by the time all data had been collected. However, since the integrated intensities of the standard reflections did not decrease monotonically during data collection, apparently only the surface of the crystal had been affected.

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Supplementary Material Available: Listings of structure factor amplitudes for compounds **1** and **2** (24 pages). Ordering information is given on any current masthead page.

Crystal and Molecular Structure of the Isobacteriochlorin: (2,3,7,8-Tetrahydro-5,10,15,20-tetraphenylporphinato)(pyridine)zinc(II) Benzene Solvate

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Abstract: The structure of the isobacteriochlorin, (2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphinato)(pyridine)zinc(II) benzene solvate, has been determined by three-dimensional X-ray diffraction. The compound crystallizes with one molecule each of benzene and reduced porphyrin per asymmetric unit in the triclinic space group $P\bar{1}$ with $a = 11.452$ (5) Å, $b = 13.332$ (4) Å, $c = 14.718$ (6) Å, $\alpha = 99.05$ (2)°, $\beta = 94.37$ (4)°, and $\gamma = 104.88$ (4)°. It is isomorphous with the corresponding chlorin, (2,3-dihydrotetraphenylporphinato)(pyridine)zinc(II) benzene solvate. The structure has been refined by least squares in three matrix blocks to $R_F = 0.073$, on the basis of 6217 reflections with $F_o > 0$. The results unambiguously confirm the structure, previously deduced by spectroscopic techniques, for the general class of isobacteriochlorins (and for siroheme, the prosthetic group of nitrite and sulfite reductases) as porphyrins in which two adjacent pyrrole rings are reduced. In addition, the data indicate that successive saturation of the pyrrole rings in porphyrins, chlorins, and isobacteriochlorins exerts no major effect on the stereochemistry of the macrocycles and suggest that the geometric details of high spin iron siroheme will not deviate substantially from those of iron(III) porphyrins.

Introduction

The many-faceted roles which porphyrin derivatives fulfill biochemically are controlled by their metals, axial ligands, protein environment, and the nature of the porphyrin itself. Respiration, electron transport, peroxide decomposition, and hydroxylations are mediated by macromolecules which contain iron porphyrins (I), Figure 1, as prosthetic groups.[2-8] Photosynthetic reactions, on the other hand, are photocatalyzed by free base and magnesium compounds evolved from dihydroporphyrins (II), pheophytins, and chlorophylls, in algae and green plants, and from tetrahydroporphyrins (III), bacteriopheophytins and -chlorophylls, in purple bacteria.[9-11] Biologically active isomers of III in which two adjacent pyrrole rings are reduced have been proposed, and a number of compounds assigned structure IV have been reported.[12-24]

Isobacteriochlorins (IV) have recently elicited considerable

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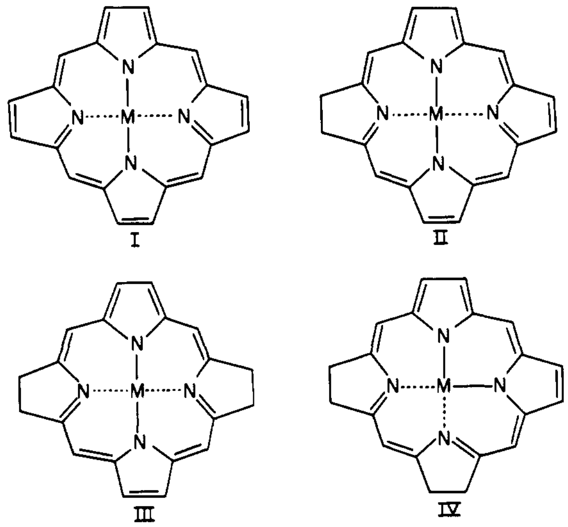

Figure 1. Structural formulas of metalloporphyrin (I), chlorin (II), bacteriochlorin (III), and isobacteriochlorin (IV).

interest[21-34] because the prosthetic groups of sulfite and nitrite reductases contain siroheme,[25,26] an iron isobacteriochlorin with eight carboxylic acid side chains. The enzymes catalyze the six-electron reductions of sulfite to hydrogen sulfide and of nitrite to ammonia.[25-31] In green plants, the latter reaction, $NO_2^- + 8H^+ + 6e^- \rightarrow NH_4^+ + 2H_2O$, is light driven with photosynthetically reduced pyridine dinucleotide serving as electron donor to the active enzyme:

$$\text{chlorophyll} \rightarrow \text{NADPH} \rightarrow \text{flavoprotein} \rightarrow \text{ferredoxin} \rightarrow \text{nitrite reductase}$$

A further biological role has been attributed to isobacteriochlorins with the realization that sirohydrochlorins, demetalated sirohemes, are intermediates in the biosynthetic pathway of the corrin, Vitamin B12.[32-34]

Structure IV has been assigned to isobacteriochlorins on the basis of molecular orbital calculations,[35] dehydrogenations,[12-14] and optical,[12,14] nuclear magnetic resonance[16,17,20-24,32,33] and mass spectral data.[23-25,32,33] As part of an investigation of the chemistry of isobacteriochlorins,[21] we present here an X-ray determination of (2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphinato)(pyridine)zinc(II) benzene solvate, ZnTPiBC(py)·C_6H_6. These results (1) unambiguously confirm the structure previously assigned to the isobacteriochlorin class by spectroscopic techniques, (2) allow an assessment of the effect of progressive ring saturation in porphyrins, chlorins, and isobacteriochlorins and of the concomitant changes in π-bond delocalization on core size, bond distances, and flexibility of the macrocycle, (3) offer a model for the high spin, pentacoordinated ferrisiroheme found in nitrite reductase by analogy with the square-pyramidal coordination of the zinc isobacteriochlorin, and (4) provide the stereochemical and structural parameters required for molecular orbital calculations[21] of the isobacteriochlorins currently used[21-24] to model the unusual chemistry of sirohemes and sirohydrochlorins.

Table I. Crystallographic Details

unit cell: space group, triclinic, $P\bar{1}$

$a = 11.452\ (5)\ \text{Å}^a$	$\alpha = 99.05\ (2)°$	$V = 2126\ \text{Å}^3$
$b = 13.332\ (4)\ \text{Å}$	$\beta = 94.37\ (4)°$	
$c = 14.718\ (6)\ \text{Å}$	$\gamma = 104.88\ (4)°$	$Z = 2$

density
obsd (aqueous KI): 1.24 g/cm^3
calcd 2 × [($C_{55}H_{43}N_5Zn$)/cell]: 1.25 g/cm^3
crystal description: platelet $\{012\}\{0\bar{1}2\}\{100\}$
$d(\underline{0}12, 0\bar{1}\bar{2}) = 0.26$ mm $d(0\bar{1}\underline{2}) = 0.31$ mm
$d(\bar{1}00, 100) = 0.03$ mm $d(01\bar{2}) = 0.22$ mm
data collection
diffractometer: Enraf-Nonius, CAD4
radiation: Mo ($\lambda = 0.710\,70$ Å)
linear abs coeff: 5.553 cm^{-1}
2θ range: $0 < 2\theta < 100°$
no. of reflctns: 16 462 measd, 7158 unique, 6217 with $F > 0$
scattering factors: Cromer and Mann[37]
anomalous dispersion: Cromer and Liberman[38]
refinement: three matrix blocks against F's[b]
$R_F = 0.073$, where $R = \Sigma|F_o - F_c|/\Sigma|F_o|$
$R_{wF} = 0.039$, where $R_F = (\Sigma(w(F_o - F_c))^2/\Sigma wF_o^2)^{1/2}$
$S = 1.36$, where $S = (\Sigma(w(F_o - F_c))^2/(N_o - N_v))^{1/2}$

[a] The figures in parentheses are the standard deviation of the least significant digit here and throughout this paper. [b] The quantities F_o and F_c are the observed and calculated structure factor amplitudes, w is the experimental weight, and N_o and N_v are the number of observations and variables, respectively. $w = 1/\sigma_{F_o}^2$ and $\sigma_{F_o}^2 = \sigma_{F_{o,c}}^2 + (0.010I)^2$ where $\sigma_{F_{o,c}}^2$ is the variance estimated from $F_{o,c}$ counting statistics and is scaled by the absorption and Lp terms. Programs used are described in the CRYSNET[39] manual of Brookhaven National Laboratory.

Experimental Section

Zinc tetraphenylisobacteriochlorin (ZnTPiBC) was prepared by a modification of the diimine reduction of zinc tetraphenylporphyrin (ZnTPP) described by Whitlock et al.[17] Two grams of tetraphenylporphyrin was refluxed with 2 g of $Zn(C_2H_3O_2)_2 \cdot 2H_2O$ in 75 mL of pyridine for about 1 h under nitrogen. After conversion to ZnTPP was completed, 12 g of K_2CO_3 and 0.6 g of *p*-toluenesulfonhydrazide (TSH) (Aldrich) were added to the solution. Then every 2 h 0.6 g of TSH was added to the reaction mixture until the characteristic absorption bands of the ZnTPP and zinc tetraphenylchlorin (ZnTPC) intermediates disappeared, and the solution contained only ZnTPiBC and bacteriochlorin (ZnTPBC). The solution was partitioned between 400 mL of methylene chloride and 400 mL of water which had been deoxygenated with nitrogen. The solutions were kept in the dark because ZnTPiBC and ZnTPBC are easily photooxidized. The methylene chloride layer was washed twice with 200 mL of 1.2 M HCl and 200 mL of 1% w/v aqueous $NaHCO_3$, dried with Na_2SO_4, filtered, and evaporated to dryness to yield 532 mg, 25%. A 100-mg sample of the crude solid was dissolved in a minimum of methylene chloride and chromatographed in the dark, with deoxygenated xylene, at ~100 psi through a 0.25-m prescrubber and two 1-m silica gel columns in series. The resulting ZnTPiBC contained no spectrophotometrically detectable ZnTPC and 1% ZnTPBC.

Suitable crystals were grown by vapor diffusion of distilled hexanes into a solution of ZnTPiBC in methylene chloride/benzene/pyridine (98:1:1). (All solvents were freshly dried and distilled.) The crystals were washed with hexanes. A purple plate approximately 0.6 mm × 0.4 mm × 0.2 mm was mounted along its long axis. Preliminary precession photographs revealed good quality diffraction patterns but no easily accessible principal zones.

The crystal was mounted on an Enraf-Nonius CAD4 diffractometer fitted with a Mo tube. The initial cell parameters indicated that the sample was nearly isomorphous with ZnTPC(py)·C_6H_6.[36] This was

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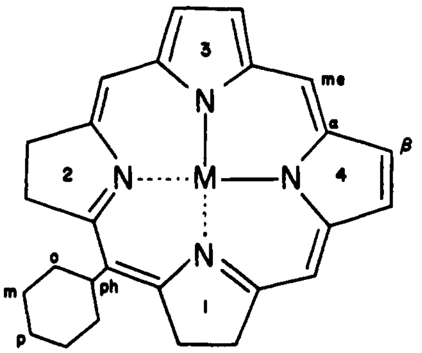

Figure 2. Atom and ring designations for ZnTPiBC.

confirmed by the final cell parameters obtained from 25 reflections ($\theta > 20°$). To exclude the possibility that the crystal was ZnTPC(py)·C_6H_6, the relative intensities of several rows of reflections were compared with those of the ZnTPC(py)·C_6H_6. Sufficient differences were found to verify that the compound was not the chlorin. In addition, when crystals from the same batch were dissolved, no ZnTPC(py) was observed spectrally.

During 3 weeks of data collection, four reflections were monitored periodically and some fluctuations in intensity (10%) were noted. These fluctuations were related to instability of the power supply and were corrected by linear interpolation between the periodic measurements of monitor reflections. No decomposition of the crystal was noted. Crystallographic details of the analysis and data collection are given in Table I.

Solution and Refinement

Because this structure is isomorphous with ZnTPC(py)·C_6H_6, the initial electron density map was calculated by using the coordinates of the Zn, N (pyrrole), and C_α and C_{meso} atoms from the ZnTPC(py)·C_6H_6 structure,[36] while the remaining carbon atoms were revealed by difference electron density maps. This model was refined by block-diagonal least-squares using 5278 reflections with $F_o \geq 3\sigma(F_o)$. From successive difference maps, all hydrogen atoms except those associated with the benzene of solvation were located at stereochemically reasonable maxima which were above background density, but lower than a residual peak near the Zn of approximately 0.8 e/Å^3.

Due to the large number of independent atoms in the structure (104), the completed model was refined in three matrix blocks by using 6217 data with $F_o > 0$. The electron density from the hydrogens of the C_{meso}-substituted phenyl rings, the pyridine, and the benzene of solvation was treated as a fixed contribution to the total density. The positions of these atoms were idealized such that they remained 1.0 Å away from their respective carbon atoms. The isotropic thermal parameter B for all hydrogens, including those on the macrocycle, was fixed at 5.7 Å^2. Refinement was terminated when shifts for the atoms were less than their nominal standard deviations. The largest shifts were observed for the x coordinates of C42 (0.37σ) and C46 (0.4σ). For the hydrogen atoms, the greatest shift occurred in the x coordinate of H7A (0.19σ). A final difference map revealed a peak of density 0.42 e/Å^3 near the zinc atom. The next largest peak corresponded to 0.41 e/Å^3, near the solvate molecule.

The regions about the C_β atoms of all pyrrole rings were examined very carefully for evidence of conformational or rotational disorder in the form of unreasonably shaped or oriented ellipsoids. No extraneous electron density was found near rings 1, 2, or 3. A few local maxima (~0.28 e/Å^3) near C(18) and C(19) of ring 4 could not be fitted to any reasonable model of disorder or thermal motion discrepancies.

The structure and numbering system for ZnTPiBC are shown in Figures 2 and and the atomic positions are given in Table II. Bond distances and angles for the benzene rings, the pyridine ring, and the benzene of solvation, as well as the positional parameters for the hydrogen

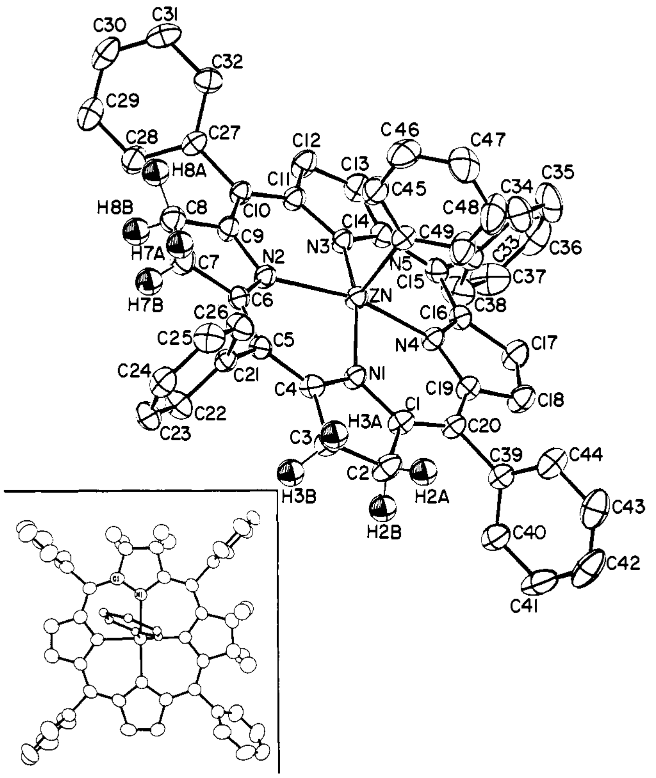

Figure 3. The structure of (2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphinato)(pyridine)zinc(II) and atom-numbering system. The hydrogen atoms are numbered according to the carbon atom to which they are bonded. The thermal ellipsoids are drawn to enclose 50% probability, except for the hydrogen atoms which are not to scale. The insert shows the structure viewed along the pyridine–Zn axis. Hydrogen atoms other than those on rings 1 and 2 are omitted for clarity.

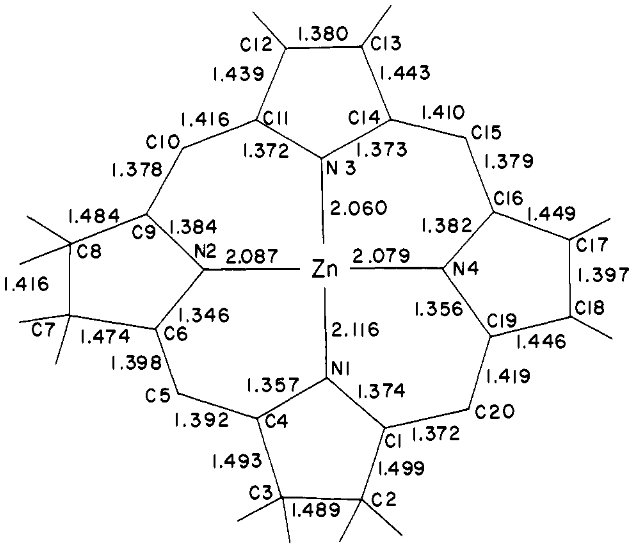

Figure 4. Selected bond distances in Å. The standard deviations are 0.005 for typical C–C or C–N bond lengths and 0.003 fo the Zn–N bonds.

atoms of these groups, are included as supplementary material. A tabulation of observed and calculated structure factors is available.[41]

Discussion

This work was prompted in part by ESR results for the cation radical of ZnTPiBC, which did not agree with unpaired spin densities predicted by molecular orbital calculations.[21] The ESR data suggested either that the postulated structure of isobacteriochlorins was wrong or, more likely, that the reduced rings of the macrocycle were capable of considerable flexibility. As shown in Figure 3, the present determination confirms the

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(41) Supplementary material available. See note at end of paper.

Table II. Atom Coordinates and Anisotropic Vibrational Parameters for the Atoms of the Isobacteriochlorin Framework[a]

ATOM	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
ZN	43200(4)	16426(4)	20625(3)	2500(2)	2906(2)	4257(3)	770(2)	-225(2)	395(2)
N1	43927(24)	799(21)	15873(19)	2560(18)	2840(18)	4446(20)	636(14)	-561(15)	274(15)
N2	34259(25)	16046(22)	7624(19)	3020(22)	2900(22)	3958(27)	894(18)	-169(20)	351(20)
N3	47285(25)	32661(22)	22941(19)	2743(19)	3039(18)	3957(19)	790(15)	-290(15)	248(15)
N4	56525(24)	17536(22)	31363(19)	2594(18)	2794(19)	4546(19)	735(15)	-116(15)	634(15)
C1	49818(31)	-4867(28)	20700(25)	2567(19)	2847(19)	5891(19)	561(15)	-142(15)	660(15)
C2	47364(40)	-16002(34)	15613(32)	3521(27)	3560(25)	7492(30)	965(21)	-1385(23)	283(22)
C3	38631(40)	-16651(32)	7373(31)	4025(29)	3164(24)	6790(29)	1103(21)	-1296(23)	-197(21)
C4	37191(30)	-5743(28)	8205(25)	2429(22)	3085(22)	4902(24)	532(18)	64(19)	-26(19)
C5	29380(30)	-3066(28)	1872(23)	2265(21)	3402(22)	4024(23)	740(17)	45(18)	60(18)
C6	28318(31)	7116(28)	1677(23)	2509(23)	3567(24)	3358(22)	930(18)	-90(18)	163(18)
C7	20249(42)	9505(35)	-5476(31)	3991(29)	4247(27)	5258(27)	1079(22)	-406(22)	137(22)
C8	22707(39)	20642(34)	-3980(29)	3520(26)	4148(27)	5991(27)	1327(21)	-200(21)	377(21)
C9	31110(32)	24517(29)	4787(24)	2945(24)	3752(24)	4035(24)	1014(19)	-103(19)	917(19)
C10	34700(31)	34863(27)	9355(24)	2758(22)	2741(21)	4279(23)	621(17)	161(18)	737(18)
C11	42340(32)	38708(28)	17885(24)	2945(23)	3131(23)	4546(24)	919(19)	187(19)	994(19)
C12	46675(39)	49693(30)	22104(29)	4223(29)	2636(22)	6280(28)	835(21)	-567(23)	1002(20)
C13	54734(39)	50260(31)	29757(30)	4559(31)	2735(23)	6002(28)	825(22)	-445(23)	-214(20)
C14	54892(32)	39560(28)	30207(24)	3113(24)	3065(23)	4001(24)	462(19)	-71(19)	-180(18)
C15	62063(31)	36712(28)	37052(23)	2728(23)	3138(23)	3957(24)	596(18)	19(19)	-163(18)
C16	62717(30)	26628(28)	37566(24)	2396(22)	3058(22)	4179(24)	417(18)	-348(18)	17(18)
C17	70675(39)	24070(34)	44448(29)	4074(29)	3897(27)	5913(28)	905(22)	-1592(23)	-240(22)
C18	68959(39)	13159(36)	42343(32)	3726(27)	4360(27)	6602(29)	1476(22)	-1115(23)	377(22)
C19	60409(31)	9466(28)	33989(24)	2531(23)	3415(23)	4546(25)	595(18)	13(19)	831(19)
C20	56970(30)	-1101(27)	29076(25)	2556(22)	2979(22)	5169(25)	915(19)	-142(19)	874(18)
C21	21336(30)	-11857(27)	-5258(24)	2399(22)	2999(22)	4390(24)	755(18)	-180(18)	420(18)
C22	25171(32)	-15525(30)	-13491(26)	3005(25)	3977(26)	5402(27)	209(20)	625(21)	-249(21)
C23	17532(37)	-23772(32)	-19864(25)	3988(28)	4386(27)	4524(26)	924(22)	155(22)	-248(21)
C24	6069(36)	-28340(30)	-18271(27)	3584(27)	3498(25)	5713(28)	328(21)	-1289(22)	-377(21)
C25	2079(33)	-24798(33)	-10148(30)	2291(24)	4756(29)	8291(33)	-94(21)	-541(23)	351(25)
C26	9708(34)	-16536(32)	-3706(26)	2948(25)	4881(28)	5791(27)	631(21)	303(21)	-223(22)
C27	30227(31)	42832(27)	4985(25)	2272(22)	2741(21)	5724(26)	417(17)	-619(19)	617(19)
C28	33984(35)	45378(33)	-3392(28)	3786(29)	5410(31)	6247(29)	1415(24)	619(23)	2091(24)
C29	29556(40)	52485(38)	-7632(29)	4866(35)	6216(35)	7036(33)	1252(27)	-200(27)	3282(27)
C30	21336(42)	56892(33)	-3651(32)	5060(35)	3930(28)	8714(36)	1312(25)	-1637(28)	1774(26)
C31	17453(37)	54540(33)	4560(33)	4096(31)	4089(28)	10059(37)	1992(24)	238(27)	943(26)
C32	21929(34)	47579(31)	8890(27)	3427(27)	3494(24)	6936(29)	989(21)	606(23)	591(22)
C33	70100(34)	45580(29)	44189(25)	3218(25)	3197(23)	4591(25)	894(19)	-606(20)	-77(19)
C34	66398(39)	49182(37)	52417(29)	5019(34)	5919(34)	5658(31)	313(27)	271(26)	94(25)
C35	73993(52)	57441(39)	58832(28)	8450(48)	5568(35)	4302(29)	1043(33)	-638(31)	-1585(25)
C36	85369(48)	61960(35)	57244(34)	6398(43)	3838(31)	8737(39)	417(28)	-3957(34)	-805(27)
C37	89345(38)	58555(38)	49342(37)	2930(29)	5694(35)	13215(47)	199(25)	-1341(30)	-900(33)
C38	81727(38)	50237(36)	42769(31)	3337(29)	5463(32)	9291(35)	711(24)	-39(25)	-1577(27)
C39	61802(32)	-8848(28)	33560(25)	2713(23)	2972(22)	5491(25)	645(18)	-574(19)	94(18)
C40	55660(36)	-14052(34)	39934(30)	3528(27)	5350(30)	8314(33)	999(23)	6(24)	2682(26)
C41	59933(47)	-21194(38)	43902(34)	6073(40)	5535(34)	9759(39)	303(30)	-612(32)	3822(30)
C42	70352(49)	-23456(35)	41687(36)	6746(43)	3408(29)	11715(44)	1193(28)	-3469(35)	1611(29)
C43	76548(42)	-18632(40)	35415(35)	4795(35)	6506(39)	11993(44)	3488(30)	-915(31)	643(32)
C44	72365(38)	-11147(36)	31338(29)	3748(29)	6566(34)	7758(32)	2221(25)	471(24)	2056(26)
N5	27050(26)	11728(24)	27278(20)	2769(19)	3983(20)	5202(21)	1069(16)	90(16)	1028(16)
C45	27231(38)	7293(41)	34655(30)	3386(29)	9030(42)	7214(33)	1500(28)	187(25)	3359(30)
C46	17172(45)	3644(45)	38964(33)	4254(34)	11692(54)	9481(39)	1555(35)	709(30)	6109(37)
C47	6309(39)	4722(40)	35517(33)	3550(31)	8164(41)	9059(37)	353(28)	1985(27)	3196(31)
C48	5784(37)	9029(38)	27877(34)	2781(27)	7081(37)	11192(41)	1416(25)	561(26)	2973(31)
C49	16241(39)	12385(37)	23940(29)	3726(29)	7458(36)	7536(32)	2499(27)	935(24)	3359(27)
C50	11279(100)	61649(65)	29572(41)	11399(98)	10734(70)	8214(47)	3916(61)	-1225(55)	2862(47)
C52	-360(65)	70189(104)	20773(46)	7138(63)	21943(125)	11015(56)	8471(78)	-574(46)	2228(72)
C53	7576(118)	77288(62)	21805(54)	15454(123)	7953(65)	14439(71)	4253(73)	3281(80)	3984(54)
C54	18534(112)	78308(72)	26417(94)	10808(109)	9803(91)	36124(167)	-3771(74)	9005(98)	-4087(87)
C55	20243(70)	69793(106)	29789(43)	6353(63)	20563(125)	10248(50)	3597(68)	-2166(45)	-2476(72)
H2 A	53792(303)	-18353(296)	13887(232)	57					
H2 B	44506(309)	-21396(292)	19469(224)	57					
H3 A	31191(298)	-22541(286)	6823(229)	57					
H3 B	41692(295)	-18424(277)	1050(238)	57					
H7 A	19594(335)	5477(294)	-11523(230)	57					
H7 B	13002(299)	5557(297)	-6639(262)	57					
H8 A	27322(296)	24120(279)	-9109(226)	57					
H8 B	16234(300)	24714(284)	-5013(231)	57					
H12	45098(306)	54867(289)	20004(235)	57					
H13	59194(299)	55657(276)	32508(231)	57					
H17	75938(295)	27940(276)	48330(228)	57					
H18	73145(307)	10346(292)	44193(242)	57					

[a] The coordinates have been multiplied by 10^5 and the vibrational terms by 10^4. The U_{ij} are coefficients in the expression $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

spectroscopic conclusions[12,14,16,17-20,25,32,33] that two adjacent pyrrole rings of isobacteriochlorins are reduced.

The reduced rings 1 and 2 are distinct from the conjugated pyrrole rings 3 and 4. The bond angles and lengths of ring 1, presented in Table III and Figure 4, are similar to those of the reduced ring of the isomorphous ZnTPC(py)$\cdot C_6H_6$.[36] The C_β–C_β bond of 1.489 (5) and C_α–C_α lengths of 1.493 (5) and 1.499 (5) agree well with those found in the chlorin: 1.478 (3), 1.493 (2), and 1.497 (2) Å. However, the corresponding bonds in ring 2 are significantly shortened: 1.416 Å for C_β–C_β and a mean of 1.479 (5) Å for C_α–C_β. The bond angles within this ring are also slightly larger than those in ring 1. While ring 1 is planar to within 0.020 Å, the atoms in ring 2 deviate by as much as 0.309 Å from the least-squares plane, with the greatest deviation in both rings at the β-carbon atoms. In addition, the $C_\alpha C_\beta C_\beta C_\alpha$ torsion angle is 2.21° in ring 1 as compared to 6.90° in ring 2; i.e., the latter is markedly more twisted than ring 1. The β-hydrogen atoms in ring 2 are equatorially and axially disposed, while those in ring 1 lie equally above and below the pyrrole ring. Their geometry is given in Table IV. This flexibility of the reduced rings appears to be consistent with the ESR observations.[21]

The two fully conjugated pyrrole rings 3 and 4 are individually planar to within 0.016 Å. They have bond distances and angles similar to those found in other porphyrin[42,43] and chlorin[36] structures. The C_β–C_β distance in ring 4 is nonetheless slightly longer (0.04 Å) than that normally encountered in porphyrins.

As noted above, we find no evidence of disorder in the carbon positions which could explain the anomalous geometry exhibited by ring 2 and, to a lesser extent, by ring 4. Nor can we ascribe any meaningful density to alternate hydrogen posiitions. Since NMR[17,44] and ESR[21] data indicate that the two reduced rings of ZnTPiBC are equivalent in solution, the differences in the conformation of the two rings must arise in the crystal. The reasons

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(42) Hoard, J. L., ref 7, 317–380.

(43) Scheidt, W. R., ref 8, 1978; Vol. 3, pp 463–511.

(44) Harel, Y. Ph. D. Dissertation, The Weizmann Institute of Science, Rehovot, Israel, 1978.

Table III. Selected Bond Angles (Deg)

N(1)-Zn-N(2)	NZnN (adjacent)	88.2 (1)	N(1)-Zn-N(5)	$NZnN_{py}$	94.6 (1)
N(1)-Zn-N(4)		88.2 (1)	N(2)-Zn-N(5)		96.5 (1)
N(2)-Zn-N(3)		88.9 (1)	N(3)-Zn-N(5)		104.0 (1)
N(3)-Zn-N(4)		89.1 (1)	N(4)-Zn-N(5)		100.7 (1)
N(1)-Zn-N(3)	NZnN (opposite)	161.5 (1)	C(1)-C(20)-C(19)	$C_{\alpha}C_{meso}C_{\alpha}$	126.6 (3)
N(2)-Zn-N(4)		162.7 (1)	C(4)-C(5)-C(6)		125.6 (3)
C(1)-N(1)-C(4)	$C_{\alpha}NC_{\alpha}$	108.7 (3)	C(9)-C(10)-C(11)		125.6 (3)
C(6)-N(2)-C(9)		109.3 (3)	C(14)-C(15)-C(16)		126.1 (3)
C(11)-N(3)-C(14)		106.2 (3)	C(1)-C(2)-C(3)	$C_{\alpha}C_{\beta}C_{\beta}$	104.4 (3)
C(16)-N(4)-C(19)		107.4 (3)	C(4)-C(3)-C(2)		103.9 (3)
N(1)-C(1)-C(2)	$NC_{\alpha}C_{\beta}$	110.9 (3)	C(6)-C(7)-C(8)		106.2 (4)
N(1)-C(4)-C(3)		112.0 (3)	C(9)-C(8)-C(7)		105.3 (4)
N(2)-C(6)-C(7)		109.9 (3)	C(11)-C(12)-C(13)		106.3 (3)
N(2)-C(9)-C(8)		108.8 (3)	C(14)-C(13)-C(12)		106.5 (3)
N(3)-C(11)-C(12)		110.6 (3)	C(16)-C(17)-C(18)		106.6 (3)
N(3)-C(14)-C(13)		110.3 (3)	C(19)-C(18)-C(17)		105.9 (3)
N(4)-C(16)-C(17)		109.3 (3)	C(5)-C(4)-C(3)	$C_{meso}C_{\alpha}C_{\beta}$	122.1 (3)
N(4)-C(19)-C(18)		110.7 (3)	C(5)-C(6)-C(7)		123.0 (3)
N(1)-C(1)-C(20)	$NC_{\alpha}C_{meso}$	125.8 (3)	C(10)-C(9)-C(8)		124.4 (3)
N(1)-C(4)-C(5)		125.8 (3)	C(10)-C(11)-C(12)		124.1 (3)
N(2)-C(6)-C(5)		127.1 (3)	C(15)-C(14)-C(13)		124.4 (3)
N(2)-C(9)-C(10)		126.7 (3)	C(15)-C(16)-C(17)		124.5 (3)
N(3)-C(11)-C(10)		125.1 (3)	C(20)-C(19)-C(18)		123.9 (3)
N(3)-C(14)-C(15)		125.3 (3)	C(20)-C(1)-C(2)		123.3 (3)
N(4)-C(16)-C(15)		126.0 (3)			
N(4)-C(19)-C(20)		125.3 (3)			

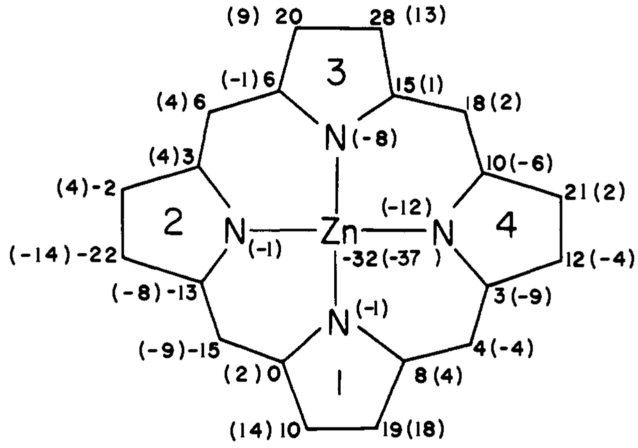

Figure 5. Deviations (Å × 10^2), in the Zn-N(5) direction, of the atoms of ZnTPiBC from two least-squares planes. The first set of numbers represents the deviations from the plane of the four nitrogens. The numbers in parentheses indicate the deviations from the plane of the 24 atoms that constitute the macrocycle skeleton. The numbering system corresponds to Figure 2. The positional uncertainties average 0.006 Å at the C and N atom and 0.001 Å at the Zn atom.

for these significant variations are not obvious, however.[45]

The distances of the nonhydrogen atoms of the isobacteriochlorin skeleton from the least-squares planes containing the four pyrrole nitrogen atoms and the 24-atom framework are displayed in Figure 5. A distortion from the usual saucer shape of zinc porphyrins occurs at ring 2, which is displaced toward the zinc atom. As was found in ZnTPC(py), the phenyl rings attached to C(5), C(15), and C(20) are perpendicular within 4° to the plane of the four nitrogen atoms. The phenyl ring attached to C(10) forms an angle of 66°.

Table IV. Bond Distances (Å) and Angles (Deg) for the Hydrogens Bonded to the Isobacteriochlorin Framework

Distances			
H2A-C(2)	0.91 (3)	H8A-C(8)	1.05 (4)
H2B-C(2)	0.99 (3)	H8B-C(8)	1.04 (4)
H3A-C(3)	0.99 (3)	H12-C(12)	0.85 (4)
H3B-C(3)	1.03 (3)	H13-C(13)	0.79 (3)
H7A-C(7)	0.95 (3)	H17-C(17)	0.81 (3)
H7B-C(7)	0.85 (3)	H18-C(18)	0.74 (3)

Angles			
H2A-C(2)-H2B	95 (3)	H3A-C(3)-H3B	101 (2)
H7A-C(7)-H7B	73 (3)	H8A-C(8)-H8B	89 (2)
H2A-C(2)-C(1)	118 (2)	H2A-C(2)-C(3)	111 (2)
H2B-C(2)-C(1)	114 (2)	H2B-C(2)-C(3)	114 (2)
H7A-C(7)-C(6)	113 (1)	H7A-C(7)-C(8)	121 (2)
H7B-C(7)-C(6)	124 (9)	H7B-C(7)-C(8)	121 (3)
H8A-C(8)-C(7)	114 (2)	H8A-C(8)-C(9)	106 (2)
H8B-C(8)-C(7)	125 (2)	H8B-C(8)-C(9)	116 (2)
H(12)-C(12)-C(11)	127 (2)	H(12)-C(12)-C(13)	127 (2)
H(13)-C(13)-C(12)	123 (3)	H(13)-C(13)-C(14)	129 (3)
H(17)-C(17)-C(16)	130 (3)	H(17)-C(17)-C(18)	123 (3)
H(18)-C(18)-C(17)	125 (3)	H(18)-C(18)-C(19)	127 (3)

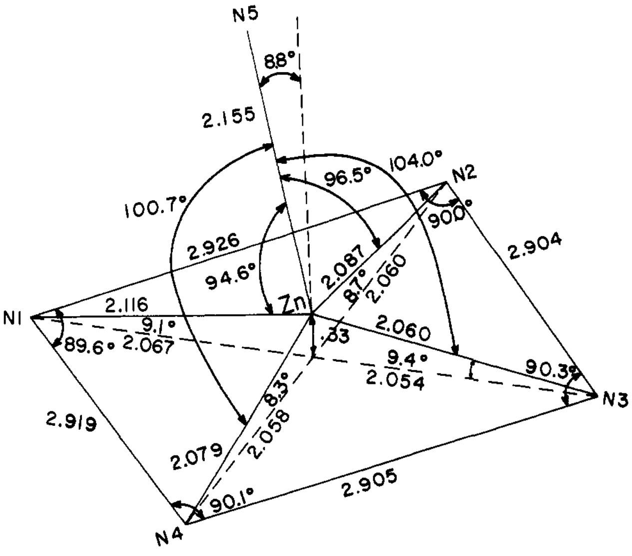

Figure 6. Coordination geometry of the zinc ion.

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[45] The unusual bond distances of rings 2 and 4 (and of Zn–N(2) and Zn–N(4) discussed further on) could be rationalized if a rotational disorder of the macrocycle is assumed such that rings 1 and 4, rather than 1 and 2, are reduced in a number of molecules. An explicit search for evidence of disorder failed to provide any conclusive proof for it although some form of packing disorder cannot be rigorously excluded. If the particular crystal used for data collection was exceptionally enriched in either chlorin or bacteriochlorin, this would also allow a simple explanation of the geometry observed. However, besides the lack of any evidence of disorder, spectroscopic tests on the same batch of crystals render this possibility highly unlikely.

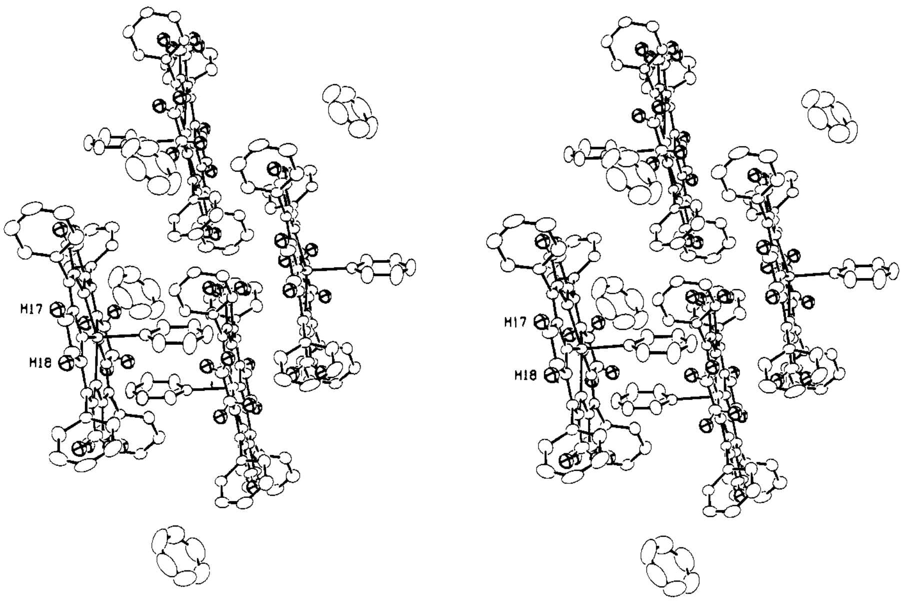

Figure 7. Stereoscopic view of all molecules within 4 Å of the central ZnTPiBC.

Reduction of the porphyrin macrocycle has no significant effect on the size of the central core. The centroid of the four pyrrole nitrogens lies 3.070 (3) Å from C_α and 3.439 (4) from C_{meso}. These distances are within experimental error of those found in ZnTPC(py) and are similar to the values of 3.061 and 3.477 Å found in (5,10,15,20-tetra-4-pyridylporphinato)(pyridine)zinc(II), ZnTPyP(py).[46]

The coordination geometry of the zinc atom is a distorted square pyramid, as observed in ZnTPyP(py) and ZnTPC(py). Details of this environment are given in Figure 6. As expected from the ZnTPC and chlorophyll[47] structures, the metal ion is bound more closely to the pyrrole nitrogens than to those of the reduced rings. The rather short Zn–N(2) and somewhat long Zn–N(4) bonds appear to reflect the "anomaly" associated with rings 2 and 4 previously discussed.[45] The 0.32-Å displacement of the central metal from the mean plane of the equatorial nitrogens is similar to those found in ZnTPC (0.32 Å) and in ZnTPyP (0.33 Å). The $Zn{-}N_{py}$ distance, 2.155 (3) Å, lies between the values of 2.171 (2) Å found in ZnTPC(py) and 2.143 (4) Å in ZnTPyP(py). The axial $Zn{-}N_{py}$ vector is tilted from the normal to the basal plane. The value of 8.8° found here is slightly larger than observed in ZnTPC(py) and in (octaethylporphinato)(pyridine)zinc(II).[48]

In agreement with the results for the isomorphous ZnTPC(py), examination of the molecular contact distances revealed no pair of atoms separated by less than van der Waals distances. Figure 7 displays the arrangement of the molecules in the unit cell.

In conclusion, this determination establishes the geometry of isobacteriochlorins and substantiates their assignment to structure IV. These results provide the first structural model for the isobacteriochlorin framework in siroheme, and, because the gross features of ZnTPiBC do not deviate significantly from those of Zn porphyrins and chlorins, they suggest that the stereochemistry of siroheme should resemble that encountered in high spin pentacoordinated iron porphyrins.

The redox chemistry of isobacteriochlorins is, however, distinctly different; i.e., they are considerably easier to oxidize and harder to reduce than porphyrins or chlorins.[21,22] These facile oxidation characteristics, rather than stereochemical features, may have favored the evolutionary hap of the isobacteriochlorin framework in nitrite and sulfite reductases in which sirohemes must mediate six-electron transfers.

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Supplementary Material Available: A listing of structure amplitudes and tables of bond angles and distances in the phenyl rings at the meso positions, the pyridine ring coordinated to Zn, and the benzene of solvation and of fractional coordinates for the hydrogen atoms not bonded to the isobacteriochlorin framework (33 pages). Ordering information is given on any current masthead page.

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