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Photochemical Reactions Inside the Electron Microscope: Preferred Dimerization of Anthracene at Dislocations

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Optical microscopic studies of UV-irradiated single crystals of anthracene, and of some of its derivatives, reveal(1,2) that nucleation of the dimer within the host matrix occurs heterogeneously; and that the cores of certain non-basal dislocations function as preferred regions for the appearance of the product. That other types of dislocations present in aromatic solids may also be involved in chemical transformations within the solid-state is indicated both by the facile photochemical decoration (with dimer nuclei) of several families of dislocations in acenaphthylene,(3) and by the unexpected stereochemical product of dimerization of 9-cyanoanthracene.(4,5) We have recently demonstrated(6) that, for 9-cyanoanthracene, stacking faults produced by partial dislocations gliding on (221) planes could account for the invariable production of *trans* dimer of 9-cyanoanthracene upon UV irradiation. In this communication we report the preliminary results of *in situ* investigations aimed at revealing directly, by transmission electron microscopy, basal dislocations and stacking faults in anthracene; and, in particular, the possible role of such imperfections in photo-stimulated reactions of the solid.

Specially prepared, ultra-thin crystals of anthracene were mounted on a goniometer cold-stage of a high-resolution electron microscope, which was modified so as to permit short pulses of UV light (>310 *nm*) to be directed on to the sample prior to and following continual electron-microscopic examination. It was so arranged that the sample suffered no deterioration from exposure to the electron beam, under the conditions of the experiment.

Figure 1 shows the single-crystal electron diffraction pattern of a typical anthracene crystal. The electron beam was perpendicular to the (001) face, and the spot-pattern is readily interpretable in terms of the *hkl* section of the reciprocal-lattice net. Figures 2(a) and (b) show the analogous patterns of partially dimerized crystals. The occasional appearance of diffuse rings within the monomer pattern and the disappearance of high-order (monomer) reflections both imply that some breakdown may occur, probably on a localized scale, of the single-crystal host into smaller imperfectly-aligned crystallites. But the most significant feature is the occurrence of some extra spots at regions in the diffraction pattern indicative of the presence of dimer single-crystals. On the basis of the various

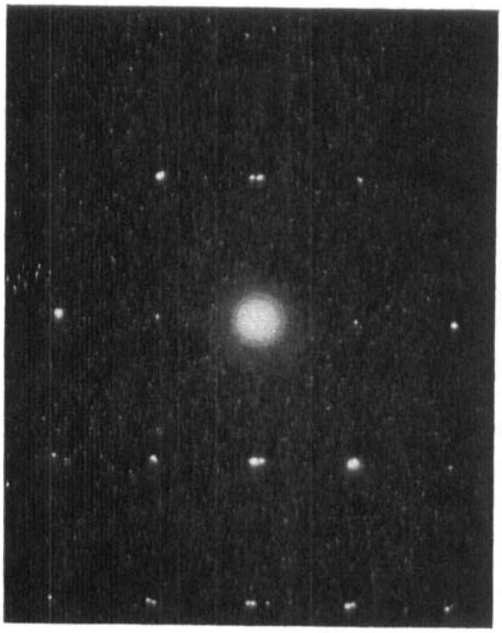

Figure 1. Selected-area diffraction pattern of a single crystal of anthracene ((001) planes perpendicular to electron beam). A certain degree of texturing is apparent.

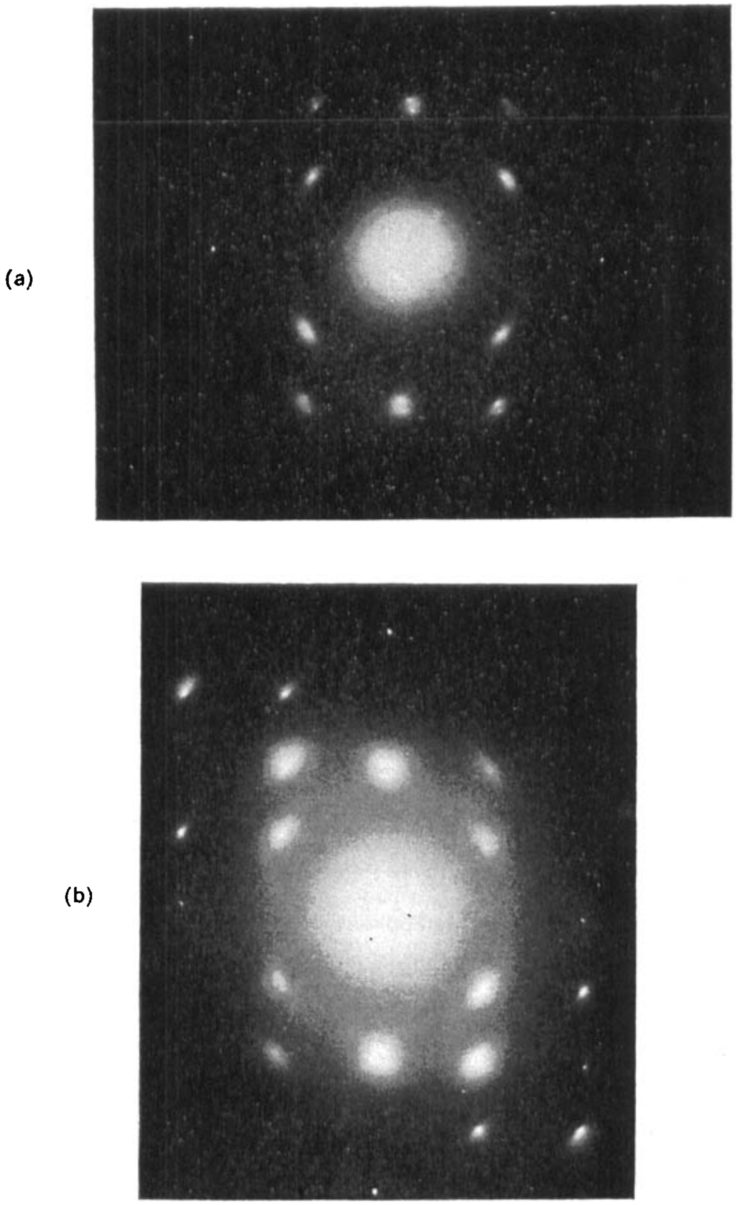

Figure 2. Selected-area diffraction patterns of anthracene (single-crystal) following UV irradiation. Note appearance of extra reflections, characteristic of the dimer, in (a) and (b), of the disappearance of high-order reflections and of the occurrence of diffuse rings.

topotactic orientations found by X-ray Weissenberg photographs for diparanthracene relative to the parent anthracene (Lonsdale, Milledge and Julian—private communication—and Julian, in preparation), the observed diffraction patterns are interpretable in terms of specific types of oriented growth of dimer within the monomer. The appearance of dimer is directly visible in the transmission electron micrograph constituting Fig. 3, and the dimer network is reminiscent of the familiar nodes and antinodes associated with basal dislocations and stacking faults.$^{(7)}$

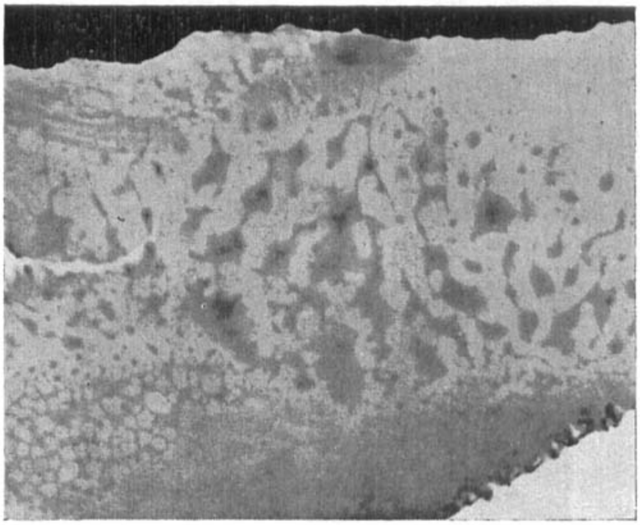

Figure 3. Transmission electron micrograph of a partially dimerized anthracene crystal showing tendency for dimer to appear in a network composed of nodes and antinodes. (Magnification 6000).

Although the previous conclusion that non-basal dislocations are of great significance in the photo-stimulated reactions of anthracene remains valid, it now seems possible that basal dislocations (which may be identified by transmission electron microscopy$^{(8)}$) are not unimportant, especially for certain types of topotactic relationships. With appropriate modification, it ought to be feasible to study many other photochemical reactions of organic solids with the technique outlined here.

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