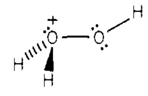
assumed that H_2O is sp^3 hybridized, which is, however, not the case.[25] It was subsequently pointed out by Symons[25] that the original ^{17}O data are supportive of a pyramidal geometry for H_3O^+ with a H–O–H bond angle of 111.3°. Indeed, Christe and coworkers[29] have previously isolated hydronium ion salts and have established by vibrational spectroscopy that H_3O^+ is pyramidal. Similar conclusions have been reached on the basis of quantum mechanical calculations.[26]

Attempts to prepare ^{17}O-labeled trimethyloxonium ion were somewhat inconclusive. The treatment of $CH_3{}^{17}OH$ with excess CH_3F–SbF_5 in SO_2 did not give rise to a clear enough absorption in the ^{17}O NMR spectrum that could be assigned to the ion. The methylation of $H_2{}^{17}O$ with excess dimethylchloronium ion was also attempted. In the ^{17}O NMR spectrum a broad absorption is observed around $\delta^{17}O$ 40.6 in addition to the $H_3{}^{17}O^+$ peak at $\delta^{17}O$ 10.0. The assignment of this signal to the trimethyloxonium ion can be, however, only tentative.

The Peroxonium Ion $H_3O_2^+$. The peroxonium ion $H_3O_2^+$ has been invoked as an intermediate in the electrophilic oxygenation of alkanes with hydrogen peroxide and strong acids.[30,31] Recently, Christe et al.[32] reported the isolation and characterization of several peroxonium salts. The infrared and Raman spectra of these salts indicated that $H_3O_2^+$ is isostructural with H_2NOH and has the geometry depicted.[32] However, no direct observation of the peroxonium ion by ^1H NMR spectroscopy[31,32] was possible due to rapid proton exchange with the solvent systems. When a mixture of equal volumes of 90% hydrogen peroxide and 30% $H_2{}^{17}O$ (stirred at room temperature for 12 h)[33] was added to a SO_2 solution of HF–SbF_5 at −25 °C, two absorptions were observed in the ^{17}O NMR spectrum. The major peak ($\delta^{17}O$ 10) is due to the oxonium ion $H_3{}^{17}O^+$. The second peak with a chemical shift of $\delta^{17}O$ 151 is attributed to the peroxonium ion $H_3O_2^+$. The peroxonium ion is shielded by 36 ppm with respect to hydrogen peroxide ($\delta^{17}O$ 187). This shielding is in contrast to the deshielding observed upon the formation of other oxonium ions such as H_3O^+ and $CH_3O^+H_2$ from their neutral precursors. No splitting was observed in the proton-coupled ^{17}O NMR spectrum of $H_3O_2^+$ (**11**), indicating an extremely fast proton exchange rate. This is consistent with the previously observed rapid exchange by ^1H NMR spectroscopy.[31,32]



11

Experimental Section

Oxygen-17-enriched water (10% and 30%, methanol (20%), acetone (20%), and acetic and propionic acids (30%) were commercially available. The enriched ketones were prepared by adding equal volumes (0.05 mL) of ketone and enriched $H_2{}^{17}O$ to dioxane (0.1 mL) and warming for several hours. The resultant solution was used directly in preparing the ions.

Preparation of Oxonium Ions. The oxonium ions were prepared by the addition of the ^{17}O-enriched precursor to a 1:1 mixture of SO_2 and HF–SbF_5 (1:1) or the appropriate methylating agent at −78 °C. Enriched $H_3O_2^+$ was prepared by the addition of equal volumes of 90% normal H_2O_2 and 30% enriched $H_2{}^{17}O$ (which had previously been stirred together for 12 h) to a HF-SbF_5/SO_2 solution at −78 °C.

The ^{13}C and ^{17}O NMR spectra were obtained by using a Varian Associates Model FT-80 NMR spectrometer equipped with a broad-band variable-temperature probe. The oxygen shifts were referenced to the SO_2 solvent peak ($\delta^{17}O$ 505 ppm[18]).

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No. H_3O^+, 13968-08-6; $H_5O_2^+$, 22206-74-2; $CH_3OH_2^+$, 17836-08-7; $(CH_3)_3O^+$, 43625-65-6; $CH_3C({=}OH)CH_3^+$, 43022-03-3; *c*-$C_4H_6{=}OH^+$, 64725-63-9; *c*-$C_5H_8{=}OH^+$, 64725-64-0; *c*-$C_6H_{10}{=}OH^+$, 64725-65-1; *c*-$C_7H_{12}{=}OH^+$, 75032-00-7; *c*-$C_8H_{14}{=}OH^+$, 80954-12-7; $CH_3C({=}OCH_3)CH_3^+$, 41798-19-0; $CH_3C({=}OH)OH^+$, 18639-92-4; $CH_3CH_2C({=}OH)OH^+$, 18639-93-5; CH_3CO^+, 15762-07-9; $CH_3CH_2CO^+$, 17158-30-4.

---

(29) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1975**, *14*, 2224-2230.

(30) Alder, R. W.; Whiting, M. C. *J. Chem. Soc.* **1964**, 4707-4712 and references therein.

(31) Olah, G. A.; Yoneda, N.; Parker, D. G. *J. Am. Chem. Soc.* **1977**, *99*, 483-488.

(32) Christe, K. O.; Wilson, W. W.; Curtis, E. C. *Inorg. Chem.* **1979**, *18*, 2578-2586.

(33) For a discussion on the possible mechanisms for the acid-catalyzed ^{17}O exchange in $H_2{}^{17}O/H_2O_2$ solutions, see: Chung, S.-K.; Decapite, P. *J. Org. Chem.* **1978**, *43*, 2935-2936.

Crystal and Molecular Structure of 2,2,8,8,12,13,17,18-Octamethylisobacteriochlorin

W. B. T. Cruse, P. J. Harrison, and Olga Kennard*[†]

Contribution from The University Chemical Laboratory, Cambridge CB2 1EW, England.

Received June 26, 1981

Abstract: The X-ray structure determination of 2,2,8,8,12,13,17,18-octamethylisobacteriochlorin has been carried out to a resolution of 0.85 Å. The compound crystallizes in the rhombohedral space group $R\bar{3}$, with cell constants $a = b = c = 16.926$ (3) Å and $\alpha = \beta = \gamma = 109.72$ (2)°. It contains one molecule of $C_{28}H_{34}N_4$ in the asymmetric unit. The structure was solved by direct methods and refined to $R_w = 4.9\%$. Four half-hydrogen atoms, within bonding distance of the nitrogen atoms, were located experimentally from a difference Fourier map. The X-ray structure is thus a superposition of two tautomeric forms in which diagonally opposed nitrogen atoms have bonded hydrogen atoms. The macrocycle is planar in contrast to metalated isobacterochlorins which are generally domed or buckled.

The isobacteriochlorin macrocycle **1** has recently become a center of chemical, structural, and biochemical interest. This is due to two developments. One was the discovery[1] that the prosthetic group of sulfite and nitrite reductases is the iron complex of an isobacteriochlorin. From the sulfite reductase of *E. coli* was isolated the iron-free form, sirohydrochlorin[1] (**2a**). A second advance was the proof that **2a**, probably as its dihydro derivative, is an important intermediate on the biosynthetic pathway to vitamin B_{12};[2,3] this work also led to the illustrated complete structure

---

[†] External staff, Medical Research Council.

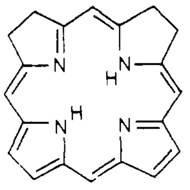
(1) Siegel, L. M.; Murphy, M. J.; Kamin, H. *J. Biol. Chem.* **1973** *248*, 251-264. Murphy, M. J.; Siegel, L. M.; Kamin, H.; Rosenthal, D. *Ibid.* **1973**, *248*, 2801-2814. Murphy, M. J.; Siegel, L. M.; Tove, S. R.; Kamin, H. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 612-616.

0002-7863/82/1504-2376$01.25/0 © 1982 American Chemical Society

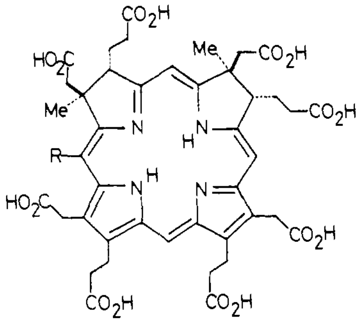
2a for sirohydrochlorin.[2,3] A surprising related development was the isolation of the 20-methylisobacteriochlorin (**2b**) from organisms producing vitamin B_{12},[4] and this substance (**2b**) was shown to be converted enzymically into the corrin system of vitamin B_{12}.[4]

Isobacteriochlorins had been prepared earlier by appropriate reduction of metalloporphyrins[5] and chlorins,[5] but no rational synthesis was available until 1979.[6] Since then, two simpler synthetic approaches have been described.[7,8]

The central role of isobacteriochlorins in the two areas mentioned above emphasizes the need for accurate structural information about this macrocycle. However, the natural substances **2a** and **2b** have not been obtained in crystalline form nor, as yet, any derivative of them. Fortunately synthetic materials have crystallized well, and we report here the results of an X-ray analysis of the isobacteriochlorin **3** synthesized by a photochemical route.[8]

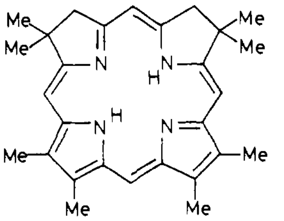


(1)



(2a) R=H

(2b) R=CH_3



(3)

Experimental Section

The isobacteriochlorin $C_{28}H_{34}N_4$, whose synthesis has been described elsewhere,[8] crystallized on standing from a CH_2Cl_2/methanol solution as dark red rhombohedra. The crystals had space group $R\bar{3}$, with cell dimensions $a = b = c = 16.926$ (3) Å and $\alpha = \beta = \gamma = 109.72$ (2) with six molecules in a cell volume of 3698.1 $Å^3$. The alternative hexagonal cell constants are $a = b = 27.682$ Å, $c = 16.717$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$. Cell dimensions were determined on a Syntex $P2_1$ diffractometer from the setting angles of 15 strong reflections by using a rhombohedral crystal with minimum and maximum dimensions of 0.12 and 0.27 mm, respectively. Intensities were measured by $\omega/2\theta$ scans at rates ranging from 29.3 to 1.25° 2θ per min, from 1° below to 1° above the 2θ angles of each $\alpha_1\alpha_2$ doublet, with graphite monochromatized Cu Kα radiation. Background intensities were measured for one-quarter of the total scan time at each end of the scan. Periodic measurement of three standard reflections indicated no significant loss of intensity during the measurement of 5114 reflections with $2\theta < 130°$. After internal scaling and Lp corrections, merging equivalent reflections yielded 4208 unique reflections; 2205 reflections had $F > 3\sigma$ and were treated as observed.

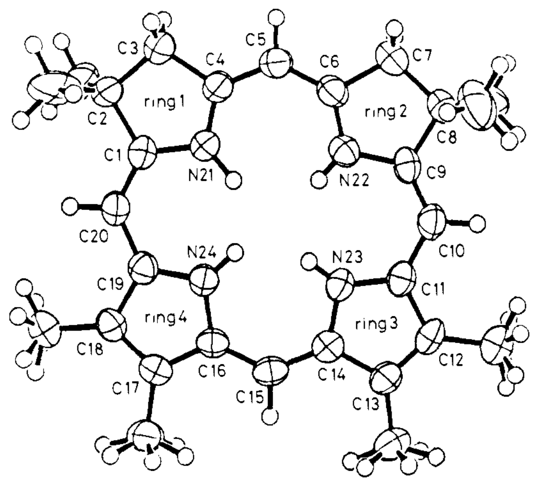


Figure 1. View of the molecule perpendicular to the mean molecular plane drawn with program ORTEP.[18] The thermal ellipsoids are scaled to 35% probability. Note the six half-hydrogen atoms attached to the pyrrole methyl substituents.

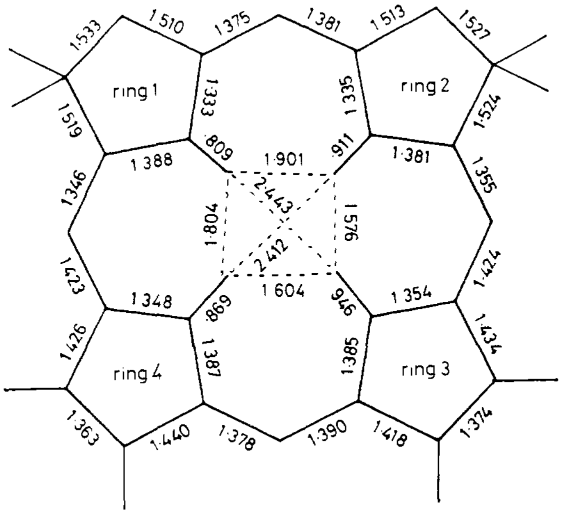


Figure 2. Selected bond lengths and interproton distances (Å).

Structure Solution and Refinement. Multisolution Σ_2 sign expansion with the program SHELX[9] determined the necessary phases from which an E map was calculated. This gave the location of all nonhydrogen atoms. Isotropic refinement by the method of full-matrix least squares, minimizing $W\Delta^2$, converged at a residual R of 0.11. A difference map showed the locations of all hydrogen atoms bonded to carbon but with each of the four pyrrole methyl groups appearing with six hydrogen atoms. These disordered methyl groups were fixed with the hydrogen atoms in a fully staggered conformation with C–H bond distances of 1.01 Å, individual occupancy factors of 0.5, and a common isotropic temperature factor. Other hydrogen atom positions were calculated by assuming an sp^3 bonding geometry, and each methyl group was refined

---

(2) Battersby, A. R.; Jones, K.; McDonald, E.; Robinson, J. A.; Morris, H. R. *Tetrahedron Lett.* **1977**, 2213–2216. Battersby, A. R.; McDonald, E.; Morris, H. R.; Thompson, M.; Williams, D. C.; Bykhovsky, V. Ya.; Zaitseva, N. I.; Bukin, V. N. *Ibid.* **1977**, 2217–2220: Deeg, R.; Kriemler, H. P.; Bergmann, K. H.; Muller, G. *Hoppe-Seylers Z. Physiol. Chem.* **1977**, *358*, 339–352. Bergmann, K. H.; Deeg, R.; Gneuss, K. D.; Kriemler, H. P.; Müller, G. *Ibid.* **1977**, *358*, 1315–1323. Scott, A. I.; Irwin, A. J.; Siegel, L. M.; Shoolery, J. N. *J. Am. Chem. Soc.* **1978**, *100*, 316–318, 7987–7994.

(3) Bykhovsky, V. Ya.; Zaitseva, N. I.; Bukin, N. V. *Dokl. Acad. Nauk SSSR* **1975**, *224*, 1431–1434. Bykhovsky, V. Ya.; Zaitseva, N. I.; Umrikhina, A. V.; Yavorskaya, A. N. *Prikl. Biokhim. Mikrobiol.* **1976**, *12*, 825–833. Battersby, A. R.; McDonald, E.; Thompson, M.; Bykhovsky, V. Ya. *J. Chem. Soc., Chem. Commun.* **1978**, 150–151.

(4) Battersby, A. R.; Matcham, G. W. J.; McDonald, E.; Neier, R.; Thompson, M.; Woggon, W.-D.; Bykhovsky, V. Ya.; Morris, H. R. *J. Chem. Soc., Chem. Commun.* **1979**, 185–186. Lewis, N. G.; Neier, R.: McDonald, E.; Battersby, A. R.; *Ibid.* **1979**, 541–542. Müller, G.; Gneuss, K. D.; Kriemler, H. P.; Scott, A. I.; Irwin, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3655–3657.

(5) Eisner, U.; *J. Chem. Soc.* **1957**, 3461–3469: Bonnet, R.: Gale, I. A. D.; Stephenson, G. F.; *Ibid. C*, **1967**, 1168–1172: Inhoffen, H. H.; Buchler, J. W.; Thomas, R. *Tetrahedron Lett.* **1969**, 1141–1144.

(6) Montforts, F.-P.; Ofner, S.; Rasetti, V.; Eschenmoser, A.; Woggon, W.-D.; Jones, K.; Battersby, A. R.; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 675–677.

(7) Naab, P.; Lattmann, R.; Angst, C.; Eschenmoser, A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 143-145.

(8) Harrison, P. J.; Fookes, C. J. R.; Battersby, A. R. *J. Chem. Soc., Chem. Commun.*, in press.

(9) Sheldrick, G. M. SHELX 76 System of Computing Programs; University of Cambridge: Cambridge, England, 1976.

Table I

(a) Atom Coordinates (×10⁴)

	x/a	y/b	z/c
C(1)	-510(3)	7543(2)	3453(2)
C(2)	513(3)	7934(3)	4250(3)
C(3)	1084(3)	7459(3)	3714(3)
C(4)	380(3)	7730(2)	2724(2)
C(5)	650(3)	7763(3)	2050(3)
C(6)	87(3)	7526(2)	1106(2)
C(7)	503(3)	7575(3)	448(2)
C(8)	-365(2)	7212(3)	-577(2)
C(9)	-1191(2)	7016(2)	-309(2)
C(10)	-2124(2)	6667(2)	-962(2)
C(11)	-2934(2)	6514(2)	-817(2)
C(12)	-3896(2)	6206(2)	-1530(2)
C(13)	-4433(2)	6162(2)	-1076(2)
C(14)	-3616(2)	6426(2)	-108(2)
C(15)	-4074(2)	6433(2)	591(3)
C(16)	-3515(2)	6643(2)	1525(3)
C(17)	-3849(3)	6597(2)	2147(3)
C(18)	-3078(3)	6813(2)	3010(3)
C(19)	-2266(3)	7022(2)	2800(3)
C(20)	-1394(3)	7326(2)	3515(3)
N(21)	-498(2)	7492(2)	2672(2)
N(22)	-654(2)	7215(2)	630(2)
N(23)	-2896(2)	6647(2)	33(2)
N(24)	-2514(2)	6918(2)	1959(2)
C(25)	913(4)	8471(3)	5057(3)
C(26)	538(3)	7285(3)	4689(3)
C(27)	-222(3)	7977(3)	-426(3)
C(28)	-576(3)	6278(3)	-1382(3)
C(29)	-4271(3)	5970(3)	-2559(3)
C(30)	-5486(3)	5881(3)	-1556(3)
C(31)	-4861(3)	6342(3)	2001(3)
C(32)	-3054(3)	6794(3)	3900(3)

(b) Anisotropic Temperature Factors[a] (Å² × 10³)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	61(2)	51(2)	44(2)	27(2)	26(2)	31(2)
C(2)	57(2)	70(3)	47(2)	35(2)	21(2)	31(2)
C(3)	61(3)	114(4)	56(3)	46(2)	26(2)	43(2)
C(4)	48(2)	56(2)	48(2)	23(2)	18(2)	25(2)
C(5)	47(2)	69(3)	53(2)	28(2)	26(2)	25(2)
C(6)	49(2)	56(2)	49(2)	24(2)	27(2)	26(2)
C(7)	56(2)	103(3)	52(2)	34(2)	33(2)	36(2)
C(8)	46(2)	69(2)	50(2)	26(2)	29(2)	26(2)
C(9)	54(2)	49(2)	46(2)	25(2)	26(2)	27(2)
C(10)	56(2)	59(2)	47(2)	28(2)	26(2)	32(2)
C(11)	51(2)	40(2)	51(2)	25(2)	26(2)	30(2)
C(12)	54(2)	54(2)	51(2)	31(2)	25(2)	31(2)
C(13)	44(2)	45(2)	50(2)	23(2)	19(2)	22(2)
C(14)	44(2)	43(2)	52(2)	24(2)	24(2)	23(2)
C(15)	46(2)	44(2)	61(2)	25(2)	29(2)	23(2)
C(16)	52(2)	42(2)	54(2)	23(2)	29(2)	24(2)
C(17)	55(2)	40(2)	57(2)	24(2)	33(2)	26(2)
C(18)	69(3)	54(2)	59(2)	32(2)	45(2)	34(2)
C(19)	60(2)	48(2)	51(2)	25(2)	32(2)	29(2)
C(20)	63(2)	54(2)	49(2)	31(2)	32(2)	35(2)
N(21)	47(2)	48(2)	45(2)	24(2)	21(1)	26(2)
N(22)	46(2)	53(2)	47(2)	26(1)	26(1)	25(1)
N(23)	49(2)	51(2)	45(2)	24(1)	25(1)	26(1)
N(24)	55(2)	56(2)	49(2)	26(1)	32(2)	30(2)
C(25)	92(3)	94(3)	60(3)	16(2)	10(2)	28(3)
C(26)	80(3)	126(4)	102(3)	94(3)	44(3)	65(3)
C(27)	81(3)	119(3)	111(4)	76(3)	61(3)	47(3)
C(28)	72(3)	99(3)	74(3)	23(3)	44(2)	44(3)
C(29)	63(3)	90(3)	55(2)	38(2)	25(2)	41(2)
C(30)	54(2)	78(3)	64(3)	38(2)	26(2)	33(2)
C(31)	64(3)	70(3)	71(3)	37(2)	43(2)	31(2)
C(32)	85(3)	87(3)	71(3)	44(3)	52(3)	40(3)

(c) Hydrogen Atom Coordinates (×10⁴) and Isotropic Temperature Factors (Å² × 10³)

	x/a	y/b	z/c	U
H(31)	1285(3)	7453(3)	3640(3)	101(7)
H(32)	1582(3)	7626(3)	4071(3)	111(7)
H(51)	1362(3)	7943(3)	2209(3)	60(5)
H(71)	1019(3)	6208(3)	723(2)	101(7)
H(72)	791(3)	7142(3)	370(2)	101(7)
H(101)	-2262(2)	6545(2)	-1632(2)	60(5)
H(151)	-4771(2)	6258(2)	384(3)	60(5)
H(201)	-1202(3)	7365(2)	4191(3)	60(5)
H(21)	-992(41)	7322(39)	2119(41)	36(8)
H(22)	-1259(40)	7143(37)	846(39)	36(8)
H(23)	-2344(41)	6854(39)	617(41)	36(8)
H(24)	-2266(41)	6947(41)	1616(42)	36(8)
H(251)	1612(4)	9286(3)	5591(3)	126(5)
H(252)	489(4)	8834(3)	5317(3)	126(5)
H(253)	656(4)	8408(3)	4779(3)	126(5)
H(261)	244(3)	6669(3)	4136(3)	126(5)
H(262)	133(3)	7278(3)	5012(3)	126(5)
H(263)	1226(3)	7517(3)	5183(3)	126(5)
H(271)	346(3)	8096(3)	-931(3)	126(5)
H(272)	-59(3)	8599(3)	-279(3)	126(5)
H(273)	-919(3)	7760(3)	-1442(3)	126(5)
H(281)	5(3)	6423(3)	-1423(3)	126(5)
H(282)	-1173(3)	6035(3)	-1963(3)	126(5)
H(283)	-691(3)	5763(3)	-1112(3)	126(5)
H(291)	-3649(3)	6128(3)	-2658(3)	72(10)
H(294)	-3655(3)	6569(3)	-2548(3)	72(10)
H(292)	-4570(3)	6344(3)	-2679(3)	72(10)
H(295)	-4515(3)	5719(3)	-2971(3)	72(10)
H(293)	-4733(3)	5258(3)	-3031(3)	72(10)
H(296)	-4682(3)	5467(3)	-2900(3)	72(10)
H(301)	-5613(3)	6071(3)	-944(3)	65(9)
H(304)	-5795(3)	5469(3)	-1320(3)	65(9)
H(302)	-5990(3)	5155(3)	-1967(3)	65(9)
H(305)	-5631(3)	5563(3)	-2213(3)	65(9)
H(303)	-5655(3)	6225(3)	-1671(3)	65(9)
H(306)	-5543(3)	6479(3)	-1225(3)	65(9)
H(311)	-5337(3)	5931(3)	1275(3)	66(11)
H(314)	-5117(3)	6610(3)	1596(3)	66(11)
H(312)	-4667(3)	5969(3)	2203(3)	66(11)
H(315)	-4630(3)	6650(3)	2611(3)	66(11)
H(313)	-5056(3)	5971(3)	2326(3)	66(11)
H(316)	-5396(3)	5612(3)	1613(3)	66(11)
H(321)	-2377(3)	7086(3)	4387(3)	74(10)
H(324)	-2650(3)	6327(3)	4002(3)	74(10)
H(322)	-3525(3)	6110(3)	3716(3)	74(10)
H(325)	-3730(3)	6583(3)	3614(3)	74(10)
H(323)	-3256(3)	7262(3)	4149(3)	74(10)
H(326)	-2581(3)	7433(3)	4485(3)	74(10)

[a] The temperature factor exponent takes the form $-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^*)$.

Table II. Bond Lengths (Å)

C(2)-C(1)	1.519(6)	C(20)-C(1)	1.346(5)
N(21)-C(1)	1.388(5)	C(3)-C(2)	1.533(7)
C(25)-C(2)	1.540(7)	C(26)-C(2)	1.524(7)
C(4)-C(3)	1.510(6)	C(5)-C(4)	1.375(5)
N(21)-C(4)	1.333(5)	C(6)-C(5)	1.381(5)
C(7)-C(6)	1.513(6)	N(22)-C(6)	1.335(5)
C(8)-C(7)	1.527(6)	C(9)-C(8)	1.524(6)
C(27)-C(8)	1.521(7)	C(28)-C(8)	1.522(7)
C(10)-C(9)	1.355(5)	N(22)-C(9)	1.381(5)
C(11)-C(10)	1.424(5)	C(12)-C(11)	1.434(5)
N(23)-C(11)	1.354(5)	C(13)-C(12)	1.374(5)
C(29)-C(12)	1.493(5)	C(14)-C(13)	1.416(5)
C(30)-C(13)	1.505(6)	C(15)-C(14)	1.390(5)
N(23)-C(14)	1.385(5)	C(16)-C(15)	1.376(5)
C(17)-C(16)	1.440(5)	N(24)-C(16)	1.387(5)
C(18)-C(17)	1.363(5)	C(31)-C(17)	1.501(5)
C(19)-C(18)	1.426(5)	C(32)-C(18)	1.506(7)
C(20)-C(19)	1.423(5)	N(24)-C(19)	1.346(5)
H(21)-N(21)	0.809(56)	H(22)-N(22)	0.911(58)
H(23)-N(23)	0.946(56)	H(24)-N(24)	0.869(58)

Table III. Bond Angles (deg)

C(20)-C(1)-C(2)	125.7(4)	N(21)-C(1)-C(2)	109.6(4)
N(21)-C(1)-C(20)	124.7(4)	C(3)-C(2)-C(1)	102.7(4)
C(25)-C(2)-C(1)	109.7(4)	C(25)-C(2)-C(3)	111.1(4)
C(26)-C(2)-C(1)	111.9(4)	C(26)-C(2)-C(3)	112.6(4)
C(26)-C(2)-C(25)	109.7(5)	C(4)-C(3)-C(2)	104.6(4)
C(5)-C(4)-C(3)	122.3(4)	N(21)-C(4)-C(3)	110.4(4)
N(21)-C(4)-C(5)	127.3(4)	C(6)-C(5)-C(4)	129.3(4)
C(7)-C(6)-C(5)	122.2(4)	N(22)-C(6)-C(5)	126.9(4)
N(22)-C(6)-C(7)	110.9(4)	C(8)-C(7)-C(6)	105.0(4)
C(9)-C(8)-C(7)	102.1(4)	C(27)-C(8)-C(7)	112.3(4)
C(27)-C(8)-C(9)	110.4(4)	C(28)-C(8)-C(7)	111.6(4)
C(28)-C(8)-C(9)	112.6(4)	C(28)-C(8)-C(27)	109.7(4)
C(10)-C(9)-C(8)	123.1(4)	N(22)-C(9)-C(8)	112.2(4)
N(22)-C(9)-C(10)	124.7(4)	C(11)-C(10)-C(9)	128.3(4)
C(12)-C(11)-C(10)	125.6(4)	N(23)-C(11)-C(10)	127.5(4)
N(23)-C(11)-C(12)	106.9(4)	C(13)-C(12)-C(11)	106.1(4)
C(29)-C(12)-C(11)	125.4(4)	C(29)-C(12)-C(13)	128.5(4)
C(14)-C(13)-C(12)	107.9(4)	C(30)-C(13)-C(12)	127.1(4)
C(30)-C(13)-C(14)	125.0(4)	C(15)-C(14)-C(13)	127.1(4)
N(23)-C(14)-C(13)	108.7(4)	N(23)-C(14)-C(15)	124.2(4)
C(16)-C(15)-C(14)	129.6(4)	C(17)-C(16)-C(15)	126.4(4)
N(24)-C(16)-C(15)	125.2(4)	N(24)-C(16)-C(17)	108.3(4)
C(18)-C(17)-C(16)	106.8(4)	C(31)-C(17)-C(16)	125.1(4)
C(31)-C(17)-C(18)	128.2(4)	C(19)-C(18)-C(17)	107.5(4)
C(32)-C(18)-C(17)	128.0(4)	C(32)-C(18)-C(19)	124.5(4)
C(20)-C(19)-C(18)	126.2(4)	N(24)-C(19)-C(18)	109.7(4)
N(24)-C(19)-C(20)	124.0(4)	C(19)-C(20)-C(1)	125.1(4)
C(4)-N(21)-C(1)	112.0(4)	H(21)-N(21)-C(1)	119.9(42)
H(21)-N(21)-C(4)	128.0(42)	C(9)-N(22)-C(6)	111.0(4)
H(22)-N(22)-C(6)	126.1(35)	H(22)-N(22)-C(9)	122.9(35)
C(14)-N(23)-C(11)	107.4(3)	H(23)-N(23)-C(11)	126.6(35)
H(23)-N(23)-C(14)	126.0(35)	C(19)-N(24)-C(16)	107.6(3)
H(24)-N(24)-C(16)	116.3(30)	H(24)-N(24)-C(19)	135.9(39)

as a rigid body. A difference map at the residual $R = 0.07$ showed four peaks of 0.25, 0.29, 0.26, and 0.25 e/Å³ at bonding distances from the nitrogen atoms. Each was assumed to be a hydrogen atom site with an occupancy factor of 0.5. Further refinement, using a common temperature factor and allowing the positions of these four atoms to change, converged at a weighted residual $R_w = 0.049$ [$R_w = \sum w^{1/2}\Delta/\sum w^{1/2}F_o$ where $\Delta = ||F_o| - |F_c||$ and $w = 1/(\sigma^2(F_0) + 0.0005F_0^2)$], corresponding to a final residual $R = 0.051$. A final difference map showed no general peaks greater than 0.15 e/Å³. Two further cycles of refinement were carried out to test the validity of the disordered hydrogen model. In one full occupancy was assigned to the two hydrogen sites attached to N21 and N23 and in the other to N22 and N24. Both refinements led to higher R_w factors than in the disordered model and to unacceptably high temperature factors for the hydrogen atoms. All calculations were performed with the program SHELX.[9] Atomic coordinates and isotropic temperature factors for the nonhydrogen atoms are given in Table Ia,b and the hydrogen coordinates and isotropic temperature factors in Table

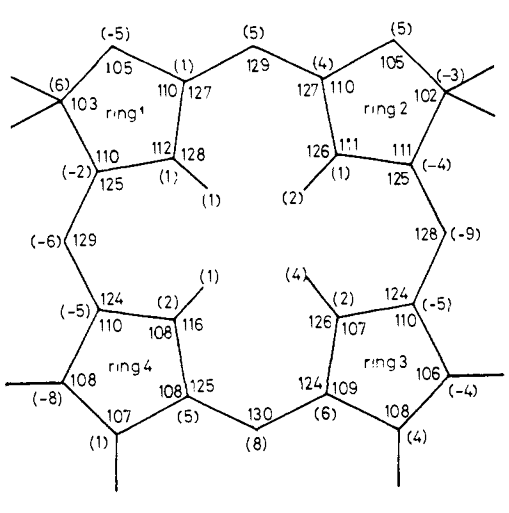
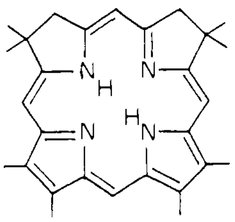


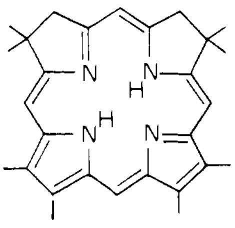
Figure 3. Selected bond angles (deg) and deviations from the mean molecular plane of the chromophore ($\times 10^{-2}$ Å).

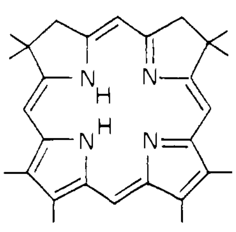
Ic. Bond lengths are listed in Table II and bond angles in Table III.

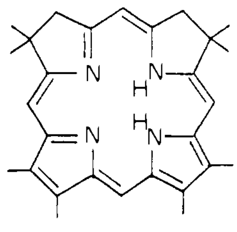
Discussion

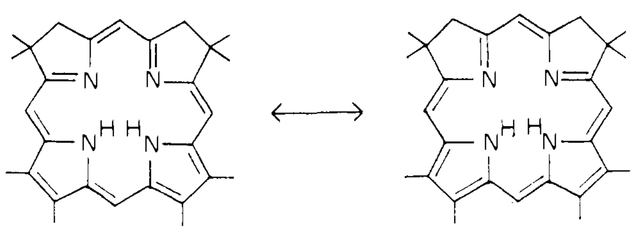
The isobacteriochlorin molecule can theoretically exist in five tautomeric forms (**4a–f**), one of which has two resonance forms.


(4a)


(4b)


(4c)


(4d)


(4e) (4f)

In three of these, however, hydrogen atoms are attached to adjacent N atoms and are thus sufficiently close to cause the entire chromophore to be considerably buckled. In the present structure the chromophore is planar, and we find experimentally two protons distributed between the four nitrogen atoms with a 50% occupancy at each site. This would suggest that the tautomeric forms (**4a,b**) contribute equally to the solid-state structure, although a slight bias toward one form or another cannot altogether be ruled out. A view of the molecule and the numbering scheme used is shown in Figure 1. The molecular dimensions (Figures 2 and 3) reflect the superposition of the tautomeric forms, **4a** and **4b**, resulting in an approximate twofold symmetry of the bond pattern about an axis through C5 and C15.

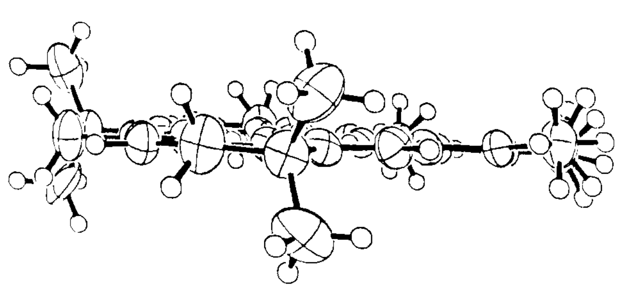


Figure 4. Edge-on view of the molecule.

The C_β–C_β distances in the two reduced rings (1 and 2) correspond to sp^3–sp^3 values (1.530 Å) while the C_α–C_β bonds (1.516 Å) show the slight shortening expected for an sp^3–sp^2 bond. The two C_α–N bonds are significantly different ($\Delta = 0.051$ Å) as a result of the superposition of the tautomeric forms. The C1–N21 and C9–N22 bonds are formally single in both tautomers (1.385 Å), while C4–N21 and C6–N22 are alternately single and double and thus shortened to 1.334 Å in the superimposed structure.

A similar situation arises with respect to bonds C1–C20 (C9–C10) and C20–C19 (C10–C11), each of which has the same formal bond order in both tautomers and appear as partial double (1.350 Å) and single (1.424 Å) bonds. Bond C4–C5 (C5–C6) has the intermediate value of 1.378 Å arising from the superposition of formal single and double bonds in the different tautomers.

A search of the literature[10] revealed four X-ray determinations of structures containing reduced rings suitable for direct comparison: the isobacteriochlorin (2,3,7,8-tetrahydro-5,10,15,20-tetraphenylporphinato)(pyridine)zinc(II) benzene solvate,[11] phyllochlorin ester,[12] nickel(II) octaethylchlorin,[13] and two isomers of octaethyl-2,3,7,8-tetrahydroporphyrin and their Ni(II) complexes[14] for which, however, no coordinate data have as yet been published. Table IV compares the relevant bond lengths and bond angles as well as the estimated standard deviations where available.

There is good agreement between the values found in the four compounds, with the exception of the C_β–C_β bonds which are significantly shorter in both reduced rings of the zinc isobacteriochlorin. In the zinc isobacteriochlorin, ring 1 is planar to within 0.02 Å while ring 2 is markedly nonplanar, with maximum deviation of 0.309 Å. In the present structure ring 1 is slightly twisted with C1 and C3 below (0.04 Å) and C2 and C4 above (0.05, 0.03 Å) the mean plane. In ring 2 the same pattern is observed but with maximum deviations of only ±0.01 Å.

In ring 1 the twist about the C_β–C_β bond is 8° (C1–C2–C3–C4), resulting in a slight staggering of the hydrogen atoms with respect to the methyl C atoms (C25–C2–C3–H32 = 10.6° and C26–C2–C3–H31 = 9.4°). In ring 2 the corresponding angles are 1.4, 0.4, or 2.5°, and thus the substituent bonds are virtually eclipsed. Similar observations were reported for the two reduced rings of the Zn–iBC whereas Kratky and co-workers report,[14] for all their compounds, axial and equatorial orientations of substituents on both rings. The dimensions of the fully conjugated rings 3 and 4 are markedly different from those of rings 1 and 2. Table V gives a comparison of values found in the present structure for these rings with the highly accurate redetermination of the structure of porphyrin,[15] octaethylporphyrin,[16] and 5,5′-(biseth-

---

(10) Allen, F. H.; Bellard, S.; Brice, M. D.; Cartwright, B. A.; Doubleday, A.; Higgs, H.; Hummelink, T.; Hummelink-Peters, B. G.; Kennard, O.; Motherwell, W. D. S.; Rodgers, J. R.; Watson, D. G. *Acta Crystallogr., Sect. B* **1979**, *B35*, 2331–2339.

(11) Barkigia, K. M.; Fajer, J.; Spaulding, L. D.; Williams, G. J. B. *J. Am. Chem. Soc.* **1981**, *103*, 176–181.

(12) Hoppe, W.; Will, G.; Gassmann, J.; Weichselgartner, H. *Z. Kristallogr.* **1969**, *128*, 18–35.

(13) Ulman, A.; Gallucci, J.; Fisher, D.; Ibers, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 6852–6854.

(14) Kratky, C.; Angst, C.; Johansen, J. E. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 211–212.

(15) Chen, B. M. L.; Tulinsky, A. *J. Am. Chem. Soc.* **1972**, *94*, 4144–4151.

(16) Lauher, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 5148–5152.

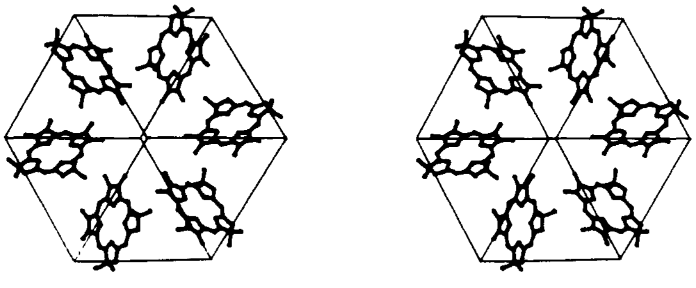
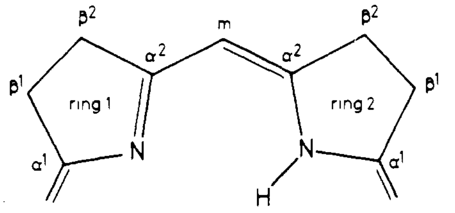


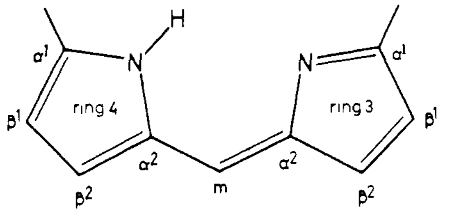
Figure 5. Stereoview of the molecular packing.

Table IV. Reduced Rings



	octamethylisobacteriochlorin (av)	Zn (pyr)iBC		phyllochlorin	nickel octaethylchlorin
		ring 1	ring 2		
		Bond Distances, Å			
N-C_α1	1.385	1.374	1.384	1.34$_2$	1.377
C_α1-C_β1	1.522	1.499	1.484	1.58$_4$	1.507
C_β1-C_β2	1.530	1.489	1.416	1.53$_3$	1.516
C_β2-C_α2	1.512	1.493	1.474	1.52$_6$	1.504
C_α2-N	1.334	1.357	1.346	1.31$_7$	1.377
C_α2-C_m	1.378	1.392	1.398		
		Bond Angles, deg			
N-C_α1-C_β1	110.3	110.9	108.8	106.0	
C_α1-C_β1-C_β2	102.4	104.4	105.3	104.0	
C_β1-C_β2-C_α2	104.8	103.9	106.2	100.0	
C_β2-C_α2-N	110.6	112.0	109.9	113.0	
C_α2-N-C_α1	111.5	108.7	109.3	113.0	
N-C_α2-C_m	127.1	125.8	127.1		
C_α2-C_m-C_α2	129.3	125.6			
σ_{bond}, Å		0.005			
σ_{angle} deg		0.3			0.002–0.005

Table V. Pyrrole Rings



	octamethylisobacteriochlorin (av)	pyrromethene (av)	porphyrin^a		octaethylporphyrin^a	
			ring 1 (av)	ring 2 (av)	ring 1 (av)	ring 2 (av)
		Bond Distances, Å				
N-C_α1	1.351	1.341	1.374	1.380	1.364	1.367
C_α1-C_β1	1.430	1.424	1.452	1.431	1.462	1.438
C_β1-C_β2	1.369	1.385	1.345	1.365	1.353	1.373
C_β2-C_α2	1.429	1.432				
C_α2-N	1.386	1.384				
C_α2-C_m	1.384	1.398	1.382		1.392	
		Bond Angles, deg				
N-C_α1-C_β1	109.8	110.9	109.8	107.9	110.8	107.7
C_α1-C_β1-C_β2	106.8	106.4	107.1	107.9	106.3	107.4
C_β1-C_β2-C_α2	107.3	106.5				
C_β2-C_α2-N	108.5	109.2				
C_α2-N-C_α1	107.5	107.1	106.1	108.6	105.7	109.6
N-C_α2-C_m	124.7	122.2	125.0	125.5	125.1	125.0
C_α2-C_m-C_α2	129.6	126.1	127.1		127.6	
σ_{bond}, Å		0.0025	0.004–0.007		0.002	
σ_{angle}, deg		0.15	0.3–0.5		0.1	

^{a} Ring 2 carries hydrogen in porphyrin and octaethylporphyrin.

oxycarbonyl)-3,3′-diethyl-4,4′-dimethyl-2,2′-pyrromethene.[17] In the pyrromethene[17] the nitrogen proton is statistically disordered between the two N atoms, and this is attributed by the authors to resonance between two possible valence tautomers, similar to the tautomers observed in the present structure. There is good agreement between the geometric parameters found in these two structures, particularly the marked differences in the N–C_α1 and N–C_α2 bond lengths ($\Delta = 0.035$ and 0.043 Å, respectively). These bonds, however, are equivalent in porphyrin[15] and octaethylporphyrin.[16] In these compounds the protons were fully localized on two diagonal N atoms, with no indication of the presence of different tautomeric species in the crystal structure.

Figure 4 shows a side view of the molecule. The entire structure, with the exception of the substituents on the reduced rings, is highly planar. This is in contrast with metal containing isobacteriochlorins such as the Zn–iBC[11] in which the macrocycle is dome shaped and the two Ni containing iBC compounds[14] which show a collapsed and highly puckered geometry of the macrocycle with approximate D_{2d} symmetry.

The individual deviations from the mean molecular plane of the octamethylisobacteriochlorin are indicated in Figure 3. The four half-protons can be accommodated in this plane with separation along the diagonals of 2.412 and 2.443 Å. This is in contrast to porphyrin where similar separation could only be achieved by substantial displacement (+0.05 and −0.9 Å) of the two protons from the mean plane. The packing of the molecules in the rhombohedral cell is illustrated in the stereodiagram (Figure 5). There is no indication of any ring stacking, and the closest approach is 3.74 Å between neighboring C and N atoms. The only deformation of the molecule which can be attributed to crystal packing forces is the slight twist observed in ring 1. The overall molecular geometry deduced from the X-ray structure gives an accurate model of two superimposed tautomeric forms of a metal-free isobacteriochlorin.

Acknowledgment. We thank the M. R. C. for financial support and the S. R. C. for studentship (to P.H.) and the provision of a diffractometer. We thank Professor A. R. Battersby for suggesting the investigation, C. J. R. Fookes for helpful discussion, and the referees for constructive comments.

Registry No. 3, 80053-11-8.

---

(17) Sheldrick, W. S.; Borkenstein, A.; Struckmeier, G.; Engel, J. *Acta Crystallogr., Sect. B* **1978**, *B34*, 329–332.