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Structural Investigation of (1-Methylimidazole)-2,3,7,8,12,13,17,18-octaethylporphinatozinc(II)

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Abstract. $[Zn(C_{36}H_{44}N_4)(C_4H_6N_2)]$, [Zn(OEP)(1-MeIm)], $M_r = 680\cdot26$, monoclinic, $P2_1/n$, $Z = 4$, $F(000) = 1448$, $a = 14\cdot099\,(3)$, $b = 17\cdot762\,(2)$, $c = 14\cdot475\,(2)$ Å, $\beta = 95\cdot48\,(1)°$, $V = 3608\cdot4$ Å^3, $T = 294 \pm 1$ K. The calculated and observed densities are 1·25 and 1·26 g cm^{-3}. 5700 observed reflections (measured with Mo $K\alpha$ radiation, $\lambda = 0\cdot71073$ Å) were used to refine the structure to a final $R_1 = 0\cdot072$ and $wR = 0\cdot098$. The complex crystallizes isomorphously with [Co(OEP)(1-MeIm)] and similarities and differences in side-chain disorder and core conformations are described. The average Zn—N_p bond distance is 2·068 (7) Å and the axial Zn—N(Im) distance is 2·106 (4) Å. The zinc(II) atom is displaced 0·42 (1) Å from the porphyrin mean plane. The 1-methylimidazole ligand plane makes a dihedral angle of 10·5° with a Zn—N_p vector. This orientation of the 1-methylimidazole ligand corresponds well with that of previously determined imidazole metalloporphyrin structures and further indicates that the preferred orientation of imidazole ligands is essentially insensitive to the d^n configuration of the metal ion of the metalloporphyrin.

Introduction. We have been actively seeking to understand the control of and the consequences of axial orientation effects in imidazole-ligated metalloporphyrin species. We distinguish two possible types of axial ligand orientation effects: (i) those involving the relative orientation of the axial ligands with respect to each other and (ii) the orientation of the axial imidazole(s) with respect to the porphinato core. A definition for the orientation of planar axial ligands was originally suggested by Collins, Countryman & Hoard (1972) as the dihedral angle φ between the ligand plane and a coordinate plane defined by a porphinato N atom, the metal atom and the coordinated axial donor atom. A φ angle of 0° corresponds to an eclipsing of the axial ligand plane with an M—N_p bond.† Recent work has demonstrated the importance of both the relative and the absolute orientations of axial imidazole ligands in defining the electron paramagnetic resonance parameters of low-spin ferric porphyrinate derivatives (Walker, Huynh, Scheidt & Osvath, 1986; Scheidt, Kirner, Hoard & Reed, 1987; Scheidt, Osvath & Lee, 1987; Quinn, Valentine, Byrn & Strouse, 1987). Other studies have shown that the absolute orientation of the axial ligands can be a factor in determining the spin state of bis-ligated iron(III) porphyrinates (Geiger, Lee & Scheidt, 1984; Scheidt, Geiger, Hayes & Lang, 1983) and possibly controlling the midpoint potentials of hemoproteins (Korszun, Moffat, Frank & Cusanovich, 1982).

It has been recognised that the axial imidazole ligands in metalloporphyrins frequently adopt structures with small values of φ. For example, the average φ value for the nine structurally characterized five-coordinate imidazole complexes is 10·4° with a range of 4–23°. The EPR investigations described above also demonstrate (Walker *et al.*, 1986; Scheidt, Kirner, Hoard & Reed, 1987; Scheidt, Osvath & Lee, 1987; Quinn *et al.*, 1987) that small φ values are thermodynamically favored for low-spin iron(III) derivatives. The question of why such sterically unfavorable orientations are found has recently been examined by Scheidt & Chipman (1986). They explained the observed orientational preference on $L \rightarrow M$ π bonding. Extended Hückel calculations for the species with experimentally known structures that encompass electronic configurations d^4 to d^8 showed that the π bond was dominated by a ligand $p\pi$ to empty metal $p\pi$ interaction that was at a maximum at $\varphi = 0°$. These calculations led to the conclusion that the bonding effects that yield imidazole orientations with φ close to 0° would be largely independent of the d^n configuration of the metal (Scheidt & Chipman, 1986). The study of the molecular structure of an imidazole-ligated zinc complex was undertaken to add a d^{10} species and to test these bonding concepts. We report herein the molecular structure of five-coordinate [Zn(OEP)(1-MeIm)]. The structure of the complex is typical of that found previously for five-coordinate pyridine-ligated species; the orientation of the axial imidazole has a relatively small value of φ (10·5°). However, extended Huckel calculations for [Zn(Porph)(HIm)] do not confirm the importance of a φ-dependent π bond in explaining the observed ligand orientation.

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† Abbreviations used: TPP, TPC, TPiBC, OEP, Porph and TPivP, dianions of *meso*-tetraphenylporphine, tetraphenylchlorin, tetraphenylisobacteriochlorin, octaethylporphyrin, porphine and picket-fence porphyrin, respectively; TPP-C_3Py, pyridine-tailed tetraphenylporphyrin dianion; 1-MeIm, 1-methylimidazole; 2-MeHIm, 2-methylimidazole; 1,2-DiMeIm, 1,2-dimethylimidazole; Py, pyridine; 3-ClPy, 3-chloropyridine; 3,5-Lut, 3,5-dimethylpyridine; 4-MePy, 4-methylpyridine; N_p, porphinato nitrogen.

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Experimental. Zn(OEP) was purchased from Aldrich Chemical Co. Crystals of the monoimidazole complex were grown by slow evaporation of a methylene chloride solution of Zn(OEP) containing a 20-fold excess of 1-methylimidazole. Crystals grew as dark purple plates. Preliminary X-ray photographic examination and data collection were carried out on an Enraf–Nonius CAD-4 diffractometer. The crystal specimen had dimensions of 0·23 × 0·72 × 0·64 mm. Precise cell constants were obtained from a least-squares refinement of 25 reflections with $25 < 2\theta < 29°$. The crystal density was measured by flotation in a mixture of hexane/carbon tetrachloride.

Intensity data were collected to a maximum 2θ of 54·9°. Of the 8839 data collected within this sphere, 8228 were unique and not systematically absent. To check for crystal stability to X-ray exposure, four reflections were measured after every hour of X-ray exposure. The crystal showed a total decay of 1·6% over 187 h of X-ray exposure; no decay correction was applied. Lorentz and polarization corrections but no absorption correction were applied to the data. Equivalent reflections were averaged. For the 462 observed reflections averaged, agreement factors are 0·7% on I and 1·2% on $F_{\rm obs}$. A total of 5700 reflections had $F_o > 3\sigma(F_o)$ and were used in the refinement of the structure. h: 0→18, k: 0→22, l: −18→18. Atomic scattering factors were taken from Cromer & Mann (1968) and Stewart, Davidson & Simpson (1965) with real and imaginary corrections for anomalous dispersion for the Zn atom (Cromer & Liberman, 1970).

Although it is to be noted that the complex is isomorphous with [Co(OEP)(1-MeIm)] (Little & Ibers, 1974), the structure was independently solved by direct methods (*MULTAN*78; Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) followed by a series of difference Fourier calculations. Some difficulties were encountered with some of the peripheral ethyl groups. Four ethyl groups were easily found and refined well; the other four were found to be disordered. The initial model for the disorder was to refine the disordered ethyl group as a pair of ethyl groups – initially each with 1/2 occupancy, one oriented up and the other down. The occupancy factors that were used in the final refinement cycles were 0·6/0·4 for the C(27,28) and C(33,34) ethyls and 0·65/0·35 for C(35,36). The doubled-up ethyl model did not work well with the C(23,24) group and this group was eventually refined as a single anisotropic ethyl group. Evidence for the *meso* hydrogens, the hydrogens of the imidazole and the methylene hydrogens of the ordered ethyl groups were found in difference Fourier syntheses. Accordingly, these H-atom positions were idealized and used as fixed contributors in subsequent least-squares refinement cycles. In the final refinement all heavy atoms were refined anisotropically except for the disordered ethyl groups. The function minimized was $\sum w(\Delta)^2$, $w = 1/\sigma^2$. At convergence $R_1 = 0{\cdot}072$ and $wR = 0{\cdot}098$, and $S = 3{\cdot}41$. Although this R may be high by some standards, it is about average for this class of compound. After the final cycle, the largest peaks in the Fourier map were 1·2, 0·8 and 0·7 e Å^{-3} and were associated with ethyl group C(23,24). The value of $(\Delta/\sigma)_{\rm max}$ was 0·48 and was associated with this ethyl group. Final values of atomic coordinates are listed in Table 1; additional information is available in the supplementary material.*

Calculations were carried out with the charge-iterative extended Hückel method with standard atomic

Table 1. *Fractional coordinates with e.s.d.'s in parentheses*

	x	*y*	*z*
Zn	−0·14570 (3)	0·15458 (3)	0·18359 (3)
N(1)	0·0342 (3)	0·1262 (3)	0·1105 (3)
N(2)	−0·2388 (2)	0·1331 (2)	0·0653 (2)
N(3)	−0·2644 (2)	0·1470 (2)	0·2589 (2)
N(4)	−0·0610 (2)	0·1331 (2)	0·3045 (2)
N(5)	−0·1379 (2)	0·2728 (2)	0·1800 (2)
N(6)	0·1693 (3)	0·3929 (2)	0·1985 (3)
C(1)	0·0585 (3)	0·1175 (3)	0·1445 (3)
C(2)	0·1175 (4)	0·1030 (4)	0·0684 (4)
C(3)	0·0577 (4)	0·1005 (4)	−0·0088 (4)
C(4)	0·0369 (4)	0·1165 (4)	0·0169 (3)
C(5)	−0·1181 (4)	0·1153 (5)	−0·0430 (3)
C(6)	0·2132 (4)	0·1236 (4)	0·0226 (3)
C(7)	−0·2965 (4)	0·1210 (4)	−0·0891 (3)
C(8)	−0·3714 (4)	0·1302 (4)	−0·0410 (4)
C(9)	−0·3354 (3)	0·1377 (3)	0·0569 (3)
C(10)	−0·3898 (3)	0·1462 (3)	0·1315 (3)
C(11)	−0·3586 (3)	0·1500 (3)	0·2247 (3)
C(12)	−0·4177 (3)	0·1555 (3)	0·3007 (3)
C(13)	−0·3592 (3)	0·1549 (3)	0·3804 (3)
C(14)	−0·2629 (3)	0·1498 (2)	0·3535 (3)
C(15)	−0·1806 (3)	0·1465 (3)	0·4147 (3)
C(16)	−0·0873 (3)	0·1377 (3)	0·3930 (3)
C(17)	−0·0028 (4)	0·1311 (5)	0·4590 (4)
C(18)	0·0713 (4)	0·1228 (5)	0·4100 (4)
C(19)	0·0360 (3)	0·1250 (3)	0·3131 (3)
C(20)	0·0906 (3)	0·1189 (4)	0·2388 (3)
C(21)	0·2235 (4)	0·0922 (5)	0·0786 (4)
C(22)	0·2767 (5)	0·1638 (5)	0·0737 (6)
C(23)	0·0788 (5)	0·0739 (6)	−0·1110 (6)
C(24)	0·0872 (6)	0·1452 (5)	−0·1492 (7)
C(25)	−0·2937 (5)	0·1067 (5)	−0·1933 (4)
C(26)	−0·2738 (6)	0·1784 (5)	−0·2407 (5)
C(27*a*)	−0·4752 (9)	0·1074 (9)	−0·0760 (8)
C(27*b*)	−0·4758 (8)	0·1519 (8)	−0·0785 (7)
C(28*a*)	−0·5132 (12)	0·1840 (10)	−0·0845 (11)
C(28*b*)	−0·5351 (8)	0·0760 (6)	−0·0745 (8)
C(29)	−0·5257 (4)	0·1612 (3)	0·2907 (4)
C(30)	−0·5730 (4)	0·0853 (4)	0·2880 (5)
C(31)	−0·3850 (4)	0·1553 (3)	0·4778 (3)
C(32)	−0·3815 (5)	0·0780 (4)	0·5224 (4)
C(33*a*)	−0·0025 (7)	0·1479 (7)	0·5646 (8)
C(33*b*)	−0·0057 (10)	0·0986 (10)	0·5582 (11)
C(34*a*)	−0·0307 (8)	0·0738 (7)	0·6083 (8)
C(34*b*)	−0·0146 (16)	0·1763 (14)	0·6010 (17)
C(35*a*)	0·1750 (7)	0·0959 (7)	0·4467 (7)
C(35*b*)	0·1797 (16)	0·1513 (13)	0·4532 (15)
C(36*a*)	0·2335 (9)	0·1730 (7)	0·4514 (8)
C(36*b*)	0·2212 (19)	0·0695 (15)	0·4510 (17)
C(37)	−0·1988 (3)	0·3215 (3)	0·2075 (4)
C(38)	−0·0639 (3)	0·3159 (3)	0·1534 (4)
C(39)	−0·0825 (4)	0·3891 (3)	0·1633 (4)
C(40)	−0·2210 (5)	0·4628 (4)	0·2212 (5)

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* A list of structure factors and tables of anisotropic temperature factors, fixed H-atom positions and complete tables of individual bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44536 (23 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

parameters (Zerner & Gouterman, 1966). Initial coordinates for [Zn(Porph)(HIm)] were taken from the crystallographic structure determination. Peripheral groups of the porphyrin were replaced by H atoms. Ligand rotations were made around the axial Zn—N(Im) bond and no additional idealization of the geometry was imposed. The computer program, coordinate system and convergence criterion used previously (Scheidt & Chipman, 1986) were employed.

Table 2. *Selected bond distances* (Å) *and angles* (°)

Zn–N(1)	2·061 (3)	N(1)–C(1)	1·361 (6)
Zn–N(2)	2·078 (4)	N(1)–C(4)	1·363 (6)
Zn–N(3)	2·065 (3)	N(2)–C(6)	1·366 (6)
Zn–N(4)	2·071 (3)	N(2)–C(9)	1·357 (5)
Zn–N(5)	2·106 (4)	N(3)–C(11)	1·374 (5)
N(5)–C(37)	1·307 (6)	N(3)–C(14)	1·368 (5)
C(37)–N(6)	1·345 (6)	N(4)–C(16)	1·370 (5)
N(6)–C(40)	1·493 (7)	N(4)–C(19)	1·369 (5)
N(6)–C(39)	1·372 (7)	C(11)–C(12)	1·445 (6)
C(39)–C(38)	1·336 (8)	C(14)–C(13)	1·451 (6)
C(38)–N(5)	1·377 (6)	C(16)–C(17)	1·460 (7)
C(11)–C(10)	1·381 (6)	C(19)–C(18)	1·444 (7)
C(14)–C(15)	1·392 (6)	C(1)–C(2)	1·465 (7)
C(16)–C(15)	1·389 (6)	C(4)–C(5)	1·446 (7)
C(19)–C(20)	1·384 (7)	C(6)–C(7)	1·446 (7)
C(1)–C(20)	1·398 (7)	C(9)–C(8)	1·465 (6)
C(4)–C(5)	1·368 (7)	C(12)–C(13)	1·353 (6)
C(6)–C(5)	1·408 (7)	C(17)–C(18)	1·325 (8)
C(9)–C(10)	1·391 (6)	C(2)–C(3)	1·334 (7)
		C(7)–C(8)	1·331 (8)
N(3)–Zn–N(4)	88·7 (1)	N(3)–C(11)–C(12)	109·7 (4)
N(3)–Zn–N(1)	162·1 (2)	N(3)–C(14)–C(13)	110·2 (4)
N(3)–Zn–N(2)	87·7 (1)	N(4)–C(16)–C(17)	109·3 (4)
N(4)–Zn–N(1)	88·0 (1)	N(4)–C(19)–C(18)	109·9 (4)
N(4)–Zn–N(2)	158·7 (2)	N(1)–C(1)–C(2)	110·1 (4)
N(1)–Zn–N(2)	89·0 (1)	N(1)–C(4)–C(3)	110·0 (4)
N(3)–Zn–N(5)	97·7 (1)	N(2)–C(6)–C(7)	110·7 (4)
N(4)–Zn–N(5)	99·8 (1)	N(2)–C(9)–C(8)	109·5 (4)
N(1)–Zn–N(5)	100·2 (2)	C(11)–C(12)–C(13)	107·4 (4)
N(2)–Zn–N(5)	101·5 (2)	C(14)–C(13)–C(12)	106·4 (4)
C(11)–N(3)–C(14)	106·3 (3)	C(16)–C(17)–C(18)	107·2 (5)
C(16)–N(4)–C(19)	106·2 (4)	C(19)–C(18)–C(17)	107·4 (5)
C(1)–N(1)–C(4)	106·2 (4)	C(1)–C(2)–C(3)	106·0 (4)
C(6)–N(2)–C(9)	106·0 (4)	C(4)–C(3)–C(2)	107·6 (5)
N(3)–C(6)–C(10)	123·8 (4)	C(6)–C(7)–C(8)	106·4 (5)
N(3)–C(14)–C(15)	124·6 (4)	C(9)–C(8)–C(7)	107·3 (4)
N(4)–C(16)–C(15)	124·4 (4)	C(10)–C(11)–C(12)	126·5 (4)
N(4)–C(19)–C(20)	124·2 (4)	C(15)–C(14)–C(13)	125·2 (4)
N(1)–C(1)–C(20)	124·2 (4)	C(15)–C(16)–C(17)	126·3 (4)
N(1)–C(4)–C(5)	125·0 (4)	C(20)–C(19)–C(18)	125·9 (4)
N(2)–C(6)–C(5)	123·3 (4)	C(20)–C(1)–C(2)	125·7 (5)
N(2)–C(9)–C(10)	124·0 (4)	C(5)–C(4)–C(3)	124·8 (5)
C(14)–C(15)–C(16)	127·6 (4)	C(5)–C(6)–C(7)	125·9 (5)
C(19)–C(20)–C(1)	127·5 (4)	C(10)–C(9)–C(8)	126·5 (4)
C(4)–C(5)–C(6)	128·5 (5)		
C(9)–C(10)–C(11)	128·1 (4)		

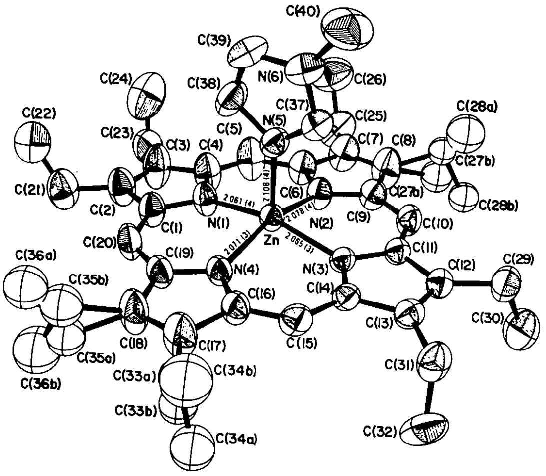

Fig. 1. An *ORTEP* drawing (Johnson, 1976) of [Zn(OEP)(1-MeIm)] illustrating coordination-group bond distances and the atom-labeling scheme. Ellipsoids are contoured at the 50% probability level.

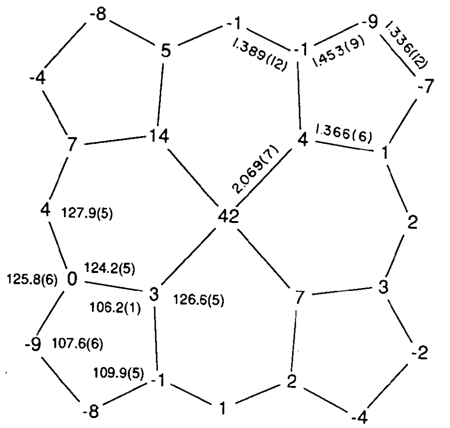

Fig. 2. Formal diagram of a porphinato core showing the averaged values of the various classes of bond distances and angles. The numbers in parentheses are the root-mean-square deviations of averaged values. The diagram also displays the displacement of each atom, in units of 0·01 Å, from the mean plane of the 24-atom core. The diagram has the same relative orientation for the molecule as Fig. 1.

Discussion. A perspective diagram of [Zn(OEP)(1-MeIm)] is given in Fig. 1. Selected bond distances and angles are listed in Table 2. Averaged values for the chemically distinct classes of bond distances and angles in the core are displayed in Fig. 2. Also shown in Fig. 2 are the displacements of each atom from the best least-squares plane of the 24-atom core. The displacement of the Zn atom from the 24-atom mean plane is 0·42 (1) Å and its displacement from the mean plane of the four porphinato N atoms is 0·35 (1) Å. There is thus some doming in the core conformation. However, as can be seen from Fig. 2, the overall conformation of the core is more like that of an umbrella tent rather than a simple C_{4v} doming. (The umbrella-tent conformation is one in which three pyrrole rings follow the displaced metal atom but the fourth pyrrole ring does not and forms the tent flap.) Interestingly, a similar core conformation has been observed in [Zn(OEP)(Py)] (Cullen & Meyer, 1976) but not in any of the analogous tetraarylporphyrin derivatives. It is also noteworthy that this core conformation is not observed in the isomorphous complex [Co(OEP)(1-MeIm)] (Little & Ibers, 1974), even though other conformational similarities are observed (see below).

The average value of the Zn—N_p bond distance is 2·068 (7) Å. This is very similar to values observed previously for other five-coordinate zinc porphyrinates, as shown in Table 3. However, the axial

Table 3. *Selected structural data for imidazole- and pyridine-ligated metalloporphyrin complexes*

Complex	M—N$_p$(Å)	M—N$_{ax}$(Å)	Reference
[Zn(OEP)(Py)]	2·067 (6)	2·200 (3)	Cullen & Meyer (1976)
[Zn(TPyP)(Py)]	2·073 (9)	2·143 (4)	Collins & Hoard (1970)
[Zn(TPC)(Py)]	2·065 (6)	2·171 (2)	Spaulding, Andrews & Williams (1977)
[Zn(TPiBC)(Py)]	2·070 (23)	2·155 (3)	Barkigia, Fajer, Spaulding & Williams (1981)
[Zn(TPP-C$_5$Py)]	2·059 (10)	2·147 (7)	Bobrik & Walker (1980)
[Zn(OEP)(1-MeIm)	2·068 (7)	2·106 (4)	Present work
[Mg(OEP)(Py)$_2$]	2·070 (8)	2·389 (2)	Bonnet, Hursthouse, Malik & Mateen (1971)
[Mg(TPP)(4-MePy)$_2$]	2·071 (2)	2·386 (2)	McKee, Ong & Rodley (1984)
[Mg(TPP)(1-MeIm)$_2$]	2·078 (6)	2·297 (8)	McKee, Ong & Rodley (1984)
[Fe(TPP)(1-MeIm)$_2$]	1·997 (4)	2·014 (5)	Steffen, Chun, Hoard & Reed (1978)
[Fe(TPP)(Py)$_2$]	1·993 (6)	2·039 (1)	Li, Petřiček, Coppens & Landrum (1985)
[Co(TPP)(1-MeIm)]	1·977 (6)	2·157 (3)	Scheidt (1974)
[Co(TPP)(3,5-Lut)]	2·000 (4)	2·161 (5)	Scheidt & Ramanuja (1975)

Zn—N(Im) distance of 2·106 (4) Å is significantly shorter than any of the Zn—N(Py) derivatives observed in the derivatives listed in Table 3. This pattern of shorter M—N(imidazole) than M—N(pyridine) bonds is also found in the d^0 magnesium complexes listed in Table 3. Smaller differences in pyridine and imidazole axial distances are seen in the transition-metal derivatives listed in Table 3. We are not certain of the cause for the difference in axial bond lengths between imidazole and pyridine ligands. Part of the difference may be steric in origin owing to the differences in steric bulk between five- and six-membered rings.

As noted in the *Experimental* section, some of the peripheral ethyl-group side chains are disordered. Interestingly, the crystallographically identical side chains are disordered in both [Co(OEP)(1-MeIm)] and the present complex. However, we have been able to define the disordered side chains better than Little & Ibers (1974), probably because our data set has a significantly increased number of observed diffraction data. We presume that these strong similarities in side-chain disorder result from the domination of crystal packing by the porphyrin entity (Scheidt & Lee, 1987). Despite these similar packing features of the side chains, we find that the detailed deviations from planarity of the porphyrin cores in the cobalt and zinc species are quite different. Since, as noted above, [Zn(OEP)(1-MeIm)] and [Zn(OEP)(Py)] share a common core conformation, we would suggest that the presently observed core conformation is intrinsic to the formation of a five-coordinate Zn(OEP) derivative rather than a consequence of crystal packing effects. Hence, we conclude that observed porphyrin core conformations are not necessarily driven by crystal packing effects, although such effects remain clearly possible.

The imidazole ligand is planar and the imidazole plane makes a dihedral angle of 86·8° with the mean plane of the porphinato core. The 1-methylimidazole ligand is close to eclipsing the N(1)—N(3) axis (Fig. 1) with a calculated φ value of 10·5°. As we have noted elsewhere (Scheidt & Chipman, 1986), it seems unlikely that all the (predominantly small) values of this orientation angle are set by crystal packing effects. Although a single value of this orientation angle clearly does not establish a trend, the present result is consistent with the notion that the preferred imidazole orientation in d^{10} complexes is close to eclipsing M—N$_p$ bonds. The present result would seem to be consistent with the bonding model proposed (Scheidt & Chipman, 1986) to explain the apparent preference for small φ values. However, a set of extended Hückel calculations, performed for several different imidazole orientations for [Zn(Porph)(HIm)], failed to show an orientation dependence for the ligand $p\pi$ to metal $4p\pi$ interaction, as had been observed for d^4 to d^8 species. The ligand-to-metal $p\pi$–$4p\pi$ overlap population, although at an apparently reasonable level of 0·009, remained constant over the range of rotations and thus failed to display the rotational dependence seen previously (Scheidt & Chipman, 1986). Thus, the results for [Zn(OEP)(1-MeIm)] lead to mixed conclusions in the understanding of the control of imidazole orientations in metalloporphyrins. The experimental structure continues the empiricial observation of small φ angles but the theoretical calculations do not support the $p\pi$–$p\pi$ mechanism previously offered (Scheidt & Chipman, 1986). It would seem that significantly more detailed calculations will be required for a theoretical understanding of ligand orientation preferences. However, given the large number of atoms that must necessarily be included in such calculations, *ab initio* calculations of adequate accuracy remain a computational challenge for the future.

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Structure of 4-Chlorobenzyl Alcohol

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Abstract. C_7H_7ClO, $M_r = 142{\cdot}6$, monoclinic, $P2_1$, $a = 12{\cdot}069\ (3)$, $b = 4{\cdot}933\ (1)$, $c = 5{\cdot}906\ (3)$ Å, $\beta = 102{\cdot}63\ (3)°$, $V = 343{\cdot}1\ (2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}380$, $D_x = 1{\cdot}381$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}46$ mm^{-1}, $F(000) = 148$, $T = 298$ K, $R = 0{\cdot}041$ for 645 unique reflections. The molecule takes a *trans* form with respect to the positions of the O hydrogen atom and the aryl group. The crystal structure is characterized by the chains of O—H···O hydrogen bonds extending along a 2_1 axis.

Introduction. The chlorine nuclear quadrupole resonance (NQR) study of the title compound has shown the presence of a phase transition from a low-temperature phase (LTP) to the room-temperature phase (RTP) at about 226 K (Hashimoto & Weiss, 1982). In the course of our thermoanalytical investigation on the phase transition, RTP was found to be supercooled without difficulty. The RTP to LTP transition temperature was about 205 K for crystals obtained by gradual evaporation of a benzene solution, while, for crystals which had undergone the phase transition several times, the transition temperature was observed in a region between 209 and 215 K depending upon the maximum temperature up to which the specimen had been heated subsequently to the LTP to RTP transition. In general, a prolonged annealing of a specimen resulted in a lowering of the RTP to LTP transition temperature. As to the LTP to RTP transition, melt-grown crystals exhibited the transition at about 225 K, while the compound recrystallized from a benzene solution exhibited the transition at about 236 K. Similar complicated phase transitions were found for 4-bromo- and 4-methylbenzyl alcohols isomorphous to the title compound. Another point of interest is the rotational isomerism of the molecule predicted by IR and dipole-moment studies (Oki & Iwamura, 1959; Pandiarajan & Sekar, 1981). In order to obtain a definite structural base for the study of the nature of the phase transition and to determine the molecular conformation in the solid state, the crystal structure of the room-temperature phase was studied by single-crystal X-ray diffractometry.

Experimental. Colorless plate-like crystal (from benzene) set in a thin glass capillary to prevent sublimation. Density by pycnometry. Approximate crystal size $0{\cdot}2 \times 0{\cdot}3 \times 0{\cdot}3$ mm. Rigaku AFC-5 automated

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