Role of Imperfections in the Dimerization of Substituted Anthracenes. Part I. 1,8-Dichloro-9-methylanthracene

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Both the separation distance and the relative orientation of neighbouring molecules in the solid 1,8-dichloro-9-methylanthracene monomer are inconducive for the photostimulated production of *trans*-dimer molecules, yet these are relatively readily formed upon u.v. irradiation. However, the presence of structural imperfections, chiefly dislocations, offers an explanation of this fact. Optical microscopic studies of the distribution of dimer nuclei, dislocation-etch-pits, and slip traces, as well as of the preferred orientation of dimer nuclei on as-grown and cleavage faces of orthorhombic 1,8-dichloro-9-methylanthracene crystals are described. The most probable operative slip systems are identified; in particular, it is possible to formulate the nature of the imperfections which lead to the almost exclusive orientation of dimer along [$\bar{2}$01], [201], and [001] directions in the monomer matrix. It is demonstrated that slip along [010], particularly when the Burgers vector in this direction is of half strength, is conducive for the photoproduction of the *trans*-dimer.

In the light of the molecular (Figure 1) and crystal (Figure 2) structures of 1,8-dichloro-9-methylanthracene (1,8-Cl_2-9MA) and on the basis of topochemical theory [1-4] (which, in its widest connotation, postulates that the reaction which proceeds within a solid is that which entails the minimum of atomic and molecular rearrangement), we should not expect any dimer to form upon the absorption of light quanta, the molecules being so far apart and inconducively oriented. The *trans*-dimer (Figure 3) is, however, formed [5] exclusively; and our task is to explain why this dimer is produced relatively readily, when the extent of lattice-control (known to be a very important factor in numerous photochemical and thermal reactions in the organic solid state) appears to be such a powerful deterrent.

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[1] M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 1996.
[2] G. M. J. Schmidt, '13th Solvay Conference, 1965,' Interscience, New York, 1967, p. 227.
[3] M. D. Cohen, Z. Ludmer, J. M. Thomas and J. O. Williams, *Proc. Roy. Soc. A*, 1971, **324**, 459.
[4] M. D. Cohen, in 'Reactivity of Solids,' (Proceedings of the 7th International Symposium on Reactivity of Solids, Bristol, 1972), Chapman and Hall, 1972, p. 456.
[5] J. P. Desvergne, H. Bouas-Laurent, R. Lapouyade, J. Gaultier, C. Hauw, and F. Dupuy, *Molecular Crystals and Liquid Crystals*, 1972, **19**, 63.

We have sought to elucidate the mechanism of this photoinduced dimerization by employing optical microscopy to analyse the role of structural imperfections rather along the lines of our earlier studies on anthracene,[6-8] 9-cyanoanthracene,[3] and, to a lesser degree, acenaphthylene.[9] Electron microscopic studies of the substituted anthracenes have been rendered more complex by the discovery (to be reported fully elsewhere) that an extensive range of polymorphic variants of 1,8-Cl_2-9MA exists; and by the fact that nucleation of dimer has not yet proved to be detectable routinely (see ref. 10) by transmission or diffractive electron microscopy.

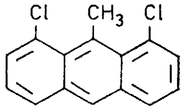

FIGURE 1 Molecular structure of 1,8-dichloro-9-methylanthracene

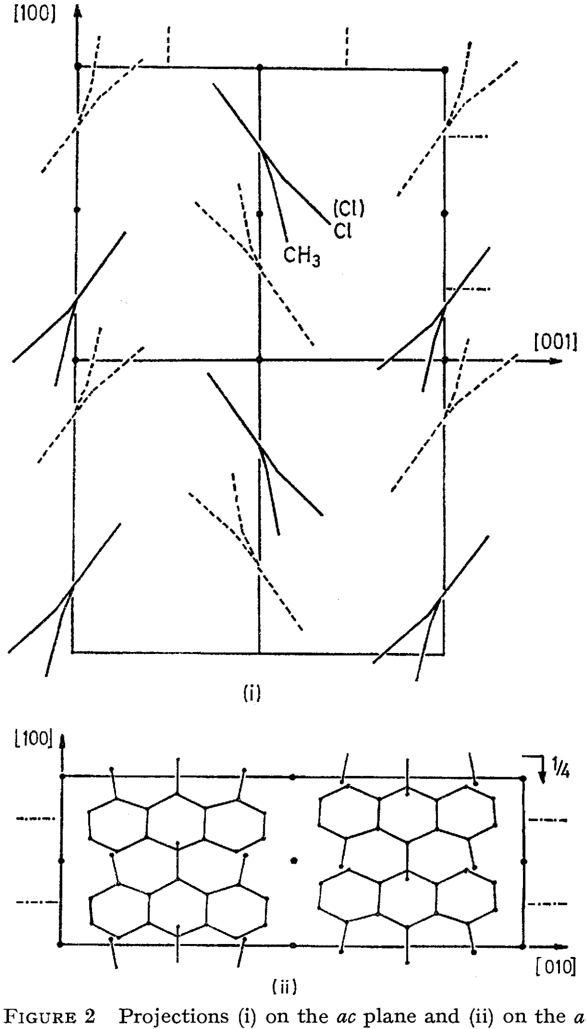

FIGURE 2 Projections (i) on the *ac* plane and (ii) on the *ab* plane of the crystal structure of 1,8-Cl_2-9MA

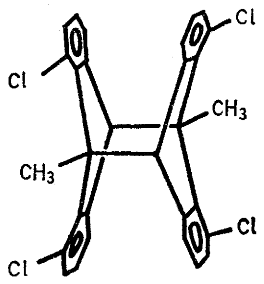

FIGURE 3 Schematic illustration of the *trans*-dimer of 1,8-Cl_2-9MA

EXPERIMENTAL

The 1,8-Cl_2-9MA was prepared [11] by the action of methylmagnesium iodide on 1,8-dichloroanthrone, formed previously by reducing 1,8-dichloroanthraquinone (Fluka technique) (fuller details of the preparation are given in ref. 5). The final product was purified by chromatography on alumina followed by recrystallization, and identified by X-ray methods (Weissenberg) as belonging to the orthorhombic symmetry class, space group $Pnma$ with $a = 7{\cdot}1$, $b = 19{\cdot}4$, $c = 8{\cdot}7$ Å, $Z = 4$, in agreement with the data of Dellaca *et al.*[12]

The morphology of the crystals grown from either benzene–light petroleum or light petroleum (hexane) is as depicted in Figure 4; their dimensions are typically $2 \times 1 \times 0{\cdot}05$ mm, too small for straightforward parallel studies of the influence of controlled deformation. Cleavage was readily effected along (010), *i.e.* the *ac* face. Dissolution-etch-pits, used to detect emergent dislocations and slip traces, were generated by using 1 : 1 v/v mixtures of either benzene and propanol or xylenes and propanol. Typical etching times were 5 s at room temperature. Dimerization was effected by irradiation, frequently with the sample on the microscope stage under nitrogen at room temperature, with light of λ 366 nm for lengths of time varying from 1—2 h (when nuclei first became detectable by optical microscopy) to about 100 h.

RESULTS

The distribution of dislocation-etch-pits (which may be pyramidal or flat-bottomed—as represented schematically in Figure 4—depending upon whether or not the line-defect responsible for the pit is 'clean' or 'contaminated', respectively [8,13]), and, in particular, the observed alignments of pits along certain preferred directions, indicate, but do not uniquely determine, which slip systems are likely for the crystal structure in question. Alignments, on the (010) face, along [001] are markedly preferred, but there is some tendency for alignments along [100], and to an even lesser extent (notwithstanding the exceptional clarity of the alignments in the micrograph of Plate 1b), along [101]; see Plate 1. Examination of matched faces of a cleaved crystal following etching and/or partial dimeriza-

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[6] J. M. Thomas and J. O. Williams, *Chem. Comm.*, 1967, 432.

[7] J. M. Thomas and J. O. Williams, *Trans. Faraday Soc.*, 1967, **63**, 1720.

[8] J. M. Thomas and J. O. Williams, *Progr. Solid-state Chem.*, 1971, **6**, 121.

[9] M. D. Cohen, I. Ron, G. M. J. Schmidt, and J. M. Thomas *Nature*, 1969, **224**, 167.

[10] J. M. Thomas, J. O. Williams, and W. Jones, ref. 4, p. 515.

[11] E. de Barry Barnett and M. A. Matthews, *J. Chem. Soc.*, 1923, 2549.

[12] R. J. Dellace, B. R. Penfold, and W. T. Robinson, *Acta Cryst.*, **B25**, 1969, 1589.

[13] J. M. Thomas, *Adv. Catalysis*, 1969, **19**, 293.

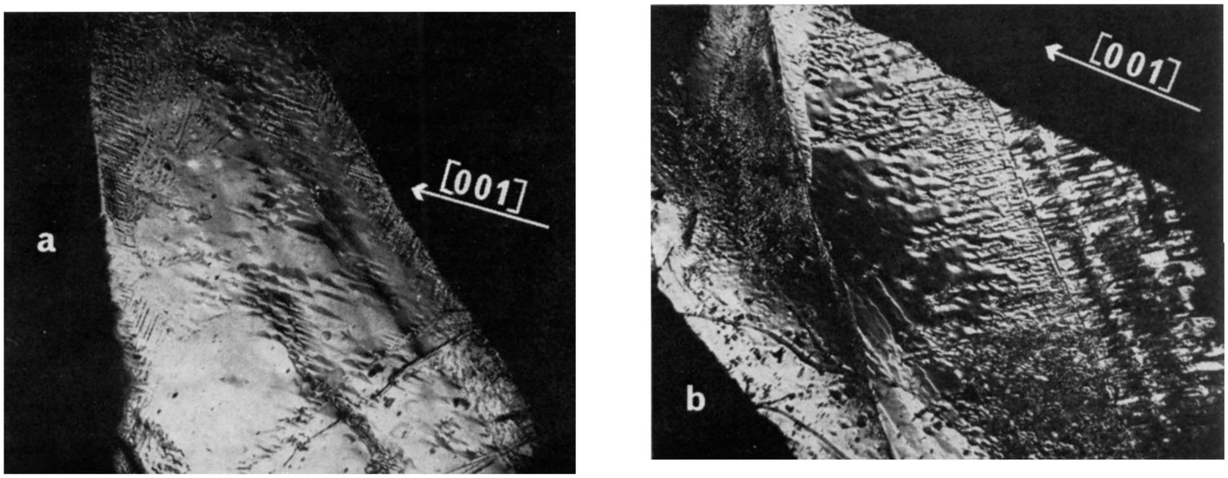

Plate 1 (a and b) Typical interference-contrast optical micrographs showing isolated and aligned dislocation-etch-pits on (010) faces of 1,8-Cl_2-9MA (magnification ×53)

Plate 2 Cleavage (010) surface after wet-etching, showing slip traces running [001] and a few dislocation-etch-pits (magnification ×53)

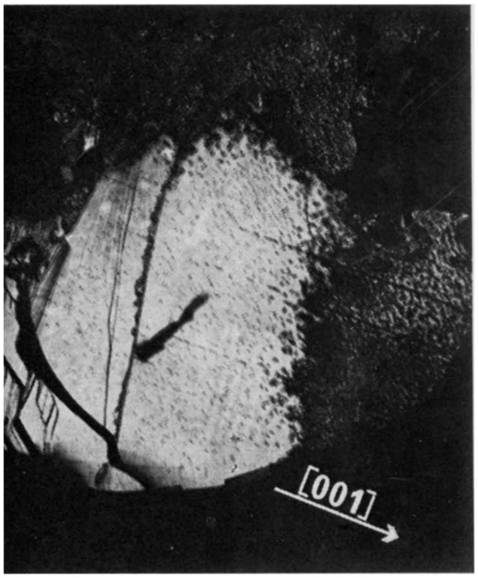

Plate 3 Matched cleavage face corresponding to that shown in Plate 2 following photoinduced dimerization; note alignment of dimer nuclei along [001] (magnification × 53)

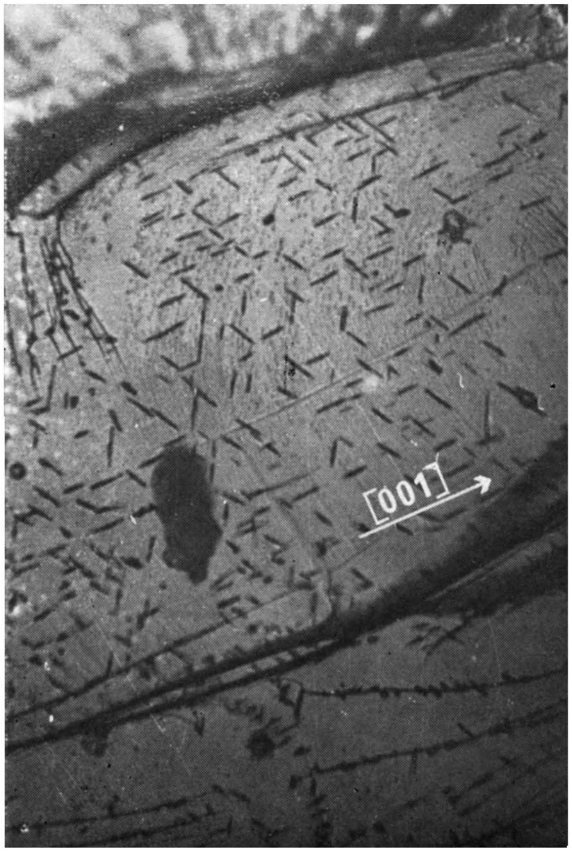

Plate 4 Typical high-resolution optical micrograph showing nature of orientational relationship between, and alignments of dimer nuclei, at the parent (010) monomer surface (magnification ×333)

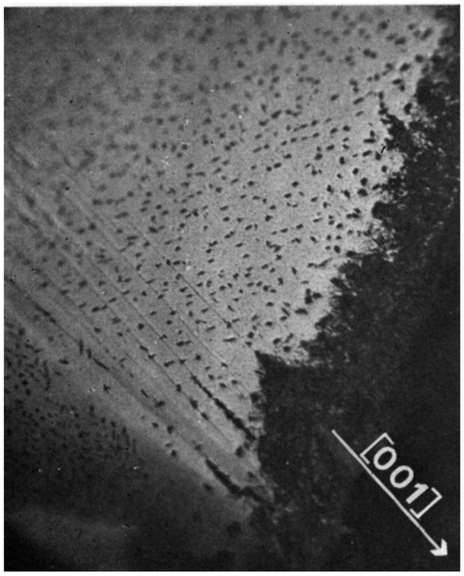

Plate 6 Micrograph of (010) surface showing tendency for dimerization to occur preferentially near to edge of crystal, as a result of introduction of dislocations upon cleavage (magnification ×213)

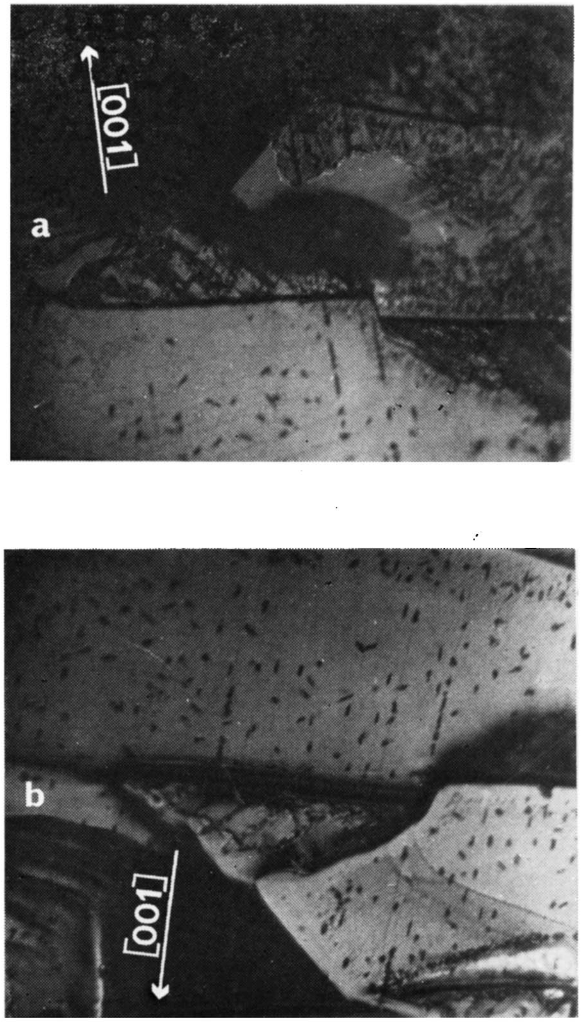

Plate 5 (a and b) Matched cleavage (010) faces after u.v. irradiation; note the alignments of dimer at slip traces along [001], and orientation of nuclei (magnification ×213)

tion (Plates 2 and 3) shows that there is a tendency for dimer nuclei to form at slip steps but that there is no general tendency for nuclei to form at the sites of isolated (aged) dislocations emergent at (010) faces. It is notable that the slip steps act as preferred sites for dissolution-etch-pits, indicating that slip on (100) has a component along [010]; there would not be such preferential dissolution if the slip on (100) were in the [001] direction.

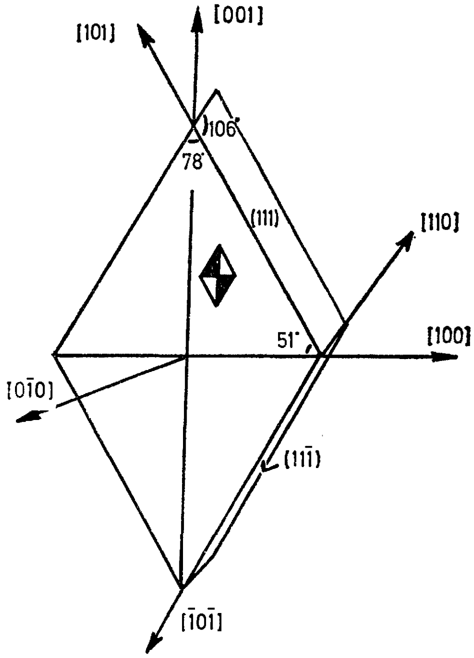

FIGURE 4 Illustration of morphology of the crystals grown from either benzene–light petroleum or from light petroleum (hexane). Orientation and shape of a typical dislocation-etch-pit on the (010) face is also shown

Apart from the preferential growth of nuclei at cleavage steps and at slip traces, which tend to run along [001], there are three major preferences for the orientation of the dimer nuclei developed on the freshly cleaved and irradiated surfaces. They grow such that their sides lie along [001], [201], and $[\bar{2}01]$ directions * (Plates 4 and 5).

Large numbers of dimer nuclei are found near the edges of cleavage faces (see Plate 6), probably because, as with certain other systems,[14,15] many defects are freshly introduced at crystal edges during the act of cleavage.

DISCUSSION

We consider first the slip systems, which, on the basis of the foregoing results, are likely to be operative in this solid. All our observations relating to alignments of etch-pits and slip traces are interpretable in terms of the slip systems: (100) [010] (mainly; the rest as subsidiaries), (100) [001], (101) [010], (101) $[10\bar{1}]$, (111) [101], (001), [010], and (001) [100]. (For fuller details of the syllogistic arguments which lead to such conclusions see the details given in previous publications [7,13,16,17] and refer to Figure 5 for a summary of the important directions. We emphasize that, although these simple slip systems are consonant with the experimental observations, from the nature of the deductions we cannot know whether the slip directions is correct in each case, or whether slip has only a component in the stated direction.) From the crystal structure[12] of 1,8-Cl_2-9MA we see that slip in the [010] direction brings molecules hitherto far removed (7·1 Å) and unfavourably oriented with respect to one another into a favourable incipient '*trans*' orientation, with the molecular planes of the anthracenic regions of the two molecules on either side of the slip plane essentially parallel. The photochemical significance of this fact will emerge shortly.

For reasons not at present understood, but possibly connected with the fact that there is contamination at the dislocation cores, isolated grown-in (aged) dislocations cores do not serve as centres for facilitating growth of the product nuclei, in contradistinction to the situation that obtains for the 1,8-Cl_2-10MA analogue (manuscript in preparation).

Freshly exposed cleavage surfaces are, however, active in facilitating dimerization at slip traces and at certain seemingly randomly distributed centres over the (010) face. Moreover there are only three directions (Plates 4 and 5) which are important as far as the orientation of the dimer nuclei is concerned: [001], [201], and $[\bar{2}01]$.

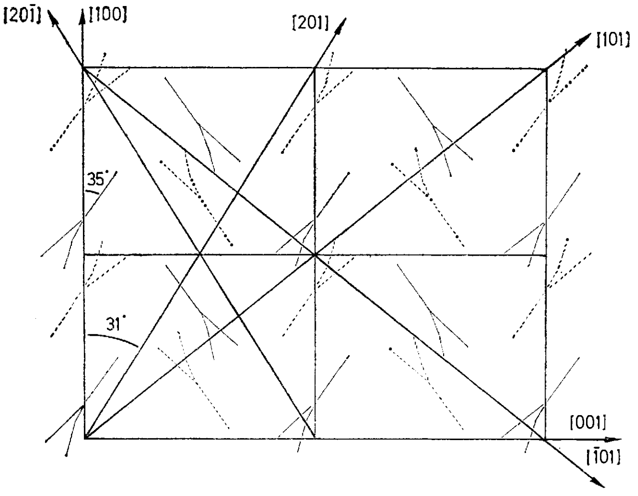

FIGURE 5 Summary of the crystallographically significant directions found in this study (and drawn on to the projection of the *ac* plane)

We now seek to explain these facts, and, at the same time, endeavour to understand why there is a marked tendency for some dimer nuclei (of no particular preferred orientation) to be formed at cleavage steps that tend to run along [001] (see *e.g.*, Plates 4—6).

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* The directions [201] and $[\bar{2}01]$ are crystallographically equivalent as may be seen from Figure 2. For the sake of clarity, however, the argument is continued by reference to both these directions. Strictly speaking we should also include $[00\bar{1}]$, but this is equivalent to [001].

[14] A. J. Forty, *Proc. Roy. Soc. A*, 1957, **242**, 392.

[15] J. M. Thomas and G. D. Renshaw, *J. Chem. Soc.* (*A*), 1967, 2058.

[16] J. M. Thomas and G. D. Renshaw, *Trans. Faraday Soc.*, **61**, 791.

[17] J. M. Thomas, E. L. Evans, and J. O. Williams, *Proc. Roy. Soc. A*, 1972, **331**, 417.

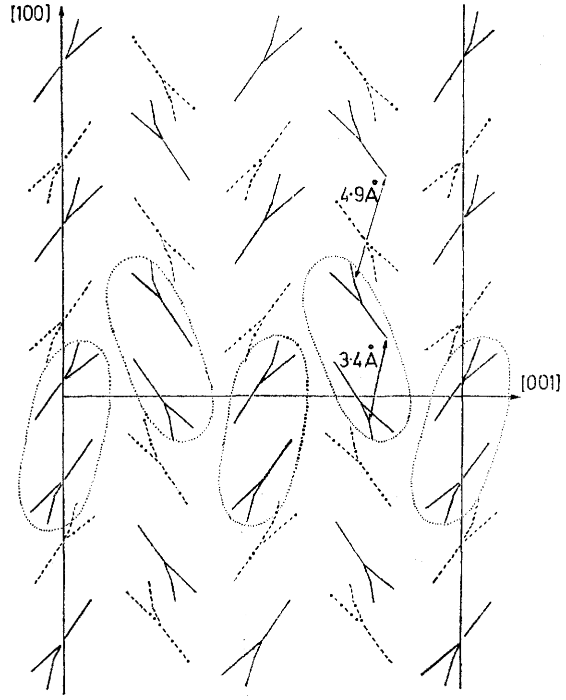

FIGURE 6 Schematic illustration, to scale, showing the favourable juxtapositioning of neighbouring molecules as a result of the introduction of (100) $\frac{1}{2}$[010] dislocations (see text)

If, at any slip trace or cleavage step, there occurs a [010] translation glide (this direction is known beyond doubt to be one of preferred slip for the solid under study) which is not exactly of unit (or an integral number of units of) strength, *i.e.* if there is a partial dislocation, and especially one characterized by a Burgers vector $\frac{1}{2}$[010], conditions become conducive for the production of the *trans*-dimer following absorption of a photon and subsequent trapping of the exciton.^{3,10,17} This is obvious from Figure 6, which shows the new stereochemical environment at partial dislocation cores of type (100) $\frac{1}{2}$[010]. At the new incipient dimer species (encircled for clarity in Figure 6) the orientation of the two monomers is optimal for dimer production and the C(9) $\cdots$ C(10′) distance is ideal (3·40 Å) for the dimerization process, in contrast to the corresponding distance of 4·9 Å for the nearest-neighbour molecules (which are most inappropriately oriented for dimerization anyway) in the ideal, defect-free, structure. It follows that surface steps at which there is an appropriate [010] translation glide will favour initial production, and subsequent nucleation of dimer. This is possibly the reason why nuclei are found to be associated with so many steps that tend to run along [001]. And the marked tendency for the orientation of nuclei to be along [001] is probably directly attributable to the presence of the (100) $\frac{1}{2}$[010] slip system, indicated schematically in Figure 6. (It is likely that dimer nuclei, once formed, will generate more dislocations so that the photoreaction should be autocatalytic. Although, for this solid, we have no direct evidence that such autocatalysis is dominant, we do know that a related solid, 9-cyanoanthracene,^{4} displays a steadily increasing quantum efficiency.)

Though we have no other (*e.g.* etch-pit) evidence for the occurrence of slip on (102) planes we note (see Figure 7) that a (102) $\frac{1}{2}$[010] slip system would lead to another optimal ' transition state ' or incipient dimer which, by trapping of a mobile exciton, would readily yield the *trans*-dimer. [Note that the ' anthracenic ' molecular planes lie almost parallel to the (102) family of planes; see Figures 2 and 5.] Distances and orientations, as with the previous example shown in Figure 6, are ideal, and vastly different from the inconducive stereochemical arrangement in the perfect structure. The pronounced tendency for dimer nuclei to grow with preferred orientations along [201] and [$\bar{2}$01] can, therefore, be interpreted, at least in part, on the basis of the existence of (102) $\frac{1}{2}$[010] slip.*

For the sake of completeness, it is necessary to consider other possible slip vectors on (102)-type planes, which would also, in principle, be capable of explaining [201] and [$\bar{2}$01] preferred orientations. Two such possibilities are (i) (102) $\frac{1}{4}$[221] (Figure 8), and (ii) (102) $\frac{1}{2}$[211] (Figure 9). Neither of these, however, is likely to be as important as the (102) $\frac{1}{2}$[010] system: for (i), the distance of closest approach between C(10′) and the carbon atom on C(9) (3·16 Å) is so small that excessive repulsive forces would be involved. For (ii) the appropriate C(10′) $\cdots$ C(9) distance for *trans*-related molecules in an incipient dimer is decreased to 5·25 Å, hardly adequate to facilitate dimerization following photo-

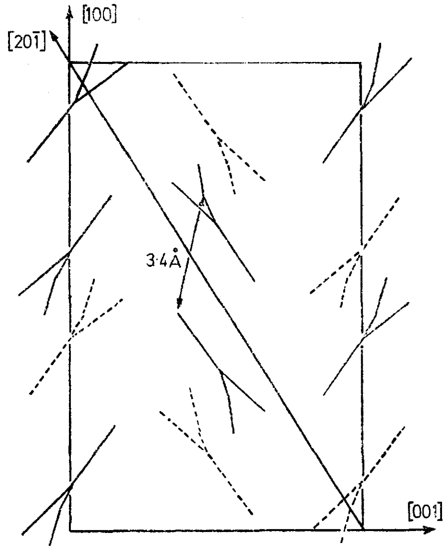

FIGURE 7 Scalar representation illustrating the favourable effect, for dimerization, of a (102) $\frac{1}{2}$[010] dislocation

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* It is impossible to assess, at present, the importance of topotaxy, *i.e.* orientational relationships between the monomer and dimer, in dictating these specific directions.

absorption, though the slip system itself may well be feasible.

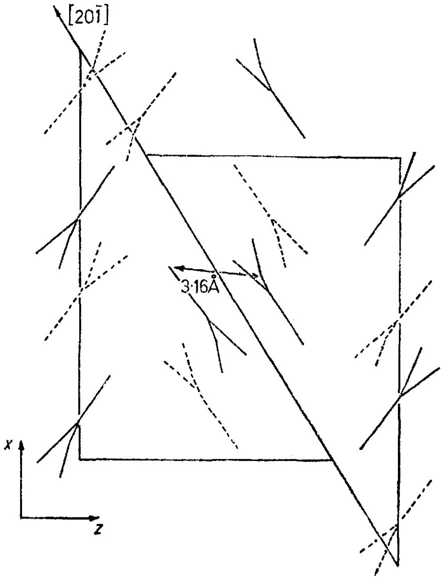

FIGURE 8 Scalar representation of the effect of introducing (102) ¼[221] dislocation

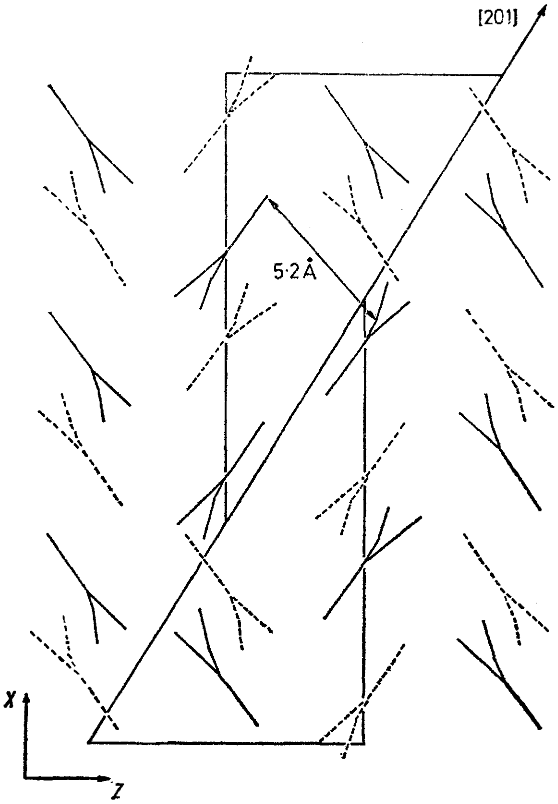

FIGURE 9 Scalar representation of the (102) ½[211] dislocation, which is less favourable for dimerization than that shown in Figure 8

It is of interest to examine why partial dislocations with Burgers vectors along [101] do not facilitate the dimerization of 1,8-Cl_2-9MA {we have no evidence for preferred photoreaction at (101) [101]- or (111) [101]-type dislocations, which are clearly shown to be present by the etch-pit studies} whereas the crystallographically analogous Burgers vectors in anthracene (*i.e.* ½[110]; see Figure 18 of ref. 17) are conducive for the photodimerization of the solid. Figure 10 clearly shows that Burgers vectors of ½[101] lead to orientations between molecules either side of the slip plane even less favourably disposed for photodimerization than neighbours in the ideal structure. In anthracene, on the other hand, merely because of the simpler unsubstituted molecules, 50% of the species on either side of the slip plane constitute incipient dimers, with their molecular planes parallel to one another.[17]

It is surprising that we have no dislocation-etch-pit evidence for the occurrence of slip on (102) planes, as we do for slip on (100). It is equally surprising that we have not yet found any evidence for preferred orientation of dimer nuclei along [101], because we do have some proof from etch-pit studies that the (101) slip plane can be active (see Plate 6). As to the first of these facts, it may well be that aged dislocations which were originally capable of glide on (102)-type planes, are not detectable by etching, possibly because of subsequent contamination of the cores. Such poisoning would at least help to explain why we do see numerous dimer nuclei [at freshly exposed (010) faces] not coincident with the sites of other etched (aged) dislocations. Dislocation half-loops freshly introduced into the solid by cleavage [at (100) and (102) planes] are not, unfortunately, readily amenable to independent electron microscopic study, for reasons to be discussed more fully elsewhere.[18,19] Briefly, samples of 1,8-Cl_2-9MA, as mentioned earlier, display a bewildering range of polymorphs and twinned structures when thin enough to allow of electron microscopic observation. Secondly, because of the thinness of the samples, it is difficult to detect the presence of dislocations, and, not least important, the organic crystals are rapidly destroyed because of electron-beam damage.

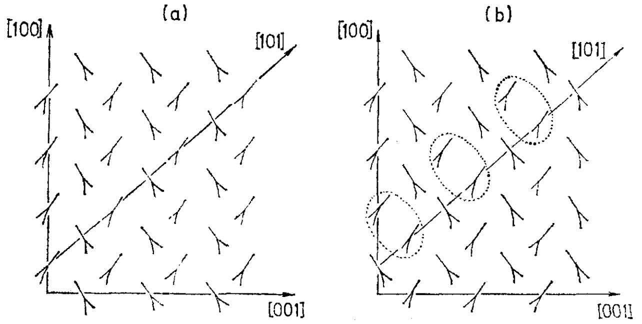

FIGURE 10 Representation (a) before and (b) after introduction of partial dislocations with ½[101] Burgers vectors on (*hkl*) planes

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[18] W. Jones, J. M. Thomas, J. O. Williams, and L. W. Hobbs, in preparation.

[19] W. Jones, J. M. Thomas, and J. O. Williams, in preparation.

When it becomes feasible to examine thin organic samples at low temperatures in electron microscopes possessing double-tilt and adequate image-intensification facilities, it should prove possible to identify and establish the importance in dimerization of dislocations that glide on (102) planes with Burgers vectors of [010] direction. At the same time we should be able to understand why aged (101) [010]-type dislocations, though in principle favourable, are not conducive towards the production of the *trans*-dimer in the solid state.

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