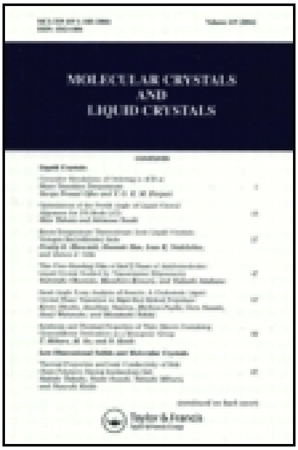

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Role of Imperfections in the Regiospecific Photodimerization of some Polynuclear Aromatic Hydrocarbons in the Solid State

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Role of Imperfections in the Regiospecific Photodimerization of some Polynuclear Aromatic Hydrocarbons in the Solid State

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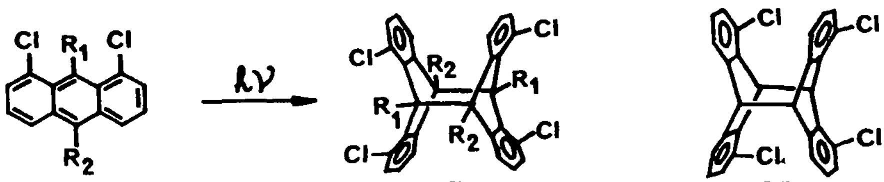
In organic crystals, molecules readily react with their nearest neighbours and the reactions may be controlled (especially the stereochemistry) by the relative arrangement of the molecules in the crystals (topochemistry).[1]

Topochemistry is exemplified by the photodimerization of the α and β polymorphs of trans cinnamic acid, which give the stereoisomer expected from the idealized crystal structure.[1] However some anthracenes, such as 9-cyano anthracene,[2] 1,8-dichloro-10 methyl anthracene (1,8 DC10MA),[3] give exclusively the head-to-tail (h-t) photodimer instead of the head-to-head (h-h) photodimer as expected from the h-h stacking observed in the bulk of the crystal structure. These cases were thought to be non topochemical photoreactions.[4,5] Further studies supported the role of crystal defects in these reactions.[2]

We wish to report on the role and the nature of the crystal imperfections in the photodimerization of 1,8 dichloro-10 methyl anthracene (1,8 DC10MA)

(I_b), its isomer (1,8 DC9MA) (I_a) and of 1,8-dichloroanthracene (1,8 DCA) (I_c), in order to precise further and extend the concept of topochemistry.



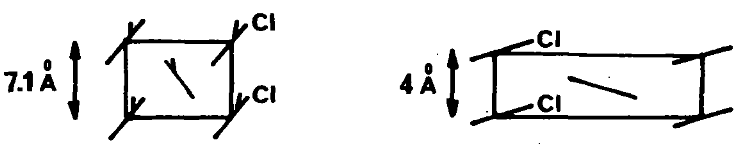
I — a $R_1 = Me, R_2 = H$; b $R_1 = H, R_2 = Me$; c $R_1 = R_2 = H$

II — (h-t) head-to-tail photodimer

III — (h-h) head-to-head photodimer

In solution (ether), I_a and I_b yield only the corresponding h-t photodimers; I_b photodimerizes about twice as efficiently as I_a;[5] this was ascribed to peri effect.[5] In the solid state, I_a was shown to react much more rapidly than I_b but no direct conclusion can be drawn from this fact.

Reactivity of 1,8 DC9MA (I_a) Crystals of I_a belong to the space group Pnma (Figure 1). Examination of the structure shows that the molecules are too far apart and unfavourably oriented to form a photodimer in the ordered crystal. Nevertheless, irradiation yields exclusively the h-t photodimer II_a.



1,8 DC9MA unit cell

1,8 DC10MA unit cell

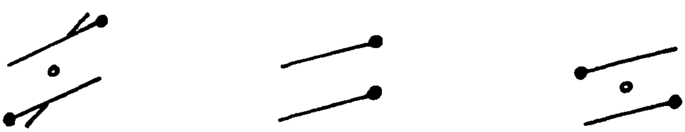
FIGURE 1

Using optical microscopic technique we have characterized the photonucleation loci, namely mechanical defects such as cracks, edges, etc., and some particular directions on cleaved faces; these specific alignments of nuclei can be rationalized by the existence of dislocations, most of which were revealed by chemical etching.[6] At these dislocations the molecular pairs are well oriented to produce the h-t photodimer. The main active slip planes may be[6] (100) 1/2 [010]; (102) 1/2 [010], (102) 1/4 [221] and (102) 1/2 [211].

Reactivity of 1,8 DC10MA (I_b) I_b crystallizes in the space group Pnma (Figure 1); the molecular stacking is h-h as already mentioned. U.V. irradiation yields exclusively the h-t photodimer II_b (identical to the photodimer obtained in solution). The photoproduct appears preferentially at emergent dislocation sites and also along the [001] direction; this particular location may be related to the following slip systems: (011) 1/4 [121] and (210) [120].[3] However it is noteworthy that the great majority of slip systems must not be conducive to h-t dimerization: very often, in line defects mutual orientation is pseudo h-h (as in ideal crystal) or h-t but in that case the distance between the reactive centres is too long to lead to a photodimer. Although energy is trapped at these dislocations[7] we do not observe any photoproduct.

We know that mesomonosubstituted anthracenes give h-t photodimers,[5] probably because of steric and electrostatic repulsion in the h-h orientation between the meso substituents.

We expected that demethylated I_b would lead to photodimer, even at the dislocations where monomers are paired h-h (Figure 2), so we have studied I_c.



majority h-h Ib — minority h-t Ib — Ia

FIGURE 2 Schematic representation of molecular orientation in crystal defects.

Reactivity of 1,8 DCA (I_c) In solution (ether) I_c is readily transformed (60% conversion) into a mixture of 80% II_c (h-t) and 20% III (h-h). This is the kinetic product in our experimental conditions.

From the preceding work by Schmidt and coworkers[1] (crystal engineering) we expected a stacking of molecules in the crystal with the chlorines head-to-head. Indeed I_c crystallizes in the space group Pnma with its unit cell parameters very close to that of I_b. Further, if we assume that the defects of crystals of aromatic hydrocarbons belonging to the same space group are of the same type (as stated elsewhere for the space group $P2_{1/a}$,[8] we may assume that the crystal defects of 1,8-DCA (I_c) are very similar to those of I_b (see Figure 2).

Our initial results appear to be in qualitative agreement with the predictions: after several days irradiation, crystals were converted (15%) to a mixture of 20% of II_c (h-t) and 80% of III (h-h). Due to its low rate, the photoreaction must occur at the crystal imperfections. The reaction is no longer regiospecific but it may be topochemical.

Thus the assertion that a reaction is topochemical can mean that the reaction is under the control of the *idealized crystal structure*, or in the case where energy transfer is very efficient, of the *local order in the crystal imperfections.*

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