

# PHOTOCHEMISTRY OF THE ORGANIC SOLID STATE

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## INTRODUCTION

Chemists, particularly organic chemists, tend to avoid the solid state as a vehicle for reaction. This treatment is especially unjustified in the case of photo-reactions, since light provides a convenient way of penetrating to the interior of the crystal, and with its aid a wide variety of reactions can be brought about. Some of these reactions, such as the photolysis of silver halide crystals, have been extensively studied and applied. In the organic field there have been a few chemists, widely separated in time and space, who have made the major contribution<sup>1-3</sup>; for the rest, references are isolated and disjointed. A review of this subject has recently appeared<sup>4</sup>.

Two properties of crystals are of particular interest to the photochemist: these are high viscosity, and the fact that the molecules have fixed (and determinable) geometries and relative orientations. The high viscosity is not unique to crystals but is found, too, in rigid-glass solutions. Thus, those properties of crystals related only to the viscosity—for example, the decreased rate of collisional deactivation—will be properties also of rigid solutions. Both types of system would therefore be suited to studies of trapped metastable intermediates<sup>5</sup>. On the other hand, properties related to geometries will be specific to the crystal, and it is these that will be treated in this paper.

The study of the relationship between the structure and reactions of a crystal has been called "Topochemistry". Cohen and Schmidt<sup>6a</sup> have discussed the consequences of topochemical control of a reaction. I wish here to describe some systems in which the rôle of crystal structure has been studied and will then turn to discuss the mechanisms available to the crystal for applying its control.

First, a word about the technique: in this Laboratory it is preferred, where possible, to study a reaction rather than a particular compound. If the reaction in question is photo-dimerization then there are selected a number of compounds of similar chemical structures, some of which are known to undergo this reaction in the solid state. Each compound is obtained in as many crystal modifications as possible, and the photo-reactions and crystallography of each modification studied. (For example, in the case of *ortho*-ethoxy-*trans*-cinnamic acid different polymorphic forms were obtained by recrystallization from ethyl acetate, benzene/petroleum ether, and ethanol/water, and each form was studied in the above way.) Additional information may be sought from comparison of reactions in the crystal and in rigid and

fluid solutions. Finally, possible correlations between structure and reaction are sought.

### EXAMPLES OF REACTIONS INVOLVING TOPOCHEMICAL CONTROL

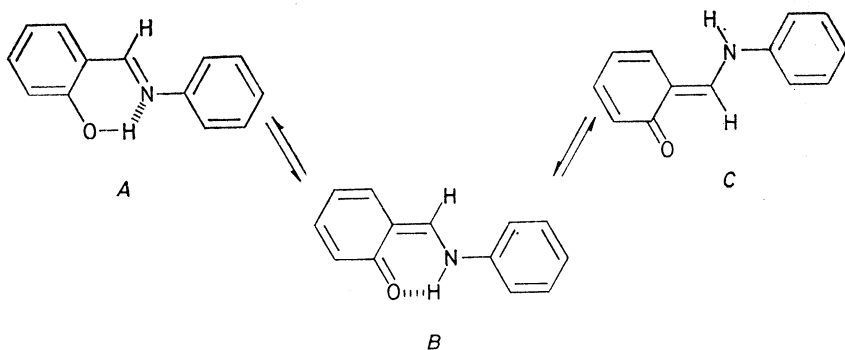
Turn now to systems which have been studied from this point of view; familiarity causes emphasis to be placed on the work done in Rehovoth.

#### (i) An apparently monomolecular process—the photochromy of anils of salicylaldehyde<sup>6b</sup>

The crystalline anils of salicylaldehydes are found to fall into two types:

	<i>Type I</i>	<i>Type II</i>
Effect of light	Reversibly coloured	Not coloured
Effect of heat	Not coloured	Reversibly coloured
Name	Photochromic	Thermochromic

In a few cases we have found anils which have two polymorphic forms, one of each type. Anils dissolved in rigid or fluid solutions are all photo-colourable with the same spectral changes as are produced by irradiation of Type I crystals. The process in the crystal can therefore be monomolecular. We have associated the photochromy with a two-step molecular rearrangement:



whereas thermochromy involves the  $A \rightleftharpoons B$  stage only.

The crystal structures determine the properties in an interesting way. In Type I crystals the molecules are non-planar and there are no close intermolecular contacts normal to the chelated ring (*Figure 1*). As a result, the activation energy for the second, isomerization, step is not very much higher than that for the free molecule. In Type II crystals, on the other hand, the molecules are planar with close (3.3 Å) normal intermolecular spacing (*Figure 2*). This not only increases the energy of the isomerization step but stabilizes the quinoid molecule *B* (by electrostatic interaction with its neighbours). This is reflected in the potential energy surface for molecules

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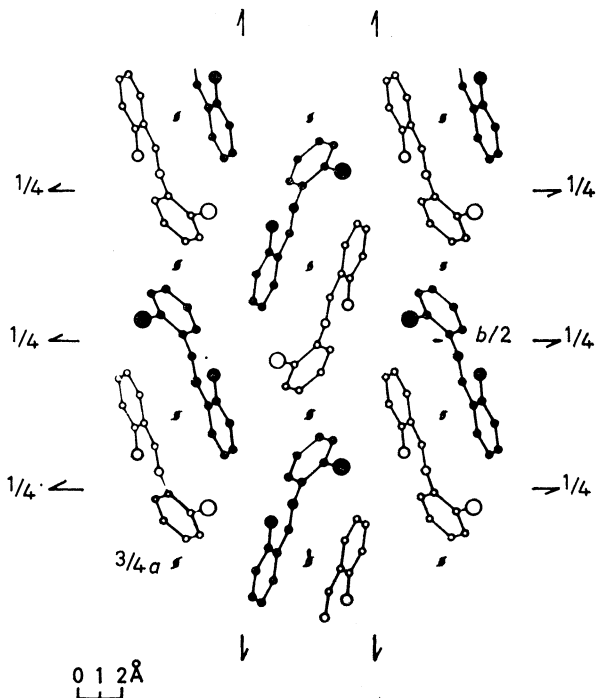


Figure 1. Packing diagram of photochromic salicylidene 2-chloroaniline seen along [001]; the marked non-planarity of the molecules is seen. (Produced by courtesy of the Editor, *J. Chem. soc.*)

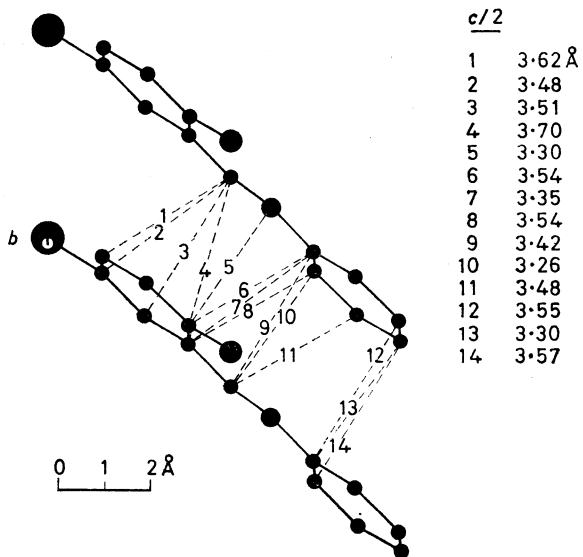
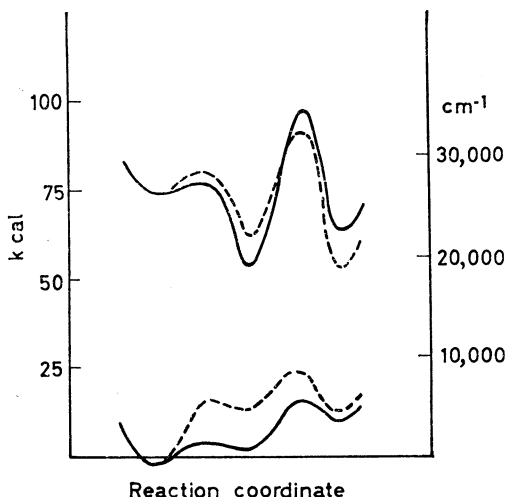


Figure 2. Partial packing diagram of thermochromic 5-chlorosalicylidene aniline seen along [100]; shown are two molecules from an infinite stack parallel to the  $b$ -axis, and contact distances between the molecules. (Produced by courtesy of the Editor, *J. Chem. soc.*)

in the two crystal types (*Figure 3*). (This figure is oversimplified since the  $B \rightleftharpoons C$  step may well involve changes in multiplicity and we have no evidence as to location of the rate-determining steps in  $B^* \rightarrow C$  and  $C^* \rightarrow B$ .)

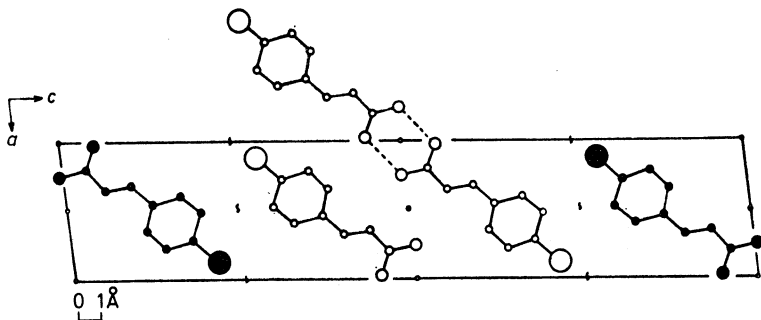


*Figure 3.* Energy diagrams for a molecule in a thermochromic (full curve) and in a photochromic (broken curve) crystal; the three minima correspond to (from left to right) the phenolic form *A*, the quinoid tautomer *B*, and the quinoid isomer *C*. (Produced by courtesy of the Editor, *J. Phys. Chem.*)

## (ii) A bimolecular process—the photo-reactions of cinnamic acids

The photochemical dimerization of *trans*-cinnamic acids in the solid-state has been long known;<sup>7</sup> it has even been pointed out that the cyclobutane derivatives obtained have symmetry elements (mirror planes and centres of symmetry) which probably arise from the arrangements of the monomer molecules in the parent lattices<sup>2</sup>.

These ideas have been confirmed and expanded<sup>6c</sup>. It has been shown that the question of whether or not reaction occurs, and the molecular structures of products when formed, are determined completely by the lattice, and in particular by the relative geometries of nearest neighbour molecules.



*Figure 4.* Packing diagram of *p*-chloro-*trans*-cinnamic acid ( $\beta$ -type structure) seen along  $[010]$ ; shortest approach between  $>C=C<$  group occurs parallel to the *b*-axis ( $3.87 \text{ \AA}$ ); all other contacts are longer than  $5 \text{ \AA}$  (Produced by courtesy of the Editor, *J. Chem. soc.* after A. L. Patterson.)

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Cinnamic acids are found to crystallize in three types of structures; of these the  $\alpha$ -type, in the structures solved, have the double bonds of adjacent molecules about 3.6 Å apart and related by a centre of symmetry. These give rise to  $\alpha$ -truxillic acids, which are centric. The  $\beta$ -type crystals again have nearest double bonds about 3.6 Å apart, but the molecules involved lie parallel; these are converted by light into  $\beta$ -truxinic acids, which have mirror symmetry (Figure 4). The third type,  $\gamma$ , have the nearest double bonds 4.7–5.1 Å apart; these are photochemically stable (Figure 5).

We see that the symmetry of the monomers in the parent crystal is maintained in the dimer; that crystal constraint is sufficient for the monomer to retain its "trans" configuration on incorporation into the dimer; and that some factor related to distance between the monomer units determines whether or not reaction occurs.

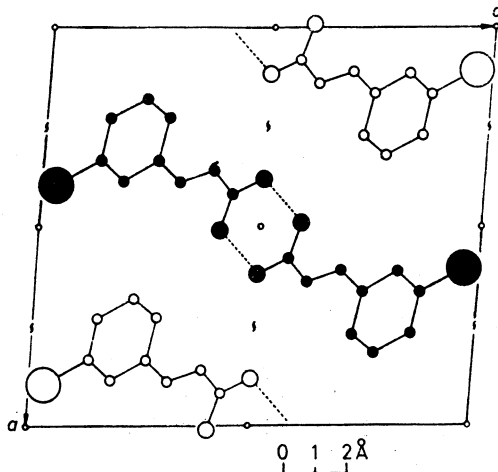
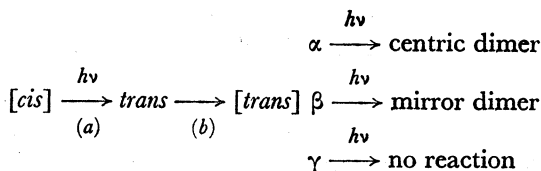


Figure 5. Packing diagram of *m*-chloro-*trans*-cinnamic acid ( $\gamma$ -type structure) seen along [010]; the shortest approach between  $>C=C<$  groups occurs parallel to the *b*-axis (4.93 Å). (Produced by courtesy of the Editor, *J. Chem. soc.*)

These studies were extended to the *cis*-acids<sup>8d</sup>. Here the reactions are more complicated and can be interpreted as follows:



The square brackets denote a material in its own crystal lattice. There is evidence that *trans* molecule formation (a) proceeds under control of the *cis*-lattice. Subsequently these molecules crystallize in their most stable lattice(s), which determine(s) the course of further reaction. The overall reaction stops at the *cis*  $\rightarrow$  *trans* isomerization step only when (b) gives a  $\gamma$ -type lattice.

The manner in which lattice control of step (a) is achieved is not immediately obvious. It appears that for isomerization to occur about the double bond a second double bond must be within "interacting distance" *i.e.* not further away than 4.3–4.4 Å. This led to the suggestion that (a) involves movement of adjacent molecules toward one another, thus freeing one or both of the molecules from lattice constraint and allowing of isomerization. One can describe this as a bimolecular reaction *via* a "pseudo-dimer", possibly a limiting form of the "excited-state dimers" postulated by Förster and Kasper<sup>8</sup>.

Interesting consequences of topochemical control in this series are that there are crystalline *cis*-acids which are light stable, and crystalline *trans*-acid which isomerize to the *cis*, even though the *trans*-molecule is thermodynamically the more stable. Further, the isomerization reactions, unlike their solution counterparts, in general go only in one direction leading to near-complete conversion.

### (iii) Other reactions

The above two systems have been dealt with in some detail since they illustrate the particular philosophy which the author wishes to emphasize here. However, this paper would be incomplete without at least passing mention to some of the other very interesting reactions which occur in the solid state.

One of these, which is being vigorously investigated in a number of laboratories, is polymerization. Here, the rôle played by the crystal structure has been the subject of some controversy<sup>9</sup>. Certainly in many cases topochemical control is not maintained throughout the period of chain growth. It is our belief that such control exists at least at the initiation stage in the case of solid-state photochemical polymerization of vinyl monomers. However, this subject deserves and requires more time than we have made available to it here.

Let us but mention a few of the many reactions awaiting thorough study. Heterogeneous reactions such as the photochemical one between gaseous oxygen and crystals of unsaturated materials have been largely ignored. More attention has been received by light-induced charge transport through organic crystals in an applied electric field, *i.e.* to photoconductivity<sup>10</sup>. Much interesting information is sure to be obtained from studies of redox reactions at the surface of such crystals<sup>11</sup>. The data would be of considerable significance in their application to biochemical systems where aggregates play so important a rôle.

A variety of intermolecular oxygen transfer reactions, some intermolecular ones, and decomposition reactions are known to occur photochemically in the crystal<sup>12</sup>. There remains, undoubtedly, a wealth of chemistry to be explored and developed.

## THE BASIS OF TOPOCHEMICAL CONTROL OF SOLID-STATE PHOTOCHEMICAL REACTIONS

In the examples cited ((i) and (ii) above) the interpretation of the influence of the crystal structure have been conventional ones. We have argued that

each molecule in a crystal makes certain contacts with its neighbours and is subjected to restraints by them. Thus, in a particular structure, different displacements will be more or less restrained by intermolecular forces; further, a particular displacement will suffer different restraints in different structures. When various reaction paths are available the one which least disrupts the lattice will be favoured.

A second, "spectroscopic", approach to the problem is available, but as yet has been little used. The structure-sensitive resonance coupling between molecules causes splitting of the energy levels and allows of transfer of energy between the interacting molecules. As a result, changes in structure can be associated with profound changes in absorption and luminescence spectra, in relative populations of different excited states, and in the time spent by the excitation on a particular molecule. These phenomena are obviously intimately related to the photochemical properties of the system.

A thorough treatment of topochemical control of solid-state photochemical reactions would have to combine the two approaches. Considering, for example, photodimerization (*ii* above): the observation that it is nearest-neighbour molecules which combine, and that they do so with a minimum of movement, is a direct ratification of the "steric" type of argument. It is not as obvious, however, what is the basic reason for the light stability of the ( $\gamma$ )-*trans*-cinnamic acids. It may be that the movement of molecules, initially 4.6 Å apart, to bonding distances involves too much disruption of the lattice. It may be that the field drawing the monomer molecules together drops rapidly with distance. Possibly the dimerization reaction requires excitation of both reacting molecules and therefore necessitates a crystal structure with a reasonable compromise between long excitation times and rapid excitation migration. A number of such interpretations come to mind; it requires careful thought and experimentation to enable choice between them.

### SOME ADVANTAGES OF SOLID-STATE REACTIONS

Apart from their more theoretical interest to the solid-state chemist and photochemist, reactions of the sort discussed here are frequently very promising for preparative purposes. In many cases the product is formed in high yield and in even higher chemical and stereochemical purity.

A further aspect of interest is that the complex organic molecules which most interest the photochemist frequently pack in crystal structures of low symmetry. As a result, many of these crystals have highly anisotropic absorption properties. By use of polarized light one may then be able to specifically induce a desired transition, with the possibility of cleaner reactions. This is particularly advantageous in cases of strongly overlapped absorption bands.

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- <sup>11</sup> For example, M. Pope and H. Kallmann. Previous reference, p. 83.
- <sup>12</sup> For example, P. Coppens and G. M. J. Schmidt "The photo-reaction of crystalline *para*-nitrophenol"; *Acta Cryst.* In press.