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Crystal and Molecular Structure of the Free Base Porphyrin, Protoporphyrin IX Dimethyl Ester

Winslow S. Caughey[1] **and James A. Ibers***[2]

Contribution from the Department of Biochemistry, Colorado State University, Fort Collins, Colorado 80523, and Department of Chemistry, Northwestern University, Evanston, Illinois 60201.

Received March 23, 1977

Abstract: The structure of the free base porphyrin, protoporphyrin IX dimethyl ester, has been determined from three-dimensional x-ray diffraction data collected from a crystal of calculated weight 0.98 μg. The porphyrin crystallizes with two molecules per unit cell in the triclinic space group C_i^1-$P\bar{1}$ with a = 11.303 (5), b = 22.553 (10), c = 6.079 (3) Å, α = 91.38 (2), β = 94.08 (2), γ = 81.96 (1)°, V = 1530 Å^3. The structure has been refined anisotropically by full-matrix least-squares methods to a final unweighted R index (on F^2) of 0.108 for 397 variables and 3889 observations. The R index (on F) for the 1982 observations having $F_o^2 \geq 3\sigma(F_o^2)$ is 0.073. Bond lengths and bond angles within the porphyrin core have been determined to estimated standard deviations of ±0.006 Å and ±0.5°. The structural results for the porphyrin core do not differ significantly from those found in the free base porphyrin, mesoporphyrin IX dimethyl ester. In the present structure the vinyl groups approach planarity with the porphyrin core more than do the ethyl groups in mesoporphyrin IX dimethyl ester, but these vinyl groups fail to achieve coplanarity owing to steric constraints. The replacement of vinyl groups with ethyl groups results in some significant changes in spectral properties, in the basicity of amide nitrogen atoms, and in the binding of ligands to a central metal without causing a detectable change in the stereochemistry of the porphyrin ring.

The asymmetric pattern of substitution of the naturally occurring porphyrins is manifested in a number of spectroscopic effects. Whether or not the substitution pattern affects the metrical details of such porphyrins, particularly of the inner core, has not been assessed owing to the lack of data on the structures of free base porphyrins. Earlier we reported the structure of the free base porphyrin, mesoporphyrin IX dimethyl ester (MPIX DME).[3] Here we describe the structure of the free base porphyrin, protoporphyrin IX dimethyl ester (PPIX DME). The structural similarities of these two porphyrins are contrasted with their spectral differences.

Experimental Section

Protoporphyrin IX dimethyl ester was obtained from bovine blood hemin chloride, the chloroiron(III) species with unesterified propionic acid groups, via a procedure described earlier.[4] This procedure permits the iron removal and esterifications to be carried out in a single step within a mixture of the hemin, HCl, methanol, chloroform, and ferrous acetate. Crystals were obtained by the diffusion of methanol into chloroform solutions of the porphyrin at 8 °C over a 5-month period. Crystals so obtained were exceedingly small.

Preliminary Weissenberg and precession photographs taken with Cu Kα radiation showed only the required center of symmetry; hence,

Table I. Positional and Thermal Parameters for the Atoms of the Free Base of Protoporphyrin IX Dimethyl Ester

ATOM	X[a]	Y	Z	B11[b]	B22	B33	B12	B13	B23
C(1)	-0.11563(57)	0.15427(24)	0.38653(92)	10.20(71)	1.65(14)	25.8(20)	-0.75(26)	0.27(99)	0.23(43)
C(2)	-0.08699(56)	0.11283(24)	0.56710(93)	10.50(71)	1.65(14)	26.7(20)	-0.52(26)	1.33(96)	1.52(44)
C(3)	0.03013(56)	0.08943(24)	0.56381(93)	11.69(72)	1.46(14)	24.5(21)	-0.87(26)	-1.34(97)	0.79(42)
C(4)	0.07891(54)	0.11514(24)	0.38271(91)	9.73(67)	1.65(14)	23.7(19)	0.21(25)	-1.18(93)	1.46(41)
C(5)	0.19373(56)	0.10423(26)	0.31622(99)	9.83(72)	1.97(15)	32.9(22)	0.30(27)	-1.2(10)	0.65(46)
C(6)	0.24230(51)	0.12902(25)	0.14209(98)	8.22(62)	1.91(15)	28.5(22)	-0.26(25)	-0.05(96)	0.21(47)
C(7)	0.36457(51)	0.11467(26)	0.0798(10)	7.61(63)	1.99(15)	34.5(23)	0.60(25)	-2.91(96)	0.32(48)
C(8)	0.37475(55)	0.14825(27)	-0.0974(11)	8.02(68)	2.41(16)	31.6(25)	0.18(27)	0.5(10)	-0.76(52)
C(9)	0.25825(50)	0.18271(25)	-0.14556(97)	8.03(58)	1.82(15)	30.7(22)	-0.12(25)	-0.57(94)	0.02(47)
C(10)	0.23030(53)	0.22227(25)	-0.31820(96)	8.66(66)	1.95(14)	28.7(21)	-0.18(26)	1.49(93)	0.01(44)
C(11)	0.12077(51)	0.25572(24)	-0.37916(89)	8.66(61)	1.72(14)	24.3(19)	-0.49(24)	1.28(90)	0.26(42)
C(12)	0.09394(54)	0.29552(24)	-0.56291(90)	9.09(67)	1.74(14)	25.8(19)	-0.43(25)	1.80(91)	0.25(42)
C(13)	-0.02330(51)	0.31976(24)	-0.55800(86)	9.84(63)	1.51(13)	20.6(18)	-0.79(24)	0.95(85)	0.43(39)
C(14)	-0.07181(51)	0.29539(23)	-0.37222(87)	8.00(63)	1.44(13)	22.4(18)	-0.06(24)	0.09(89)	0.17(40)
C(15)	-0.18718(52)	0.30811(24)	-0.30452(85)	8.80(64)	1.87(14)	21.1(17)	-0.36(25)	-0.54(85)	0.59(40)
C(16)	-0.23329(49)	0.28358(24)	-0.12569(90)	7.59(59)	1.72(14)	24.2(19)	-0.48(24)	-0.83(88)	0.04(43)
C(17)	-0.35540(48)	0.29981(24)	-0.06140(90)	7.65(58)	1.79(14)	22.2(20)	-0.75(24)	0.27(87)	-0.01(43)
C(18)	-0.36580(51)	0.26618(25)	0.11667(93)	7.78(62)	1.71(14)	25.5(20)	-0.54(24)	1.38(90)	-0.51(43)
C(19)	-0.25058(49)	0.22931(24)	0.15797(91)	7.60(58)	1.50(13)	24.1(20)	-0.59(23)	0.29(88)	0.10(42)
C(20)	-0.22316(53)	0.18664(23)	0.32968(93)	9.88(68)	1.81(13)	25.8(20)	-0.51(25)	2.35(94)	0.50(43)
C(21)	-0.17520(62)	0.10197(29)	0.7200(10)	14.25(88)	2.50(18)	35.1(22)	0.30(33)	3.8(11)	3.50(54)
C(22)	-0.17694(68)	0.05566(32)	0.8310(12)	16.7(10)	3.99(21)	58.7(29)	0.71(38)	7.2(14)	8.35(69)
C(23)	0.10303(61)	0.04556(27)	0.7189(10)	14.71(84)	2.34(15)	34.7(24)	-0.24(29)	-0.7(11)	2.78(49)
C(24)	0.45289(58)	0.06910(35)	0.1974(12)	5.88(62)	5.05(27)	50.0(30)	0.77(34)	1.0(11)	-2.76(70)
C(25)	0.56127(85)	0.06933(46)	0.2237(13)	21.9(13)	7.70(39)	50.6(33)	1.72(58)	3.5(17)	0.13(88)
C(26)	0.48101(57)	0.14974(32)	-0.2301(12)	10.29(67)	3.38(21)	46.1(29)	0.50(31)	4.2(11)	-0.47(61)
C(27)	0.18064(53)	0.30694(26)	-0.72488(95)	10.31(65)	2.62(17)	32.8(22)	-0.92(27)	4.89(97)	1.53(48)
C(28)	-0.09175(49)	0.36512(22)	-0.71553(86)	8.50(62)	1.70(12)	23.7(19)	-1.06(23)	-0.04(87)	1.07(39)
C(29)	-0.08859(56)	0.42829(22)	-0.62732(87)	13.65(79)	1.76(12)	28.7(19)	-0.73(25)	-3.11(98)	1.66(40)
C(30)	-0.12899(51)	0.47590(27)	-0.7960(11)	7.86(59)	1.90(17)	30.0(23)	-0.52(25)	-1.40(96)	1.21(50)
C(31)	-0.44541(51)	0.34805(25)	-0.16278(88)	9.21(62)	2.41(15)	22.1(19)	0.27(25)	1.13(88)	-0.34(43)
C(32)	-0.42628(53)	0.41070(24)	-0.07651(86)	9.85(67)	2.14(15)	26.1(18)	0.41(25)	1.90(87)	1.32(40)
C(33)	-0.46430(55)	0.42298(25)	0.1537(11)	7.94(66)	1.78(14)	34.2(24)	0.11(24)	-2.6(10)	-0.22(46)
C(34)	-0.47335(53)	0.26382(28)	0.24581(98)	10.51(64)	2.75(18)	33.3(23)	-0.67(26)	4.92(98)	1.13(51)
C(35)	-0.16323(56)	0.58132(23)	-0.84158(96)	15.05(78)	1.73(13)	39.5(22)	-0.64(26)	-5.9(11)	3.67(45)
C(36)	-0.63544(60)	0.44759(31)	0.3605(10)	13.37(80)	3.85(21)	34.5(22)	-0.33(33)	5.2(11)	-1.72(55)
O(1)	-0.14319(40)	0.46772(18)	-0.99112(68)	15.91(57)	2.54(11)	26.7(15)	-0.96(20)	-3.24(75)	1.44(33)
O(2)	-0.14159(37)	0.53024(18)	-0.69869(64)	13.40(49)	2.02(11)	30.9(14)	-0.55(19)	-3.08(67)	1.02(33)
O(3)	-0.40107(39)	0.42215(22)	0.31722(72)	9.96(47)	4.88(17)	31.9(16)	0.89(22)	-4.15(73)	-1.71(40)
O(4)	-0.58169(36)	0.43373(19)	0.15302(65)	9.38(46)	3.65(13)	26.6(15)	0.02(20)	-0.32(66)	-1.41(35)
N(1)	-0.01257(41)	0.15367(20)	0.28193(73)	8.79(48)	1.96(12)	25.7(17)	-0.75(20)	0.51(75)	1.64(35)
N(2)	0.17919(41)	0.17029(19)	0.00232(74)	8.91(51)	1.77(12)	26.6(16)	-0.27(20)	1.19(77)	1.21(36)
N(3)	0.01769(39)	0.25727(19)	-0.27067(70)	7.70(45)	1.85(11)	23.1(16)	-0.19(18)	1.55(70)	1.45(34)
N(4)	-0.17086(38)	0.24067(19)	0.00945(68)	7.55(48)	1.72(11)	21.2(15)	-0.12(19)	0.59(71)	0.50(33)

[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 × 10^3.

the material crystallizes in the triclinic system in space group $P1$ or $P\bar{1}$. The largest crystal available was selected for data collection. Bounding faces were of the forms {001}, {010}, and {100} with distances between the faces of these forms being 0.45, 0.016, and 0.104 mm, respectively. The crystal has a calculated volume of 0.00077 mm^3 and a calculated weight of 0.98 μg.

Lattice parameters were obtained as previously described[5] from the hand-centering of 13 reflections in the range $20 < 2\theta(\text{Cu K}\alpha_1) < 25°$ on a FACS-I diffractometer using Cu Kα_1 radiation (λ = 1.540562 Å). The lattice constants (Delaunay reduced) are a = 11.303 (5), b = 22.553 (10), c = 6.079 (3) Å, α = 91.38 (2), β = 94.08 (2), γ = 81.96 (1)°, V = 1530 Å^3, t = 24.5 °C. The calculated density for two molecules of the porphyrin in the cell is 1.282 g/cm^3 ($C_{36}H_{38}N_4O_4$) and this agrees well with a value of 1.27 g/cm^3 measured by flotation of the crystals in aqueous $ZnCl_2$.

Data were collected in shells of 2θ by the θ-2θ scan method using Cu Kα radiation prefiltered with 1-mil Ni foil. The scan range was 0.85° below the Kα_1 peak to 0.70° above the Kα_2 peak. The takeoff angle was 3.3° and the receiving aperture, placed 32 cm from the crystal, was 5.7 mm wide by 3.5 mm high. Data for reflections of the type $\pm h$, $\pm k$, l were collected. For $2\theta < 50°$ a scan speed of 2°/min was used and the basic background counting time in total was 20 s. The rescan option[6] was used with a 3σ cutoff and a limit of two rescans. Thus a once-scanned reflection would have approximately a 50-s peak scan and a 20-s total background count; corresponding values of twice- and thrice-scanned reflections are 100, 60 and 150, 100. Past 2θ of 50° the scan rate was 1°/min and the basic background counting time 40 s. Thus the peak-scan times and total background times were approximately 100, 40; 200, 120; 300, 200 for once, twice, and thrice scanned reflections. Data collection was terminated at 2θ = 110.5°, since in the region between 108 and 110.5° only a small fraction of the reflections was significantly above background. Six standard reflections were monitored during the data collection. They showed a small uniform decrease in intensity of 3% by the end of data collection. The data were accordingly corrected for this small decline.

Data were processed as previously described[5] using a value of 0.03 for p. Of the 4336 reflections measured, 3889 are unique, 3376 are unique and have $F_o^2 > 0$, 1983 are unique and have $F_o^2 > 3\sigma(F_o^2)$. The data were corrected for absorption effects.[6] Based on a linear absorption coefficient of 6.39 cm^{-1} the transmission factors ranged from 0.916 to 0.990.

The unit cell of protoporphyrin IX dimethyl ester free base bears a close relation to that of mesoporphyrin IX dimethyl ester free base[3] when the latter cell is rearranged (a = 11.378, b = 23.458, c = 5.971 Å, α = 85.77, β = 94.08, γ = 81.96°). Attempts to solve the structure of the present compound on the assumption that it is isostructural with the known structure of mesoporphyrin IX dimethyl ester free base failed. Eventually the present structure was solved from the origin-removed, sharpened Patterson function ($2x$, $2y$, $2z$ peak between

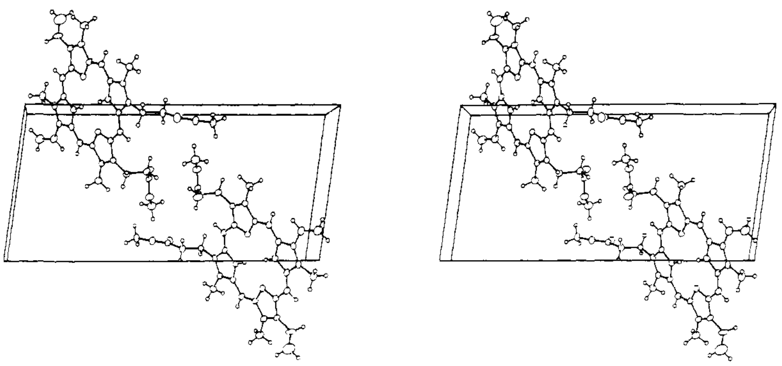

Figure 1. A stereoscopic view of the unit cell of H_2PPIX DME. In this view the x axis goes from bottom to top, the y axis from left to right, and the z axis into the paper. The atoms are drawn at their 20% probability levels, except for the hydrogen atoms which have been drawn artificially small.

Table II. Idealized Positions of the Hydrogen Atoms

Atom	x	y	z
H1C(5)	0.249	0.0756	0.404
H1C(10)	0.296	0.2278	−0.410
H1C(15)	−0.242	0.3378	−0.392
H1C(20)	−0.290	0.1840	0.422
H1N(1)	−0.004	0.1770	0.153
H1N(3)	0.010	0.2342	−0.141
H1C(21)	−0.242	0.1331	0.741
H1C(24)	0.423	0.0351	0.260
H1C(28)	−0.055	0.3611	−0.856
H2C(28)	−0.172	0.3573	−0.742
H1C(29)	−0.140	0.4350	−0.505
H2C(29)	−0.009	0.4325	−0.568
H1C(31)	−0.443	0.3461	−0.322
H2C(31)	−0.525	0.3415	−0.130
H1C(32)	−0.343	0.4150	−0.082
H2C(32)	−0.470	0.4412	−0.176
H1C(22)	−0.241	0.0515	0.925
H2C(22)	−0.117	0.0216	0.818
H1C(25)	0.617	0.0385	0.302
H2C(25)	0.600	0.1017	0.166
H1C(34)	−0.532	0.2986	0.217
H2C(34)	−0.510	0.2292	0.206
H3C(34)	−0.451	0.2631	0.400
H1C(23)	0.072	0.0500	0.864
H2C(23)	0.100	0.0053	0.670
H3C(23)	0.185	0.0522	0.734
H1C(26)	0.531	0.1114	−0.228
H2C(26)	0.457	0.1591	−0.381
H3C(26)	0.530	0.1790	−0.173
H1C(27)	0.210	0.2706	−0.800
H2C(27)	0.144	0.3351	−0.834
H3C(27)	0.248	0.3229	−0.653
H1C(35)	−0.131	0.6154	−0.771
H2C(35)	−0.124	0.5732	−0.977
H3C(35)	−0.246	0.5930	−0.878
H1C(36)	−0.606	0.4815	0.433
H2C(36)	−0.722	0.4571	0.344
H3C(36)	−0.618	0.4145	0.461

molecules of length 9.3 Å vs. 10.8 Å in MPIX DME) and from the program PATTOR[7] which yielded the orientation of the molecule from the best fit of the Fourier transform of the 24-atom inner core (whose geometry was assumed) to the diffraction pattern as given by the 12 strongest reflections.

The structure was refined by full-matrix least-squares methods described previously.[3] The refinement was on F_o^2, where $\Sigma w(F_o^2 - F_c^2)^2$ was minimized, and where all unique F_o^2, including $F_o^2 < 0$, were used. After convergence of an isotropic model for the nonhydrogen atoms at $R(F^2) = 0.17$ and $R_w(F^2) = 0.23$ a completely anisotropic model was employed, which led, after one cycle, to a difference Fourier map on which all 38 hydrogen atoms were visible as the main features of the map. The positions of these hydrogen atoms were idealized, using a C-H or N-H distance of 0.95 Å and assigning a thermal parameter to each that was 1.0 Å^2 greater than the equivalent isotropic thermal parameter of the heavy atom to which it was attached. The methyl and methylene hydrogen positions were idealized assuming tetrahedral geometry, the methine and imine hydrogen atoms assuming trigonal planar geometry, and the vinyl hydrogen atoms assuming trigonal planar geometry and a planar overall geometry for the vinyl group. The contributions of these hydrogen atoms to the overall scattering were held fixed in ensuing calculations. A final cycle of anisotropic refinement, based on 397 variables and 3889 observations, converged to values of $R(F^2)$ of 0.108, $R_w(F^2)$ of 0.161, and to an error in an observation of unit weight of 1.32e^2. The conventional R indices on F_o for the 1982 observations having $F_o^2 > 3\sigma(F_o^2)$ are 0.073 and 0.078, respectively.

An analysis of $\Sigma w(F_o^2 - F_c^2)^2$ as a function of F_o^2, setting angles, and Miller indices shows no unexpected trends. A final difference Fourier map is featureless, and ranges between 0.30 and −0.26 e/Å^3. The final atomic parameters for the heavy atoms are given in Table I. Table II lists the idealized positions of the hydrogen atoms. Values of 20 $|F_o|$ vs. 20 $|F_c|$ are given in Table III.[8] A negative entry here means that $F_o^2 < 0$.

Description of the Structure

The crystal structure of H_2PPIX DME consists of discrete, well-separated molecules. A stereoview of the unit cell, drawn in the same metrical orientation as that of H_2MPIX DME, is shown in Figure 1. Although there is a close resemblance of the two crystal structures, the positions in the cell of the centroids of the porphyrin rings differ somewhat as do the orientations of these rings. There are no exceptionally short intermolecular interactions. The shortest involving only hydrogen atoms is H2C(27)-H2C(35) at 2.37 Å. The shortest involving other atoms is O(2)-H2C(29) at 2.48 Å.

The numbering scheme[9] used in this paper is illustrated in the general view of the molecule shown in Figure 2. Individual and averaged bond distances and angles are presented in Table IV. Note that as for H_2MPIX DME this porphyrin contains isolated imino and amino pyrrole moieties and as a result the pyrrole rings are nonequivalent. The hydrogen atoms of the core are localized on opposing aminopyrrole rings. Because of this and because of the asymmetric pattern of substitution there are two possible geometrical isomers, differing only in the placement of the amino hydrogen atoms in the center of the macrocycle. As for MPIX DME only one such isomer is found here and it is the same as that found previously. In solution rapid N-H tautomerism is observed[10] for deuteroporphyrin IX dimethyl ester and tetraphenylporphyrin[10] and would be presumed to occur in MPIX DME and PPIX DME.

The 24-atom porphyrin core is nearly planar (Table V); the largest out-of-plane displacement is 0.074 (7) Å for atom C(17). The displacements here are small and nondescriptive, as they were for MPIX DME. It is very likely that distortions from planarity in these free-base porphyrins are brought about

Table IV. Bond Distances (Å) and Angles (deg) in the Free Base of Protoporphyrin IX Dimethyl Ester

		Av			Av
N(1)-C(1)	1.364 (7)	$N-C_a$[a]	N(1)-C(1)-C(2)	106.2 (5)	$N-C_a-C_b$
N(1)-C(4)	1.372 (6)	1.368 (7)[b]	N(1)-C(4)-C(3)	106.7 (5)	
N(3)-C(11)	1.375 (6)	1.367 (9)	N(3)-C(11)-C(12)	107.4 (5)	106.9 (5)
N(3)-C(14)	1.355 (6)	1.370 (7)	N(3)-C(14)-C(13)	107.2 (5)	110.9 (5)
N(2)-C(6)	1.365 (7)		N(2)-C(6)-C(7)	110.3 (5)	
N(2)-C(10)	1.372 (7)		N(2)-C(9)-C(8)	110.6 (5)	
N(4)-C(16)	1.369 (6)		N(4)-C(16)-C(17)	111.2 (5)	
N(4)-C(19)	1.372 (6)		N(4)-C(19)-C(18)	111.3 (5)	
C(5)-C(4)	1.374 (8)	C_m-C_a	C(1)-C(2)-C(3)	108.2 (5)	$C_a-C_b-C_b$
C(20)-C(1)	1.374 (7)	1.386 (9)	C(4)-C(3)-C(2)	108.1 (5)	
C(10)-C(11)	1.388 (7)	1.380 (7)	C(11)-C(12)-C(13)	107.2 (5)	107.9 (5)
C(15)-C(14)	1.385 (7)	1.392 (7)	C(14)-C(13)-C(12)	108.2 (5)	106.5 (5)
C(5)-C(6)	1.390 (8)		C(6)-C(7)-C(8)	106.9 (5)	
C(10)-C(9)	1.384 (8)		C(9)-C(8)-C(7)	106.4 (5)	
C(15)-C(16)	1.396 (7)		C(16)-C(17)-C(18)	106.4 (5)	
C(20)-C(19)	1.396 (7)		C(19)-C(18)-C(17)	106.3 (5)	
C(1)-C(2)	1.448 (7)	C_a-C_b	C(2)-C(1)-C(20)	128.1 (6)	$C_b-C_a-C_m$
C(4)-C(3)	1.435 (7)	1.446 (7)	C(3)-C(4)-C(5)	128.2 (5)	
C(11)-C(12)	1.439 (7)	1.441 (7)	C(12)-C(11)-C(10)	127.0 (5)	127.7 (6)
C(14)-C(13)	1.442 (7)	1.452 (7)	C(13)-C(14)-C(15)	127.6 (5)	124.8 (7)
C(6)-C(7)	1.450 (8)		C(7)-C(6)-C(5)	125.8 (5)	
C(9)-C(8)	1.447 (7)		C(8)-C(9)-C(10)	124.7 (6)	
C(16)-C(17)	1.456 (7)		C(17)-C(16)-C(15)	124.1 (5)	
C(19)-C(18)	1.453 (7)		C(18)-C(19)-C(20)	124.5 (5)	
C(2)-C(3)	1.356 (8)	C_b-C_b	C(4)-C(5)-C(6)	128.8 (5)	$C_a-C_m-C_a$
C(12)-C(13)	1.363 (7)	1.357 (7)	C(9)-C(10)-C(11)	128.3 (6)	128.1 (8)
C(7)-C(8)	1.352 (8)	1.360 (7)	C(14)-C(15)-C(16)	126.9 (5)	
C(17)-C(18)	1.358 (7)	1.355 (7)	C(19)-C(20)-C(1)	128.3 (6)	
C(3)-C(23)	1.501 (8)	C_b-C_{methyl}	C(4)-C(3)-C(23)	123.2 (6)	$C_a-C_b-C_{alkyl}$
C(8)-C(26)	1.499 (8)	1.498 (8)	C(9)-C(8)-C(26)	124.6 (6)	124.7 (8)
C(12)-C(27)	1.489 (7)		C(11)-C(12)-C(27)	125.1 (5)	
C(18)-C(34)	1.501 (7)		C(14)-C(13)-C(28)	125.1 (5)	
C(2)-C(21)	1.459 (8)	C_b-C_{vinyl}	C(16)-C(17)-C(31)	125.5 (5)	
C(7)-C(24)	1.487 (9)	1.474 (21)	C(19)-C(18)-C(34)	124.8 (5)	
C(21)-C(22)	1.260 (8)	Vinyl	C(2)-C(3)-C(23)	128.7 (5)	$C_a-C_b-C_{alkyl}$
C(24)-C(25)	1.225 (10)		C(7)-C(8)-C(26)	129.0 (6)	128.2 (9)
C(13)-C(28)	1.511 (7)	Propionate	C(13)-C(12)-C(27)	127.7 (5)	
C(17)-C(31)	1.494 (7)		C(12)-C(13)-C(28)	126.7 (5)	
C(28)-C(29)	1.514 (7)		C(18)-C(17)-C(31)	128.0 (5)	
C(31)-C(32)	1.534 (7)		C(17)-C(18)-C(34)	128.9 (5)	
C(30)-O(1)	1.199 (7)		C(1)-C(2)-C(21)	122.3 (6)	$C_a-C_b-C_{vinyl}$
C(33)-O(3)	1.181 (7)		C(6)-C(7)-C(24)	122.3 (6)	122.3 (6)
C(30)-O(2)	1.342 (7)		C(3)-C(2)-C(21)	129.5 (5)	$C_b-C_b-C_{vinyl}$
C(33)-O(4)	1.337 (6)		C(8)-C(7)-C(24)	130.8 (6)	130.2 (9)
O(2)-C(35)	1.443 (6)		C(2)-C(21)-C(22)	127.7 (7)	Vinyl
O(4)-C(36)	1.437 (6)		C(7)-C(24)-C(25)	126.6 (9)	
C(1)-N(1)-C(4)	110.8 (5)	C_a-N-C_a	C(13)-C(28)-C(29)	111.0 (4)	Propionate
C(11)-N(3)-C(14)	110.1 (4)		C(17)-C(31)-C(32)	112.6 (5)	
C(6)-N(2)-C(9)	105.8 (5)	110.5 (5)	C(28)-C(29)-C(30)	113.8 (5)	
C(16)-N(4)-C(19)	104.9 (4)	105.4 (5)	C(31)-C(32)-C(33)	113.0 (5)	
N(1)-C(1)-C(20)	125.7 (5)	$N-C_a-C_m$	C(29)-C(30)-O(1)	125.8 (6)	
N(1)-C(4)-C(5)	125.1 (5)	124.9 (5)	C(32)-C(33)-O(3)	126.7 (6)	
N(3)-C(11)-C(10)	125.6 (5)	125.4 (5)	C(29)-C(30)-O(2)	110.2 (5)	
N(3)-C(14)-C(15)	125.2 (5)	124.4 (5)	C(32)-C(33)-O(4)	110.4 (5)	
N(2)-C(6)-C(5)	123.9 (5)		C(30)-O(2)-C(35)	117.0 (5)	
N(2)-C(9)-C(10)	124.8 (5)		C(33)-O(4)-C(36)	117.7 (5)	
N(4)-C(16)-C(15)	124.7 (5)		O(1)-C(30)-O(2)	123.9 (5)	
N(4)-C(19)-C(20)	124.2 (5)		O(3)-C(33)-O(4)	122.8 (6)	

[a] The notation C_a, C_b, and C_m is that of J. L. Hoard, *Science*, **174**, 1296 (1971). [b] The figure in parentheses following an average value is the larger of the standard deviations estimated for an individual value from the inverse matrix or on the assumption that the values are from the same population. The first average, when given, is for the combined imino and amino pyrroles, the second for the amino pyrroles only, and the third for the imino pyrroles only.

by packing forces. Table VI provides a comparison of transannular distances in the PPIX DME and MPIX DME free bases. There are some significant differences, which simply reflect differences in the conformations of the two molecules. Such differences are also apparent from a comparison of the least-squares planes (Table V).

There is remarkable agreement between comparable metrical parameters in PPIX DME and MPIX DME (Table IV here and Table V in ref 3; Table VII here). The only significant differences arise from the presence of vinyl groups peripheral to atoms C(2) and C(7) here, compared with the presence of ethyl groups in these positions in MPIX DME. For example, the deviations from the mean 24-atom porphyrin plane of ethyl β-carbon atoms C(22) and C(25) are 1.31 and 1.59 Å in MPIX

Table V. Deviations (Å) and Equations of Weighted Least-Squares Planes[a]

	Plane 1	Plane 2	Plane 3	Plane 4	Plane 5
C(1)	−0.031 (6)[b]	0.000 (6)			
C(2)	−0.026 (6)	0.000 (6)			
C(3)	−0.010 (6)	−0.001 (6)			
C(4)	−0.002 (6)	0.001 (6)			
C(5)	0.007 (6)	−0.007	−0.006		
C(6)	0.021 (6)		0.003 (6)		
C(7)	0.013 (6)		−0.004 (6)		
C(8)	0.027 (6)		0.004 (6)		
C(9)	0.028 (6)		−0.001 (6)		
C(10)	0.020 (6)		−0.017	0.025	
C(11)	−0.014 (5)			0.002 (5)	
C(12)	−0.051 (5)			−0.002 (5)	
C(13)	−0.048 (5)			0.001 (5)	
C(14)	−0.015 (5)			0.004 (5)	
C(15)	0.009 (5)			0.014	−0.016
C(16)	0.025 (5)				0.001 (5)
C(17)	0.074 (5)				−0.003 (5)
C(18)	0.061 (5)				0.004 (5)
C(19)	−0.011 (5)				−0.003 (5)
C(20)	−0.027 (6)	0.020			0.018
N(1)	−0.017 (4)	−0.001 (4)			
N(2)	0.025 (5)		−0.001 (5)		
N(3)	0.002 (4)			−0.001 (4)	
N(4)	−0.026 (4)				0.001 (4)
C(21)	−0.019	0.020			
C(22)	−0.449				
C(23)	0.030	0.028			
C(24)	−0.049		−0.057		
C(25)	0.447				
C(26)	−0.008		−0.032		
C(27)	−0.086			−0.008	
C(28)	−0.054			0.025	
C(31)	0.230				0.091
C(34)	0.063				−0.029

Plane	A	B	C	D
1	3.708	17.360	3.422	3.603 porphyrin
2	3.574	17.427	3.431	3.601 pyrrole 1
3	3.725	17.277	3.446	3.618 pyrrole 2
4	3.768	17.674	3.299	3.722 pyrrole 3
5	4.105	16.903	3.470	3.399 pyrrole 4
6	−6.183	−10.023	−4.279	−3.020 vinyl C(2)-C(21)-C(22)
7	1.281	−10.917	−5.194	−1.120 vinyl C(7)-C(24)-C(25)

Angles between the Normals to the Planes

Plane A	Plane B	Angle, deg
1	2	0.7
1	3	0.3
1	4	1.4
1	5	2.6
1	6	154.2
1	7	147.6
2	3	0.9
2	4	1.6
2	5	3.2
3	4	1.7
3	5	2.3
4	5	3.3
2	6	153.6
3	7	147.7

[a] The entries for which an error is not indicated are for atoms which were not included in the calculation of the plane. [b] The plane $Ax + By + Cz = D$ is in triclinic coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

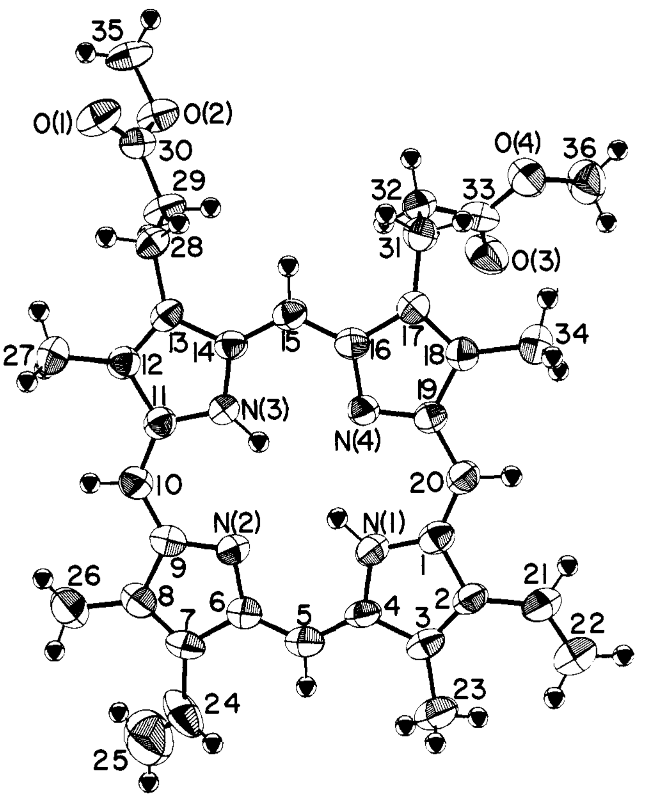

Figure 2. A drawing of the H_2PPIX DME molecule, showing the numbering scheme employed. The nonhydrogen atoms are drawn at their 50% probability levels; the hydrogen atoms are drawn artificially small.

Table VI. Transannular Distances (Å) in Two Free-Base Porphyrins

Atoms	MPIX DME[a]	PPIX DME[b]
HN(1)-HN(3)	2.15[c]	2.26[c]
N(1)-N(3)	3.941	4.199
N(2)-N(4)	4.077	4.055
N(1)-N(2)	2.862	2.917
N(2)-N(3)	2.811	2.943
N(3)-N(4)	2.861	2.890
N(4)-N(1)	2.806	2.924
C(5)-C(15)	6.574	6.849
C(10)-C(20)	6.747	6.816
C(5)-C(10)	4.538	4.813
C(10)-C(15)	4.868	4.849
C(15)-C(20)	4.550	4.829
C(20)-C(5)	4.872	4.834

[a] Reference 3; estimated standard deviation ±0.004 Å. [b] This work; estimated standard deviation ±0.006 to ±0.009 Å for nonhydrogen interactions. [c] From idealized hydrogen positions (N-H = 0.95 Å).

DME whereas the corresponding deviations of β-vinyl atoms C(22) and C(25) in the present structure are 0.45 and 0.45 Å, respectively. Thus the vinyl groups approach planarity with the porphyrin core more than do the ethyl groups, although even the vinyl groups fail to achieve planarity (and hence maximum overlap) owing to steric constraints. These steric constraints arise from at least two types of interactions: that involving an H atom on the β-C atom of a vinyl group with the H atoms on the adjacent methyl group and that involving the H atom on the α-C atom of a vinyl group with the nearby methine H atom. The former interactions are calculated to be from 2.3 to 2.4 Å, and cannot be lengthened simply by rotation of the methyl group because of interaction of the methyl group with the nearby methine H atom; the latter interactions are

Table VII. Average Bond Distances (Å) and Angles (deg) for H_2PPIX DME and H_2MPIX DME

	Amino pyrrole		Imino pyrrole	
	H_2PPIX DME	H_2MPIX DME	H_2PPIX DME	H_2MPIX DME
$N-C_a$	1.367 (9)	1.365 (3)	1.370 (7)	1.366 (3)
C_m-C_a	1.380 (7)	1.386 (3)	1.392 (7)	1.391 (3)
C_a-C_b	1.441 (7)	1.438 (3)	1.452 (7)	1.457 (3)
C_b-C_b	1.360 (7)	1.368 (3)	1.355 (7)	1.359 (5)
C_a-N-C_a	110.5 (5)	109.8 (2)	105.4 (5)	105.7 (2)
$N-C_a-C_m$	125.4 (5)	125.3 (2)	124.4 (5)	124.7 (3)
$N-C_a-C_b$	106.9 (5)	107.5 (2)	110.9 (5)	110.9 (2)
$C_a-C_b-C_b$	107.9 (5)	107.6 (2)	106.5 (5)	106.3 (2)
$C_b-C_a-C_m$	127.7 (6)	127.2 (2)	124.8 (7)	124.4 (3)
$C_a-C_m-C_a$	128.1 (8)	127.7 (2)		

Table VIII. Spectral Data for H_2PPIX DME and H_2MPIX DME[a]

H_2PPIX DME		H_2MPIX DME	
λ_{max}, nm	A_{mM}	λ_{max}, nm	A_{mM}
630	5.0	619	4.9
576	6.5	566	6.5
541	11.1	532	9.9
506	13.8	498	14.0
407.5	161	399.5	168
275	13.0	270	7.9

[a] Spectra determined in chloroform at 30 °C. From ref 12.

2.27 and 2.28 Å for vinyl groups C(21)–C(22) and C(24)–C(25), respectively. If a C–H distance of 1.09 Å is assumed these latter interactions shorten to 2.18 and 2.20 Å. It appears as though the peripheral H atoms tightly interlock and that rotation of the vinyl groups into the porphyrin plane is not possible without shortening of a number of already short H···H interactions. Reference to the appropriate tables indicates that there are indeed metrical differences, especially angular differences, between the two structures in the area of the ethyl-vinyl groups. But the substitution of ethyl for vinyl has no significant effect on bond distances or angles away from the point of substitution. Although this result may have been anticipated on structural grounds, it is essential to establish since the significant differences observed in spectroscopic and other properties suggest that there may also be discernible stereochemical differences.

The modification of the natural vinyl groups by reduction to ethyl groups results in marked effects upon several properties and reactions of the free-base porphyrins, the metal complexes, and reconstituted hemoproteins.[11-18] It has long been recognized that the absorption maxima in electronic spectra (visible and Soret regions) are shifted about 10 nm to higher energy for the metal-free (Table VIII), iron,[15,18,19] and other metal[11-13] complexes. That the vinyl groups can exert a greater "electron-withdrawing" effect upon the porphyrin system than can ethyl groups has been shown in several systems. Examples are (1) the protonation reactions which reveal the amide nitrogen atoms of MPIX DME to be the more basic,[12,20] (2) the lower affinity of nitrogenous ligands (e.g., pyridine, 1-methylimidazole) for metal complexes of MPIX DME than of PPIX DME,[12,13,18] and (3) the lower C–O stretching frequency in carbonyls of Fe(II) MPIX DME than of Fe(II) PPIX DME within, or free from, the globins of hemoglobin and myoglobin.[18] Such a difference in inductive effect has also been offered in explanation of differences in ring current field effects in ^1H NMR spectra of free-base and iron(II) dipyridine species; this effect is not seen in ^1H NMR spectra of the fully protonated dication.[21] It was pointed out earlier[12] that the shifts in visible and Soret band maxima need not reflect a difference in electron-withdrawing effect, as has often been stated to be the case.[22] Increased electron withdrawal will cause a red shift if the energy of the excited state is lowered to a greater extent than is the ground state. The vinyl groups (compared with ethyl groups) may lower the excited state energy level without appreciably affecting the ground state level. Thus, an effect on the ground state stereochemistry can be minimal.

Vibrational spectra have revealed small, but possibly significant, differences between the two porphyrins. The N–H stretching frequencies in the infrared differ only slightly if at all.[23] In the aromatic C–C and C–N regions, the infrared spectra suggest a greater nonequivalence among pyrrole rings in the metal-free than in the metal porphyrins and are also consistent with less symmetry in PPIX DME than in MPIX DME.[4,16] In the Raman spectra, differences between the iron complexes of the two porphyrins have not been considered important.[24] Present evidence from infrared and Raman spectra are thus consistent with the stereochemistry for the porphyrin rings of PPIX DME and MPIX DME being nearly identical, as observed.

Several conclusions may be drawn from the present study. The first is one of crystallographic interest: it is possible to derive satisfyingly consistent metrical details on a complex organic crystal whose weight is a mere 0.98 μg, although clearly it would be preferable to have a larger crystal. The second is that this study allows for the first time a direct comparison of the molecular structures of two asymmetrically substituted porphyrin free bases (MPIX DME and PPIX DME); the results suggest that except in the specific region of differing substituents there are no significant differences in metrical details. This result must be contrasted with the differing spectroscopic and reactivity manifestations of such substitutions.

Acknowledgments. This research was supported at Colorado State University by Grant HL-15980 and at Northwestern University by Grant HL-13157 of the National Institutes of Health. We are indebted to Dr. Shie-Ming Peng for some preliminary film studies of the crystals.

Supplementary Material Available: Table III of observed and calculated structure amplitudes (28 pages). Ordering information is given on any current masthead page.

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Silylmethyl and Related Complexes. 5.[1] Metallocene Bis(trimethylsilyl)methyls and Benzhydryls of Early Transition Metals [M(η^5-C_5H_5)$_2$R] (M = Ti or V) and [M(η^5-C_5H_5)$_2$(X)R] (M = Zr or Hf and X = Cl or R), and the Crystal and Molecular Structures of [M(η^5-C_5H_5)$_2$($CHPh_2$)$_2$] (M = Zr or Hf)

Jerry L. Atwood,*[2a] Geoffrey K. Barker,[2b,c] John Holton,[2b] William E. Hunter,[2a] Michael F. Lappert,*[2b] and Ronald Pearce[2d]

Contribution from the School of Molecular Sciences, University of Sussex,
Brighton BN1 9QJ, England, and the Department of Chemistry,
The University of Alabama, University, Alabama 35486.
Received January 19, 1977

Abstract: The reactions of some d^0 or d^1 metallocene dichlorides or [{V(η^5-C_5H_5)$_2$Br}$_2$] with the sterically hindered β-hydrogen-free lithium alkyls $LiCHPh_2$ or LiCH($SiMe_3$)$_2$ have been investigated. The following new compounds were isolated as analytically pure, thermally stable crystals: [M(η^5-C_5H_5)$_2$R] [M = Ti and R = Ph_2CH or (Me_3Si)$_2$CH; or M = V and R = (Me_3Si)$_2$CH], [M(η^5-C_5H_5)$_2$(Cl){CH($SiMe_3$)$_2$}] (M = Zr or Hf), [M(η^5-C_5H_5)$_2$($CHPh_2$)$_2$] (M = Zr or Hf), and [Zr(η^5-C_5H_5)$_2$(Bu-*n*){CH($SiMe_3$)$_2$}]. It is interesting that the titanocene(IV) or vanadocene(IV) dichlorides (unlike the Zr^{IV} or Hf^{IV} analogues) are reduced; for Ti, the Ti^{III} chloride was an isolable intermediate; in the V^{IV} or V^{III}/$LiCHPh_2$ system, reduction gave [V(η^5-C_5H_5)$_2$] and $Ph_2CHCHPh_2$. The benzhydryl ligand is evidently less sterically demanding than (Me_3Si)$_2\overline{C}$H; thus, LiCH($SiMe_3$)$_2$ failed to react with [M(η^5-C_5H_5)$_2$(Cl){CH($SiMe_3$)$_2$}] (M = Zr or Hf), although LiBu-*n* gave the stable mixed alkyl which at 150 °C gave H_2 and C_4H_{10} but no C_4H_8. By contrast the bis(benzhydryls) of Zr^{IV} or Hf^{IV} were readily accessible. The Ti^{III} and V^{III} compounds show magnetic moments consistent with spin-only values and [Ti(η^5-C_5H_5)$_2${CH($SiMe_3$)$_2$}] is a monomer in benzene by cryoscopy. IR, ESR, and NMR data are reported. A single crystal x-ray analysis has been carried out for the isostructural Zr^{IV} and Hf^{IV} compounds [M(η^5-C_5H_5)$_2$($CHPh_2$)$_2$] (M = Zr or Hf). For the former, the metal-carbon σ-bond length {2.388 (12) Å compared with 2.251 (6) Å in [Zr(η^5-C_9H_7)$_2Me_2$]} is markedly influenced by the bulk of the benzhydryl ligand, whereas this is not the case for the latter {2.36 (4) Å compared with 2.332 (12) Å in [Hf(η^5-C_9H_7)$_2Me_2$]}. A comparison of the M-C (indenyl) lengths shows that the approach is closer for Hf [2.46 (5) Å] than Zr [2.513 (15) Å].

This paper results from complementary and overlapping interests of two laboratories. At Sussex attention has focused on ligands such as $Me_3SiCH_2^-$ and (Me_3Si)$_2CH^-$, to provide unusually stable homoleptic transition metal alkyls and subvalent main group element alkyls[3-15] (see also ref 16 and 17). At Alabama extensive structural investigations have been carried out on a large number of organotransition metal complexes.[18-25]

Although there has been considerable interest in the benzyls of transition metals,[15] little work has been done (but see ref 26) using the bulkier benzhydryl ligand, Ph_2CH^-.

A large number of d^0 and d^1 metallocene dialkyls [M(η^5-C_5H_5)$_2R_2$] (M = Ti, Zr, Hf, Nb, or Ta) are now known,[17] but attempts to make vanadium analogues were unsuccessful unless R_2 is a chelate or R = PhC≡C. It is interesting that [Ti(η^5-C_5H_5)$_2Cl_2$] and the allyl-Grignard reagent yielded a Ti^{III} product [Ti(η^5-C_5H_5)$_2$(η^3-C_3H_5)] and biallyl,[27a] whereas the corresponding experiment with [Zr(η^5-C_5H_5)$_2Cl_2$] gave [Zr(η^5-C_5H_5)$_2$(η^1-C_3H_5)$_2$].[27b] Various monoalkyls [V(η^5-C_5H_5)$_2$R] are known, but for corresponding Ti alkyls only a few (R = Me_3SiCH_2) derivatives are well characterized.[28,41]

The chemistry of zirconium and hafnium is well known to be quite similar[29] because of the closeness of atomic radii (1.45 and 1.44 Å, respectively). However, x-ray crystallographic studies of organometallic analogues have produced several interesting structural differences. The most dramatic of these is found with the tetracyclopentadienyl derivatives: tetracyclopentadienylzirconium(IV) is reported[30] to exist as [Zr(η^5-C_5H_5)$_3$(η^1-C_5H_5)], while tetracyclopentadienylhafnium(IV) is thought[31] to be [Hf(η^5-C_5H_5)$_2$(η^1-C_5H_5)$_2$] {but not isostructural with [Ti(η^5-C_5H_5)$_2$(η^1-C_5H_5)$_2$]}.[32] Unfortunately, the crystallographic quality of the structural studies has generated doubts.[33] More subtle differences can be found in bond length comparisons. The Hf-C(η^5-cyclopentadienyl) bond lengths are invariably slightly shorter than the Zr-C(η^5-cyclopentadienyl) distances. For the particularly well-determined structures [MCl_2{(CH_2)$_3$(C_5H_4)$_2$}],[34] the values are Hf-C (average) = 2.482 (4) Å and Zr-C (average) = 2.494 (4) Å. However, the opposite trend has been found for the metal-carbon σ bond lengths in [M(η^5-C_9H_7)$_2Me_2$].[21] Here, the Hf-C (σ) length of 2.332 (12) Å is significantly longer than the Zr-C (σ) distance of 2.251 (6) Å. In order to clarify the factors responsible for the σ- and π-bond length

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