Photochemical Transformations in Crystalline Anthracenes: the Importance of Crystal Defects

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ANTHRACENES may be transformed into the corresponding dimers, and other degradation products, by photolysis with u.v. light.[1-3] But, contrary to the predictions of the theory of topochemical preformation,[4,5] some substituted anthracenes yield the *trans*- rather than the *cis*-photodimers, which are the compounds more nearly "preformed" in the host lattice. It has, consequently, been suggested[4] that crystal defects may function as the preferred centres for reaction, it being possible that anthracene molecules have their excitation energies slightly reduced when they are displaced from regular lattice sites. Here we report the identity of several kinds of co-operative defects (dislocations) in anthracene crystals, and direct evidence for preferred photolysis at such centres.

The sites of emergence, at {00*l*} faces, of isolated dislocations and sub-grain boundaries consisting of various arrangements of dislocations, have been identified by etching[6] and topographical[7] techniques. The most widely occurring type of dislocation is that in which slip (translation gliding) takes place on (010) planes in the [001] direction. Dislocations of this kind, designated (010) [001], give rise to pure screw dislocations and twist boundaries when they emerge at the {00*l*} faces. Another kind of dislocation is that which involves slip on (100) planes in the [010] directions. Dislocations of this kind, symbolized (100) [010], give rise to pure edge dislocations and tilt boundaries when they emerge at {00*l*} faces. Subsidiary dislocations which, in association with the above types, constitute asymmetrical small-angle boundaries are: (010) [100] and (001) [010].

A series of separated halves (obtained by cleavage) of melt-grown crystals were treated as follows. One half was etched to reveal the distribution of emergent dislocations; the other was irradiated, through quartz windows in the absence of oxygen, with a medium pressure mercury vapour lamp (sometimes without the 2537 Å component[3]). The distribution of product nuclei was observed using high power interference contrast (Nomarski) microscopy,[8] and the degree of matching of the patterns on corresponding faces compared. Isolated and aligned dislocations of all the above types, as well as some surface steps, were found to facilitate photolytic conversion thus confirming previous speculations. It transpired that photolysis with u.v. is at least as good a method of detecting dislocations as other techniques; and that little or no dislocation multiplication occurs during the initial stages of growth of products.

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