The Crystal and Molecular Structure of Tetrabenzmonazaporphin

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Tetrabenzmonazaporphin, $C_{35}H_{21}N_5$, crystallizes with unit-cell dimensions $a = 17.63$, $b = 6.58$, $c = 12.50$ Å, $\beta = 123°24'$, space group $P2_1/a$ and $Z = 2$. Optical transform methods have been freely used to derive the approximate structure using two-dimensional X-ray intensity data and the structure is refined by Fourier and difference Fourier syntheses in projections.

Introduction

Tetrabenzmonazaporphin ($C_{35}H_{21}N_5$) is a stable organic pigment belonging to the porphin series. It closely resembles phthalocyanine in physical and chemical properties and has identical constitution excepting that it contains three methin groups in place of three of the four nitrogen atoms in the central ring (Fig. 1).

A preliminary X-ray study of tetrabenzmonazaporphin was made by Woodward (1940) who pointed out the importance of its structural investigation to obtain information of interest for theories of molecular structure and packing of molecules in relation to the effect of modified resonance forces due to small chemical changes. The remarkable differences in unit-cell dimensions (as shown in Table 1) and X-ray intensities that were observed between phthalocyanine and tetrabenzmonazaporphin were attributed to different molecular packings. Detailed analysis, however, had not been reported.

Table 1. *Comparison of unit-cell dimensions of phthalocyanine and tetrabenzmonazaporphin*

	a	b	c	β
Phthalocyanine	19.85 Å	4.72 Å	14.8 Å	122.25°
Tetrabenzmonazaporphin	17.6	6.61	12.5	122.7

Our attention was drawn to the problem through a different consideration. Tetrabenzmonazaporphin like the phthalocyanines has a planar molecule of approximately known shape and dimensions with atoms of similar scattering power. Symmetry considerations require only one molecule as the unit of pattern. The problem is thus well suited for investigation by optical-transform methods (Hanson, Lipson & Taylor, 1953) in which this department is particularly interested. Menarry & Lipson (1957) who used electronically presented optical transforms to derive the orientation of the molecule in the unit cell, considered the available intensity data grossly inadequate for complete structure analysis. An attempt at full crystal-structure determination by optical-transform methods with two-dimensional data was considered worth while.

Experimental

The compound originally received from the late Professor R. P. Linstead of Imperial College, London, was in the form of fine powder and was not suitable for single-crystal X-ray study. By low-pressure sublimation in a stream of dry CO_2, as described by Barret, Dent & Linstead (1936) deep-violet crystals were obtained as laths elongated along the b axis. The unit-cell dimen-

Fig. 1. (*a*) Molecule of phthalocyanine. (*b*) Molecule of tetrabenzmonazaporphin.

sions were redetermined from oscillation and Weissenberg photographs calibrated with silver ($a = 4\cdot0862$ Å) powder lines.

Tetrabenzmonazaporphin, $C_{35}H_{21}N_5$
M.W. 511·21
Monoclinic
$a = 17\cdot63 \pm 0\cdot02$, $b = 6\cdot58 \pm 0\cdot01$, $c = 12\cdot50 \pm 0\cdot02$ Å,
$\beta = 123°24' \pm 6'$
$Z = 2$
$d_{exp} = 1\cdot41$ g.cm^{-3}, $d_{calc} = 1\cdot39$ g.cm^{-3}
$\mu = 7\cdot96$ cm^{-1} ($\lambda = 1\cdot5418$ Å)
$F(000) = 532$
Space group $P2_1/a$.

For measurement of X-ray intensities unfiltered Cu $K\alpha$ radiation was used to record $h0l$ and $hk0$ reflexions on zero-layer-line Weissenberg photographs using the multiple-film technique. The intensities of the reflexions were measured by visual comparison with calibrated reflexions of known relative exposures obtained from the same crystal. Absorption correction was not considered necessary as the crystal specimens chosen were small and had an almost square cross-section perpen-

dicular to the rotation axes (the dimensions of the cross-section perpendicular to the b axis were $0\cdot31 \times 0\cdot29$ mm, and $0\cdot16 \times 0\cdot15$ mm perpendicular to the c axis). Correction for Lorentz and polarization factors was applied.

Structure determination

Projection on (010)

The space group $P2_1/a$ with two molecules in the unit cell places the molecules on centres of symmetry at $(0,0,0)$ and $(\frac{1}{2},\frac{1}{2},0)$. This demands a molecular centre of symmetry, whereas from the point of view of chemical constitution the molecule of tetrabenzmonazaporphin does not strictly satisfy the requirement of a centrosymmetrical molecule. The deviation, however, is small, as substitution of N by CH may have little effect on X-ray scattering, or a random distribution of the unique nitrogen atom in the four equivalent positions in the molecule may be assumed.

The effective unit cell of projection on (010) contains only one molecule. The structural investigation by the optical-transform method may therefore be made in relation to the transform of only one molecule. The optical transform of the idealized molecule of

Table 2. *Observed and calculated structure factors*

* Indicates structure factors corrected for extinction.

tetrabenzmonazaporphin is shown in Fig. 2(a) which displays a prominent central region, the square-shaped ring of strong peaks at a distance of 0·4 Å^{-1} and finally the outermost prominent ring of peaks at a distance of almost 0·84 Å^{-1} from the origin. For the optical-transform approach these features have to be considered in relation to the h0l weighted reciprocal-lattice section [Fig. 2(b)], the main features of which are firstly the group of strong reflexions around the origin, secondly a group of comparatively strong reflexions lying about the line PQ at a distance of 0·4 Å^{-1} from the origin and thirdly a second group of reflexions lying about the line ST at a distance of about 0·84 Å^{-1} from the origin. Obviously the last two features in the weighted reciprocal lattice account for the two rings of prominent peaks of the transform. The stretching of the reflexions along the line PQ and ST suggests that the molecule is steeply tilted about the tilt axis XY out of the plane of projection, so that the rings in the transform become elongated. From the point of view of structure determination, all that was considered necessary was to find the orientation of the tilt axis in the idealized molecule and to estimate the angle of tilt. A trial rotation of the weighted reciprocal lattice section with respect to the transform of the idealized molecule immediately revealed the direction of the tilt axis in the molecule and its orientation relative to the crystallographic axes. The estimated value of the tilt angle of the molecule for producing the necessary expansion of the transform, so that it fitted with the weighted reciprocal lattice section, was found to be 60°. This estimate of tilt agrees with the value predicted by Woodward (1940) from packing consideration. The projection of the tilted molecule on to (010) plane is shown in Fig. 2(c) where the orientation of the tilt axis XY is also shown inset on the idealized molecule. The match between the weighted reciprocal lattice section and the transform of the trial structure thus obtained for the (010) projection [Fig. 2(d)] was considered reasonable enough for routine refinements. Fig. 2(e) shows the final agreement for the refined structure.

Refinement of (010) projection

The first $F_o(h0l)$ synthesis computed with only 55 reflexions, the phases of which were quickly derived optically (Lipson & Taylor, 1951) revealed the complete molecule.

The final electron-density projection on (010) is shown in Fig. 3. The agreement residual $R = \sum|F_o| - |F_c|]/\sum|F_o|$ at this stage, using the same isotropic temperature-factor parameter $B = 4·0$ Å^2 was found to be 24%. In three cycles of refinement by $(F_o - F_c)$ synthesis (Fig. 4) the agreement residual decreased to 20%. The final $(\varrho_o - \varrho_c)$ map shows reasonably flat topography but suggests the necessity of adjustments of individual isotropic temperature factors of a few atoms. Besides, a few peaks appear at sites where hydrogen atoms are expected. Assuming C–H bond length to
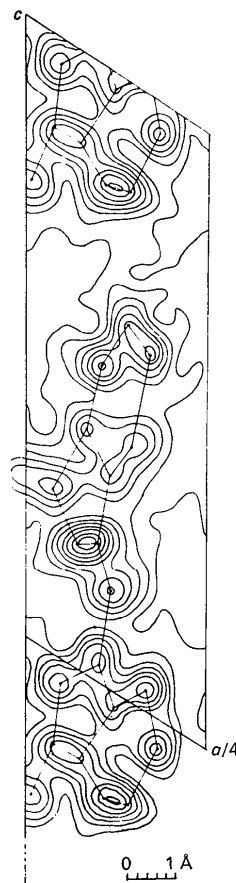
Fig. 3. Electron-density projection on (010). Contours are drawn at intervals of 1 e.Å^{-2}.

be 1·09 Å and taking into consideration the tilt of the molecule, the positions of the hydrogen atoms are assigned by the optical-transform test (Pinnock & Lipson, 1954) with reference to these peaks. The adjustment of the individual isotropic temperature factor parameters of the atoms C(3), C(10), C(11), C(14), C(18) and inclusion of the hydrogen atoms in the structure factor calculation reduced the R value to 18%. In the structure-factor calculation the atomic scattering factors were adopted from International Tables for X-ray Crystallography (1962). The effect of secondary extinction was observed in a few low-angle reflexions for which the calculated structure factors were found to be consistently higher than the observed values. Extinction correction of these reflexions by an empirical method suggested by Pinnock, Taylor & Lipson (1956) reduced the R value to 16%. In Table 2 these reflexions are marked by asterisks and the uncorrected values are shown in parentheses.

Solution and refinement of the (001) projection

The solution of the (001) projection followed in a straightforward manner. An approximate model was immediately obtained by projecting along the c axis
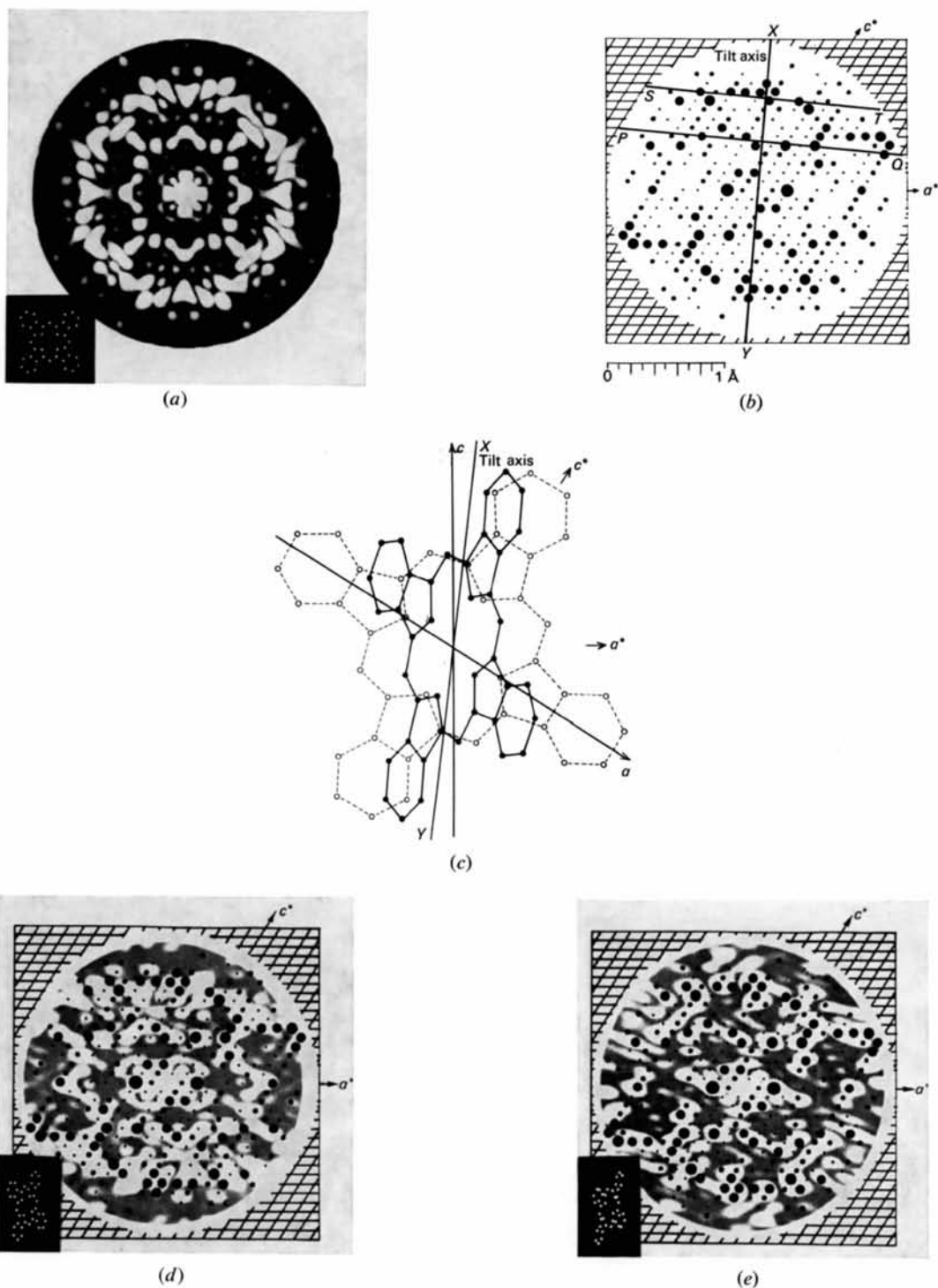
Fig. 2. (a) Optical transform of the idealized molecule of tetrabenzmonazaporphin. (b) h0l section of the weighted reciprocal lattice of tetrabenzmonazaporphin with weights proportional to approximate unitary structure factors. (c) Projection of the tilted molecule (bold line) on to (010) plane. (d) Optical transform of the tilted molecule in projection with the weighted reciprocal lattice section superimposed to demonstrate optical agreement obtained for the trial structure. (e) Optical agreement for the refined structure.

the shadow of a wire model of the molecule, which was so oriented that its shadow, cast on the electron-density projection on to (010), fitted fairly well. Assuming the x parameters from the (010) projection, the model thus derived gave an agreement residual of 38 % for the $hk0$ reflexions. Two cycles of Fourier refinement using the ϱ_o map and three cycles of difference Fourier synthesis reduced the R value for the $hk0$ reflexions to 23 %. The final electron density map (Fig. 5) shows a considerable amount of overlap resulting in poor resolution of the
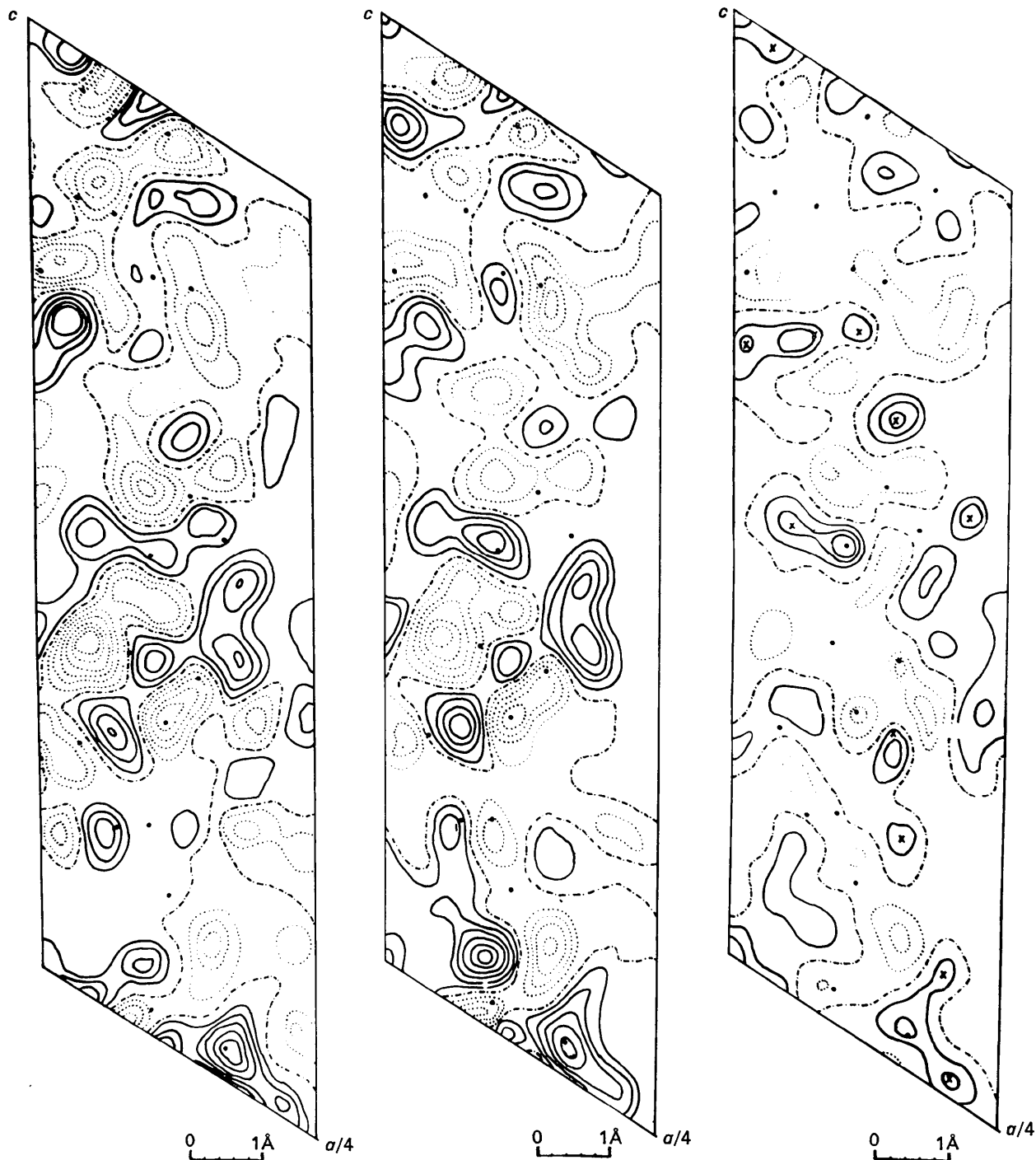
Fig. 4. $(F_o - F_c)$ syntheses projected on (010). The proposed hydrogen atom positions are indicated by x.

Fig. 5. Electron-density projection along [001]. Contours are drawn at intervals of 1 e.Å^{-2}. The 1 e.Å^{-2} contour is shown by a broken tine.

projected atoms. The $(\varrho_o - \varrho_c)$ map did not show any features for objective determination of the positions of the hydrogen atoms. However, assuming C–H bond length to be 1·09 Å and using the x and z coordinates

Table 3. *Final atomic coordinates*

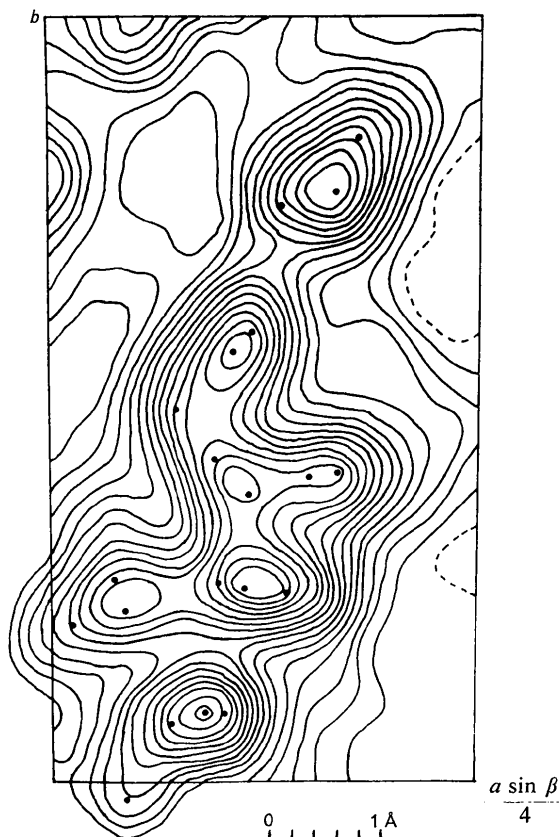|	x (Å)	y (Å)	z (Å)	B (Å^2)
C(1)	2·39	5·02	−2·24	4·0
C(2)	3·18	5·57	−0·65	4·0
C(3)	2·94	5·14	0·45	3·1
C(4)	2·10	3·85	−0·27	4·0
C(5)	1·27	3·22	−1·84	4·0
C(6)	1·90	3·69	−2·34	4·0
C(7)	1·71	2·73	0·45	4·0
C(8)	2·05	2·55	2·05	4·0
C(9)	1·73	1·86	2·84	4·0
C(10)	2·02	1·80	4·36	5·1
C(11)	2·68	2·70	5·50	4·6
C(12)	2·98	2·74	7·22	4·0
C(13)	2·45	1·70	7·60	4·0
C(14)	1·81	0·56	6·46	2·5
C(15)	1·60	0·58	5·06	4·0
C(16)	0·78	−0·14	3·47	4·0
C(17)	0·66	1·89	−2·02	4·0
C(18)	0·22	1·27	−3·28	5·1
N(1)	1·24	0·54	2·54	4·0
N(2)	0·76	1·49	−0·55	4·0
H(1)	2·60	1·12	8·54	4·0
H(2)	3·76	3·53	7·92	4·0
H(3)	2·60	3·25	4·40	4·0
H(4)	2·76	3·13	3·06	4·0
H(5)	3·46	4·81	1·62	4·0
H(6)	3·60	6·28	0·26	4·0
H(7)	2·00	5·77	−3·10	4·0
H(8)	1·24	3·37	−3·52	4·0
H(9)	0·94	−0·33	6·28	4·0
H(10)	0·20	1·82	−4·22	4·0
H(11)	0·60	1·00	−0·16	4·0

Table 4. *Values of bond lengths and bond angles*

Bond lengths (Å)

C(1)—C(2)	1·44 (5)	C(12)–C(13)	1·31 (5)
C(2)—C(3)	1·32 (3)	C(13)–C(14)	1·49 (5)
C(3)—C(4)	1·49 (5)	C(14)–C(15)	1·30 (3)
C(4)—C(5)	1·46 (5)	C(10)–C(15)	1·58 (5)
C(5)—C(6)	1·11 (4)	C(15)–C(16)	1·53 (5)
C(1)—C(6)	1·44 (5)	C(16)–C(18')	1·49 (5)
C(4)—C(7)	1·49 (5)	C(5)—C(17)	1·46 (5)
C(7)—C(8)	1·45 (4)	C(17)–C(18)	1·25 (5)
C(8)—C(9)	1·22 (4)	C(9)—N(1)	1·38 (5)
C(9)—C(10)	1·38 (3)	C(16)–N(1)	1·40 (4)
C(10)–C(11)	1·32 (5)	C(7)—N(2)	1·55 (5)
C(11)–C(12)	1·58 (3)	C(17)–N(2)	1·47 (4)

Bond angles (°)

C(1)—C(2)—C(3)	124	C(10)–C(11)–C(12)	132
C(2)—C(3)—C(4)	101	C(11)–C(12)–C(13)	116
C(3)—C(4)—C(5)	136	C(12)–C(13)–C(14)	117
C(4)—C(5)—C(6)	100	C(13)–C(14)–C(15)	124
C(5)—C(6)—C(1)	128	C(14)–C(15)–C(10)	125
C(6)—C(1)—C(2)	113	C(15)–C(10)–C(11)	105
C(4)—C(7)—N(2)	121	C(9)—C(10)–C(15)	125
C(7)—N(2)—C(17)	96	C(10)–C(15)–C(16)	91
N(2)—C(17)–C(5)	109	C(15)–C(16)–N(1)	106
C(17)–C(5)—C(4)	117	C(16)–N(1)—C(9)	121
C(5)—C(4)—C(7)	93	N(1)—C(9)—C(10)	92
N(2)—C(17)–C(18)	132	N(1)—C(9)—C(8)	127
C(17)–C(18)–C(16')	111	C(9)—C(8)—C(7)	143
N(2)—C(7)—C(18)	108	N(1)—C(16)–C(18')	135

from the (010) projection, the y coordinates of the hydrogen atoms were calculated. The inclusion of these calculated y parameters reduced the R value still further to 21 %. The observed and the calculated structure factors are presented in Table 2.

Results and discussions

The final atomic coordinates and the isotropic temperature factors are listed in Table 3.

The average standard deviations in the atomic coordinates as estimated according to the formula of Cruickshank (1960) are as follows:

$$\sigma(x)=0\cdot025 \qquad \sigma(y)=0\cdot052 \qquad \sigma(z)=0\cdot025 \text{ Å}.$$

In view of the poor resolution of the atoms in the projections, particularly in (001) projection, the average standard deviations are definitely underestimated.

Fig. 6 presents the molecular arrangement in the crystal lattice as viewed along the b axis and indicates the intermolecular distances. The intramolecular bond lengths and bond angles deduced from the atomic coordinates of Table 3 are given in Table 4. The indicated errors in bond lengths are the standard deviations estimated using the formula given by Ahmed & Cruickshank (1953).

A high degree of accuracy in bond length and bond angle measurements is not claimed. However, values of most of the bond lengths do not depart very much from normal aromatic bond lengths except the value 1·58 Å for C(11)–C(12) and C(10)–C(15) which is somewhat greater. Hall & Maslen (1965) have attributed such lengthening of C–C bonds in condensed ring hydrocarbons to the degree of substitution in the carbon atoms involved in the bond and long-range steric strain in the molecule due to attachment of the five-membered pyrrole ring with the six-membered benzene ring. The C(5)–C(6) and C(8)–C(9) bonds are found to be shorter than the normal values, although double-bond character may be assigned to C(8)–C(9) bond.

The equation of the best plane which passes through the molecule and which also passes through the origin is

$$-0\cdot103x+0\cdot058y+0\cdot023z=0 .$$

The calculated value of the angle between the mean molecular plane and the (010) plane is found to be 62°. The perpendicular distances of the atoms from the best plane as given in Table 5 bear distinct evidence of departure from planarity of the molecule. This may be considered quite probable for an overcrowded condensed ring hydrocarbon like tetrabenzmonazaporphin. Such distortions may produce weakening of the adjacent bonds as described by Pauling (1960), resulting in deviations from normal values. However, in view of the limitations usual in the accuracy of the atomic coordinates obtained from two-dimensional analysis, the comments regarding non-planarity of the molecule and the observed deviations in the bond

length and bond angle values have to be made with due reservation.

Table 5. *Perpendicular distances of the atoms from the mean plane*

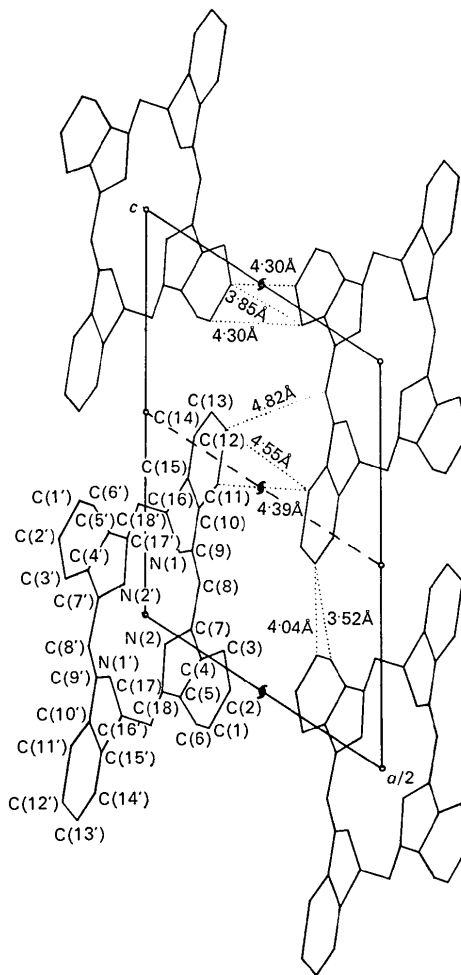|	Distance		Distance
C(1)	−0·048 Å	C(11)	0·064 Å
C(2)	−0·159	C(12)	0·143
C(3)	0·40	C(13)	0·175
C(4)	0·008	C(14)	−0·040
C(5)	0·111	C(15)	−0·119
C(6)	−0·287	C(16)	−0·064
C(7)	−0·064	C(17)	−0·032
C(8)	−0·127	C(18)	−0·191
C(9)	−0·040	N(1)	−0·311
C(10)	−0·032	N(2)	−0·040

Fig. 6. The structure of tetrabenzmonazaporphin viewed along [010] axis. Intermolecular distances are indicated.

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The Structure of (−)-Kaur-15-en-19-al, an Aldehyde Isolated from *Espelitia Weddeli*

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An aldehyde, $C_{20}H_{30}O$, isolated from the Venezuelan plant *Espelitia weddeli*, has been identified by its crystal structure analysis to be (−)-kaur-15-en-19-al,
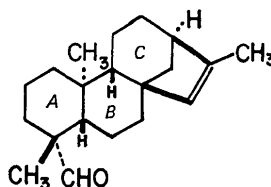
Ring junction *A–B* is *trans* while *B–C* is *cis*. Comparison with related compounds of known absolute configuration indicates that this molecule has a configuration opposite to that of the steroids. The intensities of reflexions decreased rapidly with scattering angle, and there is considerable positional disorder in the cell. The material crystallizes in space group $P2_12_12_1$ with cell dimensions $a = 11·654 \pm 0·005$, $b = 22·644 \pm 0·007$, $c = 6·370 \pm 0·004$ Å and $Z = 4$. The structure was solved by the application of the symbolic addition procedure for the phase determination in noncentrosymmetric space groups.

The original aim of this study was to establish the structural formula of a diterpenoid, whose empirical formula is $C_{20}H_{30}O$, which had been isolated from the tubers of *Espelitia weddeli*, a Composita which grows at 10,000 feet in the Venezuelan Andes. The elucidation of the structure showed the formula to be:

(I)
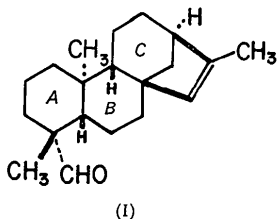
It is identical to the aldehyde extracted from *Espelitia tenore*, also occurring in the Venezuelan Andes (Usubillaga & Morales, 1970). The fungus *Fusarium moniliforme* Sheld also produces a number of diterpenoids closely related to (I) (Serebryakov, Simolin & Kuche-

rov, 1970). These diterpenoids belong to the (−)-kaurane group (see, *e.g.*, Cross, Galt, Hanson, Curtis, Grove & Morrison, 1963; Briggs, Cambie & Rutledge, 1963) and are of particular interest in the biosynthesis of gibberellins (Hanson & White, 1969). They are also related to steviol (II), prepared by the enzymatic hydrolysis of stevioside, whose absolute configuration has been established by chemical means (Mossettig, Beglinger, Dolder, Lichti, Quitt & Waters, 1963). In spite of their superficial resemblance to steroids, the kaurane diterpenoids have the antipodal absolute configuration.

(II)