

Fig. 2. (a) Bond lengths and angles for centrosymmetric molecule. (b) Bond lengths, (c) angles, for molecule in general position.

The thermal vibrations have not been analysed further. It is evident from the figures in Table 1 that for the carbon atoms the greatest amplitudes of vibration are along *b*, while for the oxygen atoms the greatest amplitudes are along *c*. The low values in the *a* direction are to be expected from the hydrogen bonding, but the values in the other directions would seem to imply an oscillation of the carboxyl group about the carbon to carbon bond.

Acta Cryst. (1966). **21**, 5

A New Kind of Twinning

BY KATHLEEN LONSDALE

University College, Gower St., London, W.C.1, England

(Received 20 December 1965)

Where a single crystal undergoes chemical decomposition into a twinned crystal of another chemical substance, the twinning may be due to geometrical relationships between the parent crystal and the (secondary) twin individual of the decomposition product and not between the main and secondary twin individuals themselves.

A study has recently been made, by X-ray diffraction techniques, of the decomposition of anthracene peroxide, $C_{14}H_{10}O_2$, when single crystals are irradiated by

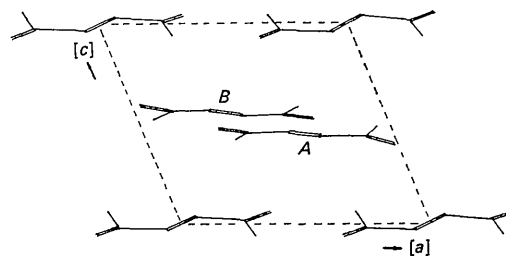


Fig. 3. Diagrammatic representation of nearest-neighbour contacts across the (001) cleavage plane. Molecule *A* has its mid-point near $\frac{1}{3}, \frac{1}{6}, \frac{1}{2}$; molecule *B* has its mid-point near $\frac{1}{3}, -\frac{1}{6}, \frac{1}{2}$.

This work was made possible by means of a grant from the Department of Scientific and Industrial Research, and we also acknowledge with thanks the help received from Ferranti Limited and International Computers and Tabulators Limited for the gift and servicing of the Pegasus computer.

References

- BAILEY, M. & BROWN, C. J. (1966). To be published.
 BEDNOWITZ, A. & POST, B. (1965). A.C.A., summer meeting abstracts.
 COOK, R. J., ROWLANDS, J. R. & WHIFFEN, D. H. (1963). *J. Chem. Soc.* p. 3520.
 CRUICKSHANK, D. W. J. (1961). In *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.
 HIGGS, M. A. & SASS, R. L. (1963). *Acta Cryst.* **16**, 657.
 MORRISON, J. D. & ROBERTSON, J. M. (1949). *J. Chem. Soc.* p. 980.
 NOWACKI, W. & JAGGI, H. (1957). *Z. Kristallogr.* **109**, 272.
 REIS, A. & SCHNEIDER, E. (1928). *Z. Kristallogr.* **68**, 543.
 SHAHAT, M. (1951). *Acta Cryst.* **4**, 571.
 SHAHAT, M. (1952). *Acta Cryst.* **5**, 763.
 SIM, G. A., ROBERTSON, J. M. & GOODWIN, T. H. (1955). *Acta Cryst.* **8**, 157.
 TANATAR, S. & CHELEBIEV, C. (1890). *J. Russ. Phys.-Chem. Soc.* **22**, 548.
 YARDLEY, K. (1925). *J. Chem. Soc.* **127**, 2207.

Cu *K* or Mo *K* X-rays, or heated, or both (Lonsdale, Nave & Stephens, 1966). The final product is a severely mosaic twinned mixed crystal of variable proportions

of anthraquinone, $C_{14}H_8O_2$, and anthrone, $C_{14}H_{10}O$, which are isomorphous (Srivastava, 1962) and form mixed crystals in all proportions (Harris, 1965).

The relationships between the unit cell of the original substance and those of the various individuals of the decomposition product are shown in Fig. 1.

The twinning of the mixed ($C_{14}H_8O_2$, $C_{14}H_{10}O$) crystal across the plane $(\bar{2}01)$, the trace of which is OE , is easily understood in terms of structure. For both anthraquinone and anthrone, and for mixed crystals in all proportions, the molecules, which have pseudo-mirrorsymmetry, lie almost normal to $(\bar{2}01)$ (Fig. 2). Twinning on this plane is common in both pure substances and in the mixed-crystal series. The structure of anthraquinone itself is pseudo-orthorhombic, with $(\bar{2}01)$ as one axial plane of the pseudo-orthorhombic unit cell (Fig. 3). Moreover the unit-cell dimensions of anthraquinone and of anthrone are

	a	b	c	β
$C_{14}H_8O_2$	15.83 Å	3.97 Å	7.89 Å	102.5°
$C_{14}H_{10}O$	15.80	4.00	7.86	101.7

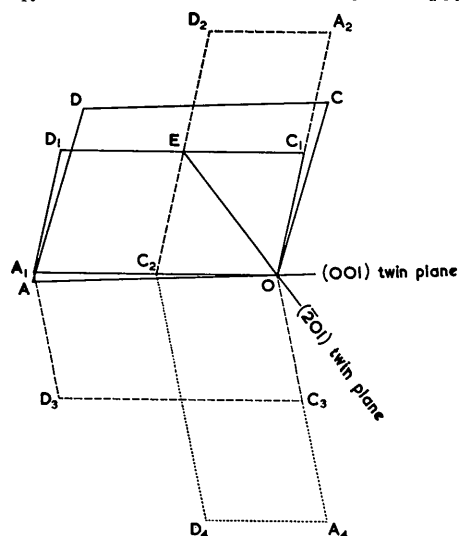


Fig. 1. [010] projections of the unit cells of the parent $C_{14}H_{10}O_2$, $OADC$, and of the derived individuals $OA_1D_1C_1$, $OC_2D_2A_2$, $OA_1D_3C_3$, $OC_2D_4A_4$ of the mixed-crystal ($C_{14}H_8O_2 + C_{14}H_{10}O$) decomposition product.

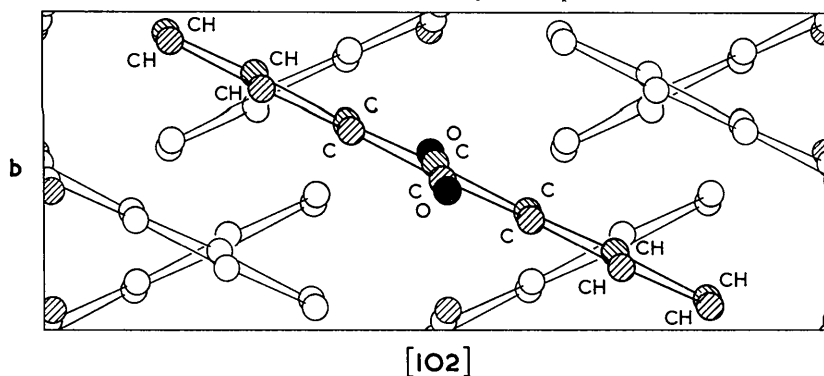


Fig. 2. Projection of the structure of anthraquinone on $(\bar{2}01)$. That of anthrone or of mixed crystals is almost identical apart from the change of H_2 for one O atom.

and hence for any mixed crystal (now called A:A) we have approximately $a=2c$.

The twinning across (001), trace OA_1 in Fig. 1, cannot be explained either in terms of the crystal structure of anthraquinone (or A:A) or of the dimensions of the

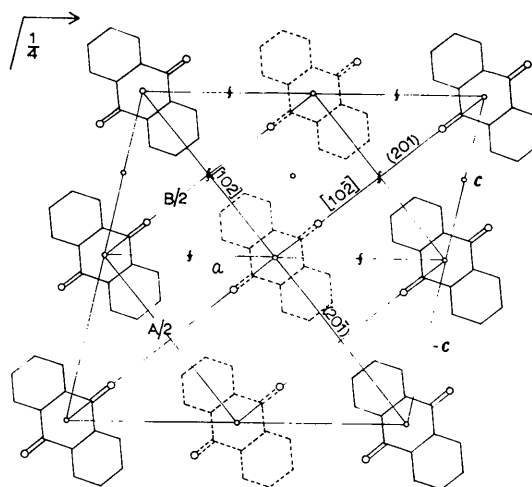


Fig. 3. Projection of the structure of anthraquinone on (010) showing the pseudo-orthorhombic axes $[102][102]$. That of anthrone or of A:A is similar, but disordered.

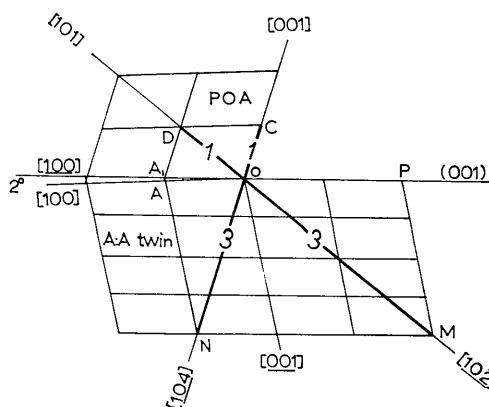


Fig. 4. Relationships between (010) projections of the anthraquinone photo-oxide and of the (001) twin individual of the mixed (anthraquinone, anthrone) crystal which is its decomposition product.

unit cell. It is, however, easily understood *in relation to the dimensions of the unit cell of the parent substance*, the anthracene photo-oxide (now called POA).

The derived A:A has a variable composition but usually consists of a higher proportion of anthraquinone than of anthrone. Its *b* axis, although very different in length (for POA, $b = 5.86 \text{ \AA}$) exactly coincides in direction with that of the parent POA. The unit-cell relationships in (010) are as follows

	<i>a</i>	<i>c</i>	β
POA	15.94 \AA	11.43 \AA	108.2°
A:A	15.82	7.88	102.2

The *a* of A:A is inclined at about 2° in obtuse β to that of POA.

The consequences of these relationships are that [101], [001] of POA almost coincide in direction with [10 $\bar{2}$], [104] of the (001) twin individual A:A, and there are also very close numerical relationships as follows (Fig. 4) between their dimensions.

$$\left\{ \begin{array}{l} OD = 16.46 \text{ \AA} \quad OM = 49.15 = 3 \times 16.38 \text{ \AA} \\ \angle DOA_1 = \angle DOA - 2^\circ = 39.3^\circ \quad \angle POM = 38.8^\circ \\ OC = 11.43 \text{ \AA} \quad ON = 32.14 = 3 \times 10.71 \text{ \AA} \\ \angle COA = 108.2^\circ - 2^\circ = 106.2^\circ = 180^\circ - \angle COP \\ \angle COP = 73.8^\circ \quad \angle A_1ON = 73.5^\circ \end{array} \right.$$

These relationships of course involve others, but these are sufficient to prove that the existence of this

twin (and of the doubly twinned individual $OC_2D_4A_4$ shown in Fig. 1) is not due to any direct relationship with $OA_1D_1C_1$ or with $OC_2D_2A_2$, but that *it is the consequence of decomposition from the parent substance $C_{14}H_{10}O_2$* . Apart from the coincidence of *b*-axial directions, which is due to the particular chemical reaction mechanism involved (Lonsdale, Nave & Stephens, 1966), and the near-equality of length of the *a* axes (POA 15.94, A:A 15.82 \AA), there is little resemblance between the two structures; and it is difficult to see why the *a* axis of the main A:A individual should be displaced from that of POA by 2°. The geometrical relationships of the (001) twin A:A with the parent POA may provide just the reason required. On the other hand the *reorientation of molecules* necessary to form this twin is greater than that required to form the main A:A individual and this, presumably, is the reason for its lesser importance, although it invariably occurs in the same specimen, sometimes in nearly equal strength, sometimes only to about one-eighth of the strength of the main individual.

References

- HARRIS, J. (1965). *Nature, Lond.* **206**, 1038.
 LONSDALE, K., NAVE, E. & STEPHENS, J. (1966). *Phil. Trans.*
 In the press.
 SRIVASTAVA, S. N. (1962). *Z. Kristallogr.* **117**, 386.

Acta Cryst. (1966). **21**, 7

A Simple Method of Setting a Single Crystal on One of its Principal Axes

BY JOHN IBALL

Chemistry Department, Queen's College, Dundee, Scotland

(Received 8 November 1965)

In order to mount a small single crystal about one of its principal axes it is mounted on a small mount which can be rotated on the top of the goniometer head of an X-ray Weissenberg camera. A series of oscillation photographs with the Weissenberg screens set at 1.0 cm is taken, and by observing the position of the goniometer head when small angle reflexions appear it is possible to set the corresponding planes parallel to the axis of rotation of the camera.

Many small crystals have no outward indication of the position of the unit-cell axes, and even when there are faces visible it is often necessary to cut a small fragment from a larger one or to grind it into a sphere. There are several suggestions in the literature (Wooster, 1964) about how to proceed in order to orientate such a crystal about a principal axis, but we have found the following method much simpler.

The crystal is mounted on a glass fibre which is supported in a small mount as shown in Fig. 1. The larger hole in the stem is filled with plasticine and the fibre

is pushed into it through the small hole. All our goniometer heads were modified many years ago to accept such mounts and the top of the goniometer head has marks every 30° around the circumference of the hole into which the mount fits. A set screw through the side of the hole fixes the mount in any desired orientation with respect to the arcs of the goniometer head. With the screens of the Weissenberg camera set at approximately 1.0 cm apart and with the camera stationary and at one end of its travel an oscillation photograph over (say) 25° is taken from a position where one