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Supplementary Material Available: Listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of 2,3-Dihydro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrinatopyridinezinc(II)-Benzene Solvate¹

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Abstract: The structure of 2,3-dihydro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrinatopyridinezinc(II)-benzene solvate, ZnTPC(Py)·C₆H₆, has been determined from three-dimensional x-ray diffraction. The compound crystallizes with one molecule of benzene and one ZnTPC(Py) per asymmetric unit in the triclinic space group *P* $\bar{1}$ with $a = 11.414$ (2) Å, $b = 13.334$ (2) Å, $c = 14.809$ (1) Å, $\alpha = 99.18$ (1)°, $\beta = 94.14$ (1)°, and $\gamma = 105.08$ (1)°. The structure has been refined by block-diagonal least-squares to $R = 0.046$ based on 8792 measured intensities with a 13:1 parameter-to-variable ratio. Agreement of chemically similar bond distances and angles is excellent. The reduced pyrrole ring is clearly distinct with a C $_{\beta}$ -C $_{\beta}$ distance of 1.478 (3) Å and C $_{\alpha}$ -C $_{\beta}$ distance of 1.495 (2) Å. Comparison of ZnTPC(Py) with analogous porphyrins shows the effect of reduction on the porphyrin macrocycle and on the zinc coordination. Differences in the orientations of the reduced pyrrole ring hydrogen atoms in chlorophylls and ZnTPC(Py), previously predicted by ESR experiments, are confirmed.

Metallotetraphenylporphyrins, MTPP, Figure 1a, have been widely studied by x-ray diffraction as models of naturally occurring porphyrins.³ The dihydrotetraphenylporphyrins (tetraphenylchlorins), Figure 1b, have been used to model chlorophyll;⁴ however, no structure of a metallotetraphenylchlorin has been determined to date. Such a structure would illustrate the effect of reducing the porphyrin conjugated π -electron system, and allow direct comparison with the recently determined structures of ethylchlorophyllides a⁵ and b.⁶ We present here the structural determination of 2,3-dihydrotetraphenylporphyrinatopyridinezinc(II)-benzene solvate.

Experimental Section

Tetraphenylchlorin (TPCH₂) was prepared by standard methods⁷ and reacted with zinc acetate in pyridine to form 2,3-dihydro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrinatopyridinezinc(II), ZnTPC(Py).⁸ The reaction mixture was partitioned between benzene and water, and the organic layer washed with water. The product was crystallized from benzene and dried in vacuum at room temperature. A combination of diffusion and evaporation at room temperature using Fisher Certified hexanes and dichloromethane, distilled from calcium hydride, as solvents yielded crystals suitable for diffraction studies.

A purple prism (0.3 × 0.7 × 0.4 mm) was mounted along its long axis and the crystallographic properties were examined on a precession camera. Good quality diffraction patterns, exhibiting only inversion symmetry, were obtained. After approximate cell dimensions were measured, the crystal was mounted on an Enraf-Nonius CAD4 diffractometer. Some crystallographic details are given in Table I.

During the 2 weeks of data collection, three reflections were mon-

itored periodically. The intensities of these reflections showed no significant trends or fluctuations; therefore no time-dependent correction for experimental instability was made.

Solution and Refinement. The position of the zinc atom was determined from a vector map, and electron-density and difference-electron-density syntheses were used to obtain positions for all other nonhydrogen atoms. This model was refined by block-diagonal least-squares against the 7760 data with $|F_o| > 12\sigma|F_o|$. A further difference map indicated positions for all hydrogen atoms except those of the benzene molecule of solvation. Refinement was continued against all the unique intensity data (*I*s), except 3-4.4 which was omitted because of an unusually large weighted discrepancy. All nonhydrogen atoms were permitted anisotropic expression of their thermal motion, but each hydrogen atom was restricted to a single isotropic vibration parameter. Hydrogen atoms of the benzene solvate were placed in their calculated positions and periodically updated. Because of the apparently very high thermal motion of the benzene ring, refinement of the occupancy factors for its atoms was attempted. Values near unity resulted, and so full occupancy was assumed.

Refinement was terminated when the parameter shifts for all nonhydrogen atoms, except those for the benzene solvate, were reduced to less than their nominal standard deviations. The largest positional shift in the final cycle was 1.08 σ for two hydrogen atoms, and the largest change in a vibrational parameter was 1.9 σ for U_{23} of C(55). A final difference synthesis revealed a peak of height $\sim 0.6 e/\text{\AA}^3$ near the benzene ring as its most prominent feature. The region near the reduced pyrrole ring was carefully examined for evidence of conformational or rotational disorder, but no evidence for these phenomena was found. Final residuals are given in Table I.

The structure and numbering system are shown in Figure 2 and the atomic positions are given in Tables II and III. The bond distances

Table I. Crystallographic Details

Unit cell: space group, triclinic, $P\bar{1}$		
$a = 11.414 (2) \text{ \AA}^a$	$\alpha = 99.18 (1)^\circ$	$V = 2133 \text{ \AA}^3$
$b = 13.334 (1) \text{ \AA}$	$\beta = 94.14 (2)^\circ$	$Z = 2$
$c = 14.809 (1) \text{ \AA}$	$\gamma = 105.08 (1)^\circ$	
Density		
Obsd (aqueous K1), 1.23 g/cm ³		
Calcd for $2 \times [(C_{55}H_{36}N_5Zn)/\text{cell}]$, 1.25 g/cm ³		
Crystal description: triclinic prism, $\{100\}$, $\{010\}$, $\{001\}$, $\{011\}$		
$d(100, 100) = 0.15 \text{ mm}$	$d(001, 001) = 0.19 \text{ mm}$	
$d(010, 010) = 0.37 \text{ mm}$	$d(011, 011) = 0.34 \text{ mm}$	
Vol = 0.085 mm ³		
Data collection		
Diffractometer, Enraf-Nonius, CAD4		
Radiation, Cu K α -graphite monochromated, $\lambda = 1.54051 \text{ \AA}$		
Attenuator, nickel foil, $I_0/I_{\text{Airy}} = 15.55$		
Linear absorption coefficient, 12.28 cm ⁻¹ (Cu K α)		
Two θ range, $0 \leq 2\theta \leq 140^\circ$		
No. of reflections, 11 563 measured $h \geq 0$, 8792 unique		
Scattering factors, Cromer and Mann ⁹		
Anomalous dispersion, Cromer and Liberman ¹⁰		
Refinement: block-diagonal least-squares against I_s		
$R_F = 0.03 (F > 0)$	$R_I = 0.06$	
$R_{wF} = 0.06 (F > 0)$	$R_{wI} = 0.11$	
Programs used		
Absorption correction and averaging BNLABS/AVSORT ²³		
Thermal motion analysis TLS6 (Schomaker and Trueblood) ^{23,24}		
Figure 5 (PRJCTN) (McCandlish, Andrews, Bernstein, 1975) ²³		
All others XRAY76 (Stewart et al.) ²⁵		

^a Here and subsequently the standard deviations of the least significant figure are given in parentheses.

and angles are embodied in Tables IV, V, and VI. Throughout this analysis there was no indication that the structure had symmetry lower than that of space group $P\bar{1}$. A tabulation of the observed and calculated amplitudes is available.¹¹

Results and Discussion

In structures with a high degree of internal redundancy, the agreement between chemically similar bond lengths can be used to indicate the reliability of the analysis, and also to provide an indication of the true standard deviations in these quantities. Table IV indicates that for this analysis the agreement is, in general, very good, although the least-squares estimates of the standard deviations appears to be too low by a factor of ~ 2.5 .

The reduced pyrrole, ring 1, is clearly distinct from the other three as indicated by the bond distance involving the saturated carbon atoms C(2) and C(3). The C_α - C_β distances of the reduced ring (average 1.495 (2) \AA) are longer than those of the other three pyrroles by an average of 0.052 \AA . The C_β - C_β bond of the saturated pyrrole in this structure (1.478 (3) \AA) is markedly longer than the other three C_β - C_β bonds (average 1.363 (4) \AA). It is, however, significantly shorter than the comparable linkage observed in the other crystallographic studies of chlorin compounds. In the ethylchlorophyllides a and b, 1.56 \AA ^{5,6} was found and, for ethylpheophorbide,¹² the analysis yielded 1.55 \AA . The difference between these latter values and that found here seemed abnormally large, and perhaps indicative of some unrecognized error. A careful examination of the difference—electron-density map as noted above and an inspection of the apparent thermal motion of the atoms in this region revealed no evidence of experimental or procedural error. Therefore, we conclude that for the case of only hydrogen atoms as exocyclic substituents of the C_β atoms, the C_β - C_β bond has the expectation value we report here. The chlorophyllide and pheophorbide structures alluded to bear

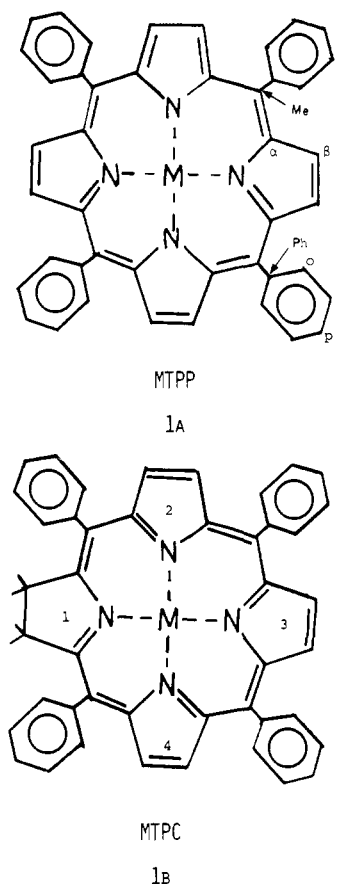


Figure 1. Structural formulas and atom designation for a metallotetra-phenylporphyrin (**1a**) and a metallotetra-phenylchlorin (**1b**).

alkyl substituents exocyclic to the saturated ring, and the C_β atoms of these rings are displaced above and below the ring planes by 0.076 \AA on average. In ZnTPC(Py) these deviations average 0.017 \AA . The C_β - C_β distance given here falls in the range 1.42 to 1.54 \AA found in simple pyrrolidine derivatives.^{13,14}

The reduction of a double bond in the porphyrin macrocycle to form a chlorin has very little effect on the geometry of the macrocycle. The average bond lengths within the porphyrin ring for $\alpha,\beta,\gamma,\delta$ -tetra-4-pyridylporphyrinatopyridinezinc(II), ZnTPyP(Py),¹⁵ are given in Table IV along with the values for the phenyl rings from SnTPP(Cl₂).¹⁶ These values agree to within one standard deviation as do the corresponding bond angles given in Table VI.

There appears to have been no change in size of the central hole of this molecule upon reduction. From the center, C_1 , of the macrocycle, determined from the average of N(1), N(2), N(3), and N(4) coordinates, the average C_1 - C_{Me} distance is 3.445 \AA and the average C_1 - C_α distance is 3.070 \AA . The corresponding values in ZnTPyP(Py) are 3.477 \AA and 3.061 \AA .¹⁵

The coordination geometry of the Zn(II) ion is that of a distorted square pyramid, Figure 3. The metal ion forms bonds 2.061 (1), 2.072 (1), and 2.063 (1) \AA in length to the nitrogen atoms of rings 2, 3, and 4 and is 2.130(1) \AA from the reduced pyrrole ring. This pattern of metal-macrocycle bond lengths was also observed in the ethylchlorophyllide structures. These observations support the x-ray photoelectron spectroscopy studies¹⁷ and molecular orbital calculations¹⁸ on MTPC which indicate that N(1) is electron deficient relative to the other pyrrole nitrogen atoms and may be expected to bond less strongly to a metal ion. Because of this decreased electron donation from the equatorial ligands in ZnTPC over that in ZnTPP it is expected that the former compound is a stronger

Table II. Atomic Coordinates and Anisotropic Thermal Vibration Coefficients for the Nonhydrogen Atoms

ATOM	X	Y	Z	U11	U22	U33	U12	U13	U23
ZN	43138.9(1.7)	16315.6(1.5)	20653.9(1.3)	420.6(1.0)	336.2(1.0)	390.5(1.0)	88.7(0.8)	-24.7(0.8)	13.4(0.8)
N(1)	43990(12)	614(10)	15868(9)	432(6)	321(6)	433(7)	83(5)	-45(5)	10(5)
N(2)	34543(12)	16004(9)	7850(8)	463(6)	320(6)	370(6)	98(5)	-24(5)	7(5)
N(3)	47333(12)	32661(10)	23003(8)	485(7)	342(6)	380(6)	88(5)	-41(5)	8(5)
N(4)	56421(12)	17427(10)	31270(9)	440(6)	339(6)	407(6)	95(5)	-22(5)	20(5)
N(5)	26676(13)	11551(11)	27204(10)	476(7)	439(7)	478(7)	114(6)	30(6)	61(6)
C(1)	49812(14)	-5024(12)	20584(11)	436(7)	335(8)	524(9)	94(6)	-31(6)	33(6)
C(2)	47488(18)	-16127(14)	15491(14)	605(10)	395(9)	652(11)	138(8)	-120(8)	-5(8)
C(3)	38736(18)	-16825(14)	7405(14)	651(10)	375(9)	666(11)	166(8)	-99(9)	-12(8)
C(4)	37231(14)	-5938(12)	8174(11)	438(7)	321(7)	478(8)	71(6)	-15(6)	-14(6)
C(5)	29567(13)	-3166(11)	1887(10)	419(7)	351(7)	392(7)	69(6)	-5(6)	-18(6)
C(6)	28474(14)	7057(12)	1698(10)	435(7)	381(7)	365(7)	86(6)	-13(6)	-4(6)
C(7)	20815(17)	9624(14)	-5276(11)	592(9)	458(9)	430(8)	135(7)	-93(7)	6(7)
C(8)	22756(16)	20370(14)	-3449(12)	576(9)	455(9)	463(9)	151(7)	-97(7)	28(7)
C(9)	31221(14)	24339(12)	4931(10)	465(7)	377(7)	382(7)	114(6)	3(6)	51(6)
C(10)	34837(14)	34846(12)	9464(10)	478(8)	353(7)	413(7)	118(6)	19(6)	66(6)
C(11)	42541(15)	38692(12)	17881(11)	505(8)	333(7)	423(8)	104(6)	-2(6)	34(6)
C(12)	47028(17)	49689(13)	22175(12)	653(10)	352(8)	496(9)	118(7)	-44(8)	26(6)
C(13)	54779(18)	50167(13)	29777(12)	655(10)	350(8)	498(9)	105(7)	-56(8)	-19(6)
C(14)	54903(15)	39557(12)	30277(10)	506(8)	338(7)	402(8)	80(6)	-25(6)	-21(6)
C(15)	61951(14)	36713(12)	37099(10)	466(8)	379(8)	385(7)	82(6)	-5(6)	-25(6)
C(16)	62608(14)	26487(12)	37478(10)	455(7)	387(8)	374(7)	86(6)	-27(6)	-4(6)
C(17)	70400(17)	23812(14)	44262(12)	604(10)	487(9)	448(8)	141(8)	-107(7)	3(7)
C(18)	68883(17)	13239(14)	42076(12)	614(10)	479(10)	493(9)	152(8)	-110(8)	48(7)
C(19)	60212(14)	9334(12)	33885(11)	461(7)	393(8)	429(8)	109(6)	-18(6)	52(6)
C(20)	56950(14)	-1245(12)	29066(11)	453(7)	368(8)	495(8)	105(6)	-22(6)	76(6)
C(21)	21447(14)	-11973(12)	-5268(10)	417(7)	350(7)	403(7)	73(6)	-17(6)	-2(6)
C(22)	25400(16)	-15768(14)	-13389(12)	509(9)	496(9)	491(9)	43(7)	74(7)	-33(7)
C(23)	17676(19)	-24024(15)	-19782(12)	697(11)	540(10)	443(9)	106(9)	35(8)	-82(7)
C(24)	6075(17)	-28583(14)	-18123(13)	595(10)	431(9)	554(10)	58(8)	-165(8)	-50(7)
C(25)	1942(16)	-24820(16)	-10151(14)	444(9)	541(10)	709(12)	4(8)	-18(8)	10(9)
C(26)	9515(16)	-16551(15)	-3800(12)	467(8)	542(10)	534(10)	61(7)	54(7)	-48(8)
C(27)	30310(14)	42633(12)	5015(11)	465(8)	357(8)	476(8)	79(6)	-25(6)	75(6)
C(28)	33812(18)	44912(16)	-3347(13)	591(10)	576(11)	546(10)	173(8)	39(8)	176(8)
C(29)	29363(22)	51959(17)	-7538(15)	799(13)	632(13)	654(12)	148(10)	-37(10)	282(10)
C(30)	21235(21)	56745(16)	-3477(16)	785(13)	466(11)	818(14)	174(10)	-187(11)	160(9)
C(31)	17710(21)	54633(16)	4877(16)	723(12)	488(11)	864(15)	271(10)	3(11)	75(10)
C(32)	22338(18)	47693(14)	9162(13)	622(10)	415(9)	638(11)	170(8)	66(8)	76(8)
C(33)	70036(16)	45494(13)	44264(11)	525(8)	380(8)	453(8)	104(7)	-74(7)	-18(6)
C(34)	65995(22)	49031(17)	52402(13)	832(14)	602(12)	483(10)	54(10)	43(10)	-90(9)
C(35)	73600(28)	57270(19)	58927(15)	1204(21)	637(13)	494(11)	85(14)	-59(12)	-119(9)
C(36)	85140(24)	61902(17)	57362(15)	970(16)	488(11)	677(13)	123(11)	-367(12)	-89(9)
C(37)	89298(21)	58457(20)	49457(20)	588(12)	659(14)	1116(19)	13(10)	-181(12)	-137(13)
C(38)	81761(20)	50271(18)	42826(17)	574(11)	664(13)	832(15)	44(10)	-29(10)	-201(11)
C(39)	61781(15)	-8931(12)	33457(11)	499(8)	345(8)	511(9)	88(6)	-69(7)	52(6)
C(40)	55698(20)	-13740(16)	40128(15)	650(11)	561(11)	676(12)	91(9)	2(9)	210(9)
C(41)	59997(26)	-20984(19)	44126(17)	1003(18)	585(13)	818(15)	23(12)	-122(13)	308(11)
C(42)	70272(27)	-23475(17)	41728(18)	1104(19)	438(11)	946(17)	206(12)	-376(15)	114(11)
C(43)	76369(24)	-18858(21)	35181(19)	860(16)	770(16)	993(18)	483(14)	-124(14)	23(13)
C(44)	72179(20)	-11623(18)	31018(15)	672(12)	712(13)	729(13)	325(10)	47(10)	163(10)
C(45)	15939(18)	12264(18)	23698(15)	527(10)	741(14)	780(13)	220(9)	89(9)	270(11)
C(46)	5278(19)	9154(20)	27496(18)	499(10)	840(16)	1017(18)	133(10)	111(11)	270(13)
C(47)	5673(21)	4885(21)	35343(18)	581(11)	867(16)	869(16)	43(11)	196(11)	162(13)
C(48)	16502(24)	3981(25)	38932(18)	731(14)	1232(23)	780(15)	141(15)	-142(12)	478(15)
C(49)	26859(19)	7435(20)	34761(15)	561(10)	937(16)	618(12)	151(10)	41(9)	294(11)
C(50)	10897(41)	61250(29)	29593(21)	1743(37)	1175(27)	814(19)	490(27)	185(22)	247(18)
C(51)	339(37)	61840(39)	24555(26)	1141(28)	1938(44)	1030(25)	-191(28)	183(22)	-11(25)
C(52)	-97(39)	70434(39)	20717(23)	1470(33)	2110(44)	963(23)	1133(33)	130(22)	269(25)
C(53)	9071(62)	78261(32)	21952(30)	3454(77)	951(27)	1398(34)	883(39)	881(43)	358(24)
C(54)	20156(45)	77826(36)	27073(35)	1502(37)	1216(32)	2059(47)	-168(27)	780(37)	-124(30)
C(55)	20688(35)	69335(36)	30343(22)	1176(27)	1904(41)	746(18)	411(28)	-77(18)	-71(21)

^aThe coordinates have been multiplied by 10⁵ and the vibration coefficients by 10⁴. The U_{ij} are coefficients in the expression $\exp[-2\pi^2(U_{11}a^2h^2 + \dots + 2U_{12}a^*b^*hk \dots)]$.

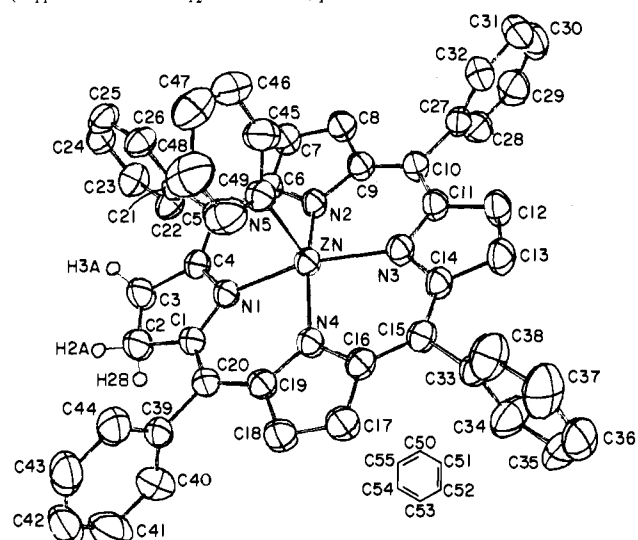


Figure 2. The structure of 2,3-dihydro- $\alpha,\beta,\gamma,\delta$ -tetraphenylporphyrinato-pyridinezinc(II) and atom numbering system. The hydrogen atoms are numbered according to the carbon atom to which they are bonded. The thermal ellipsoids are drawn for 50% probability, except for those of hydrogen atoms which are not to scale. H(3B) is hidden behind C(3).

Lewis acid than the latter. The experimental binding constants for pyridine to these two compounds¹⁹ support this thesis.

The Zn-N(Py) distances found for ZnTPyP(Py),¹⁵ ZnTPC(Py) (this study), and ZnOEP(Py)²⁰ form the series 2.143 (4), 2.171 (2), and 2.200 (3) Å. An explanation of these observations is that steric interaction of the pyridine ortho-hydrogen atoms with the pyrrole rings result in lengthening of the Zn-N_{py} bond.²⁰ The interaction would be largest if the hydrogen atoms were directly over two of the nitrogen atoms, $\phi = 0^\circ$, and least for ϕ of 45° . The N(2)-Zn-N(5)-C(45) torsion angle, ϕ , is 18.6° in ZnTPC(Py) which is smaller than the 23° ϕ in ZnTPyP(Py) and larger than that of ZnOEP(Py), 4° .

The distances of the nonhydrogen atoms of the chlorin system from their least-squares plane are given in Figure 4. These indicate that the molecule is saucer shaped as well as being slightly ruffled. The individual pyrrole rings are planar to within 0.01 Å and no nonhydrogen atom of the reduced ring deviates from its best plane by more than 0.02 Å. The hydrogen atoms of ring 1 are 0.74 Å above and below the best plane of the pyrrole ring. The dihedral angles between the plane of the four pyrrole N atoms and the planes of the four five-membered rings are all of the same sign and range between 3 and 6° .

There are two distortions exhibited by this molecule for

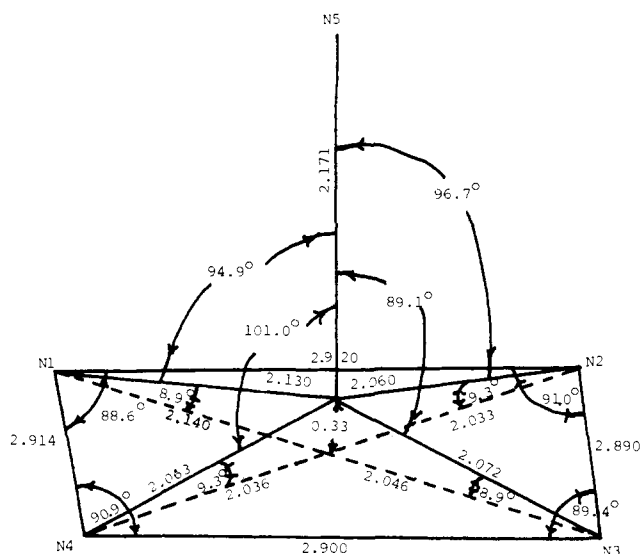


Figure 3. Coordination geometry of the zinc ion.

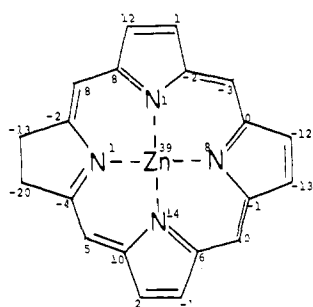


Figure 4. Deviations of the atoms of the metallochlorin macrocycle ($\text{\AA} \times 10^3$) from the least-squares plane of the chlorin system.

which no explanation has been discerned. These are (1) the phenyl rings bonded to meso carbon atoms C(5), C(15), and C(20) form dihedral angles of 93 to 94° with the plane of the four nitrogen atoms, while that bonded to C(10) is 67°, and (2) the axial zinc–nitrogen vector is tilted by 7° from the

Table III. Atomic Coordinates and Isotropic Thermal Vibration Parameters for the Hydrogen Atoms

ATOM	X	Y	Z	B
H(2A)	4446(25)	-2181(21)	1950(17)	80(7)
H(2B)	5454(28)	-1744(24)	1374(19)	105(9)
H(3A)	3145(28)	-2138(24)	723(19)	102(9)
H(3B)	4069(23)	-1983(19)	121(16)	73(6)
H(7)	1647(22)	480(18)	-976(15)	65(5)
H(8)	1893(19)	2414(16)	-608(14)	55(5)
H(12)	4601(19)	5570(16)	1958(13)	51(5)
H(13)	6002(21)	5594(18)	3415(15)	65(6)
H(17)	7519(23)	2842(19)	4944(15)	71(6)
H(18)	7288(19)	922(16)	4498(14)	55(5)
H(22)	3393(19)	-1206(16)	-1464(13)	53(5)
H(23)	2049(22)	-2638(19)	-2535(16)	71(6)
H(24)	65(18)	-3398(15)	-2245(12)	46(4)
H(25)	-583(24)	-2808(20)	-877(16)	78(7)
H(26)	669(22)	-1417(20)	196(16)	73(6)
H(28)	3931(20)	4179(17)	-618(15)	60(5)
H(29)	3264(24)	5325(19)	-1327(16)	73(6)
H(30)	1733(20)	6190(17)	-684(14)	59(5)
H(31)	1169(24)	5770(20)	825(17)	80(7)
H(32)	2028(20)	4635(17)	1524(14)	57(5)
H(34)	5788(24)	4543(20)	5398(17)	83(7)
H(35)	7042(25)	6037(21)	6512(18)	87(7)
H(36)	9011(23)	6737(19)	6151(15)	70(6)
H(37)	9683(29)	6166(24)	4734(20)	104(8)
H(38)	8429(26)	4752(21)	3704(18)	87(7)
H(40)	4817(22)	-1193(18)	4173(16)	68(6)
H(41)	5556(24)	-2382(20)	4942(17)	76(7)
H(42)	7455(24)	-2854(20)	4545(17)	78(7)
H(43)	8253(25)	-2003(21)	3297(17)	82(7)
H(44)	7603(21)	-858(19)	2660(15)	69(6)
H(45)	1557(25)	1547(21)	1779(18)	82(7)
H(46)	-165(23)	1081(20)	2494(16)	74(6)
H(47)	-222(28)	363(23)	3873(19)	99(8)
H(48)	1771(27)	160(22)	4453(19)	94(8)
H(49)	3475(22)	645(18)	3722(15)	65(6)
H(50)	1039(34)	5514(29)	3304(24)	145(12)
H(51)	-761(41)	5608(34)	2300(29)	179(15)
H(52)	-778(41)	6988(36)	1886(29)	183(15)
H(53)	840(41)	8233(35)	2029(29)	156(14)
H(54)	2884(38)	8445(33)	2923(29)	160(14)
H(55)	2873(43)	6863(38)	3256(31)	191(16)

^aThe coordinates have been multiplied by 10^4 and the vibration terms by 10.

normal to the basal plane of the metal ligands toward the benzene of solvation. This tilt was also observed in ZnOEP(Py).²⁰ Examination of lists of intramolecular contact distances reveals only two approaches $<3 \text{ \AA}$. These are H(54)–H(2B) of 2.590 \AA and H(38)–H(55) of 2.640 \AA . The closest carbon–hydrogen contact is 3.3 \AA and all intermolecular carbon–carbon distances are $>3.3 \text{ \AA}$. There is no evidence of any π – π orbital interactions between neighboring molecules. The shortest distance between the planes of symmetry related chlorin systems is 3.92 \AA .

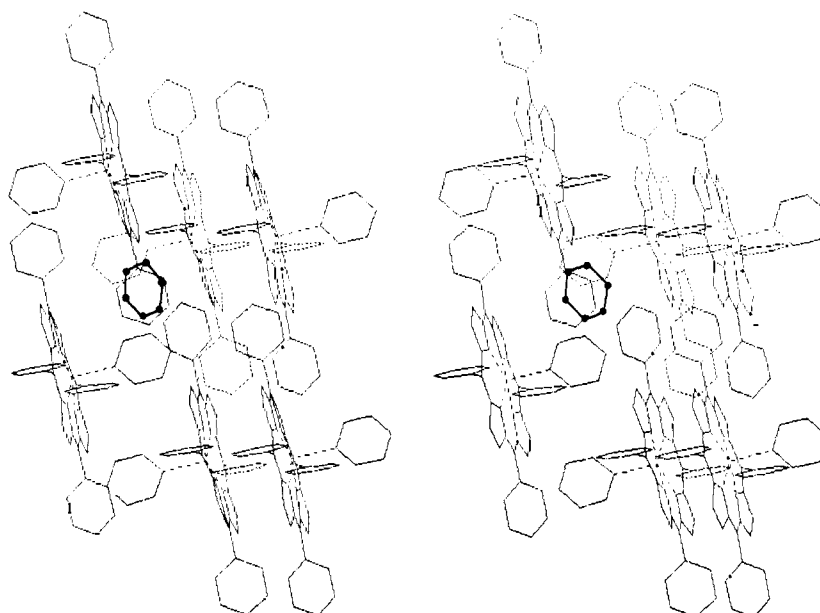


Figure 5. A packing diagram showing the environment of the benzene molecule and the interactions of the ZnTPC(Py) molecules. All molecules which have one or more atoms within 5 \AA from the centroid of the benzene molecule are drawn.

Table IV. Bond Distances between Nonhydrogen Atoms^a

Bond	Type	Distance	Mean ^b	Bond	Type	Distance	Mean ^b	Bond	Type	Distance	Mean ^b
Zn-N(1)	Zn-N	2.130 (1)		C(13)-C(14)	C _α -C _β	1.432 (3)	1.442 (2)	C(34)-C(35)	C _o -C _m	1.392 (3)	(1.392) ^c
Zn-N(2)		2.060 (1)		C(16)-C(17)		1.442 (3)	1.447 (3) ^d	C(37)-C(38)		1.394 (3)	1.397 ^e
Zn-N(3)		2.072 (1)	2.065	C(18)-C(19)		1.442 (2)		C(40)-C(41)		1.383 (4)	
Zn-N(4)		2.063 (1)	2.073 ^d	C(7)-C(8)	C _β -C _β	1.370 (3)		C(43)-C(44)		1.388 (4)	
Zn-N(5)		2.171 (2)		C(12)-C(13)		1.363 (3)	1.362	C(23)-C(24)	C _m -C _p	1.363 (3)	
				C(17)-C(18)		1.357 (3)	1.355 ^d	C(24)-C(25)		1.372 (3)	
				C(9)-C(21)	C _{Me} -C _{Ph}	1.502 (2)		C(26)-C(30)		1.377 (4)	
	Saturated pyrrole			C(10)-C(27)		1.493 (3)	1.497 (2)	C(30)-C(31)		1.377 (4)	1.365
				C(15)-C(33)		1.499 (2)	1.494 (4) ^e	C(35)-C(36)			(9)
				C(20)-C(39)		1.494 (3)		C(36)-C(37)		1.355 (4)	(1.380) ^c
N(1)-C(1)	N-C _α	1.362 (2)	1.363							1.352 (4)	1.366 ^e
N(1)-C(4)		1.364 (2)						C(41)-C(42)		1.355 (4)	
C(1)-C(2)	C _α -C _β	1.497 (2)	1.495					C(42)-C(43)		1.367 (4)	
C(3)-C(4)		1.493 (2)									
C(2)-C(3)	C _β -C _β	1.478 (3)									
	Unsaturated pyrroles										
				N(5)-C(45)		1.329 (3)					
				N(5)-C(49)		1.324 (3)					
				C(45)-C(46)		1.372 (3)		C(50)-C(51)		1.319 (5)	
N(2)-C(6)	N-C _α	1.366 (2)		C(48)-C(49)		1.373 (3)		C(50)-C(55)		1.314 (7)	
N(2)-C(9)		1.384 (2)		C(46)-C(47)		1.376 (4)		C(51)-C(52)		1.398 (6)	
N(3)-C(11)		1.373 (2)	1.374 (4)	C(47)-C(48)		1.360 (4)		C(52)-C(53)		1.368 (7)	
N(3)-C(14)		1.365 (2)	1.369 (9) ^d					C(53)-C(54)		1.249 (6)	
N(4)-C(16)		1.372 (2)						C(54)-C(55)		1.447 (8)	
N(4)-C(19)		1.382 (2)									
C(1)-C(20)	C _α -C _{Me}	1.390 (2)									
C(4)-C(5)		1.389 (2)									
C(5)-C(6)		1.405 (2)									
C(9)-C(10)		1.394 (2)									
C(10)-C(11)		1.412 (2)	1.401 (4)								
C(14)-C(15)		1.405 (2)	1.406 (6) ^d								
C(15)-C(16)		1.395 (2)									
C(19)-C(20)		1.416 (2)									
C(6)-C(7)	C _α -C _β	1.444 (3)									
C(8)-C(9)		1.451 (2)									
C(11)-C(12)		1.443 (2)									

^a Figures in parentheses are errors derived from the coordinate errors as obtained from the block-diagonal least-squares refinement. ^b Unweighted averages for the chemically similar bonds are given along with their standard deviation, σ_d , where $\sigma_d = [\sum(d_i - \bar{d})^2/(n-1)]^{1/2}$. ^c The average value of the indicated bonds after correction for rigid body motion. ^d From ZnTPyP(Py). ^e From SnTPPCl₂.¹⁶

Table V. C-H Bond Lengths

C(2)-H(2A)	0.99(5)	C(30)-H(30)	1.02(5)
C(2)-H(2B)	0.99(5)	C(31)-H(31)	0.98(4)
C(3)-H(3A)	1.07(5)	C(32)-H(32)	1.00(4)
C(4)-H(3B)	0.93(4)	C(34)-H(34)	1.05(5)
C(7)-H(7)	0.93(4)	C(35)-H(35)	1.16(5)
C(8)-H(8)	0.94(5)	C(36)-H(36)	1.05(3)
C(12)-H(12)	1.00(4)	C(37)-H(37)	0.98(5)
C(13)-H(13)	0.98(6)	C(38)-H(38)	0.96(5)
C(17)-H(17)	0.99(4)	C(41)-H(41)	1.17(5)
C(18)-H(18)	0.97(5)	C(42)-H(42)	1.02(6)
C(22)-H(22)	0.98(4)	C(43)-H(43)	0.98(5)
C(23)-H(23)	0.99(4)	C(44)-H(44)	1.01(5)
C(24)-H(24)	1.05(3)	C(45)-H(45)	1.05(5)
C(25)-H(25)	1.02(4)	C(46)-H(46)	1.02(5)
C(26)-H(26)	1.04(4)	C(47)-H(47)	1.06(5)
C(28)-H(28)	1.06(5)	C(48)-H(48)	1.01(5)
C(29)-H(29)	1.07(5)	C(49)-H(49)	1.06(5)

As can be seen from the stereoscopic packing diagram, Figure 5, the benzene molecule fits neatly into a hole formed

by the phenyl rings and the coordinated pyridine. The closest approaches of the benzene molecule to the macrocycle are given above. All remaining atomic contacts are >3.0 Å.

One of the reasons for undertaking this determination was to discern a structural basis for the large difference between the electron paramagnetic resonance hyperfine coupling constant (a_H) of the aliphatic protons of the reduced ring in the cation radicals of zinctetraphenylchlorin (ZnTPC⁺) and chlorophyll a (Chl⁺). At 100 K, $a_H = 7.4$ and 4.2 G for ZnTPC⁺ and Chl⁺,^{4,21} respectively. This coupling is given by the McConnell equation,²² $a_H = (\text{constant}) \rho_\alpha \cos^2\theta$ where ρ_α is the unpaired spin density on the α -carbon atoms of the reduced ring and θ is the dihedral angle between the plane containing the p_z orbital lobes of C_α and atom C_β and the planes containing the atoms C_α, C_β, and the hydrogen atoms bonded to C_β. Because of the planarity of ring 1, the NC_αC_βH_β torsion angles were used to calculate an average value of $\theta = 34(4)^\circ$.

Assuming θ is the same in ZnTPC⁺ and ZnTPC, and using the theoretically calculated ρ_α of 0.138, a value of $a_H = 7.9$ G was predicted⁴ in reasonable agreement with the experimentally observed 7.4 G. If the spin densities are similar in

Table VI. Selected Bond Angles in Degrees^{a,b}

N(1)-Zn-N(2)	NZnN (adjacent)	88.3 (1)	
N(1)-Zn-N(4)		87.0 (1)	
N(2)-Zn-N(3)		88.7 (1)	
N(3)-Zn-N(4)		104.0 (1)	
N(1)-Zn-N(3)	NZnZ (opposite)	161.0 (1)	
N(2)-Zn-N(4)		162.1 (1)	
N(1)-Zn-N(5)	NZnN _{Py}	94.9 (1)	
N(2)-Zn-N(5)		96.7 (1)	
N(3)-Zn-N(5)		89.1 (1)	
N(4)-Zn-N(5)		101.0 (1)	
C(1)-N(1)-C(4)	Reduced ring	108.7 (1)	
N(1)-C(1)-C(2)		111.2 (1)	
N(1)-C(4)-C(3)		111.3 (1)	
C(1)-C(2)-C(3)		104.2 (2)	
C(2)-C(3)-C(4)		104.3 (1)	
C(6)-N(2)-C(9)	C _α NC _α	107.0 (1)	
C(11)-N(3)-C(14)		106.5 (1)	106.8 (2)
C(16)-N(4)-C(19)		106.8 (1)	106.61 ^c
N(1)-C(1)-C(20)	NC _α C _{Me}	125.7 (1)	
N(1)-C(1)-C(5)		125.5 (2)	
N(2)-C(6)-C(5)		126.2 (1)	125.8 (3)
N(3)-C(11)-C(10)		125.5 (1)	125.7 ^c
N(3)-C(14)-C(15)		125.4 (1)	
N(4)-C(19)-C(20)		126.1 (1)	
C(4)-C(5)-C(6)	C _α C _{Me} C _α	126.3 (1)	
C(9)-C(10)-C(11)		125.0 (2)	
C(14)-C(15)-C(16)		125.6 (1)	125.6 (3)
C(19)-C(20)-C(1)		125.6 (2)	125.2 ^c
C(20)-C(1)-C(2)	C _{Me} C _α C _β	123.0 (1)	
C(20)-C(19)-C(18)		123.9 (1)	
C(5)-C(4)-C(3)		123.1 (1)	
C(5)-C(6)-C(7)		124.2 (1)	124.1 (6)
C(10)-C(9)-C(8)		124.5 (2)	125.7 ^c
C(10)-C(11)-C(12)		124.7 (2)	
C(15)-C(14)-C(13)		124.7 (1)	
C(15)-C(16)-C(17)		124.7 (1)	
N(2)-C(6)-C(7)	NC _α C _β	109.9 (1)	
N(3)-C(11)-C(12)		109.7 (1)	109.6 (3)
N(3)-C(14)-C(13)		109.8 (1)	109.8 ^c
N(4)-C(19)-C(18)		109.2 (1)	
N(4)-C(19)-C(17)		109.8 (1)	
C(6)-C(7)-C(8)	C _α C _β C _β	107.0 (1)	
C(9)-C(8)-C(7)		106.7 (2)	
C(11)-C(12)-C(13)		106.7 (2)	106.9 (2)
C(14)-C(13)-C(12)		107.2 (1)	106.9 ^c
C(16)-C(17)-C(18)		107.1 (1)	
C(19)-C(18)-C(17)		107.0 (2)	
C(4)-C(5)-C(21)	C _α C _{Me} C _α	116.9 (1)	
C(6)-C(5)-C(21)		116.8 (1)	
C(9)-C(10)-C(27)		117.4 (1)	
C(11)-C(10)-C(27)		117.6 (1)	
C(14)-C(15)-C(33)		117.2 (1)	117.2 (3)
C(16)-C(15)-C(33)		117.1 (1)	117.3
C(19)-C(20)-C(39)		117.5 (1)	
C(1)-C(20)-C(39)		116.8 (1)	

^a Figures in parentheses are errors derived from the coordinate errors as obtained from the block-diagonal least-squares refinement.

^b Unweighted averages for the chemically similar bonds are given along with their standard deviation, σ_d ; where $\sigma_d = [\sum(d_1 - \bar{d})^2 / (n - 1)]^{1/2}$. ^c From ZnTPyP(Py).¹⁵

ZnTPC⁺ and Chl⁺, then θ should be larger in Chl⁺ than in ZnTPC⁺.⁴ From the x-ray structure of ethylchlorophyllide a⁵ a value for $\theta = 45 (5)^\circ$ was calculated confirming the trend suggested by the ESR data.

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Supplementary Material Available: A listing of structure amplitudes (33 pages). Ordering information is given on any current masthead page.

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