

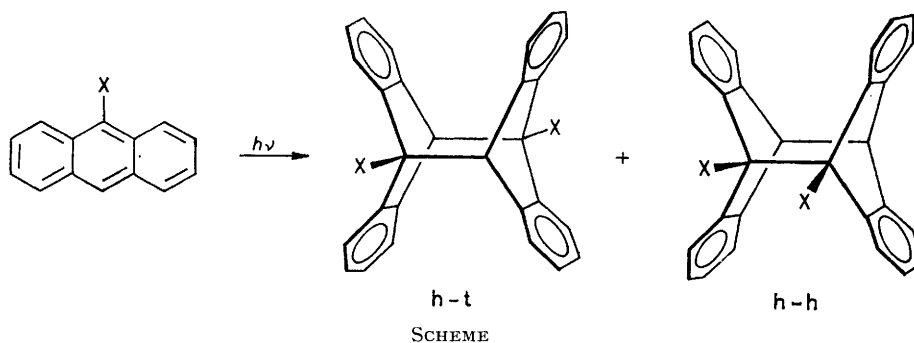
Dimerization Stereochemistry and Local Order in Organic Crystal Imperfections. Part 1. Photodimerization of Some Dichloroanthracenes in the Solid State and in Fluid Solution

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A study of solid state and fluid solution photodimerization of three dichloroanthracenes (I)—(III) shows that the 'head-to-head' photodimers are predominant in crystals whereas the 'head-to-tail' photodimers are favoured in fluid solutions; in these media, where solvating molecules leave the monomers free to take up all possible mutual orientations, the 'head-to-tail' dimer is preferred, because, we believe, of the repulsion between the chlorine atoms in the 'head-to-head' activated complex; in the solid state, this repulsion can be compensated by crystal forces in the reaction cavity. It is shown that, in that state, the reaction occurs in disorder sites, and it is argued that these regions maintain, however, a high degree of 'head-to-head' mutual orientation of the monomers, reflecting the ideal β type crystal structure. This might be of general significance for crystals of aromatic molecules where facile exciton migration occurs.

A NUMBER of organic solid state reactions have been rationalized by Schmidt and his co-workers in terms of the topochemical postulate which states that reactions in crystals occur with a minimum of atomic and molecular movement and are therefore governed by the structure of the starting materials.¹ Thus the stereochemistry of the photodimers of *trans*-cinnamic acid

anthracene (1,8-Cl₂-10-MeA), the stereochemistry of the photodimer [head-to-tail (h-t)] is not that expected from the molecular arrangement in the perfectly ordered crystal.^{3,4} It is known that the photodimerization of anthracene and most of its derivatives occurs through the 9- and 10-positions, according to the Scheme. Thus for the 9,10-disubstituted derivatives, two photodimers are



is determined by the geometric arrangement of the overlapped molecules in the α and β forms of the crystals.^{1,2}

However, for a variety of anthracenes, and in particular 9-cyanoanthracene (9-CNA), 1,8-dichloro-9-methylanthracene (1,8-Cl₂-9-MeA), and 1,8-dichloro-10-methyl-

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¹ G. M. J. Schmidt, *Pure Appl. Chemistry*, 1971, **27**, 647 and references therein; M. D. Cohen and B. S. Green, *Chem. in Britain*, 1973, **9**, 490.

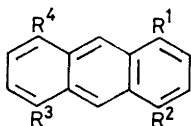
² M. D. Cohen and G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 1996.

³ D. P. Craig and P. Sarti-Fantoni, *Chem. Comm.*, 1966, 742.

⁴ J. P. Desvergne, H. Bouas-Laurent, R. Lapouyade, J. Gaultier, C. Hauw, and F. Dupuy, *Mol. Cryst. Liquid Cryst.*, 1972, **19**, 63.

These solid state photodimerizations^{3,4} denoted non-topochemical, were shown to occur at zones of crystalline imperfections. Such defects bring adjacent molecules situated at the core of the defects into a favourable mutual orientation and separation distance conducive to the production of the h-t dimer.^{5,6} It was also shown that energy transfer occurs in crystalline anthracenes such as 9-CNA (β type crystals) and that the transfer continues until there occurs radiative or non-radiative deactivation or the energy reaches an appropriate structural defect where reaction occurs.⁷

A detailed study of the defects of 1,8-Cl₂-10-MeA revealed, *inter alia*, sites where molecules are paired h-h and thus non-reactive because of the presence of the 10-methyl groups.⁶ We anticipated that the demethylated compound, *i.e.* 1,8-Cl₂A (I) would yield also the h-h photodimer (I_{D_a}) provided its crystal structure and defects are similar to that of 1,8-Cl₂-10-MeA. This similarity in lattice was expected from the resemblance in molecular structure and the possibility of the two chlorine atoms inducing β type molecular stacking (crystal engineering¹).



(I) R¹ = R⁴ = Cl, R² = R³ = H

(II) R¹ = R³ = Cl, R² = R⁴ = H

(III) R¹ = R² = Cl, R³ = R⁴ = H

We believed that the existence of chlorine bonds in the overlapped mirror symmetry mode would also induce β type lattice crystallization of two other anthracene derivatives 1,5-Cl₂A (II) and 1,4-Cl₂A (III) and we investigated the photochemistry of (I)—(III) in the crystalline state in order to observe a connection between the regioselectivity and the local order of the crystal imperfections. In a parallel study, the photochemistry was examined in fluid solution to compare the molecular and the solid state reactivity.

METHODS AND RESULTS

1 Crystallographic Data.—We have determined the crystallographic constants and packing type of (I)—(III) (Table 1). The space group and characteristics of the unit cell have been determined from Weissenberg photographs. The measured and calculated densities are in close agreement.

Compound (I) is isomorphous with 1,8-Cl₂-10-MeA previously studied. From our data, compound (II)

⁵ J. P. Desvergne, J. M. Thomas, J. O. Williams, and H. Bouas-Laurent, *J.C.S. Perkin II*, 1974, 363; J. M. Thomas, *Phil. Trans.*, 1974, **A277**, 251 and references therein.

⁶ J. M. Thomas, J. O. Williams, J. P. Desvergne, G. Guarini, and H. Bouas-Laurent, *J.C.S. Perkin II*, 1975, 84; J. P. Desvergne, H. Bouas-Laurent, R. Lapouyade, J. M. Thomas, J. Gaultier, and C. Hauw, *Mol. Cryst. Liquid Cryst.*, 1976, **32**, 107.

belongs to the triclinic space group. Despite the number of ways we have grown the crystals (crystallization from EtOH, PrⁿOH, Et₂O, CH₃COCH₃, CH₃COOEt, C₆H₆ or microsublimation⁸) we have not found the monoclinic space group *A*_{2/a} reported by Kitaigorodsky.⁹ Our unit cell parameters (*a*, *b*, *c*) can be roughly compared with those published by the author (*a'*, *b'*, *c'*) as follows: *a* \simeq *c'*/2; *b* \simeq *a'*/2; *c* \simeq *b'*. It is possible that (II) is polymorphic.

TABLE 1

Crystallographic constants and packing type of (I)—(III)

| Compound | Space group | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | β (°) | <i>Z</i> | Packing arrangement |
|---------------------|--|--------------|--------------|--------------|-------------|----------|---------------------|
| (I) (needles) | <i>P</i> _{mma} | 15.25 | 18.90 | 4.00 | 98 | 4 | h-h ^a |
| (II) (platelets) | <i>P</i> ₁ or <i>P</i> ₁ | 7.20 | 9.75 | 4.00 | 101 | 1 | h-h ^a |
| (III) (needles) | <i>P</i> _{21/c} | 3.92 | 16.27 | 17.22 | 92, 5 | 4 | h-h ^a |

^a Head-to-head means that all the chlorine atoms are superimposed.

2 Irradiation in Solution and Structure of the Photodimers.—Compounds (I)—(III) are smoothly photodimerized in degassed solutions (*ca.* 10⁻²M) in Pyrex vessels, by irradiation with a high pressure mercury lamp, at room temperature (60—80% conversion in 4 h) (see Table 2).

TABLE 2

Photodimerization of (I)—(III) in fluid solution

| Compound | Solvent | Conversion rate (%) | Photodimer isomer ratio h-h : h-t * |
|----------|--------------|---------------------|-------------------------------------|
| (I) | Ether | 72 | 20 : 80 |
| | Benzene | 62 | 23 : 77 |
| | Acetonitrile | 62 | 34 : 66 |
| (II) | Benzene | 83 | 36 : 64 |
| | Benzene | 75 | 33 : 67 |

* We use h-h and h-t by analogy with the 9,10-disubstituted compounds and for the sake of simplicity

Attribution of the structure to (I_{D_a}) and (I_{D_b}) is straightforward from inspection of n.m.r. spectra. In the h-h photoproduct (I_{D_a}), the 9,10-protons are not coupled and appear as two singlets at δ 5.92 (2 H) and 4.55 (2 H). By contrast, the 9,10-protons of (I_{D_b}) form an AB spectrum, δ_A 5.60, δ_B 4.67 (*J*_{AB} *ca.* 11 Hz).

The photodimers of (II) could be separated by crystallization in benzene and were identified by Heller and Schmidt¹⁰ by symmetry considerations of the crystallographic data. The authors assigned the centrosymmetric configuration to the more insoluble photodimer (II_{D_a}).

Starting from these established structures, we deduced the structure of the isomers of (III_D) by comparison of n.m.r. chemical shifts of the 9,10-protons of the four compounds as indicated in the Figure.

⁷ M. D. Cohen 'Reactivity of Solids,' eds. J. S. Anderson, M. W. Roberts, and F. S. Stone, Chapman and Hall, London, 1972, p. 456; M. D. Cohen, *Angew. Chem. Internat. Edn.*, 1975, **14**, 386.

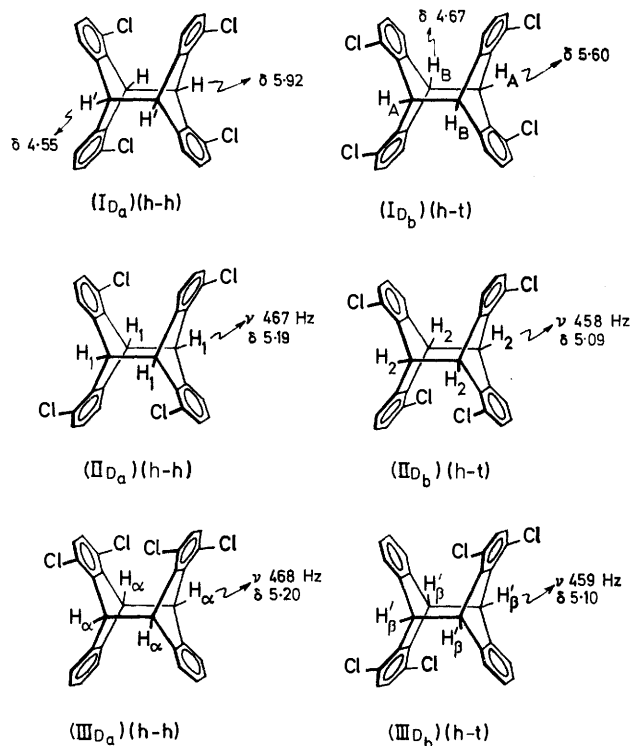
⁸ W. H. Melhuish, *Nature*, 1959, **184**, 1933.

⁹ A. I. Kitaigorodsky and S. S. Kabalkina, *Zhur. Fiz. Khim.*, 1951, **25**, 185.

¹⁰ E. Heller and G. M. J. Schmidt, *Israel J. Chem.*, 1971, **9**, 449.

Estimation of the h-h : h-t ratio was made by comparison of the intensities corresponding to the 9,10-proton n.m.r. signals of the two isomers. Because of the low solubility of the photodimers these measurements were made possible by use of Fourier transform n.m.r. (50—500 scans). Mass and u.v. spectra of the six compounds are in agreement with the proposed structures.

3 Irradiation of Single Crystals.—Compounds (I)—(III) as microcrystalline powders were irradiated in sealed Pyrex



N.m.r. data for 9,10-protons of photodimers (I_D)—(III_D): Bruker WH 90, solvent CDCl₃, saturated solutions, 30 °C, reference Me₄Si (50—500 scans)

tubes under vacuum (10⁻⁵ Torr) at room temperature, with a high pressure mercury lamp. Experiments were repeated on several samples. For (III) we estimated the h-h : h-t ratio after 8% conversion and showed that it is not far from the ratios obtained after 95% conversion. N.m.r. estimations were made on entirely solubilized irradiated samples (no attempt was made to separate the dimers, to prevent thermal decomposition during work-up). The results are given in Table 3.

4 Microscopic Examination of Crystals.—The experiments were carried out with an interferential phase contrast optical microscope (Zeiss-Normarski differential interference contrast) with magnification × 70, 200, and 400. Crystals were irradiated under nitrogen, or in sealed tubes under vacuum for 1—8 h before examination.

A preliminary study of crystal imperfections shows the following main features. Compound (I) has etch-pits (ethanol) similar to those of the isomorphous 1,8-Cl₂-10-MeA. We have not found an adequate solvent for etching compound (II). Finally compound (III) displays some alignment of etch-pits (ethanol-benzene mixture) mainly oriented along the short axis of the crystal.

In a parallel study and with the same optical device, we have examined irradiated crystals. Compound (I) exhibits

TABLE 3
Conversion rate and isomer ratios of photodimers obtained by irradiation of microcrystals

| Compound | Exposure time | Sample mass (mg) | Conversion rate (%) | Photodimer h-h : h-t ratio |
|----------|---------------|------------------|---------------------|-------------------------------|
| (I) | 7 days | 200 | 15—20 | 80 : 20 80 : 20 70 : 30 |
| (II) | 7 days | 200 | 25—30 | 66 : 33 |
| | 3 days | 10 | 20 | 86 : 14 |
| (III) | 6 h | 10 | 8 | 72 : 28 |
| | 3.5 days | 4 | 95 | 80 : 20 75 : 25 |

photodimers near the edges, cracks, and along a specific direction parallel to the short axis of the crystal (stacking direction). On the crystal of compound (II) the photodimers appear at mechanical defects and no specific alignment on crystalline faces has so far been detected. For compound (III) the photodimers again appear at mechanical defects; however it is also possible to detect some specific alignment of the photodimers along the short crystalline axis (stacking direction).

DISCUSSION

The photodimers obtained in fluid solution or in the solid state by irradiation through a Pyrex filter are not at photostationary equilibrium because they are transparent to light of $\lambda > 300$ nm. In addition, they are thermally stable at room temperature, at least within the time scale of the experiments. Consequently the ratios of isomers (h-h : h-t) recorded in Tables 2 and 3 are relevant to the kinetic factors controlling their formation.

Crystal photodimerization occurs at room temperature, *i.e.* well below any melting or eutectic point.* No liquid phase was observed during the reaction but solid photoproduct appeared along specific sites without destruction of the crystal geometry. Moreover, it has been shown, for anthracene and some of its derivatives that vapour phase cannot have a significant contribution to the reaction^{1,7,11} and we believe the same to apply to (I)—(III).

All the crystals belong to space groups where molecules are stacked in a β type packing, the shortest distance between two overlapped neighbouring molecules being 4.0 [(I) and (II)] and 3.92 Å [(III)]; this apparently is conducive to lattice-controlled topochemical reactions.^{1,10}

Examination of Tables 2 and 3 show that h-t photodimers are obtained predominantly in fluid solution whereas h-h photodimers dominate in the solid state.

* All melting points were measured with a Kofler block. Compound (I) has m.p. *ca.* 160—161°, a mixture of 15% photodimers and 85% monomer melts at *ca.* 159—160°. Compound (II) has m.p. *ca.* 191—193°, a mixture of 15% photodimers and 85% monomer melts at *ca.* 192—193°. Compound (III) has m.p. *ca.* 183—184°, a mixture of 15% photodimers and 85% monomer melts at *ca.* 183—184°.

¹¹ E. Klein, Thesis, Weizmann Institute of Science, 1969.

A priori one might state that, in crystals, the h-h dimers come from lattice-controlled reactions and that the h-t dimers are generated at defect sites. But this statement is consistent neither with the known rapid energy transfer in β type crystals with the result that photoreactions take place at imperfection sites,⁷ nor with our optical observations of the early photonucleation along specific lines corresponding to crystal imperfections. We rather believe that the photodimerization occurs, not in the bulk, but at imperfections where the mutual orientation of monomers governs the relative amount of monomers.

Indeed, we have seen that (I) and 1,8-Cl₂-10-MeA are isomorphous. If we accept that the defects of crystals of aromatic hydrocarbons belonging to the same space group are of the same type (as stated elsewhere¹² for the space-group $P_{21/a}$) we may assume that the crystal defects of (I) are very similar to those of 1,8-Cl₂-10-MeA in which an extensive study has revealed that mutual orientations of the nearest neighbouring molecules at the majority of the various types of imperfection sites are pseudo-h-h (as in an ideal crystal).

The same trend to generate h-h rather than h-t mutual orientations in crystal defects of (II) and (III) is inferred from the greater facility for β type lattices to develop dislocations with h-h alignment. This is indeed also the case for 9-cyanoanthracene for which a great number of imperfections have been characterized to display a h-h arrangement of molecules.¹³

Based on the above assumptions on the similarity of defect core structure in the three compounds under study and in 1,8-Cl₂-10-MeA, we argue that the imperfection sites responsible for photodimerization (energy traps) maintain a high degree of h-h mutual orientation of the monomer molecules, reflecting the ideal β type

¹² W. Jones, J. M. Thomas, J. O. Williams, and L. W. Hobbs, *J.C.S. Faraday, II*, 1975, 138.

crystal structure. This result might be of general significance for crystals of aromatic molecules where facile exciton migration takes place.

It is noteworthy that, for the three compounds, the fluid solutions show a preference for h-t photodimer formation (Table 2). Isomer ratios of (I_D) are not very sensitive to the polarity of the solvent. We believe that the h-h activated complex leading to the photodimer is less stable than the h-t one, because of Cl ··· Cl repulsion (in the transition state, the distance between the two chlorine atoms is shorter than in the excimer or in the crystal where the chlorine atoms attract each other).

Green¹⁴ has observed a similarity between intermolecular forces that operate in the crystal and in fluid solution in the photodimerization of dichlorostyrylthiophens and dichloro-*trans*-stilbene. Our results allow further insight into the comparison of fluid-solution and solid-state reactivity for compounds able to form crystals with highly overlapped molecules. In our case, sandwich pairs are presumably also formed in solution but the product regioselectivity depends on solvation forces which are different in solution than in the solid state. In solution, there is a competition between h-h and h-t photodimerization because monomers are free to undergo any mutual orientation. In the solid state, monomers must react as they stand at specific sites: the unfavourable h-h activated complex is probably stabilized by the surrounding monomers of the reaction cavity.

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¹³ M. D. Cohen, Z. Ludmer, J. M. Thomas, and J. O. Williams, *Proc. Roy. Soc.*, 1971, **A324**, 459

¹⁴ B. S. Green and L. Heller, *J. Org. Chem.*, 1974, **39**, 196.