Dislocations and the Photodimerization of 9-Cyanoanthracene

By M. D. COHEN and Z. LUDMER
(*Department of Chemistry, Weizmann Institute of Science, Rehovoth, Israel*)
and J. M. THOMAS*† and J. O. WILLIAMS†
(*Department of Chemistry, University College of North Wales, Bangor, Caerns.*)

Summary The dislocations emergent at *bc* and *ac* faces have been characterized and shown to be the preferred sites of photodimerization; in particular, partial dislocations on (211) planes give rise to a *trans* registry of molecules across contiguous planes, and thereby facilitate the formation of the *trans* dimer.

THE stereochemistry of the solid-state photodimerization[1,2] of 9-cyanoanthracene has led us to examine the complementary roles of the topochemical preformation theory[3,4] and dislocation theory in the interpretation of the reactions of organic solids. Upon u.v. irradiation 9-cyanoanthracene yields the *trans*-photodimer, implying that molecules in the monomer lattice[5] have to be displaced from their regular head-to-head arrangement along the *c*-axis, either prior to or during irradiation so as to bring the molecules into the required *trans*-conformation. It is difficult to envisage how the monomer species may rotate within the bulk crystal, and it has, therefore, been suggested that reaction is centred at regions of disorder, *e.g.* at lattice defects such as dislocations.

In a previous communication,[6] it was reported that dipara-anthracene, produced photochemically from single crystals of unsubstituted anthracene, appears preferentially

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† Present address: Edward Davies Chemical Laboraory, University College of Wales, Aberystwyth, Cardiganshire.

in the monomer lattice at emergent dislocations, which have since been rather fully characterized.[7] It is impossible to decide, as yet, whether the anthracene photodimer is formed, or merely crystallizes out, at dislocation cores. Moreover, it is dangerous to extrapolate results obtained with unsubstituted anthracene to the 9-cyano-derivative. Accordingly, we have carried out a topographical[7,8] (conventional optical and fluorescence microscopic) study of cleaved, etched, and partially photodimerized surfaces of melt-grown and vapour-grown single crystals of 9-cyanoanthracene.

We find that the principal families of dislocations which intersect the *bc* and *ac* planes (the two predominant cleavage faces) glide on (010) in the [100] and [001] directions, on (100) in [010] and on (211) with a component of slip in [100] [the precise direction being difficult to determine unequivocally on (211)]. We draw attention to the fact that the dissociation of particular perfect dislocations on (211) into partial ones according, for example, to the reaction:—

$$[100] \rightarrow \tfrac{1}{4}[214] + \tfrac{1}{4}[2\bar{1}\bar{4}]$$

offers a ready means of producing the *trans* registry of molecules prior to photoabsorption. The associated stacking faults provide regions in which 50% of the 9-cyanoanthracene molecules are stacked head-to-tail across contiguous planes. This implies that the unusual *order* associated with the fine structure of dislocation may be more important in reaction pathways than the unusual *disorder* associated with the core of a perfect dislocation. Such ideas would help to explain why some photodimerizations[9] proceed more easily in KBr discs than in uncompressed solids; the method of preparation of the sample (by analogy with other systems[10]) facilitates the introduction of the requisite dislocations.

We also report that photodimer nuclei appear in isolation (*ca.* 10^6 cm.$^{-2}$) and in pronounced alignments within the monomer host. The alignments are readily interpretable in terms of dislocations but the well-defined directions (on the *bc* face) along which some of the nuclei grow, *e.g.*, [021], $[02\bar{1}]$, $[01\bar{4}]$, [018], $[01\bar{8}]$ can be rationalized only by invoking concepts such as that of topotactic growth.[11] There appears to be a difference in the way certain nuclei develop: some, which appear crystallographic in outline, are elongated along the *c*-direction, whereas others develop a more amorphous structure. Excellent correspondence between the sites of nucleation has been obtained on matched *bc* cleavage faces, but in some regions on the two faces the directions in which the nuclei grow are different. Contrariwise, on another pair of matched halves, the nuclei may develop in identical patterns.

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