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Twinned Crystals. I. 10-Methyl-1,2-benzanthracene

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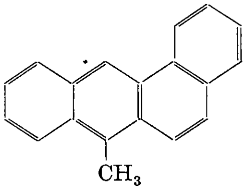
The apparently complicated diffraction patterns from 10-methyl-1,2-benzanthracene (10-methylbenz[*a*]anthracene) (Mason, *Acta Cryst.* (1958), **11**, 329) can be explained completely in terms of ordinary twinning. The crystals are reflexion-twinned by pseudo-merohedry, (001) being the twin plane.

Introduction

Two crystals have recently been reported to give complicated diffraction patterns which could not be indexed satisfactorily in terms of simple unit cells. These are 10-methyl-1,2-benzanthracene (I) (Mason, 1958) and the α phase (stable below 185 °K) of 1,2:4,5-tetrachlorobenzene (Gafner & Herbstein, 1960). These crystals differ in symmetry and their diffraction patterns differ in detail. Nevertheless there is one striking feature common to both *descriptions* of the diffraction patterns: for both crystals unit cells are quoted which have one edge much longer than usual. In addition non-space-group absences occur. The resemblances between the reports suggest that the same phenomenon is being encountered in both instances. I have now examined the diffraction patterns from both crystals and find that the apparently complicated photographs can be explained in terms of ordinary twinning. The results for the first compound are given in this paper; α-1,2:4,5-tetrachlorobenzene will be described later.



(I)

Previous crystallographic work on 10-*methyl-1,2-benzanthracene*

Mason (1958) has reported that the following unit cell satisfies the large majority of the X-ray reflexions from (I):

$$a=24\cdot2\pm0\cdot2,\ b=5\cdot77\pm0\cdot03,\ c=94\cdot4\pm0\cdot9\ \text{Å};$$
$$\beta=90^\circ\ 0'\pm15',\ \varrho_{\text{obs}}=1\cdot20\ \text{g.cm}^{-3}.$$

Systematic absences $h0l$ when h odd, $0k0$ when k odd. Hence space group $P2_1/a$ (C_{2h}^5). The observed density gives 40 molecules in the unit cell, *i.e.* 10 in the asymmetric unit. The $0kl$ reflexions are absent when $l\neq5n$ and $00l$ absent when $l\neq10n$. The above cell was considered to be approximate only as a number of hkl reflexions were observed which could only be indexed if c were 283·2 Å, which would give 120 molecules in the unit cell. An ill-defined superlattice arrangement, reminiscent of that proposed by Ito (1950) for trinitrotoluene, was suggested but the structure was not worked out in any further detail.

Experimental

Fine needles showing straight extinction were obtained by slow cooling of a solution in a mixture of ethanol and methyl ethyl ketone. An oscillation photograph about the needle axis showed that this was an axis of symmetry and was 5·77 Å long, in agreement with Mason's value for b. Zero and first-layer Weissenberg photographs were then taken about b, using Cu $K\alpha$ and then Fe $K\alpha$ radiation. The greater dispersion afforded by Fe $K\alpha$ made the latter photographs more satisfactory and they were used most in the subsequent analysis; there were no differences in the data given by the two sets of photographs.

Inspection of the photographs (Fig. 1) showed that a number of reflexions occurred close together along the $h0l$ and $h1l$ (h constant) festoons, suggesting a large value for c, but that the separation between adjacent reflexions varied for the different festoons. In addition there were two lines of almost exact symmetry in both $h0l$ and $h1l$ photographs. These symmetry lines, which were 90° apart, are marked pseudo-**a*** and **c*** in Fig. 1. The first reflexions along pseudo-**a*** on the $h0l$ and $h1l$ Weissenberg photographs were 10,00 and 10,10 according to Mason's unit cell. Values of (pseudo) d_{100} and d_{001} measured from the two symmetry lines with a Buerger template agreed with Mason's values.

The ω, Υ values of each reflexion were then measured

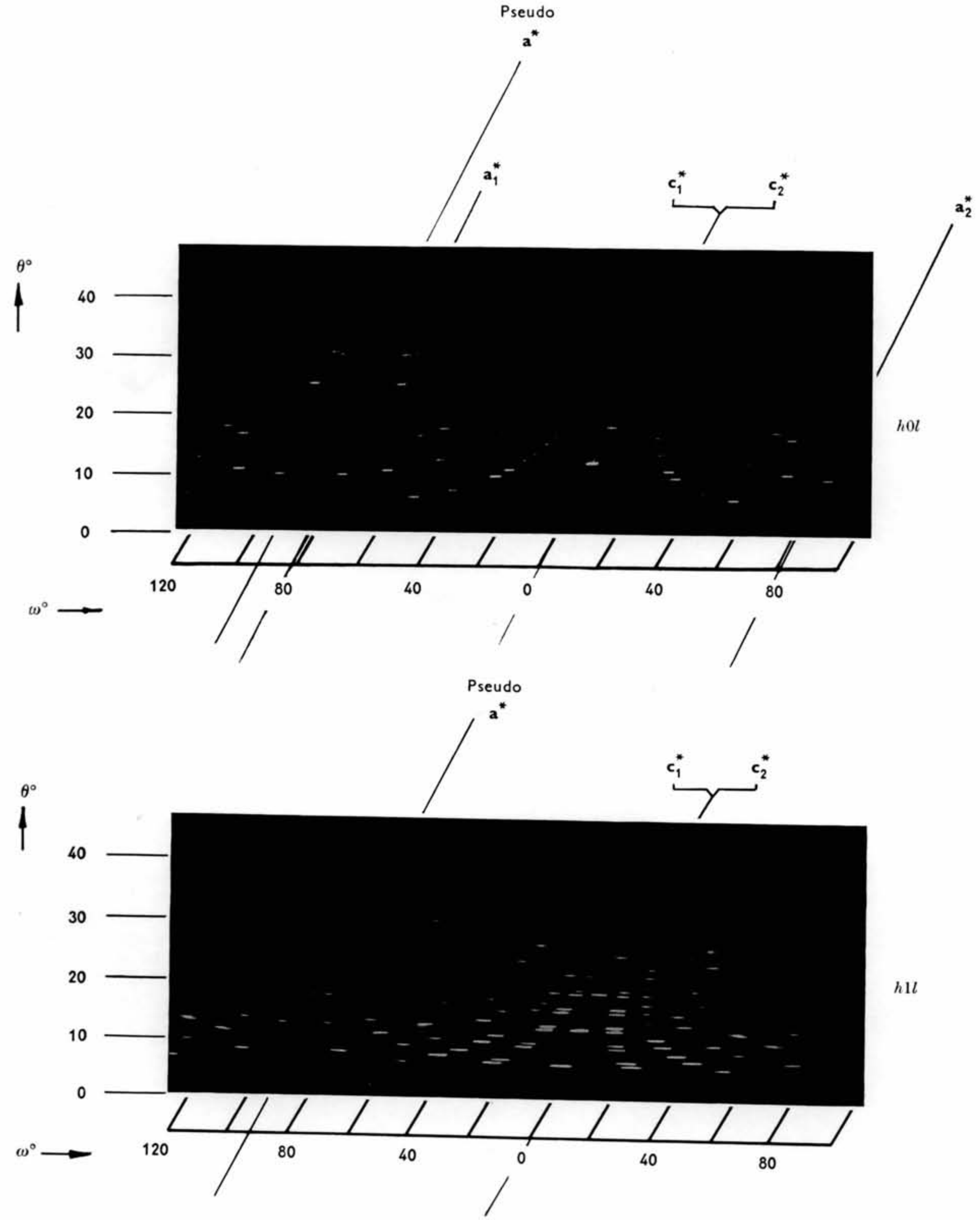


Fig. 1. *h0l* and *h1l* Weissenberg photographs, Fe$K\alpha$ (Mn filter) 35 kV, 900 mA.hr exposure.

with an appropriately drawn template and the reciprocal lattice sections were plotted. (An attempt was made to use the Buerger template for indexing but its non-linear scale made interpolation difficult.) The $h0l$ and $h1l$ reciprocal lattice layers are shown in Fig. 2. Examination of these, and particularly the latter, shows that all the reflexions can be explained in terms of two twinned reciprocal lattices, with **b*** axes antiparallel. The relationship between the reciprocal axes of the two individuals is shown in Fig. 3 together with the corresponding relationship for the axes of the two direct cells. It should be noted that the requirements that the three axes form a right-handed set and that $\beta > 90°$ enable one to define the $+\mathbf{b}$ directions of the two individuals unequivocally from the Weissenberg photographs. The small separations between some neighbouring reflexions along lines of constant h in reciprocal space are simply consequences of the mutual disposition of the reciprocal lattices of the two individuals of the twin and have nothing to do with the length of **c***. The apparent symmetry of the photographs is also a result of the twinning and the reciprocal lattice layers of the individuals do not have any symmetry other than a centre.

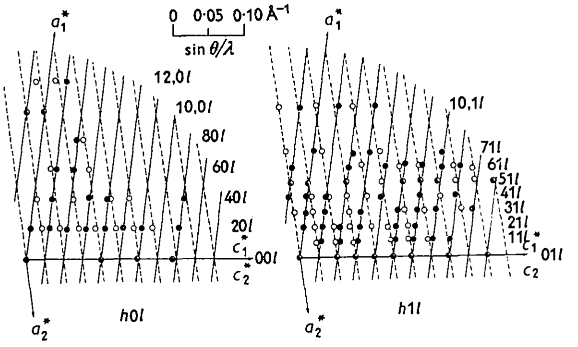


Fig. 2. The $h0l$ and $h1l$ reciprocal lattice sections deduced from the photographs of Fig. 1. The measured values of ω, Υ have been used to insert the points through which the best average lattices have been drawn. The reciprocal lattice of one individual is denoted with full circles and full lines, of the second individual with open circles and dashed lines. Half-filled circles show points common to both reciprocal lattices and also points whose assignment is ambiguous. No attempt has been made to indicate the relative intensities of the reflexions but unobserved reflexions are omitted.

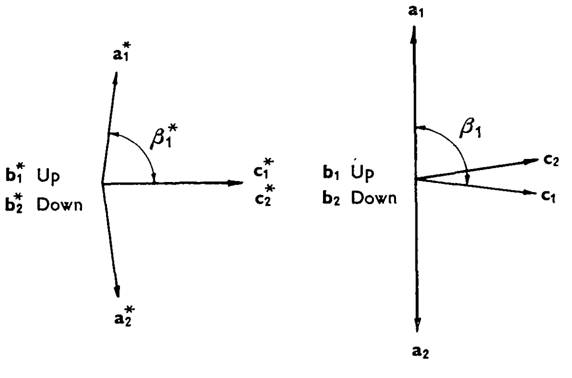


Fig. 3. The relationships between the axes of the twinned reciprocal and direct lattices.

Crystallographic data

The following cell dimensions were deduced from the reciprocal lattices of the individuals (it was not possible to derive very accurate values because of the lack of high-angle reflexions):

$a = 23{\cdot}6 \pm 0{\cdot}1$ Å
$b = 5{\cdot}77 \pm 0{\cdot}03$ Å
$c = 19{\cdot}0 \pm 0{\cdot}1$ Å
$d_{001} = 18{\cdot}9 \pm 0{\cdot}1$ Å
$\beta = 97{\cdot}5 \pm 0{\cdot}5°$
$\varrho_o = 1{\cdot}230 \pm 0{\cdot}002$ g.cm^{-3}
$\varrho_c = 1{\cdot}25$ g.cm^{-3} for 8 molecules in the unit cell.

Systematic absences: $h0l$ absent for h odd, $0k0$ absent for k odd, hence space group $P2_1/a$. There is also a non-space-group absence $00l$ absent for l odd, while $01l$ reflexions are very weak for l odd. The resemblance between the present crystallographic data and those given by Mason can be summarized as follows:

a: different values because of different choice of axes.
b: good agreement.
c: agreement of d_{001} values apart from an integral factor. The same axes were chosen but the absences (for $00l$ and $01l$) interpreted differently.
β: different values.

Space group: the same.
Measured densities: these do not agree well. The present value was measured by flotation in K_2HgI_4 solution.
Number of molecules: these are quite different, owing to the different interpretations of the diffraction patterns.

Optical goniometric data were obtained for a crystal rotated about **b**; the quality of the reflexions was poor. The value obtained show that (201) and $(20\bar{1})$ faces of one individual occur on the crystal examined.

Description of the twinning

Reference to Fig. 3 shows that the **a**, **b** and **c** axes of the two individuals can be made to coincide by a rotation of 180° about the normal to (001). This is one of the two possible rotations in the monoclinic system (Donnay & Donnay, 1959). According to Friedel's classification (Cahn, 1954), the crystals are reflexion-twinned by pseudo-merohedry, (001) being the reflexion plane. The obliquity is about $7\frac{1}{2}°$. Mallard's Law applies, *i.e.* the twins can be accurately described in terms of a twin plane parallel to a lattice plane (here (001)) which is almost a symmetry plane of the lattice.

Discussion

The photographs of (I) shows three features (an apparently large value for one axial length, two apparent symmetry lines 90° apart, many absences along one symmetry line) which were also found on the *hk*0 Weissenberg photograph of α-1,2:4,5-tetrachlorobenzene. Fig. 2 shows that these three features arise from the twin relationship between reciprocal lattice layers with $\beta^* \neq 90°$. In (I) the oblique reciprocal lattice layers are monoclinic $\mathbf{a}^*\mathbf{c}^*$ nets while in α-1,2:4,5-tetrachlorobenzene they are triclinic $\mathbf{a}^*\mathbf{b}^*$ nets. Mason (1956) has reported crystallographic data for 5-methyl-1,2-benzanthracene ($a=8{\cdot}20$, $b=6{\cdot}55$, $c=48{\cdot}77$ Å, $\beta=90°$, space group $P2/c$ or Pc, 2 or 4 molecules in the asymmetric unit) which show at least the first two of the three features listed above, and it is therefore possible that these crystals are twinned in similar fashion. Details of the diffraction patterns have not been published so that it has not been possible to check this point.

Complicated diffraction patterns have been reported from 2,4,6-trinitrotoluene (Ito, 1950; Gol'der, Zhdanov, Umanskii & Glushkova, 1952; Burkardt & Bryden, 1954), 1,3,6,8-tetranitronaphthalene (Gol'der *et al.*, 1952) and some other crystals studied by Ito. In particular there appear to be resemblances between the patterns obtained from trinitrotoluene and those studied in the present series of papers. One difference is, however, the variability of the trinitrotoluene patterns; the patterns from (I) and α-1,2:4,5-tetrachlorobenzene were always found to be the same, despite variations in experimental conditions. Burkardt & Bryden (1954) state that *These variations are best explained by considering the crystals to be composed of twinned fragments of simple or variant forms which are nearly aligned with respect to their pseudo-orthorhombic axes.* No other details were given.

Mason (1956) has suggested that the 'aggregation factor' (the number of molecules in the asymmetric unit) varies in a semi-quantitative way with the carcinogenic activity of certain methyl-1,2-benzanthracenes and bis-cyclic dibenzacridines. The main experimental evidence for this suggestion was the large activity of (I) and its supposed aggregation factor of 10. It was later suggested (Mason, 1958) that a large aggregation factor might lead to increased intermolecular delocalization of π-electrons and thus to measurable effects on the electrical and magnetic properties of the crystals. The present results show that (I) has an aggregation factor of 2. The relationship of carcinogenic activity to aggregation factor is thus much less strongly based than was thought. Chalvet & Mason (1961) have recently given a quantum-mechanical theory of the carcinogenic activity of some substituted methyl-1,2-benzanthracenes in which no mention is made of aggregation factors.

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