)	C (55)	0.01048 (26)	0.11372 (31)	0.97064 (23)	2.13 (10)
C (13)	0.19434 (24)	0.31998 (29)	0.69653 (21)	1.81 (9)	O (11)	0.01037 (17)	0.11633 (20)	0.90671 (15)	1.97 (6)
C (14)	0.14348 (23)	0.30189 (28)	0.73857 (20)	1.44 (8)	C (56)	-0.00084 (24)	0.04724 (29)	0.87687 (21)	1.71 (9)
C (15)	0.16743 (24)	0.29542 (28)	0.80194 (21)	1.58 (8)	O (12)	-0.00665 (18)	-0.01734 (21)	0.89875 (16)	2.20 (7)
N (4)	0.05546 (19)	0.29337 (22)	0.82999 (17)	1.47 (7)	C (57)	-0.06178 (25)	0.05678 (30)	0.76444 (22)	1.88 (9)
C (16)	0.12635 (23)	0.29069 (28)	0.84347 (21)	1.53 (8)	C (58)	-0.05828 (24)	0.05958 (28)	0.70360 (21)	1.69 (9)
C (17)	0.15433 (25)	0.28870 (29)	0.90945 (22)	1.83 (9)	C (59)	0.00447 (24)	0.06015 (28)	0.6891 (21)	1.62 (9)
C (18)	0.10139 (25)	0.29300 (29)	0.93544 (22)	1.85 (9)	C (60)	0.06614 (24)	0.06157 (28)	0.73550 (21)	1.60 (9)
C (19)	0.03860 (24)	0.29654 (28)	0.88495 (21)	1.67 (9)	C (61)	0.06238 (24)	0.06185 (29)	0.79602 (21)	1.80 (9)
C (20)	-0.02782 (24)	0.30257 (29)	0.89314 (21)	1.72 (9)	C (62)	-0.00013 (24)	0.05781 (28)	0.81070 (21)	1.59 (8)
O (1)	-0.27051 (18)	0.14651 (21)	0.67657 (16)	2.57 (7)					

^a Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. ^b The form of the anisotropic thermal ellipsoid is: $\exp[-(B_{11})h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]$. The quantities given in the table are the thermal coefficients $\times 10^4$.

atom parameters are given in Table IV.²⁵ Table V lists the value of $10|F_o|$ vs. $10|F_c|$.²⁵

Description of the Structure and Discussion

General Information. The crystal structure consists of dis-

crete monomeric molecules of the "capped" porphyrin, H₂Cap, as illustrated in Figure 3, immersed in a matrix of solvate molecules with 5(CHCl₃):1(CH₃OH):1(H₂Cap). The molecular connectivity of H₂Cap is that expected.⁸ Hydrogen bonding of the methanol and interactions of some of the

Table III. Derived Parameters for the Rigid Group Atoms for H₂Cap·5CHCl₃·CH₃OH

ATOM	X	Y	Z	B ^a	ATOM	X	Y	Z	B ^a
C(21)	-0.25931(11)	0.28896(18)	0.66189(15)	1.63(9)	C(39)	0.24409(11)	0.30170(17)	0.82726(14)	1.53(8)
C(22)	-0.28971(15)	0.36257(15)	0.64020(16)	2.02(9)	C(40)	0.27150(14)	0.37489(15)	0.85446(15)	1.97(9)
C(23)	-0.36128(16)	0.36773(16)	0.61671(16)	2.59(10)	C(41)	0.34265(15)	0.38138(15)	0.87965(15)	2.10(10)
C(24)	-0.40246(12)	0.29927(20)	0.61490(17)	3.04(11)	C(42)	0.38638(11)	0.31630(19)	0.87764(15)	2.45(10)
C(25)	-0.37206(15)	0.22566(16)	0.63659(17)	2.81(11)	C(43)	0.35897(14)	0.24391(16)	0.85044(16)	2.36(10)
C(26)	-0.30049(16)	0.22050(14)	0.66008(15)	1.88(9)	C(44)	0.28783(15)	0.23662(14)	0.82525(14)	1.79(9)
C(30)	0.02063(17)	0.32169(18)	0.53328(10)	1.67(9)	C(48)	-0.03636(17)	0.31514(18)	0.95665(11)	1.06(9)
C(31)	-0.00734(17)	0.39011(17)	0.50018(14)	2.13(9)	C(49)	-0.00942(17)	0.38581(17)	0.98825(14)	2.16(10)
C(32)	-0.08080(18)	0.40096(16)	0.44068(13)	2.47(10)	C(50)	-0.01762(18)	0.39877(16)	1.04692(14)	2.51(10)
C(33)	0.03370(18)	0.34339(20)	0.41428(11)	2.42(10)	C(51)	-0.05276(19)	0.34266(20)	1.07399(11)	2.51(10)
C(34)	0.06166(17)	0.27498(17)	0.44738(13)	2.26(10)	C(52)	-0.07970(17)	0.27278(18)	1.04239(14)	2.44(10)
C(35)	0.05513(16)	0.26413(15)	0.50688(13)	1.78(9)	C(53)	-0.07151(17)	0.25982(15)	0.98372(13)	1.78(9)

RIGID GROUP PARAMETERS						
GROUP	X _C ^A	Y _C	Z _C	DELTA ^B	EPSILON	ETA
PH-1	-0.33889(11)	0.29411(13)	0.638396(93)	-0.8882(17)	2.9317(21)	0.1262(21)
PH-2	0.02716(10)	0.33254(13)	0.473781(94)	-2.6177(21)	3.0745(16)	1.4275(21)
PH-3	0.31524(11)	0.30900(12)	0.852448(90)	0.1375(16)	-2.8294(20)	-2.9810(21)
PH-4	-0.04456(11)	0.32890(13)	1.015320(95)	-0.5212(21)	3.0548(16)	-1.3981(21)

^A X_C, Y_C, and Z_C are the fractional coordinates of the origin of the rigid group. ^B The rigid group orientation angles delta, epsilon, and eta (radians) have been defined previously: La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.*, **1965**, *18*, 511-519.

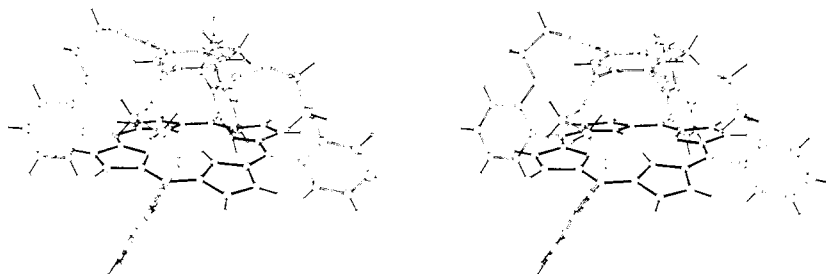


Figure 3. Stereodiamgram of H₂Cap. Probability ellipsoids are drawn at the 36% level, except for the hydrogen atoms, which are shown artificially small.

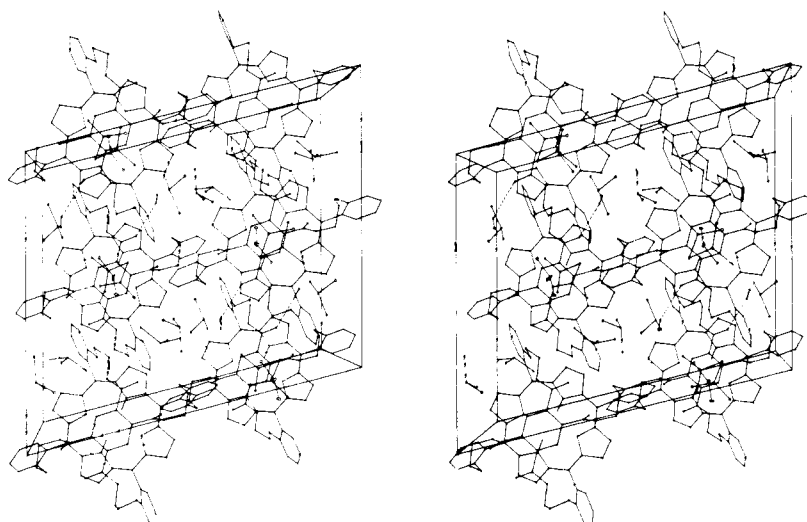


Figure 4. Crystal packing diagram for H₂Cap·5CHCl₃·CH₃OH looking down the *b* axis.

chloroform solvate molecules with the H₂Cap molecule dominate the crystal packing arrangement which is illustrated in Figure 4. In addition numerous contacts of the van der Waals type exist, some of which are very short (such as the O(6) · · ·

C(41) separation of 3.200 (5) Å). Notwithstanding the above example, the large majority of such contacts are solvate-solvate or solvate-H₂Cap rather than H₂Cap-H₂Cap (see Tables VI²⁵ and VII²⁵ for intermolecular contacts). Despite domination

Table VIII. Bond Distances (Å) for H₂Cap·5CHCl₃·CH₃OH

atoms	separation	av ^a	atoms	separation	av
N(1)-C(1)	1.373(6)	N-C _a ^b 1.370(6)	O(2)-C(29)	1.329(6)	1.327(7)
N(1)-C(4)	1.367(6)		O(5)-C(38)	1.326(5)	
N(2)-C(6)	1.362(6)		O(8)-C(47)	1.336(6)	
N(2)-C(9)	1.369(6)		O(11)-C(56)	1.319(6)	
N(3)-C(11)	1.374(6)		C(29)-O(3)	1.216(6)	
N(3)-C(14)	1.374(6)		C(38)-O(6)	1.201(5)	
N(4)-C(16)	1.370(6)		C(47)-O(9)	1.206(6)	
N(4)-C(19)	1.367(6)	C(56)-O(12)	1.197(6)	1.205(8)	
C(1)-C(2)	1.421(7)	C(29)-C(57)	1.483(8)		
C(4)-C(3)	1.430(7)	C _a -C _b 1.430(7)	C(47)-C(60)	1.480(7)	1.482(8)
C(11)-C(12)	1.438(7)		C(38)-C(59)	1.503(7)	
C(14)-C(13)	1.431(7)	1.454(10)	C(56)-C(62)	1.509(7)	1.506(7)
C(6)-C(7)	1.448(7)		C(57)-C(58)	1.395(7)	
C(9)-C(8)	1.445(7)		C(58)-C(59)	1.371(7)	
C(16)-C(17)	1.455(7)		C(59)-C(60)	1.401(7)	
C(19)-C(18)	1.468(7)		C(60)-C(61)	1.389(7)	
C(2)-C(3)	1.353(7)		C(61)-C(62)	1.370(7)	
C(12)-C(13)	1.347(7)		C(62)-C(57)	1.400(7)	
C(7)-C(8)	1.338(7)	C _b -C _b 1.350(7)	C(63)-Cl(1)	1.741(8)	1.388(14)
C(17)-C(18)	1.333(7)		C(63)-Cl(2)	1.761(7)	
C(5)-C(4)	1.399(6)	C(63)-Cl(3)	1.766(8)		
C(5)-C(6)	1.400(7)	C(63)-Cl(1)	1.73(3)		
C(10)-C(9)	1.398(7)	C(63)-Cl(2)'	1.73(3)		
C(10)-C(11)	1.390(6)	C(63)-Cl(3)'	1.66(4)		
C(15)-C(14)	1.395(6)	C(64)-Cl(4)	1.766(7)		
C(15)-C(16)	1.395(6)	C(64)-Cl(5)	1.729(7)		
C(20)-C(19)	1.394(7)	C(64)-Cl(6)	1.743(7)		
C(20)-C(1)	1.397(7)	C(65)-Cl(7)	1.750(7)		
C(5)-C(21)	1.499(5)	C(65)-Cl(8)	1.743(7)		
C(10)-C(30)	1.505(6)	C(65)-Cl(9)	1.760(8)		
C(15)-C(39)	1.495(5)	C(66)-Cl(10)	1.756(7)		
C(20)-C(48)	1.499(6)	C(66)-Cl(11)	1.759(7)		
C(26)-O(1)	1.374(4)	C(66)-Cl(12)	1.731(7)		
C(35)-O(4)	1.372(4)	C(67)-Cl(13)	1.78(1)		
C(44)-O(7)	1.362(4)	C(67)-Cl(14)	1.51(1)		
C(53)-O(10)	1.369(4)	C(67)-Cl(15)	1.74(1)		
O(1)-C(27)	1.399(6)	C(67)-Cl(13)'	1.54(2)		
O(4)-C(36)	1.436(6)	C(67)-Cl(14)'	1.47(1)		
O(7)-C(45)	1.420(6)	C(67)-Cl(15)'	1.62(2)		
O(10)-C(54)	1.439(6)	O(13)-C(68)	1.418(9)		
C(27)-C(28)	1.496(7)	H(C63)...N(2)	2.48		
C(36)-C(37)	1.515(7)	H(C64)...O(9)	2.53		
C(45)-C(46)	1.503(7)	H(C64)...O(4)	2.59		
C(54)-C(55)	1.511(7)	H(C65)...O(13)	2.25		
C(28)-O(2)	1.454(6)	H(C66)...O(1)	2.29		
C(37)-O(5)	1.443(6)	O(13)...O(3)	2.857(7)		
C(46)-O(8)	1.444(6)				
C(55)-O(11)	1.445(6)				

^a Here, and elsewhere, the estimated standard deviation given in parentheses is the larger of that calculated for an individual observation on the assumption that the values averaged are from the same population or of that calculated for an individual parameter from the inverse of the least-squares matrix. ^b The nomenclature is that of Hoard.¹

of the diffraction pattern by the solvate molecules—these constitute nearly $\frac{2}{3}$ of the scattering power—the porphyrin has been defined reasonably precisely. Inspection of Tables VIII and IX of bond distances and angles shows that the structure is internally consistent with chemically equivalent bond parameters generally showing statistically insignificant differences. The unusually large deviations of the porphyrin skeleton from planarity which are observed (see Figure 5 and Tables X and XI) are a consequence of the ester-ether linkages between the porphyrin and its “cap”. The separation between these two planes, which are coplanar to within 0.03°, is 3.96 Å, taken as the distance between the centroids of porphyrin and “cap”. At this separation a π - π interaction between porphyrin ring and phenyl cap, if it exists at all, must be very weak. The porphyrin skeleton is substantially domed toward the cap; the distance between the centroids of the four pyrrole nitrogen atoms and of the phenyl “cap” is 3.86 Å.

Conformation of the Porphyrin. Averaged parameters associated with the porphyrin core for known free-base porphyrin structures are collected in Table XII. Bond distances in the porphyrin skeleton and the internal bond angles for the pyrrole rings of H₂Cap are within experimental error of those for both the pyrrole- and meso-substituted porphyrins. But, in common with the other TPP-based molecules, bond angles involving the mesocarbon atoms are different from those for the pyrrole-substituted class of porphyrins. The transannular N...N separations are very similar to those observed for other free-base porphyrins.

Bond angles are rather insensitive to large deviations from planarity of the porphyrin core. Whereas the other porphyrins are all planar to within 0.074 Å, with the exception of H₂TPP in its triclinic form,^{21a,b} where deviations from planarity of up to 0.159 Å are observed (see Table XII), H₂Cap is decidedly nonplanar, although the 24-atom porphyrin skeleton still

Table IX. Bond Angles (deg) for H₂Cap·5CHCl₃·CH₃OH

atoms	angle	av	atoms	angle	av
C(1)-N(1)-C(4)	110.1(4)	C _a -N-C _a	C(26)-O(1)-C(27)	114.5(4)	115.3(18)
C(11)-N(3)-C(14)	109.7(4)		C(35)-O(4)-C(36)	114.9(3)	
C(6)-N(2)-C(9)	105.3(4)	105.7(4)	C(44)-O(7)-C(45)	118.0(3)	107.4(11)
C(16)-N(4)-C(19)	106.0(4)		C(53)-O(10)-C(54)	113.9(3)	
N(1)-C(1)-C(2)	107.0(4)	N-C _a -C _b	O(1)-C(27)-C(28)	108.1(4)	111.8(8)
N(1)-C(4)-C(3)	106.5(4)		O(7)-C(45)-C(46)	106.6(4)	
N(3)-C(11)-C(12)	106.7(4)	106.8(4)	O(4)-C(36)-C(37)	111.2(4)	110.3(7)
N(3)-C(14)-C(13)	107.0(4)		O(10)-C(54)-C(55)	112.3(4)	
N(2)-C(6)-C(7)	110.9(4)	110.4(5)	C(27)-C(28)-O(2)	110.1(4)	116.5(6)
N(2)-C(9)-C(8)	110.4(4)		C(45)-C(46)-O(8)	109.5(4)	
N(4)-C(16)-C(17)	109.7(4)	108.3(4)	C(36)-C(37)-O(5)	111.0(4)	125.1(7)
N(4)-C(19)-C(18)	110.4(4)		C(54)-C(55)-O(11)	110.7(4)	
C(1)-C(2)-C(3)	108.1(4)	C _a -C _b -C _b	C(28)-O(2)-C(29)	117.2(4)	123.2(6)
C(2)-C(3)-C(4)	108.4(4)		C(46)-O(8)-C(47)	116.7(4)	
C(11)-C(12)-C(13)	108.2(4)	108.3(4)	C(37)-O(5)-C(38)	115.8(4)	120.2(11)
C(12)-C(13)-C(14)	108.3(4)		C(55)-O(11)-C(56)	116.3(4)	
C(6)-C(7)-C(8)	106.4(4)	106.9(9)	O(2)-C(29)-O(3)	124.3(4)	111.6(4)
C(7)-C(8)-C(9)	107.1(4)		O(5)-C(38)-O(6)	125.3(4)	
C(16)-C(17)-C(18)	108.0(4)	106.0(4)	O(8)-C(47)-O(9)	125.0(4)	123.2(6)
C(17)-C(18)-C(19)	106.0(4)		O(11)-C(56)-O(12)	125.9(4)	
N(1)-C(1)-C(20)	125.7(4)	N-C _a -C _m	O(2)-C(29)-C(57)	112.1(4)	120.0(9)
N(1)-C(4)-C(5)	127.2(4)		O(5)-C(38)-C(59)	111.7(4)	
N(3)-C(11)-C(10)	126.0(4)	126.4(7)	O(8)-C(47)-C(60)	111.2(4)	120.0(9)
N(3)-C(14)-C(15)	126.6(4)		O(11)-C(56)-C(62)	111.3(4)	
N(2)-C(6)-C(5)	125.6(4)	125.8(6)	O(2)-C(29)-C(57)	123.6(4)	120.0(9)
N(2)-C(9)-C(10)	125.3(4)		O(6)-C(38)-C(59)	122.8(4)	
N(4)-C(16)-C(15)	126.6(4)	125.8(4)	O(9)-C(47)-C(60)	123.8(4)	120.0(9)
N(4)-C(19)-C(20)	125.8(4)		O(12)-C(56)-C(62)	122.6(4)	
C(2)-C(1)-C(20)	127.4(5)	C _b -C _a -C _m	C(29)-C(57)-C(58)	120.6(4)	120.0(9)
C(3)-C(4)-C(5)	126.2(4)		C(29)-C(57)-C(62)	120.5(4)	
C(12)-C(11)-C(10)	127.3(4)	126.8(6)	C(38)-C(59)-C(60)	121.1(4)	120.0(9)
C(13)-C(14)-C(15)	126.3(4)		C(38)-C(59)-C(58)	118.3(4)	
C(7)-C(6)-C(5)	123.2(4)	123.7(5)	C(47)-C(60)-C(59)	119.7(4)	120.0(9)
C(8)-C(9)-C(10)	124.3(4)		C(47)-C(60)-C(61)	121.5(4)	
C(17)-C(16)-C(15)	123.5(4)	124.4(5)	C(56)-C(62)-C(61)	118.8(4)	120.0(9)
C(18)-C(19)-C(20)	123.8(4)		C(56)-C(62)-C(57)	120.9(4)	
C(4)-C(5)-C(6)	126.3(4)	C _a -C _m -C _α	C(57)-C(58)-C(59)	120.7(4)	120.0(9)
C(14)-C(15)-C(16)	126.0(4)		C(58)-C(59)-C(60)	120.2(4)	
C(9)-C(10)-C(11)	124.5(4)	126.2(4)	C(59)-C(60)-C(61)	118.8(4)	120.0(9)
C(19)-C(20)-C(1)	124.3(5)		C(60)-C(61)-C(62)	121.1(4)	
C(4)-C(5)-C(21)	116.3(4)	124.4(5)	C(61)-C(62)-C(57)	120.1(4)	120.0(9)
C(6)-C(5)-C(21)	117.0(4)		C(62)-C(57)-C(58)	118.9(5)	
C(14)-C(15)-C(39)	116.1(4)	C _a -C _m -C _α	Cl(1)-C(63)-Cl(2)	113.1(5)	120.0(9)
C(16)-C(15)-C(39)	117.6(4)		Cl(1)-C(63)-Cl(3)	107.8(4)	
C(9)-C(10)-C(30)	118.3(4)	116.7(7)	Cl(2)-C(63)-Cl(3)	109.0(4)	120.0(9)
C(11)-C(10)-C(30)	117.1(4)		Cl(1)-C(63)-Cl(2)'	109(2)	
C(19)-C(20)-C(48)	118.3(4)	117.8(6)	Cl(1)-C(63)-Cl(3)'	114(2)	120.0(9)
C(1)-C(20)-C(48)	117.3(4)		Cl(2)'-C(63)'-Cl(3)'	113(2)	
C(5)-C(21)-C(22)	118.7(3)	120.0(12)	Cl(4)-C(64)-Cl(5)	111.5(4)	120.0(9)
C(5)-C(21)-C(26)	121.3(3)		Cl(4)-C(64)-Cl(6)	110.5(3)	
C(10)-C(30)-C(31)	120.1(3)	120.0(12)	Cl(5)-C(64)-Cl(6)	110.8(4)	120.0(9)
C(10)-C(30)-C(35)	119.9(3)		Cl(7)-C(65)-Cl(8)	112.1(4)	
C(15)-C(39)-C(40)	118.6(3)	120.0(12)	Cl(7)-C(65)-Cl(9)	109.3(4)	120.0(9)
C(15)-C(39)-C(44)	121.4(3)		Cl(8)-C(65)-Cl(9)	109.3(4)	
C(20)-C(48)-C(49)	119.0(3)	121.0(3)	Cl(10)-C(66)-Cl(11)	109.0(4)	120.0(9)
C(20)-C(48)-C(53)	121.0(3)		Cl(10)-C(66)-Cl(12)	111.8(4)	
C(25)-C(26)-O(1)	119.5(3)	120.3(3)	Cl(11)-C(66)-Cl(12)	110.3(4)	120.0(9)
C(21)-C(26)-O(1)	120.3(3)		Cl(13)-C(67)-Cl(14)	117.1(8)	
C(34)-C(35)-O(4)	120.7(3)	120.0(23)	Cl(13)-C(67)-Cl(15)	112.2(5)	120.0(9)
C(30)-C(35)-O(4)	119.3(3)		Cl(14)-C(67)-Cl(15)	122.8(7)	
C(43)-C(44)-O(7)	124.2(3)	120.0(23)	Cl(13)'-C(67)-Cl(14)'	111.7(9)	120.0(9)
C(39)-C(44)-O(7)	115.6(3)		Cl(13)'-C(67)-Cl(15)'	117.9(10)	
C(52)-C(53)-O(10)	120.0(3)	120.0(3)	Cl(14)'-C(67)-Cl(15)'	129.8(11)	120.0(9)
C(48)-C(53)-O(10)	120.0(3)				

conforms very closely to D_{2d} symmetry. Displacements of up to 0.354 Å and a mean displacement of 0.134 Å are observed (see Figure 5). The latter value is more than twice as large as that for H₂TPP. In common with H₂TPP but to a much greater extent, the aminopyrrole rings make a greater angle with the 24-atom porphyrin plane than do the imino rings (see

Tables X and XI). Since H₂TPrP has similar transannular N...N separations and is essentially planar, avoidance of the NH...HN contact does not appear to be the reason for this. Despite the highly buckled porphyrin skeleton the pyrrole rings are, as usual,¹ essentially planar.

Conformation of the "Cap". That there is considerable steric

Table X. Least-Squares Planes for H₂Cap·5CHCl₃·CH₃OH

name	coefficients $Ax + By + Cz - D = 0^a$				atoms defining the plane displacement					
	A	B	C	D						
l	0.693	-16.558	-0.384	-5.128	N(1)	N(2)	N(3)	N(4)		
ll	0.548	-16.562	-0.286	-5.152	010(4)	-010(4)	010(4)	-010(4)		
py-1	2.717	16.290	-3.436	1.733	C(5)	C(10)	C(15)	C(20)		
py-2	2.175	-16.467	-1.014	-5.640	124(5)	-129(5)	121(5)	-131(5)		
py-3	3.318	-16.181	-3.927	-7.306	N(1)	C(1)	C(2)	C(3)	C(4)	
py-4	1.019	16.547	-0.294	4.677	-003(4)	003(5)	000(5)	-003(5)	004(5)	
cap	0.542	-16.562	-0.304	-1.214	N(2)	C(6)	C(7)	C(8)	C(9)	
ph-1	6.939	-3.595	-21.930	-17.354	008(4)	-011(5)	006(5)	001(5)	-008(5)	
ph-2	15.923	8.066	3.220	4.640	N(3)	C(11)	C(12)	C(13)	C(14)	
ph-3	6.970	5.339	-21.233	-14.253	001(4)	002(5)	-005(5)	005(5)	-003(5)	
ph-4	15.720	-7.892	4.047	0.813	N(4)	C(16)	C(17)	C(18)	C(19)	
ester-1	2.003	-15.814	5.577	3.240	-010(4)	014(5)	-010(5)	000(5)	009(5)	
ester-2	18.560	5.177	-1.103	-0.358	C(57)	C(58)	C(59)	C(60)	C(61)	C(62)
ester-3	1.563	14.854	9.092	7.707	008(5)	-018(5)	011(9)	007(5)	-018(5)	010(5)
ester-4	19.236	-2.420	-0.657	-0.682	C(21)	C(22)	C(23)	C(24)	C(25)	C(26)
porph	0.553	-16.562	-0.302	-5.157	0	0	0	0	0	0
					C(30)	C(31)	C(32)	C(33)	C(34)	C(35)
					0	0	0	0	0	0
					C(39)	C(40)	C(41)	C(42)	C(43)	C(44)
					0	0	0	0	0	0
					C(48)	C(49)	C(50)	C(51)	C(52)	C(53)
					0	0	0	0	0	0
					O(2)	C(29)	O(3)	C(57)		
					000(3)	-003(5)	001(3)	001(5)		
					O(5)	C(38)	O(6)	C(59)		
					-004(3)	028(5)	-006(3)	-008(5)		
					O(8)	C(47)	O(9)	C(60)		
					-001(3)	006(5)	-001(3)	-002(5)		
					O(11)	C(56)	O(12)	C(62)		
					004(3)	-025(5)	005(3)	007(5)		

^a The plane is a crystal coordinates as defined by Hamilton, W. C. *Acta Crystallogr.* **1961**, *14*, 185-189. ^b The displacement (Å) is generated by placing a decimal point prior to the first digit.

Table XI. Dihedral Angles (deg) between Selected Least-Squares Planes for H₂Cap·5CHCl₃·CH₃OH^a

	porph	l	cap	py-1	py-2	py-3	py-4	ph-1	ph-2	ph-3	ph-4
porph		0.4	0.0	168.0	4.7	11.0	175.5	76.6	117.8	107.9	60.3
l			0.4	167.6	4.3	10.6	175.1	ester-1	ester-2	ester-3	ester-4
cap				168.0	4.8	11.0	175.5	17.3	106.8	153.8	80.2
py-1					163.8	157.0	8.6				
py-2						7.6	170.8				
py-3							165.2				

^a For definition of the planes see Table X.

strain involved in accommodating the "cap" is apparent in some short 1-4 interactions (e.g., O(1)···O(2), 2.717 (5) Å), 1-5 interactions (e.g., O(4)···C(11), 3.045 (6) Å), 1-6 interactions (e.g., O(3)···O(12), 3.049 (5) Å), and 1-8 interactions (e.g., O(11)···C(19) 3.100 (6) Å). Steric strain is manifested most obviously, but not necessarily primarily, through buckling of the *meso*-tetraphenylporphyrin moiety from its preferred planar conformation (see Figure 5). In contrast to other free-base porphyrin compounds, the C_a-C_m-C_a bond angles may be divided into two dyadically related pairs for H₂Cap (and also for the grossly unsymmetrical 5-R-OEP^{22a}). This conformation can be associated with the phenyl "cap" which, in contrast to the porphyrin, lacks even a rudimentary approximation to fourfold symmetry. With two of the ester groups approximately coplanar with the phenyl "cap" and the other two approximately perpendicular (see Table XI), steric crowding around this tetrasubstituted phenyl "ring" is avoided. The former pair of ester groups are both planar; the latter pair show a slight tetrahedral distortion. Although the difference is of marginal significance, the C_{phenyl}-C_{ester} bond lengths for the ester groups which are coplanar and hence ca-

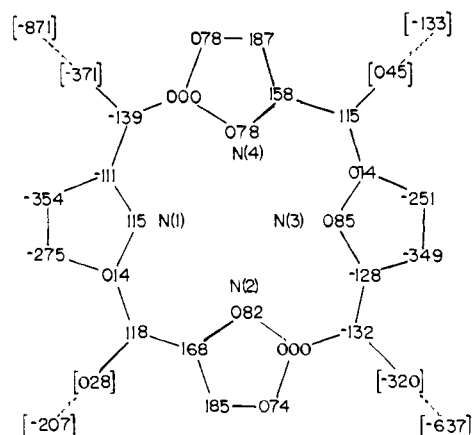


Figure 5. Displacements ($\times 10^3$) of atoms from the least-squares plane of the 24-atom porphyrin skeleton. The estimated standard deviations are 0.004 Å for nitrogen atoms and 0.005 Å for carbon atoms. Displacements in square parentheses were not included in the calculation of the least-squares plane.

Table XII. Averaged Parameters for Several Free-Base Porphyrins

	A. Atomic Separations (Å)										displacements from porphyrin plane mean max	
	N-C _a		C _a -C _b		C _b -C _c		C _a -C _m		N...N			
	imino	amino	imino	amino	imino	amino	imino	amino	imino	amino		
MPiXDME ^{a,b}	1.366	1.365	1.457	1.438	1.359	1.368	1.391	1.386	4.060	4.181	0.020	0.066
PPiXDME ^c	1.370	1.367	1.452	1.441	1.355	1.360	1.392	1.380	4.055	4.199	0.025	0.074
H ₂ OEP 1 ^d	1.364	1.367	1.462	1.438	1.353	1.373	1.394	1.390	4.052	4.195	0.021	0.049
porphine ^e	1.377	1.380	1.452	1.431	1.345	1.365	1.376	1.387	4.058	4.112	0.02	0.05
H ₂ TPrP ^f	1.372	1.376	1.443	1.437	1.341	1.352	1.399	1.394	4.08	4.16	0.03	0.06
H ₂ TPP ^g	1.364	1.374	1.455	1.428	1.347	1.355	1.400	1.400	4.06	4.20	0.054	0.159
H ₂ Cap ^h	1.367	1.372	1.454	1.430	1.336	1.350	1.397	1.395	4.038	4.182	0.134	0.354
5-R-OEP ⁱ	1.367	1.362	1.452	1.443	1.357	1.361	1.395	1.386	4.052	4.195	0.040	0.116

	B. Bond Angles (deg)										
	C _a -N-C _a		N-C _a -C _b		C _a -C _b -C _b		N-C _a -C _m		C _b -C _a -C _m		C _a -C _m -C _a
	imino	amino	imino	amino	imino	amino	imino	amino	imino	amino	
MPiXDME	105.7	109.8	110.9	107.5	106.3	107.6	124.7	125.3	124.4	127.2	127.1
PPiXDME	105.4	110.5	110.9	106.9	106.5	107.9	124.4	125.4	124.8	127.7	128.1
H ₂ OEP	105.7	109.6	110.8	107.7	106.3	107.4	125.1	125.0	124.0	127.3	127.6
porphine	106.1	108.6	109.8	107.9	107.2	107.9	125.0	125.4	125.1	126.9	127.1
H ₂ TPrP	106.6	110.0	109.5	106.7	107.3	108.3	126.2	127.1	124.5	126.2	125.0
H ₂ TPP	106.2	109.2	110.3	107.3	106.8	108.1	126.3	126.0	123.5	126.6	125.6
H ₂ Cap	105.7	109.9	110.4	106.8	106.9	108.3	125.8	126.4	123.7	126.8	125.3 ^k
5-R-OEP	105.3	110.4	111.1	107.1	106.3	107.7	<i>j</i>	<i>j</i>	<i>j</i>	<i>j</i>	128.2 ^j

^a Reference 18; estimated errors ± 0.004 Å, ± 0.2 – 0.3° . ^b The N...N separations reported here are correct; those in Table VII of ref 18 are erroneous. (See: Little, R. G.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 7437.) ^c Reference 19; estimated errors ± 0.007 Å, ± 0.5 – 0.8° . ^d Reference 17; estimated errors ± 0.002 Å, $\pm 0.2^\circ$. ^e Reference 16; estimated errors ± 0.007 Å, ± 0.3 – 0.5° . ^f Reference 15; estimated errors ± 0.004 Å, ± 0.2 – 0.4° . ^g Reference 21a; estimated errors ± 0.005 – 0.01 Å, ± 0.5 – 0.8° . ^h This work; estimated errors ± 0.007 Å, ± 0.4 – 0.9° . ⁱ Reference 22a; estimated errors ± 0.01 Å, ± 0.8 – 1.1° . ^j Marked asymmetry because of the 5-substituents on the porphyrin ring. ^k The four such angles can be split into two pairs; see Table IX.

Table XIII. Torsional Angles^a in the Linkages for H₂Cap-5CHCl₃·CH₃OH

atoms ^b	chain 1	chain 3	chain 2	chain 4
C(25)–C(26)–O(1)–C(27)	–77.8(5)	18.8(6)	–65.3(5)	–69.0(5)
C(26)–O(1)–C(27)–C(28)	173.1(3)	–171.1(4)	–72.1(5)	–68.1(5)
O(1)–C(27)–C(28)–O(2)	53.6(5)	–55.9(5)	–59.5(5)	–59.7(5)
C(27)–C(28)–O(2)–C(29)	79.4(5)	109.8(4)	–77.4(5)	–82.8(5)
C(28)–O(2)–C(29)–O(3)	6.4(7)	6.9(7)	–4.5(7)	–4.8(7)
C(28)–O(2)–C(29)–C(57)	–174.1(4)	–174.1(4)	–179.5(4)	179.7(4)
O(3)–C(29)–C(57)–C(58)	–161.9(5)	–152.8(5)	71.6(6)	79.1(6)
O(2)–C(29)–C(57)–C(58)	18.5(6)	28.2(6)	–113.2(5)	–105.2(5)

^a The sign is positive if, for a chain of atoms 1–2–3–4, when looking from 2 to 3 a clockwise motion of atom 1 would superimpose it on atom 4. ^b Only the atoms of chain 1 are listed here; atoms in chains 2, 3, and 4 are defined analogously as shown in Figure 2.

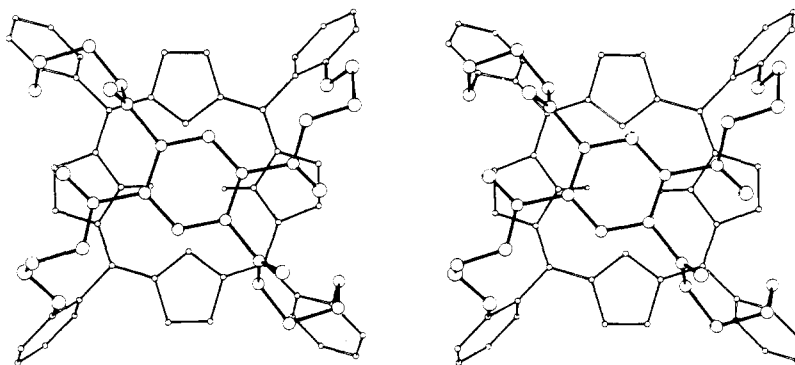


Figure 6. Stereodiagram of H₂Cap perpendicular to the porphyrin plane. The "cap" moiety is highlighted, and hydrogen atoms, except for the amino hydrogen atoms, are omitted for clarity. Chain 1 is at bottom left, chain 2 at bottom right.

pable of resonance interaction with the phenyl "cap" are both slightly shorter than those for the ester groups perpendicular to the phenyl "cap". Atoms C(38) and C(56) of the latter pair are also significantly displaced (0.197 and 0.165 Å, respectively) from the least-squares plane of the phenyl "cap"; atoms C(29) and C(47) are displaced only 0.015 and -0.008 Å. The phenyl cap itself is slightly but significantly nonplanar (see Table X), with the carbon atoms at the unsubstituted 3 and 6 positions being displaced toward the porphyrin plane. The departures from D_{6h} symmetry of the bond distances and angles are of marginal significance.

Two linking chains, chain 2 (atoms O(4), C(36)···C(39)) and chain 4 (similarly defined by reference to Figure 2), share a similar conformation, and chemically equivalent bond distances and angles have statistically insignificant differences. However, the conformations of chain 1 and chain 3 are very different for the ether-ethyl portions of the chains, although the ester-phenyl "cap" conformations are similar, as noted above. This may be appreciated qualitatively in Figure 6, which is a view of the molecule looking down the pseudo-twofold axis, and quantitatively in Table XIII of torsional angles. Although bond angles in chain 1 could be distorted by hydrogen bonding

between atom O(3) and the methanol solvate molecule, it is in chain 3 that steric strain is apparent. The torsional angle about bond C(26)-O(1) is only 18.8° (i.e., a nearly eclipsing conformation) with no factor such as resonance stabilization to encourage such a sterically active conformation. As a result there is a marked increase in the asymmetry of the C(43)-C(44)-O(7) and C(39)-C(44)-O(7) bond angles, and the C(47)-O(7)-C(45) bond angle is more than 3° larger than those observed in the other three chains where the torsional angle about the C_{phenyl}-O_{ester} bond is considerably removed from 0°. This chain indulges in far fewer intermolecular contacts than do the other three.

Because of the space-group ambiguity (*C2/c* or *Cc*), detailed discussion on the possible crystal and molecular structure of the room-temperature phase based on the known structure of the low-temperature phase is necessarily speculative. If the H₂Cap molecules remain similarly disposed with respect to unit-cell origin between the low- and high-temperature phases, then they could be arranged about the twofold axes in space group *C2/c*. Moreover, the solvate molecules A (especially) and E are disordered (see Figure 3) such that they are pseudodyadically related. However, the lone methanol molecule which has no pseudodyadically related mate and the different conformations of chain 1 and chain 3 indicate that additional disorder would exist in space group *C2/c*. That some medium-intensity reflections of the type *hkl*, $h + k = 2n + 1$, are observed—these reflections are absent in space groups *Cc* or *C2/c*—is evidence of substantial rearrangement of at least the solvate molecules.

Relationship between the Structure of H₂Cap and the Ligand Binding Properties of Its Metal Complexes. The separation between the centroids of the phenyl "cap" and the 24-atom porphyrin core is a remarkably close 3.96 Å; the two planes are essentially parallel. The separation between the centroids of the four pyrrole nitrogen atoms and of the phenyl "cap" is 3.86 Å. We believe that a generally similar stereochemistry will occur for metal complexes of H₂Cap in solution, although the observation of three, and not two or one, conformations for the ester-ether linkages between the "cap" and the porphyrin cautions against overinterpretation. In particular, we believe that a buckled porphyrin ring and a porphyrin-phenyl "cap" separation in the range 3.85–4.05 Å will be maintained. Budge et al.¹⁰ have observed that Fe(Cap) binds an axial base with a lower affinity than do Fe(TPP),^{26,27} Fe(TpivPP),^{28,29} and some of the Fe(MP-L) systems where the axial base is attached to the porphyrin by a covalent chain of varying length and composition.²⁶ This observation¹⁰ is consistent with ours that for H₂Cap the porphyrin is not only buckled but also somewhat domed toward the "cap" such that the approach of an axial base would be hindered (see Figure 3). The affinities of Fe(Cap)(Base) complexes for a second axial ligand are also less than the analogous Fe(TPP)(Base) and Fe(TpivPP)(Base) systems. Indeed the structure of H₂Cap confirms deductions made from space-filling molecular models that a second axial base, such as 1-methylimidazole, cannot be accommodated under the "cap", and that there is severe hindrance to the binding of small molecules such as dioxygen and carbon monoxide. In particular, CO cannot be accommodated under a "cap" only 3.85 Å from the porphyrin plane in a linear and perpendicular geometry and determination of the structure of a Fe(CO)(Cap)(Base) complex is clearly of high priority.

The domed and bent geometry of H₂Cap combined with the ligand binding properties of its metal complexes are not inconsistent with the hypothesis²³ that in hemoproteins per-

urbation of the heme group from a planar geometry by the protein matrix may be important in controlling ligand affinity.

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Supplementary Material Available: Table IV, idealized hydrogen atom parameters; Table V, calculated and observed structure amplitudes; Tables VI and VII, intermolecular contacts (34 pages). Ordering information is given on any current masthead page.

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