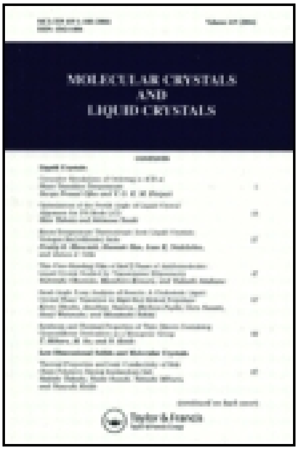

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Topochemistry in Crystalline Imperfections.: The Photodimerization of Two Acenaphthylene Derivatives

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Topochemistry in Crystalline Imperfections.

The Photodimerization of Two Acenaphthylene Derivatives

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The topochemical rule states that, in organic solids, the reactions occur with a minimum of atomic and molecular movements and are controlled by the crystalline structure of the starting materials.[1] The photochemical behaviour of α and β modifications of trans cinnamic acid crystals is a good illustration of the topochemical concept, each crystalline form gives the stereoisomer expected from the idealized crystal structure.[1]

However for a variety of anthracene derivatives the photodimerization has been proved to be non topochemical. The reaction occurs at defect sites where molecules are in appropriate mutual orientations to give the observed photoproducts.[2]

Moreover, for some dichloro-anthracenes which adopt similar molecular stacking types (crystal engineering[1]), we have recently shown that both head-to-head (topochemical product) and head-to-tail (non topochemical product) photodimers are obtained at the defects in accordance with the relative distribution of molecular pairs within the reactive sites,[3] although the molecules are well oriented in the perfect lattice to permit a topochemical dimerization.

This photochemical behaviour is consistent with an efficient energy transfer process toward defect zones occurring in certain anthracenic crystals,[2c] and it may be assumed to be the same for other aromatic crystals of β type.

In order to check the preceeding assumption we wish here to report on the photodimerization in the solid state of two acenaphthylene* derivatives I

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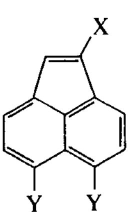
* Acenaphthylene has been photodimerized in the solid state[4] but the crystal structure is not conducive for a topochemical reaction and is disordered.[5]

TABLE I

Crystallographic constants of compounds I and II

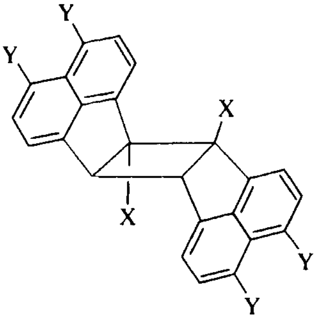
	a (Å)	b (Å)	c (Å)	β (°)	Space group	Z
I[8]	8, 29	3, 85	28, 61	95	P_{2_1}/c	4
II	16, 8	3, 8	17, 5	122	$P_{2_1}c$	4

and II of which crystal structure (β type, see Table I) permits a topochemical reaction. The compounds I and II smoothly photodimerize in solution. I leads (in degassed ether) to the syn 1–3 photodimer (IV syn 1,3),[6] whereas II (in degassed cyclohexane) gives 30% of syn (V syn) and 70% of anti (III anti) photodimers.[7]

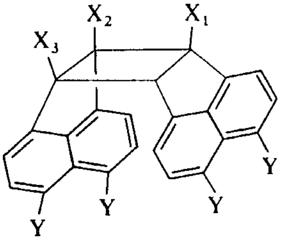


I X = CO_2H, Y = H

II X = H, Y = Cl



III anti {X = H, Y = Cl}



IV syn 1,2 {$X_1 = X_2 = CO_2H$, $X_3 = Y = H$}

IV syn 1,3 {$X_1 = X_3 = CO_2H$, $X_2 = Y = H$}

V syn {$X_1 = X_2 = X_3 = H$, $Y = Cl$}

The irradiation of solids yields *quantitatively the topochemical photoproducts* (planosymmetric dimers), IV syn 1,2 and V syn respectively. Optical microscopic examinations of irradiation crystals indicate that the reaction is not homogeneous; the photoproduct appears namely at mechanical defects (edges, cracks . . .) and along particular directions on the crystals main face.

The compound I shows on the main face of the crystal (001), two perpendicular directions for the nucleation of the product, [010] and [100] which correspond with the alignments of emergent sites of dislocations and slip planes traces on this face revealed by chemical etching (benzene[9]). Numerous slip systems have been identified, (100) [*uvw*], (102) [*uvw*], ($\bar{1}$03) [*uvw*], (013) [*uvw*] and (011) [*uvw*] and, in their majority, these defects present molecules which are in the same mutual orientation than those in the ideal lattice and so lead to the "topochemical photoproduct."

The chemical etching of compound II reveals a lot of emergent dislocation sites on the main face of the crystal, they are aligned along the [010] direction (stacking axis), and these emergent sites of defects are those of the photonucleation.

Thus the topochemical reactions for compounds I and II appear to be controlled by lattice imperfections which probably act as energy traps.

However we may wonder why we obtained only one photoproduct from the defect zones in contrast with dichloroanthracenes where, as in fluid media, two photodimers are formed. Moreover for compound I, some slip systems ((011) [$3\bar{1}1$] for instance) exhibit an anti mutual orientation between neighbour molecules which might be precursor of anti photoproducts. We know for some acenaphthylenes that the formation, in solution, of anti and syn photodimers originates from excited states of different multiplicities, respectively triplet and singlet[6] and as it has been recently claimed for anthracenes we may suppose that energy transfer in acenaphthylenes is an excimeric process[10] (singlet character) which is mainly conducive for the syn photoproduct.

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