Crystal Structure of Octaethylxanthoporphinogen Dihydrate [1]

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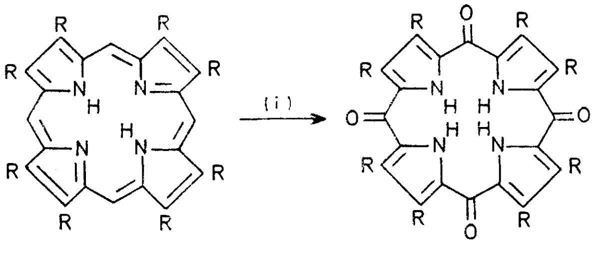
Crystals of the title compound (I) are tetragonal, space group $I4_1/a$, with a = 13.801(1), c = 18.575(6) Å, Z = 4. The chromophore molecule has crystallographic S_4 symmetry with the oxygen atoms of the associated water molecules positioned on this symmetry axis above and below the porphinogen and linked in each case to two opposing pyrrole nitrogen atoms by hydrogen bridge bonds of length 3.016 Å (N–H 0.92, H · · · O 2.13 Å). The atoms bonded to a bridging carbon atom form dihedral angles of −8.9 and 41.6° with the planes of the neighbouring pyrrole rings. Each of the four hydrogen atoms of the two water molecules interacts with a ketone-oxygen atom of a neighbouring molecule such that each molecule of (I) is linked to four other similar molecules (O–H · · · O 2.832, O–H 0.89, H · · · O 2.01 Å), resulting in the formation of water-containing tubular cavities. The structure was solved by direct methods and refined to R 0.075 for 1 115 diffractometer measured unique reflections.

XANTHOPORPHINOGENS [Greek xanthos = yellow, porphinogen = porph(yr)in producer] were first obtained by Fischer in 1927 by the oxidation of porphyrins under drastic conditions with lead dioxide.[2] At that time the question of the structure of the porphyrin skeleton had not finally been resolved, for, in addition to the sixteen-membered tetrapyrrole macrocycle originally suggested for haemin by Küster in 1913,[3] the possibility of the 'indigoid' structure of a tetrapyrrolethylene was also under consideration. Although Fischer was by 1927 convinced of the correctness of Küster's suggested structure, he nevertheless continued to search for an experimental means of confirming one of these structures to the exclusion of the other. Thus the stimulus for his synthesis of the xanthoporphinogens came, in fact, from an extension to the porphyrins of oxidation procedures using lead dioxide, which had proved successful with indigo (equation). Almost quantitative yields were obtained of these yellow crystalline compounds, which were shown to be four oxygens richer than the parent porphyrin. The major reason why almost 40 years were to pass before their structure as tetraoxoporphinogens was finally elucidated by spectroscopic methods,[4] lay in the fact that the four oxygens appeared to display differing chemical reactivities. For instance, only two could be eliminated upon reaction with zinc and glacial acetic acid.



(I) R = Et

Reagents: (i), PbO_2 in $CHCl_3$–HOAc.

The n.m.r. spectrum showed that the ring current of the porphyrin nucleus no longer exists in the xanthoporphinogens even though the tetrapyrrole macrocycle has been retained. In further contrast to the porphyrins it was noted that two molecules of water of crystallisation could not be removed even on heating in a high vacuum at 150 °C; such stable hydrates have never been observed among porphyrins. This investigation of (I) was accordingly initiated in order to characterise the structure of the tetrapyrrole macrocycle and the nature of the bonding role of the water molecules.

EXPERIMENTAL

Well formed tetragonal bipyramidal crystals of (I) were obtained upon its recrystallisation from ethanol. Intensity data from a crystal with dimensions *ca.* 0.32 × 0.32 × 0.53 mm mounted with the c axis parallel to the goniometer axis, was collected on a Syntex $P2_1$ four-circle diffractometer by use of graphite monochromated Mo-K_α radiation. Measurements were carried out in the ω-mode ($3.0 \leqslant 2\theta \leqslant 50.0°$) at scan speeds varying linearly between 4.0 and 19.53° min^{-1}. Scan and total background times were equal. Three standard reflections, monitored regularly, showed no significant variations due to crystal deterioration during data collection. 1 115 Of the 1 775 reflections recorded (one quadrant of reciprocal space) were considered to be observed, having $F > 2.5\sigma(F)$ (internal consistency index R 0.031). Lorentz and polarisation, but no absorption corrections were applied to the raw intensity data. Accurate unit-cell dimensions were obtained from measurements of 15 reflections ($\pm hkl$) by use of Mo-K_α radiation.

Crystal Data.—$C_{36}H_{44}N_4O_4,2H_2O$, M = 632.81. Tetragonal, a = 13.801(1), c = 18.575(6) Å, U = 3 537.7(12) Å^3, Z = 4, D_c = 1.19. Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 0.43 cm^{-1}. Systematic absences hkl ($h + k + l = 2n$), $00l$ ($l = 4n$) and $hk0$ [h, (k) = $2n$] indicate the centrosymmetric space group $I4_1/a$ (No. 88).

Structure Solution and Refinement.—Crystallising in the space group $I4_1/a$ with Z = 4, the molecules of (I) must contain inverse tetrad crystallographic axes (0,0.25,z, *etc.*, for the origin at $\bar{1}$). The structure was solved by a multi-solution technique in which 2^{18} sign permutations were expanded by the Σ_2 formula.[5] A permutation is rejected in this method if its internal consistency falls at any stage below a preset value. Additionally, a similarity test is applied to avoid the calculation of too many closely similar E maps. In this case two E maps were computed, of which the best (in terms of Σ_2 consistency) revealed the positions of all 12 heavy atoms in the asymmetric unit. The oxygen, nitrogen, and carbon positional parameters,

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[1] W. S. Sheldrick and J.-H. Fuhrhop, *Angew. Chem.*, 1975, **87**, 456.

[2] H. Fischer and A. Treibs, *Annalen*, 1927, **457**, 209.

[3] W. Küster and P. Deihle, *Z. physiol. Chem.*, 1913, **82**, 463.

[4] H. H. Inhoffen, J.-H. Fuhrhop, and F. von der Haar, *Annalen*, 1966, **700**, 92.

[5] G. M. Sheldrick, unpublished results.

TABLE 1

Atom co-ordinates and anisotropic vibrational amplitudes (Å^2 × 10^3),* with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(21)	0.8763(2)	0.3411(2)	0.1288(2)	24(2)	28(2)	33(2)	4(2)	−2(2)	1(1)
C(1)	0.7865(2)	0.3006(2)	0.1229(2)	24(2)	27(2)	36(2)	1(2)	11(2)	1(2)
C(2)	0.7300(2)	0.3590(3)	0.0781(2)	25(2)	30(2)	39(2)	−1(2)	1(2)	3(2)
C(3)	0.7875(3)	0.4381(3)	0.0576(2)	27(2)	34(2)	39(2)	0(2)	2(2)	3(2)
C(4)	0.8782(2)	0.4270(3)	0.0905(2)	28(2)	29(2)	33(2)	2(2)	1(2)	2(2)
C(5)	0.9594(3)	0.4925(3)	0.0911(2)	27(2)	30(2)	44(2)	−2(2)	1(2)	3(2)
O(5)	0.9532(2)	0.5744(2)	0.0651(2)	39(2)	30(2)	86(2)	−24(2)	−10(2)	0(1)
C(21)	0.7575(3)	0.2094(3)	0.1589(2)	30(2)	27(2)	44(2)	−1(2)	−2(2)	3(2)
C(22)	0.6272(3)	0.3395(3)	0.0549(3)	34(2)	44(3)	65(3)	5(2)	−7(2)	−4(2)
C(31)	0.5536(4)	0.4019(4)	0.0941(4)	33(3)	61(4)	136(6)	3(4)	10(3)	5(3)
C(32)	0.7569(3)	0.5191(3)	0.0085(3)	35(2)	50(3)	57(3)	22(2)	−4(2)	−1(2)
O(2)	0	0.25	0.2443(2)	35(2)	77(3)	37(3)	0	0	4(2)

* In the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}kha^*b^*)]$.

together with their associated anisotropic temperature factor components, were refined by full-matrix least-squares, the function $\Sigma w\Delta^2$ being minimised. At this stage of the refinement, a difference-Fourier synthesis clearly revealed the positions of the hydrogen atoms which were then included, together with their isotropic temperature factors, as parameters in the final cycles of refinement. The terminal value of the generalised index R_G [$= \Sigma w\Delta^2/\Sigma wF_o^2]^{1/2}$ was 0.073, with a weighted residual R' [$= \Sigma w^{1/2}\Delta/\Sigma w^{1/2}F_o$] of 0.067, and a corresponding unweighted R of 0.075. The weights applied were given by the expression $w = k/[\sigma^2(F_o) + gF_o^2]$, where k and g refined to 1.845 2 and 0.000 66 respectively. In the final cycle of refinement, the largest observed shift-to-error ratio was −0.007. A final difference-Fourier synthesis displayed no peaks or troughs of density >0.31 eÅ^{-3}.

TABLE 2

Hydrogen atom co-ordinates and isotropic vibrational amplitudes (Å^2 × 10^3), with estimated standard deviations in parentheses

	a/x	y/b	z/c	U
H(N)	0.9188(28)	0.3270(25)	0.1656(20)	38(11)
H(211)	0.6190(30)	0.2676(32)	0.0700(21)	61(13)
H(212)	0.6163(25)	0.3448(25)	−0.0024(21)	40(11)
H(221)	0.4840(37)	0.3778(36)	0.0792(25)	84(16)
H(222)	0.5574(41)	0.4698(48)	0.0818(30)	114(22)
H(223)	0.5757(57)	0.3847(54)	0.1490(44)	170(34)
H(311)	0.8130(30)	0.5367(28)	−0.0187(21)	52(12)
H(312)	0.6995(32)	0.4938(31)	−0.0329(23)	70(14)
H(321)	0.6727(40)	0.5998(38)	0.0767(29)	87(21)
H(322)	0.7059(45)	0.6610(53)	0.0019(36)	147(24)
H(323)	0.7786(46)	0.6298(47)	0.0892(35)	132(25)
H(0)	1.0466(44)	0.2483(56)	0.2773(31)	143(28)

TABLE 3

Molecular geometry

(*a*) Interatomic distances (Å)

N(21)–C(1)	1.364(4)	N(21)–C(4)	1.384(4)
C(1)–C(2)	1.396(5)	C(3)–C(4)	1.401(5)
C(4)–C(5)	1.440(5)	C(5)–C(1$^{\text{I}}$)	1.481(5)
C(2)–C(3)	1.403(5)	C(5)–O(5)	1.232(4)
C(2)–C(21)	1.507(5)	C(21)–C(22)	1.519(7)
C(3)–C(31)	1.503(5)	C(31)–C(32)	1.515(7)
C(21)–H(211)	1.04(4)	C(21)–H(212)	1.08(4)
C(22)–H(221)	1.05(5)	C(22)–H(222)	0.97(6)
C(22)–H(223)	1.09(8)	C(31)–H(311)	0.96(4)
C(31)–H(312)	1.05(4)	C(32)–H(321)	0.91(5)
C(32)–H(323)	1.15(7)	C(32)–H(323)	1.09(7)
N–H(N)	0.92(4)	O(2)–H(0)	0.89(6)
H(N) ··· O(2)	2.13	H(0) ··· O(5$^{\text{II}}$)	2.01
N ··· O(2)	3.016	O(2) ··· O(5$^{\text{II}}$)	2.832

(*b*) Bond angles (°)

C(1)–N(21)–C(4)	109.0(3)	C(1)–N(21)–H(N)	123(2)
C(4)–N(21)–H(N)	123(2)	N(21)–C(1)–C(2)	108.7(3)
C(1)–C(2)–C(3)	107.2(3)	C(2)–C(3)–C(4)	107.6(3)
C(3)–C(4)–N(21)	107.6(3)	C(4)–C(5)–O(5)	121.5(3)
C(4)–C(5)–C(1$^{\text{I}}$)	119.5(3)	O(5)–C(5)–C(1$^{\text{I}}$)	119.0(3)
C(2)–C(21)–C(22)	113.0(4)	C(3)–C(31)–C(32)	113.4(4)
C(1)–C(2)–C(21)	126.4(4)	C(3)–C(2)–C(21)	126.4(4)
C(2)–C(3)–C(31)	125.8(3)	C(4)–C(3)–C(31)	126.7(3)

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x,y,z:

I $0.75 + y, 0.25 - x, 0.25 - z$
II $0.5 + x, y, 0.5 - z$

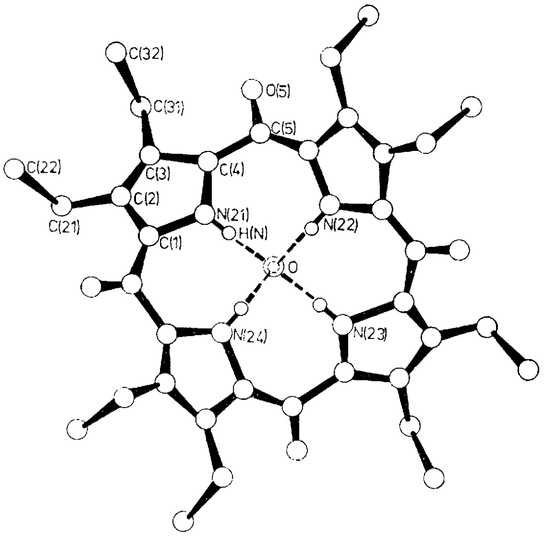

FIGURE 1 Projection of (I) perpendicular to the S_4 axis

47 Reflexions showed a deviation between F_o and F_c of $>2.0\sigma(F_c)$. Complex neutral-atom scattering factors [6,7] were employed for the non-hydrogen atoms. The results from the final least-squares cycle, summarised in Tables 1 and 2, were used, together with the full covariance matrix, to calculate the bond lengths and angles, and their estimated standard deviations listed in Table 3. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21585 (8 pp., 1 microfiche).* Figure 1 shows the molecule together with the numbering system, projected perpendicular to the S_4 axis (z direction).

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* See Notice to Authors No. 7, in *J.C.S. Perkin II*, 1975, Index issue.

[6] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[7] D. T. Cromer and D. Libermann, *J. Chem. Phys.* 1970, **53**, 1891.

DISCUSSION

The octaethylxanthoporphinogen molecule (I) possesses crystallographic S_4 symmetry. The protons on the two opposing nitrogen atoms N(21) and N(23) lie 0.75 Å above the least-squares plane through the molecule ($z = 0.25$ Å), whilst the protons on N(22) and N(24) lie the same distance below the plane. The nitrogen atoms themselves are displaced only 0.071 Å above and below this plane. The planes of the pyrrole rings are mutually twisted such that neighbouring members of the macrocycle make dihedral angles with the atoms bonded to a bridging carbon atom {*e.g.* C(5) of −8.9° [N(21) ring] and 41.6° [N(22) ring]}. This state of affairs is reflected in the two significantly different macrocycle bond lengths at C(5) [C(4)–C(5) 1.440(5) and C(5)–C(6) 1.481(5) Å], which indicate a much greater degree of π-delocalisation between the C=O bond and the pyrrole ring containing N(21), correlating nicely with the smaller dihedral angle of −8.9°. The bond lengths in the pyrrole rings are very similar to those observed in free pyrrole [C–N 1.370(5), C=C 1.387(5), C–C 1.420(5) Å; C_α–N–C_α 109.8(5), N–C_α–C_β 107.7(5), C_α–C_β–C_β 107.4(5)°] [8] as would be predicted from the n.m.r. measurements.

Figure 2, which depicts the molecule viewed in the y direction, shows clearly the nature of the bonding between the water molecules and the pyrrole NH protons. The oxygen atoms of the bonded water molecules lie on the S_4 symmetry axis each linked by hydrogen bonds to two opposing NH protons (NH · · · O 3.016, N–H 0.92, H · · · O 2.13 Å). The strength of this hydrogen bonding is demonstrated by the fact that the two water molecules are not removed even on heating in a high vacuum at 150 °C. It is reasonable to attribute the twisting of the chromophore mainly to the formation of these four hydrogen bridges. The appearance of these bridge bonds which, as mentioned above, are not observed in the related porphyrins, may be explained as being due to the relatively high acidity of α-acyl-substituted pyrroles.

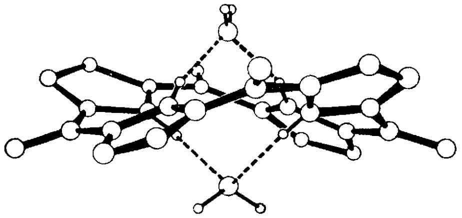

FIGURE 2 Projection of (I) (without ethyl groups) perpendicular to [010]

A second bonding effect of the water of crystallisation leads to the formation of a clathrate-like crystal structure. Hydrogen bonds are also formed between the hydrogen atoms of the water molecules and the carbonyl-oxygen atoms of the bridges in the chromophore (I) (OH · · · O 2.832, O–H 0.89, H · · · O 2.01 Å). Each of the four hydrogen atoms of the two water molecules interacts with a different ketone-oxygen atom of a

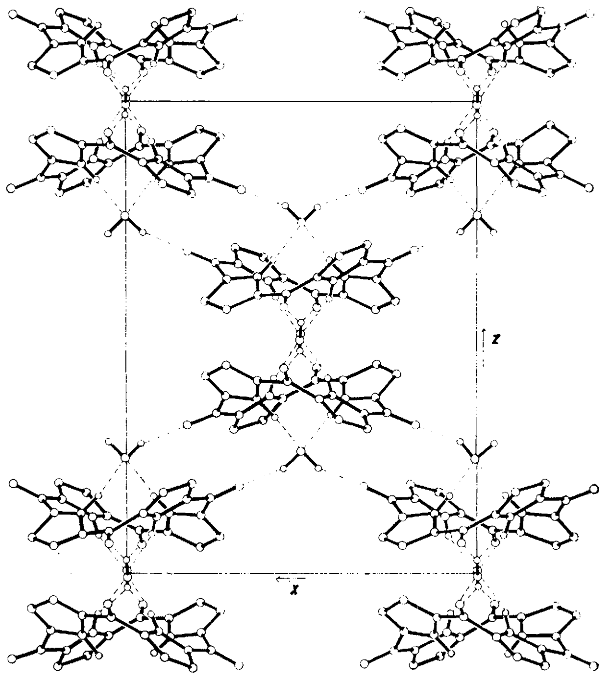

FIGURE 3 Projection of the unit-cell contents perpendicular to [001]

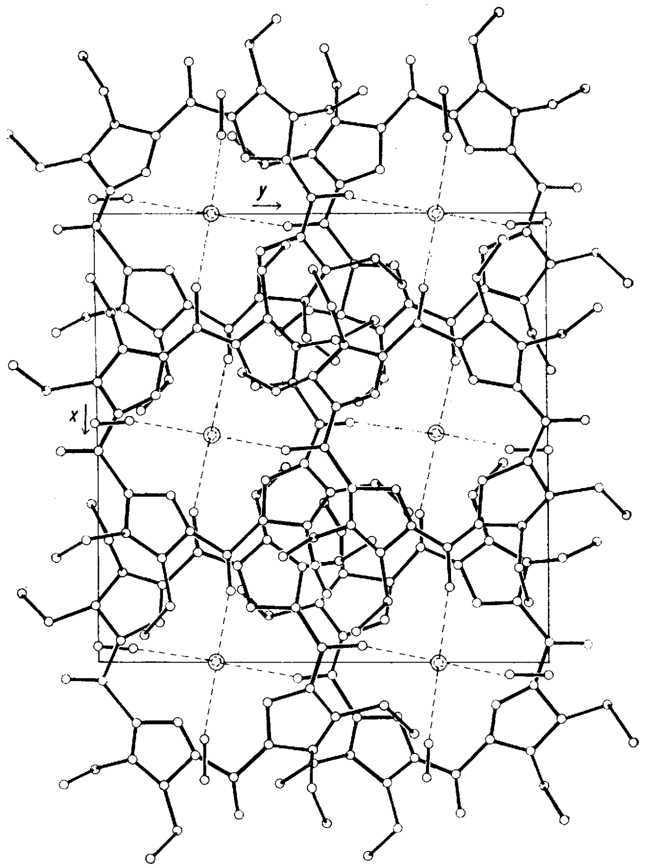

FIGURE 4 Projection of the unit-cell contents perpendicular to [010]

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[8] L. Nygaard, J. T. Nielsen, J. Kirchheiner, G. Maltesen, J. Rastrup-Andersen, and G. O. Sørensen, *J. Mol. Structure*, 1969, **3**, 491.

neighbouring molecule, so that each xanthoporphinogen dihydrate is linked to four other such molecules. Each chromophore molecule thus fixes two molecules on its S_4 axis and each of these in turn bonds two further porphinogen molecules at its periphery. This mode of arrangement leads to the formation of water-containing tubular cavities, as depicted in Figure 3. The nature of the hydrogen bonding may also be readily appreciated from Figure 4 which shows the structure perpendicular to the y direction.

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