Acta Cryst. (1958). **11**, 325

The Crystal and Molecular Structure of 3:4:5:6:9:10:11:12-Octahydrochrysene

By W. G. Ferrier and J. Iball*

University of St. Andrews, Queen's College, Dundee, Scotland

(*Received* 15 *May* 1957 *and in revised form* 21 *November* 1957)

3:4:5:6:9:10:11:12-Octahydrochrysene crystallizes in the monoclinic system with $a = 10{\cdot}06 \pm 0{\cdot}01$, $b = 7{\cdot}24 \pm 0{\cdot}01$, $c = 9{\cdot}14 \pm 0{\cdot}01$ Å, $\beta = 101^\circ\, 8' \pm 2'$; space group = $P2_1/a$, $Z = 2$, $d(\text{obs.}) = 1{\cdot}170$, $d(\text{calc.}) = 1{\cdot}178$ g.cm.$^{-3}$. The atomic coordinates have been established by two-dimensional Fourier methods applied to the three principal axial zones. The reliability indices are $R(0kl) = 0{\cdot}16$, $R(h0l) = 0{\cdot}16$, $R(hk0) = 0{\cdot}15$. With the exception of atoms 4, 5, 10 and 11, the molecule is planar; the r.m.s. deviation from the mean plane is 0·022 Å. Atoms 4 and 5 are at approximately 0·43 Å from the mean plane, atom 4 is on one side and atom 5 on the other. (Atoms 10 and 11 are related to atoms 4 and 5 by a centre of symmetry.)

Introduction

Very few polycyclic compounds containing reduced benzene rings have been investigated in detail by X-ray diffraction methods. The study of the present compound (Fig. 1) was begun many years ago by one of us but the structure analysis has only recently been completed. Unfortunately the crystals which were obtained were very 'imperfect' and each plane reflected over a rather large angle. This caused the spots on the Weissenberg photographs to be diffuse and elongated, and consequently it was difficult to estimate the intensities. However, the agreement which has been obtained between the observed structure factors and those calculated from the atomic coordinates given by the analysis is relatively good. The structure can therefore be said to be reasonably accurate though it is not claimed that the coordinates of any particular atom are known to a high accuracy.

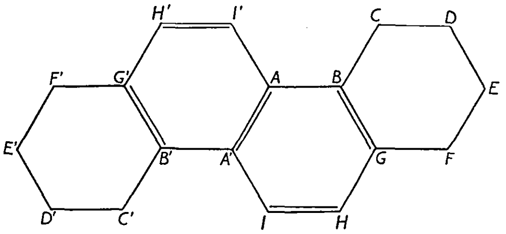

Fig. 1. Octahydrochrysene.

Experimental

Octahydrochrysene crystallizes in monoclinic prisms flattened on (001); other faces observed were (100) and (110). The crystals are optically negative, the optic axial plane is (010) and the optic axial angle is almost 90°. β is parallel to b and γ is nearly parallel to c. The unit cell and space group were first given by Bernal (1933) in the report of a discussion of the chemical constitution of oestrin.

The unit-cell dimensions are:

$$a = 10{\cdot}06 \pm 0{\cdot}01,\ b = 7{\cdot}24 \pm 0{\cdot}01,\ c = 9{\cdot}14 \pm 0{\cdot}01\ \text{Å},\ \beta = 101^\circ\, 8' \pm 2'.$$

$$d(\text{obs.}) = 1{\cdot}170,\ d(\text{calc.}) = 1{\cdot}178\ \text{g.cm.}^{-3};$$
2 molecules per unit cell.

The space group is $C_{2h}^5\text{-}P2_1/a$.

Since there are only two molecules in the unit cell each molecule must have a centre of symmetry.

Most of the intensity measurements were made by visual estimation on equi-inclination Weissenberg photographs. A few intensities had previously been measured with the integrating photometer described by Robinson (1929). In addition we are indebted to Dr B. W. Robinson for measuring the absolute intensity of the reflexion from (001) with an ionization chamber. Another determination of the absolute intensities of reflexion of a few planes was made by comparison with a standard anthracene crystal on Robertson's double-crystal moving-film camera (Robertson, 1934). Thus it was possible to put the visually estimated intensities on an absolute scale without reference to any calculated structure factors. No attempt to correct for absorption was made as the crystals were small and of fairly uniform dimensions.

Determination of the structure

Since there were several planes in the $h0l$ zone with fairly large unitary structure factors, an attempt was made to apply the Harker–Kasper inequality method to the determination of signs. However, this proved unsuccessful although several sign relationships were obtained which were useful when various trial structures were considered.

The general orientation of the molecule was clear from the optical data and from some magnetic measurements, for which we are indebted to Dame

---

* British Empire Cancer Campaign Research Fellow.

Kathleen Lonsdale. The latter measurements indicated that the mean molecular plane intersects the (010) plane at approximately 47° to the a axis and the normal to the molecular plane makes an angle of 83° to the b axis. This means that the molecule would lie very close to the (201) plane, and this is confirmed by the large structure factor of (201); $F(201) = 105{\cdot}8$; $F(000) = 256$. It also means that its sign will be positive. Even with this sign determined, the Harker–Kasper relations failed to give any more signs.

Further help in deciding on the general orientation of the molecule was given by plotting the $0kl$ unitary structure factors on a reciprocal-lattice net (Fig. 2).

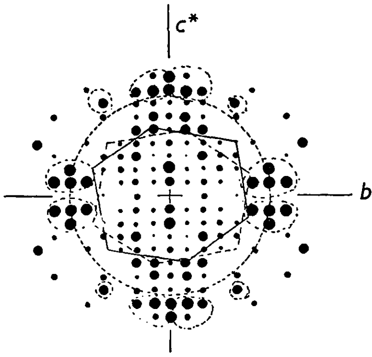

Fig. 2. 'Weighted' reciprocal-lattice plane $0kl$.

The dotted circle represents the reciprocal of 1·22 Å, i.e. the spacing of the lines of atoms in a benzene ring. Twelve groups of spots are marked and these were assumed to represent the rings in the two related molecules. The corresponding hexagons were drawn, and are indicated on the diagram. Since the outside rings of octahydrochrysene cannot be plane hexagons it was not expected that this procedure would be very accurate, but the twelve groups of spots are in fact fairly definite. The orientation of the rings given by this interpretation of the 'weighted' reciprocal-lattice plane agreed with the above indications from optical and magnetic data, and the complete molecule was reconstructed. The atoms in the outer ring were given positions which they would be expected to have on the assumption of normal bond lengths and angles.

The structure factors of 29 planes having the largest F_o were then calculated. The corresponding value of $R\ (= \Sigma||F_o|-|F_c|| \div \Sigma|F_o|)$ was 0·37. (The scattering curve used for these preliminary calculations was that of anthracene (Mathieson, Robertson & Sinclair, 1950).) However, if the $00l$ planes alone are considered, it was possible to find by trial and error a set of z coordinates which gave much better agreement for these planes. When the latter z coordinates were combined with the y coordinates obtained from the above consideration of the weighted reciprocal lattice and the structure factors were recalculated, the value of R fell to 0·22 (for the same 29 planes).

At this stage a Fourier synthesis of the $0kl$ zone was calculated, using those structure factors whose signs seemed most likely to be correct. Only three atoms were resolved. The positions of the resolved peaks were determined as accurately as possible and the other atomic positions were estimated. The structure factors of all those $0kl$ planes for which there was an F_o were calculated. The value of R was 0·24.

With some assumptions regarding the shape of the molecule it was now possible to calculate approximate x coordinates. With these and the z coordinates obtained from the $0kl$ Fourier projection, structure factors were calculated for the $h0l$ zone. There was fairly good agreement with the F_o for those reflexions with the larger values, and the signs satisfied the

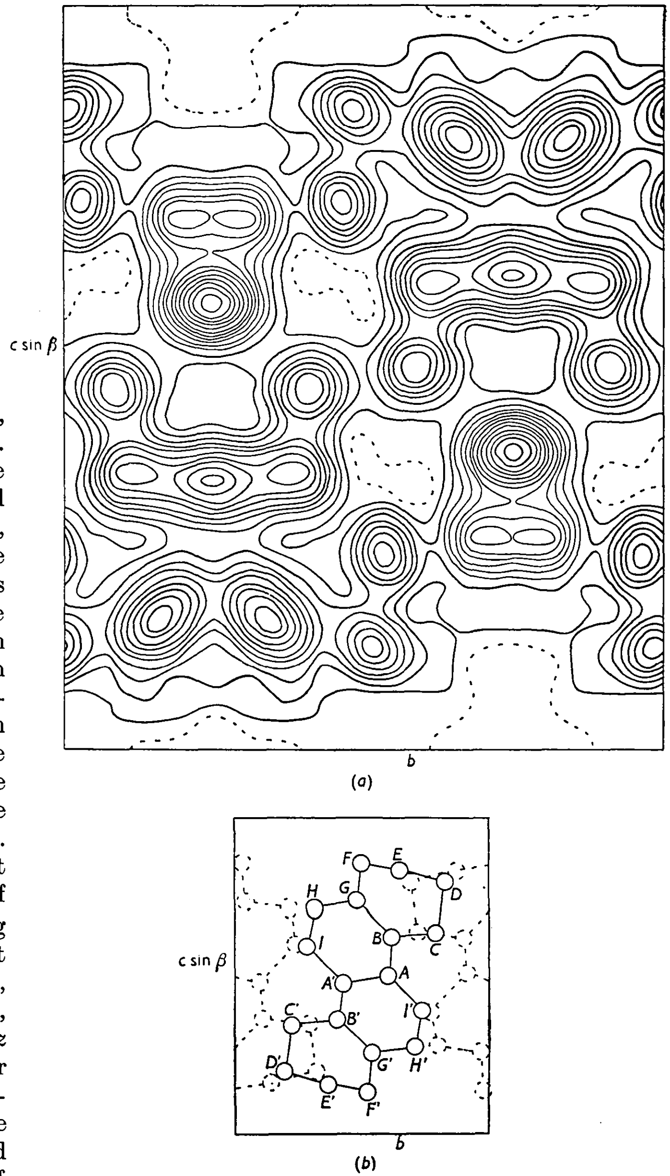

Fig. 3. (a) Fourier synthesis of $0kl$ zone. Contours at intervals of 1 e.Å^{-2}; the 1 e.Å^{-2} line is broken. Scale: 1 cm. = 1 Å. (b) Positions of the atoms.

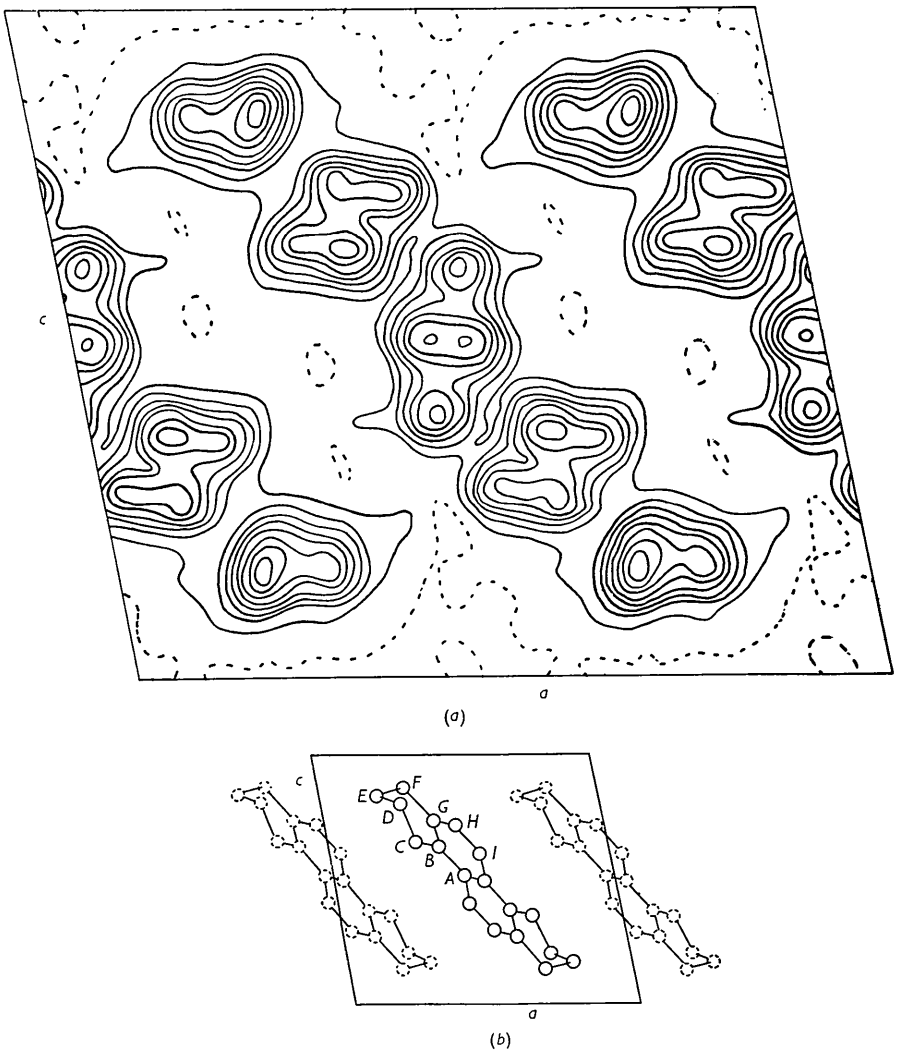

Fig. 4. (a) Fourier synthesis of $h0l$ zone. Contours at intervals of 1 e.Å^{-2}; the 1 e.Å^{-2} line is broken. Scale: 1 cm. = 1 Å. (b) Positions of the atoms.

Harker–Kasper sign relationships which had previously been derived. A Fourier projection was calculated but only one atom (I, Fig. 1) gave a resolved peak. The atomic positions were estimated and the x coordinates thus obtained were accepted, but the z coordinates obtained from the $0kl$ projection were considered to be more accurate. With these coordinates the $hk0$ structure factors were calculated. The value of R for all the observed F's was 0·35.

A Fourier projection with the larger F_o for the $hk0$ zone was computed and the coordinates of two atoms (E and G, Fig. 1) were obtained with reasonable accuracy, the positions of the other atoms being estimated.

The best set of coordinates from all the above Fourier projections was then obtained, due weight being given to well resolved atoms. The structure factors for the three axial zones were recalculated and the following values of the index R were obtained:

$$R(0kl) = 0{\cdot}24;\quad R(h0l) = 0{\cdot}30;\quad R(hk0) = 0{\cdot}23\ .$$

The atomic coordinates were refined by successive F_o Fourier projections of the $hk0$ and $h0l$ zones, including more and more planes as the signs were considered established. When it was thought that all the signs had been determined, Fourier projections on all three axial zones were computed and the contour maps obtained are shown in Figs. 3, 4 and 5.

The peak positions of resolved atoms were determined by the semi-analytical method of Burns & Iball (1955) and the effect of neighbouring peaks was calculated using the technique described by the same authors. The coordinates of the hydrogen atoms were calculated by assuming a C–H bond length of 1·0 Å and normal bond angles.

The structure factors were now re-calculated, including the contribution of the hydrogen atoms. A difficulty arose, however, as it appeared impossible to

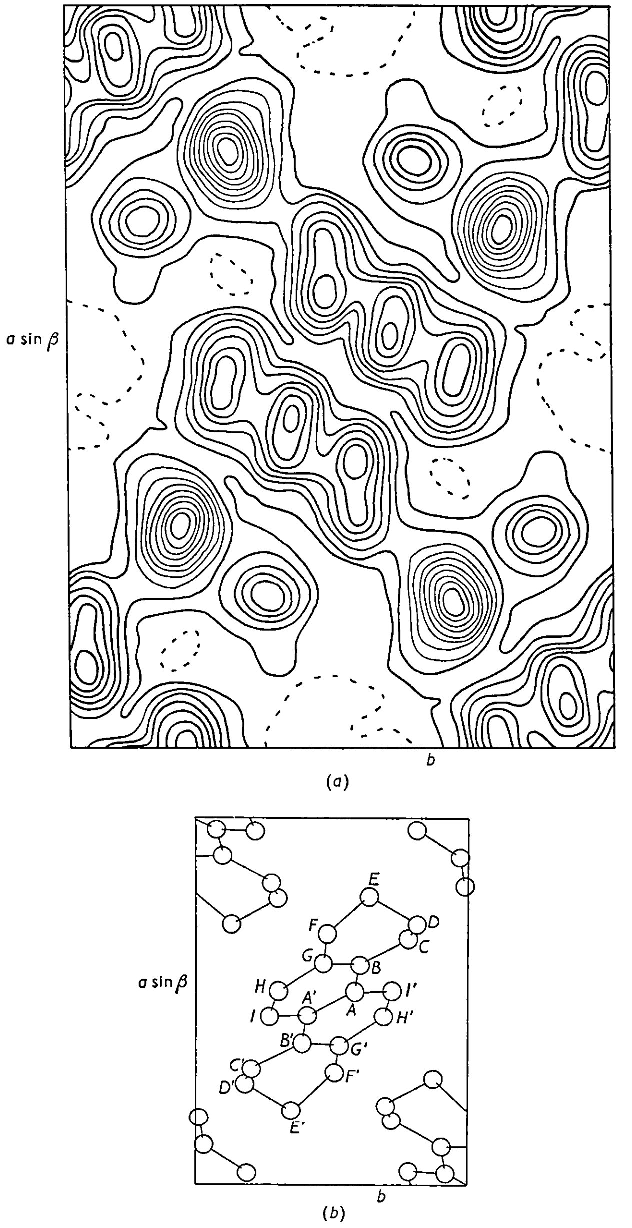

Fig. 5. (a) Fourier synthesis of $hk0$ zone. Contours at intervals of 1 e.Å^{-2}; the 1 e.Å^{-2} line is broken. Scale: 1 cm. = 1 Å. (b) Positions of the atoms.

obtain good agreement between F_o and F_c over the whole range of sin θ if a theoretical f_C curve was used. So, in the first instance an empirical carbon scattering curve was constructed as follows. The calculated value of the contribution of the hydrogen atoms (F_H) was computed using the theoretical hydrogen scattering curve with a temperature factor B of 4·75 Å^2. Then the ratio of $(F_o - F_H)$ to $\Sigma \cos(hx+ky+lz)$ for the carbon atoms over ranges of sin θ, 0–0·1, 0·1–0·2, etc. was plotted against the value of sin θ for the middle of each range.

The structure factors were then computed using this empirical curve. The values of the reliability indices were:

$$R(0kl) = 0{\cdot}16(0{\cdot}20);\ R(h0l) = 0{\cdot}16(0{\cdot}19);$$
$$R(hk0) = 0{\cdot}15(0{\cdot}19).$$

The figures in brackets are the indices obtained when the hydrogen atoms are omitted from the calculations.

When the structure factors were computed using the theoretical scattering curves of Berghuis *et al.* (1955) with a temperature factor B of 3·85 Å^2 for carbon, and of 4·5 Å^2 for hydrogen, the values of the reliability indices were:

$$R(0kl) = 0{\cdot}22;\quad R(h0l) = 0{\cdot}20;\quad R(hk0) = 0{\cdot}22.$$

The final atomic coordinates are given in Table 1.

Discussion of the structure

The bond lengths and bond angles are indicated in Fig. 6. These seem reasonable with the limited accuracy of the coordinates.

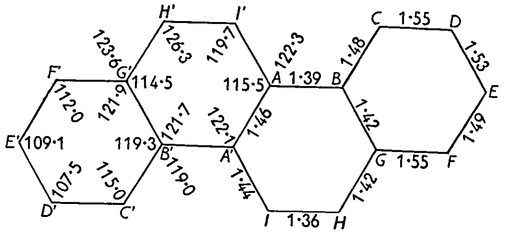

Fig. 6. Bond lengths (Å) and bond angles (°).

With reference to rectangular axes, x' parallel to a, y parallel to b and z' perpendicular to (001), the mean plane of the carbon atoms of the molecule, excluding atoms D and E (Fig. 1), is

$$0{\cdot}7303x' + 0{\cdot}3777y + 0{\cdot}5693z' = 0\,,$$

and the deviations of the atoms from this plane are as follows:

Atom	A	B	C	D	E
Deviation (Å)	0·017	0·010	0·030	0·412	−0·451

Atom	F	G	H	I
Deviation (Å)	−0·036	−0·007	0·038	0·019

The r.m.s. deviation (excluding D and E) is 0·022 Å.

The atoms C and F are therefore approximately in the same plane as the two benzene rings while the atoms D and E are displaced from this plane by approximately equal amounts, one on either side. This is what might have been expected though there does not seem to be any *a priori* reason why the two atoms should not be both on the same side of the mean plane. Either arrangement could satisfy the stereochemical requirements, and result in a molecule with a centre of symmetry. The shortest intermolecular distance is

Table 1. *Atomic coordinates*

Values in Ångström units. See Fig. 1 for key

Carbon atoms

Atom	x	y	z
A	−0·356	0·618	0·104
B	−1·052	0·769	1·169
C	−1·765	2·048	1·305
D	−2·165	2·276	2·710
E	−2·891	1·008	3·060
F	−1·893	−0·108	3·310
G	−1·092	−0·265	2·132
H	−0·323	−1·421	1·941
I	0·352	−1·634	0·908

Hydrogen atoms

Atom	x	y	z
$(C)H_1$	−2·633	2·030	0·614
$(C)H_2$	−1·119	2·781	1·181
$(D)H_1$	−2·776	3·070	2·676
$(D)H_2$	−1·333	2·455	2·422
$(E)H_1$	−3·279	1·167	3·894
$(E)H_2$	−3·644	0·773	2·285
$(F)H_1$	−1·217	0·091	4·166
$(F)H_2$	−2·398	−0·957	3·383
$(H)H$	−0·311	−2·139	2·589
$(I)H$	0·847	−2·480	0·816

3·68 Å between atom A of the molecule at 0, 0, 0 and the atom C of the molecule at $\frac{1}{2}, \frac{1}{2}, 0$.

We are indebted to Prof. J. D. Bernal and to Prof. J. W. Cook for supplying crystals and to the Royal Society and the British Empire Cancer Campaign for apparatus grants. One of us (W. G. F.) wishes to thank the University of St. Andrews and Queen's College for a Research Scholarship. We should also like to thank Mrs N. M. Stott for help in calculating the final list of structure factors.

References

Berghuis, J., Haanappel, I. M., Potters, M., Loopstra, B. O., MacGillavry, C. H. & Veenendaal, A. L. (1955). *Acta Cryst.* **8**, 478.

Bernal, J. D. (1933). *Chem. Ind.* 267.

Burns, D. M. & Iball, J. (1955). *Proc. Roy. Soc.* A, **227**, 200.

Mathieson, A. M., Robertson, J. M. & Sinclair, V. C. (1950). *Acta Cryst.* **4**, 516.

Robertson, J. M. (1934). *Phil. Mag.* (7), **18**, 729.

Robinson, B. W. (1929). *J. Sci. Instrum.* **10**, 233.

Acta Cryst. (1958). **11**, 329

The Crystal Structure of 10-Methyl 1.2 Benzanthracene

By R. Mason

Department of Chemical Crystallography, University College, London W.C. 1, *England*

(*Received* 22 *November* 1957)

The molecular 'aggregation' in the crystal structure of 10-methyl 1.2 benzanthracene is discussed in relation to the electron distribution in the crystal and associated effects.

Introduction

X-ray crystallographic analyses of the monomethyl substituted 1.2 benzanthracenes were initiated with the purpose of examining the adequacy of the quantum mechanical predictions of the electron distribution in these molecules (Pullman, 1946), but the complexity of the crystal structures has prevented such a detailed survey. Some features of the crystal structure of 10-methyl 1.2 benzanthracene are, however, of interest in connexion with the hypothesis that some of the polycyclic carcinogens may act in a state of aggregation (Mason, 1956) and in a study of the polymorphism of organic crystals.

Experimental

10-Methyl 1.2 benzanthracene, the most active agent in the isomeric series, crystallizes in the monoclinic system (fine needles from ethanol) with the following unit cell satisfying the large majority of X-ray reflexions:

$$a = 24{\cdot}2 \pm 0{\cdot}2,\ b = 5{\cdot}77 \pm 0{\cdot}03,\ c = 94{\cdot}4 \pm 0{\cdot}9\ \text{Å}\ ,$$
$$\beta = 90^\circ\ 0' \pm 15' .$$

The observed density, $\varrho(20^\circ\ \text{C.}) = 1{\cdot}20$ g.cm.$^{-3}$, corresponds to 40 molecules in the unit cell, and the systematic absences ($h0l$ when $h = 2n+1$, $0k0$ when $k = 2n+1$) require the space group $P2_1/a\text{–}C_{2h}^5$ to relate the ten independent sets of four molecules.

A more detailed examination of the $\{h0l\}$ Weissenberg data suggests that the crystal structure is based on a rather ill-defined superlattice arrangement. The $\{00l\}$ reflexions occur for $l = 10n$ only, and the further accidental absences which are observed among the general reflexions can be largely explained in the following way (Fig. 1). The co-ordinates of any reference