

# The Relationship Between Dislocations and Molecular Structure in Aromatic Crystals

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Topographical studies of cleaved anthraquinone crystals provide evidence for twinning on  $(20\bar{1})$  in accordance with the predictions of the sense of angle (SA) mechanism. Supplementary studies on etched, as-grown and cleaved crystals of anthraquinone and *p*-terphenyl, and a comparison of the results with the available data on anthracene, reveal that the dislocation arrangements in the three isostructural solids can be interpreted in terms of the relative dimensions of the unit cells. In anthraquinone, the  $(100)$   $[010]$  slip system is found to be of greater significance than the  $(001)$   $[010]$  system, which is dominant in anthracene, whereas the near orthorhombic nature of the *p*-terphenyl structure results in slip being favoured on  $(1\bar{1}0)$ . Twinning and glide are common to  $(20\bar{1})$  of anthraquinone, whereas glide alone has been observed on  $(20\bar{1})$  of anthracene and  $(201)$  of *p*-terphenyl. Possible partial dislocations and associated stacking faults are discussed.

## 1. Introduction

It is well known that the mechanical strength of metals and ionic crystals is greatly affected by the structural defects present in the lattice. However, apart from investigations into the plasticity of polymers [1, 2], little information has so far been obtained on the nature of dislocations in other solids, for example, molecular crystals. Detailed studies have been confined to the polynuclear hydrocarbons such as naphthalene [3] and anthracene [4-6] although line defects have also been identified in crystals of metaldehyde [7], cyclotrimethylene trinitramine (cyclonite) [8] and sucrose [9]. As part of a general survey of the physico-chemical consequences of lattice imperfections in organic solids, we have extended our earlier studies on anthracene to the closely related materials 9,10 anthraquinone and *p*-terphenyl. Both these materials are isostructural with anthracene; they crystallise in the monoclinic symmetry class with space group  $P2_1/a$  and have two molecules to the unit cell. A closer examination of the three structures reveals interesting differences. In addition to a replacement of the hydrogen atoms at the 9 and

10 positions by oxygen atoms, anthraquinone differs appreciably from anthracene in the relative magnitude of the unit cell axes and in the value of the  $\beta$ -angle. The unit cell dimensions of *p*-terphenyl, on the other hand, are very similar to those of anthracene, but the value of the  $\beta$ -angle is very significantly diminished, making the crystal symmetry very nearly orthorhombic. The relevant information is summarised in table I.

TABLE I

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$
Anthracene	8.58	6.02	11.18	124° 24' $c > a > b$
Anthraquinone	15.85	3.98	7.92	102° 43' $a > c > b$
<i>p</i> -Terphenyl	8.08	5.60	13.59	91° 55' $c > a > b$

Whereas molecular interactions across low-index planes in anthracene are governed to a large extent by intermolecular hydrogen-hydrogen contacts [10], the presence of the oxygen atoms at the 9 and 10 positions of the anthraquinone molecule offers a structure suitable for

the study of the effects of oxygen-oxygen contacts on the deformation behaviour. Again, the linear *p*-terphenyl molecules, crystallising as they do, may be expected to have active slip planes and slip directions not unlike those of ionic solids with cubic symmetry, viz.  $(110) a/2 [1\bar{1}0]$  for sodium chloride and  $(001) a/2 [1\bar{1}0]$  for calcium fluoride. In particular, an examination of the crystal structure shows that the molecular interactions encountered across  $(20\bar{1})$  – a plane known [11] to be actively involved in slip in anthracene – would be restricted to those between the oxygen atoms of neighbouring anthraquinone molecules, and it is of interest to enquire how this will manifest itself in the deformation behaviour of anthraquinone. The marked resemblance of the  $(001)$  face of *p*-terphenyl and of anthracene [12] is indicative that similar deformation behaviour on the  $(001)$  planes is to be expected for the two materials when in states of comparable purity [13].

## 2. Experimental

Transparent, yellow, single crystals of anthraquinone and colourless, blue fluorescent crystals of *p*-terphenyl were grown, using purified starting material, from solutions in benzene, from the vapour phase and from the melt by the Bridgman technique [14, 15]. Anthraquinone crystals grown from solution or from the vapour are needle-like and elongated along the *b*-axis with  $\{001\}$ ,  $\{100\}$  and  $\{20\bar{1}\}$  as prominent faces. Cleavage is pronounced on  $(001)$  and  $(100)$  and poor on  $(010)$ . *p*-Terphenyl crystallises from the vapour or from solution as  $(001)$  tablets and melt-grown crystals show  $(001)$  cleavage. Cleavage and etched surfaces were examined, using optical microscopy and interference contrast microscopy.

## 3. Results and Discussion

Fig. 1 shows a photograph, taken between crossed polars, of a section cut normal to the needle axis of a solution-grown anthraquinone crystal. The morphology described above is apparent, with angle ABC equal to the  $\beta$ -angle of the anthraquinone structure. Several parallel bands, in which the direction of light extinction is different from that in the surrounding material, can be seen to run across the crystal in a  $[102]$  direction. An identical band pattern is obtained on the opposite  $(010)$  face, indicating that the structures responsible extend along the  $[010]$  direction. These structures are growth twins,

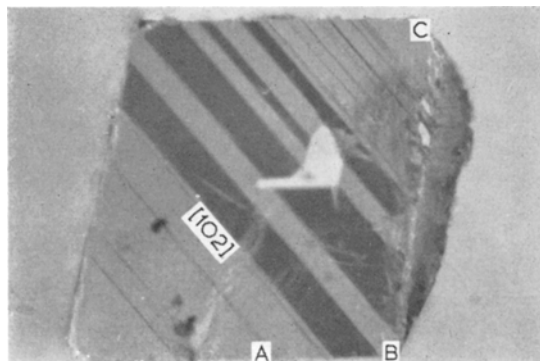
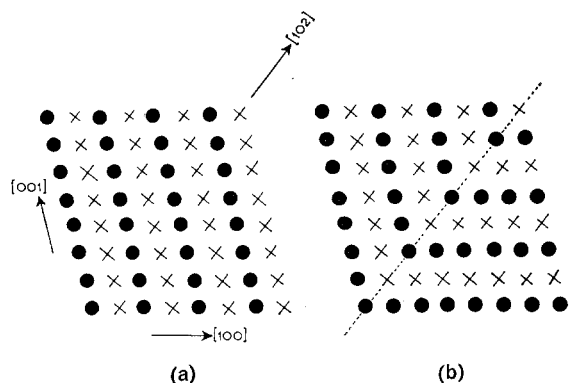


Figure 1 Optical micrograph of a  $(010)$  cleavage face of a solution grown anthraquinone crystal taken between crossed polars. Angle ABC equals the  $\beta$ -angle in anthraquinone structure and the twin bands extend along  $[102]$  ( $\times 50$ ).

the twin composition plane being  $(20\bar{1})$ .

Twinning in organic crystals, particularly those of low symmetry, has not been extensively dealt with in the literature although analogies may be made with the more rigorous treatments of the subject in connection with metals and minerals [16]. Twinning in monoclinic crystals as a function of habit type and centrosymmetry was recently treated by Wolten and Chase [17]. According to their classification, anthraquinone crystals would belong to the rather rare Type D – a class characterised by being elongated along the *b*-axis, and almost equidimensional in the *ac*-plane – whereas anthracene, crystallising as thin  $(001)$  plates, is a member of Type B. Twinning by the “sense of angle” (SA) mechanism of Wolten and Chase [17] would be expected on  $(001)$  for anthracene and  $\{h0l\}$  for anthraquinone. There is ample experimental support for  $(001)$  twinning in anthracene [18] and from the present work it appears that planes of the type  $(20\bar{1})$  are favoured in anthraquinone. The occurrence of these growth twins in anthraquinone suggests that the faulting energy on  $(20\bar{1})$ , which is required for their formation, is relatively low [16] and suggests that other faults may also be tolerated on  $(20\bar{1})$  planes. Fig. 2a is a schematic representation of the projection of the perfect anthraquinone structure on the  $(010)$  plane and fig. 2b represents a twinned structure formed by reflection across a  $(20\bar{1})$  plane, the rotation of the lattice planes being equal to the  $\beta$ -angle ( $102^\circ 43'$ ). Fig. 3 is an interference contrast micrograph across a twin boundary such as that seen in fig. 1. It illustrates



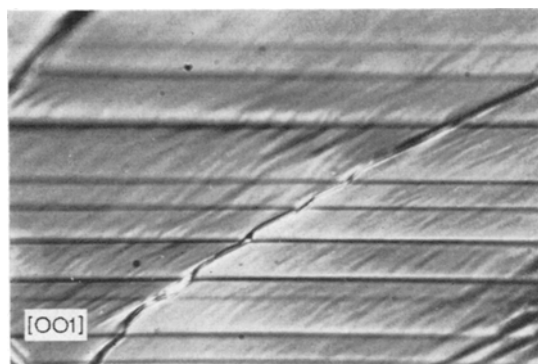
**Figure 2** (a) A schematic representation of the projection of the perfect anthraquinone structure on (010). Molecules represented by crosses (x) have their centres in planes  $b/2$  below those of molecules represented by filled circles. (b) A schematic representation of the twinned structure across a (201) in anthraquinone. Note that the twin involves a rotation of the molecular planes by an amount that equals the  $\beta$ -angle ( $102^\circ 43'$ ).



**Figure 3** An interference contrast micrograph of a (010) face across a twin boundary illustrating the deviation of [001] slip steps across the boundary ( $\times 225$ ).

the deviation of [001] slip steps across the (201) twin boundary.

Fig. 4 is an interference contrast micrograph of a non-twinned portion of a cleavage (010) face showing slip lines – a result of the growth process and/or cleavage – running in [001] directions. (Similar features are observed on the opposite (010) face). It was established that slip occurred on (100) planes, the slip vector having a component in the [010] direction. The most likely slip direction in the (100) plane of anthraquinone is [010] since this is by far the shortest lattice translation (see table I). The (100) [010]

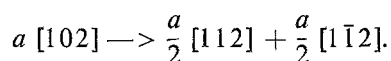


**Figure 4** An interference contrast micrograph of a cleaved (010) face showing [001] slip steps ( $\times 500$ ).

slip system has already been found to be active in as-grown crystals of anthracene but was considered to be of secondary importance to the system (001) [010]. It appears that in anthraquinone the order of importance of these two slip systems has been reversed, a state of affairs which is not unexpected in view of the ratio of the  $a$ - and  $c$ -axes for the two structures (see table I).

Dissolution and chemical attack in various organic solvents and inorganic acids leads to the production of dislocation etch pits (recognised from prescribed experimental criteria [9, 19]) at (001) and (100) cleavage and as-grown faces of anthraquinone, and at (001) cleavage and as-grown faces of *p*-terphenyl. Figs. 5a, b and c show typical etch patterns produced by exposing (a) a (001) as-grown face of anthraquinone to sulphuric acid, and (b) and (c) (001) cleavage faces of anthraquinone to benzene. From a detailed study of etch pit shapes, symmetry and pronounced alignments on (001) and (100) faces, we conclude that dislocations in anthraquinone may glide in (100) and (001) planes with [010] as the most likely slip direction. Dislocations also glide on (201) but the precise magnitude and direction are difficult to determine unequivocally. The [010] direction is the shortest lattice translation in the (201) plane, but slip in this direction cannot account for dislocations emergent at (100) faces in the screw orientation (cf. emergence points at A and B of fig. 5b). Slip in the [102] direction, although involving a long lattice translation, would give perfect dislocations of the required orientation. It might, however, be energetically advantageous for complete (201) [102] dislocations to dis-

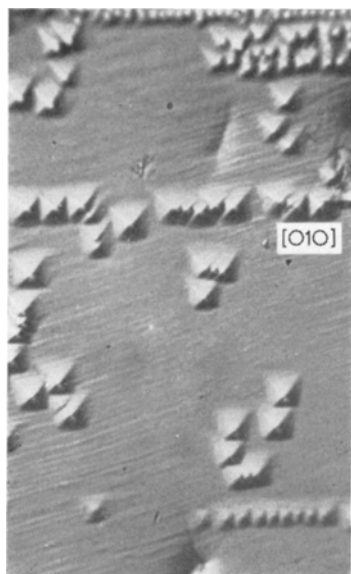
sociate into partials according to the reaction



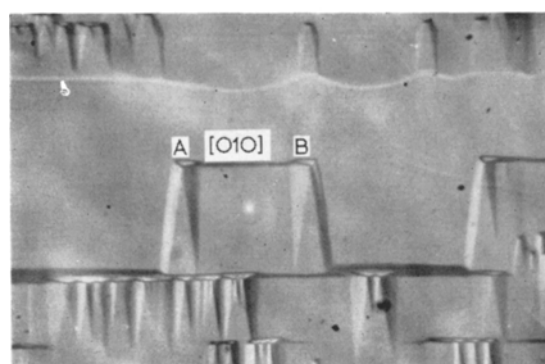
Furthermore, partials of the type  $(20\bar{1}) a/2 [102]$  might be favoured. The energy changes involved in the formation of such partial dislocations and associated stacking faults in anthraquinone is unknown, although, from the observation of

twinning on  $(20\bar{1})$  planes, there is some indication that stacking faults on  $(20\bar{1})$  planes may have a low specific energy. The extent of formation of such defects on  $(20\bar{1})$  planes in anthraquinone will be controlled to a large extent by the repulsive forces between the oxygen atoms of neighbouring molecules.

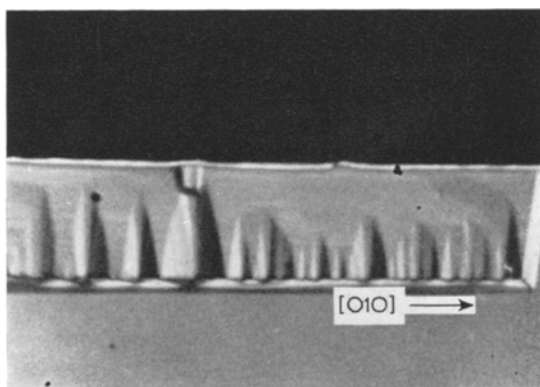
Fig. 6 shows a typical etch pattern on a  $(001)$



(a)



(b)



(c)

Figure 5 (a) An interference contrast micrograph of the  $(001)$  face of an anthraquinone crystal grown from solution and etched with concentrated sulphuric acid. Note the alignments of etch pits along  $[010]$  ( $\times 500$ ). (b) An interference contrast micrograph of a  $(001)$  cleavage face of a solution-grown anthraquinone crystal etched with benzene. The pits at A and B, joined by a cleavage step, demarcate the emergence points of screw dislocations of opposite sign ( $\times 500$ ). (c) Alignment of etch pits along  $[010]$  on a  $(001)$  cleavage face of anthraquinone after exposure to benzene. The pits demarcate the emergent points of dislocations gliding on  $(20\bar{1})$  planes and emergent at the  $(001)$  face in the screw orientation ( $\times 400$ ).

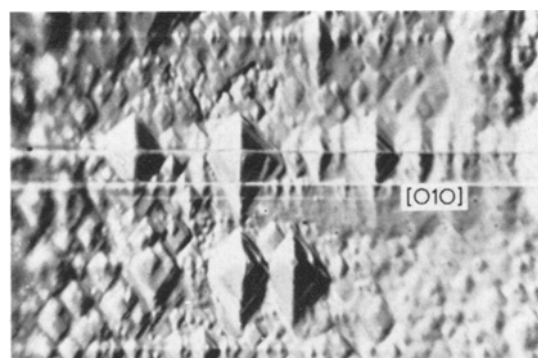


Figure 6 An interference contrast micrograph showing a typical etch pattern on a  $(001)$  cleavage face of a melt-grown *p*-terphenyl crystal after exposure to concentrated sulphuric acid ( $\times 500$ ).

cleavage face of *p*-terphenyl after exposure to sulphuric acid. A preliminary study has shown that pronounced alignments of dislocation etch

pits occur in [010] and [110] directions on (001) cleavage surfaces. Analysis of the results show that the (201) [010] slip system, similar to the one found for anthracene, can also be operative in *p*-terphenyl. However, the slip system (1 $\bar{1}$ 0) [110], found to be active in *p*-terphenyl, is completely absent in the deformation behaviour of anthracene. In all probability this is a direct consequence of the difference in the  $\beta$ -angle of the two structures. It is not possible to assess whether full [110] dislocations occur in *p*-terphenyl or whether dissociation into partials, as has been observed in orthorhombic polymeric materials [1], is feasible. Etching studies alone cannot provide the answer to this problem.

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