ELECTRON MICROSCOPIC IDENTIFICATION AND CHEMICAL CONSEQUENCES OF EXTENDED DEFECTS IN ORGANIC MOLECULAR CRYSTALS

G. Parkinson, Edward Davies

To cite this version:


HAL Id: jpa-00217355
https://hal.archives-ouvertes.fr/jpa-00217355
Submitted on 1 Jan 1978

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
ELECTRON MICROSCOPIC IDENTIFICATION
AND CHEMICAL CONSEQUENCES OF EXTENDED DEFECTS
IN ORGANIC MOLECULAR CRYSTALS

G. M. PARKINSON (*)

University of Oxford, Department of Metallurgy and Science of Materials,
Parks Road, Oxford OX1 3PH, England

Abstract. — The course of organic reactions in the solid state may be successfully predicted in many cases by the principle of topochemical preformation, which states that reactions in crystals proceed with a minimum of atomic and molecular movement. However, well defined exceptions to this rule, notably in the substituted anthracenes, have pointed to the involvement of extended defects in such reactions. Transmission electron microscopy has been used to characterize linear and planar faults in organic crystals and has also shed light on phase transitions in these materials. The stress-induced transformation undergone by anthracene is described in detail and the concept of a new family of crystal defects, made feasible by the nature of packing between organic molecules, is outlined.

1. Introduction. — In recent years scientists from many disciplines have become increasingly aware of the unique opportunities afforded by a study of the organic solid state. Particularly in the crystalline phase, organic molecules are held in precisely known locations and conformations, as determined by x-ray crystallography, and thus any consequent reactions of these molecules and the nature of the concomitant changes in intermolecular forces may be studied to a degree of precision not accessible in the fluid or amorphous phases. By studying ultra-pure single crystals of organic materials fundamental understandings have been gained concerning the interactions of photons with molecules, together with the possible delocalization of this energy throughout a crystal as an exciton, followed by its subsequent trapping: the identity of the trapping site and the locus of an ensuing photochemical reaction become crucial questions, as will be seen later.

Cogent studies of a wide range of materials have led to the formulation of the principle that for many organic crystals which undergo solid state reactions, the nature of the product (if any) is determined by the original monomer lattice. This powerful idea leads to the concept of crystal engineering by which, in principle, one may design an arrangement of reactant molecules within a crystal structure such that the lattice control would ensure that the desired product was obtained. This opens up the exciting possibility of the facile preparation of compounds which are very difficult or even impossible to obtain by conventional solution techniques.

However, the main emphasis of this talk is to be on materials which are exceptions to the rule of monomer lattice control because a fundamental investigation of such materials is likely to give an insight into several of the basic features of reactions in the organic solid state. It is in these materials that the reaction is dominated by imperfections in the crystal, rather than by the perfect lattice.

2. Principles of organic solid state chemistry. — Thomas [1] has pointed to the analogical value of considering processes and defect structures in inorganic solids as a means of enriching our understanding...
of the organic solid state. The observation, mentioned earlier, that certain crystalline organic compounds are found to react in a manner suggestive that the process is dependent on the geometry of the disposition of reactive groups in the crystal lattice, was first noted with inorganic reactions and has been designated by Kohlschütter [2] as topochemical.

Two powerful criteria are indicative of whether a reaction may be so described: firstly, if the reactivity of chemically similar crystalline substances is unrelated to the relative reactivity of these substances in the fluid state (an especially convincing analogue of this is encountered when different crystalline modifications of the same reagent are found to exhibit widely different reactivities); secondly, if the product obtained from the solid state reaction of a molecule is chemically distinct from the reaction product obtained in the fluid state, or else, within a series of related solid reactants, is dependent upon properties of the corresponding crystal structures. A most striking example of this is given by the now classic studies of Schmidt and his colleagues [3] on the photodimerization of cinnamic acid derivatives.

The reactions of the cinnamic acids are examples of \((2 + 2)\) photocyclo-addition, a widely studied reaction in a large number of organic crystals embracing a variety of molecular species. All the crystalline compounds within this family studied to date may be classified in terms of only three arrangements of molecular packing, and the photochemical behaviour of each reagent is found to be determined by which structure type is adopted [4]. This is illustrated schematically for \(\alpha\), \(\beta\)-unsaturated carboxylic acids in figure 1. Hydrogen bonding occurs between molecules of these acids forming nearly planar pairs across centres of symmetry. These pairs stack parallel to one another and classification of the three structure types may be based on the angles made between the normals to the molecular planes and the stack axis; this distinction corresponds to a difference in separation between equivalent points on the molecules.

Translationally related molecules in \(\beta\)-type structures experience a large degree of overlap, their separation being the short lattice repeat distance of 3.8 to 4.2 Å, this also being the double bond contact distance. There is offset between adjacent molecules in the \(\gamma\)-type structure resulting in the large double bond contact distance of 4.8 to 5.2 Å. This offset is so large in the \(\alpha\)-type lattice that overlap occurs between the double bond of the molecule in one stack and that of a centrically related molecule in an adjacent stack; thus, although the distance between equivalent double bonds is \(\approx 5.5\) Å, that between the overlapping double bonds is about 4 Å. Those structures in which there is overlap of closely-spaced double bonds give photodimers, and the stereochemistry of the product molecule is determined by the geometric arrangement of the overlapped molecules. It was as a rationalization of these and other experimental observations that Schmidt and his co-workers [5] formulated the topochemical postulate, which states that reactions in crystals proceed with a minimum of atomic and molecular movement, and are thus determined by the structures of the starting crystals. A number of other systems behave in ways similar to that of the cinnamic acids, for example the chalcones, and several butadienedicarboxylic acids and their derivatives (e.g. cis, cis muconic acid).

The effect of molecular packing on reactivity is clearly demonstrated in lattice controlled polymerization where it leads to the formation of polymers of extended conformation. Wegner [6] and colleagues have demonstrated the topotactic photo- and thermal polymerization of crystalline monomers containing conjugated triple bonds, notably the 1,3-diacylenes. The term topotactic has been introduced by Lotgering [7] to include all chemical solid state reactions that lead to a material with crystal orientations correlated with the crystal orientation of the reagent; again, there are several instances of this phenomenon in inorganic systems, for example the oxidation of magnetic \(\text{Fe}_3\text{O}_4\) to \(\gamma\)-\(\text{Fe}_2\text{O}_3\), which has been shown to proceed by the addition of oxygen layers to the surface of the crystal with a migration of the cations to their new lattice positions. The distinction between topochemical and topotactic phenomena is an important one to make as they have sometimes erroneously been taken to be synonymous; the review by Thomas [1] deals with this topic in detail.

![Fig. 1.](image-url) The three types of molecular packing found in \(\alpha\), \(\beta\)-unsaturated carboxylic acids (after Cohen, M. D. and Green, B. S., Chem. Br. 9 (1973) 400).
Turning now to a very interesting class of compounds, anthracene and its derivatives, it is found that these grow in a variety of crystal structure types, some analogous to those of the materials previously described. In substituted anthracenes, except those in which the substituents are in positions 9 or 10, solid state photodimerization is topochemically controlled, the molecules linking at their 9 and 10 positions to give dianthracenes (Fig. 2). Thus for example, 1-chloroanthracene is potentially capable of forming four distinct photodimers, all of which are produced in solution, whereas in the solid state only one photodimer is formed, probably the one expected on the basis of the crystal structure [8], when reaction takes place with crystals of the $\alpha$-type. This material is dimorphic and the second phase is of $\gamma$-type which is found to be light stable.

However, in the case of anthracene itself and many of its 9-substituted derivatives, it is found that the topochemical idea is contravened. For anthracene there is only one possible dianthracene; for the 9-substituted monomers there are two possible structures for the dimer molecule namely the mirror symmetric (head to head) and centrosymmetric (head to tail) ones. In solution only the latter are formed, suggesting that steric repulsion between opposed substituents makes the head to head approach energetically unfavourable. Crystals of the $\alpha$-type (e.g. 9-methyl anthracene) yield, as expected, the same centrosymmetric dimer as do solutions. Those of the $\beta$-type, however, either do not react, or, if they do, give the wrong dimer, i.e. the centrosymmetric one (e.g. 9-cyano anthracene). Some examples of the $\gamma$-type which the topochemical principle predicts to be light-stable, e.g. anthracene, do, in fact, photodimerize in the crystalline state. It has been suggested [9, 10] that those reactions which give non-topochemical products may occur preferentially at defect sites in the crystal. Defects are known to exist in all organic molecular crystals so far investigated [11, 12] and so the implications of this idea are dealt with in detail.

3. Consequences of structural faults on chemical reactivity. — The early application of topographic and etching techniques to organic crystals soon revealed that extended defects and, in particular, dislocations play an important role in determining sites of preferential attack for photoinduced reactions within the solid state. The photoreactivity of many solids is now better understood as a result of the elucidation of the nature of the structural imperfections which they contain, and it is helpful to select a number of illustrative examples of these. However, before dealing with specific compounds, it is appropriate to outline methods of characterizing extended defects in solids.

It is now well established that a diverse range of solid-state phenomena of chemical interest, for example, exciton and charge-carrier trapping, fluorescence, self-diffusion, photochemical and thermal rearrangements, and crystal dissolution, can be governed or modified by the presence of dislocations, and this modification has been harnessed to a greater or lesser extent as a means of revealing the presence and nature of such defects. For example, the electrical studies of anthracene carried out by Helfrich and Lipsett [13] and the novel decoration of dislocations inacenaphthylene by Cohen et al. [14] (a process analogous with the classic studies of Mitchell [15] on ionic solids), to mention but two instances.

However, the most precise methods of characterizing extended faults rely on the manner in which the presence of such defects in a crystal perturb the diffraction of radiation by the otherwise perfect lattice. One method to utilise this, x-ray topography, has met with some success, although its major limitation is that it is of inadequate resolution to cope with the identification of individual dislocations present in small specimens. Thus, we have turned to the most powerful direct technique, transmission electron microscopy, which has afforded valuable information (principally from diffraction-contrast techniques, see Hirsch et al. [16]) on the microstructure of metallic and many inorganic solids. Unfortunately, the extreme sensitivity of organic crystals to electron beam damage renders difficult the application of this technique to these types of materials. However, electron microscopy has been used recently with some success as a result of the minimisation of the rate of this damage by experimental techniques and by selecting model systems [17, 18]. Thus, the characterization of slip planes and Burgers vectors of dislocations in p-terphenyl and substituted anthracenes have been carried out [19, 20], and more recently many of the slip systems in anthracene itself have been precisely characterized, as described briefly below.

Figure 3a shows a typical array of basal dislocations in anthracene, imaged in bright field; figure 3b shows the same area after slightly tilting the specimen, and imaging the area (in dark field) with the $g=(202)$ reflection. The dislocation image AB is not visible.
in figure 3b and this is known as a disappearance condition, expressed mathematically as \( g \cdot b = 0 \). A similar disappearance with \( g = (201) \) was also established, thus unambiguously identifying the Burgers vector as [010]. From the orientation of the crystal and the length of the dislocation line we know that this is a basal dislocation, and hence the slip system is fully described as (001)[010]. This has been found to be the most common dislocation in anthracene. The other widely occurring basal dislocation has been found to be (001)[100] by similar methods. Most interestingly, from a photochemical point of view, several families of non-basal dislocations have also been observed in anthracene. Figure 4 shows examples of such dislocations: some are distributed apparently randomly throughout the solid whereas others are quite clearly aligned on crystallographic planes. Deserving of particular mention in this respect is the hitherto unsuspected slip system (103)[010]. The role of dislocations per se in the photodimerization of anthracene (as earlier suggested [10]) has very recently been somewhat overshadowed by the discovery of a new phase of this material, the very special properties of which will be discussed later, when we shall return to consider in more detail dislocations in anthracene.

A related compound, 1,8-dichloro-9-methyl anthracene, undergoes rather rapid photodimerization in the crystalline state to yield the trans-dimer. A rational understanding of this, when the space symmetry of the ideal structure is so inconducive for the production of this dimer (Fig. 5a) (on the basis of the topochemical principle) except in terms of the influence
of feasible slip systems, is difficult to conceive [21].
In particular, partial slip with Burgers vector [010]
seems particularly favourable — see, for example,
figure 5b, which shows that the (102) \( \frac{1}{2} [010] \) system
brings neighbouring molecules into a registry favourable
for the production of trans-dimer. Similarly, it is very likely, as has been discussed fully else-
where [22], that the presence of stacking faults on (221)
planes of crystalline 9-cyanoanthracene can also
account for the production of the centrosymmetric
photodimer in this solid, rather than the mirror-
symmetric one topochemically predicted on the basis
of the idealized crystal structure.

Turning to heterogeneous reactions, it is found
that for both trans-stilbene and diethylstilboestrol
the gas-solid ozonolysis reaction, to yield, respecti-
vely benzaldehyde and parahydroxy propiophenone,
takes place preferentially at structural imperfections
in the solid, there being strong correlations between
alignments of dislocation etch pits and alignments
of accumulated products on the faces of the partially
oxidized solids [23]. The build up of product within
the parent matrix expedites the production of more
dislocations which in turn function as further sites
of preferred attack. Very considerable strain is
inferred to be imposed upon the structure by the
product accumulation as monitored by the fact that
it succeeds in activating slip systems which are other-
wise difficult to stimulate.

One fascinating aspect of organic molecular crystals
is the profusion of polymorphic phases which they
display; the influence of crystal defects on their
production and their subsequent chemical role deserve
detailed study (Fig. 6).

Largely because of the greater molecular and
conformational complexities involved, the generation
of a new polymorph within an organic crystal can be
appreciably more complicated than a comparable
process in metallic and mineralogical systems; more-
over, the total range of polymorphs involved is gene-
rally much broader. Nonetheless, such a situation
may be brought about by the application of external
stress, in a manner analogous to well-known metallic
transitions. The conversion of the orthorhombic
form of polyethylene on straining to the monoclinic
structure, for example, has been recognized to bear
all the symptoms of a stress-induced martensitic trans-
formation [24]. One fascinating aspect of this system
is that a single crystal, in its orthorhombic form,
may be partially converted to a biphasic material
in which the monoclinic structure occurs in two of
the four sectors of the flat crystal [25]. This presents
direct experimental proof of the so-called hybrid-
crystals which have been invoked [26, 27] to assist
in the interpretation of hysteresis in crystalline phase
transformations. Also, a new phase which is produced
by a stress-induced transformation lies in a well-
deﬁned orientational relation with that phase from
which it was produced. For example, studies of the
stress-induced martensitic transformation in 1,8
dichloro-10-methyl anthracene by transmission elec-
tron microscopy [28] have revealed a precise example
of such a situation (Fig. 7).

The introduction of dislocation theory into organic
solid-state chemistry has had, inter alia, one quite
far-reaching consequence in that it now seems possible
to explain on this basis complicated topotactic
relations exemplified by the perchlorate salt of the
cation 5-methyl-1-thia-5-azacyclooctane 1-oxide. Paul
and Go [29] have reported that this material under-
goes a single-crystal \( \Rightarrow \) single-crystal transformation,
with complete retention of morphological integrity,
between 3 °C and room temperature. It appears as
if ring inversion and rotation is required of one half
of the total number of cations in each row and each

**FIG. 6.** (a) Domains of the low-temperature form of pyrene resulting from the cooling of the sample to 110 K [36]. (b) An array of planar faults in one polymorph of 1,8-dichloro-9-methyl anthra-
cene. The associated diffraction pattern (see insert) indicates that these are microtwins \{100\} [37] (courtesy W. Jones).
column of the modification stable at room temperature to effect the transformation as the temperature is lowered (Fig. 8a). We have proposed [30], however, that it is possible to offer a simple mechanism for the facile interconversion of this rather complicated cyclooctane derivative based on the notion of cooperative shear involving the successive passage of partial dislocations on recurrent crystallographic planes (Fig. 8b).

Through a familiarity with phase transitions in other organic crystals (see above) it was found that this transformation is topotactic: an exact knowledge of the mutual crystallographic orientations led to the complete triclinic unit cell parameters, the space group being P1. With the aid of accurate space-filling models and following the ideas of close packing outlined by Kitaigorodskii [33], a trial structure was proposed for packing the molecules within this unit cell. Subsequent atom-atom potential calculations by Ramdas [32] have provided inexpugnable evidence for the reality of this structure, the loss in cohesive energy as a result of the transition being less than 10 kJ mole⁻¹ (cf. the total cohesive energy of anthracene ∼ 180 kJ mole⁻¹). The change in the unit cells is shown in figure 10. The topotactic relationship between the crystal structure of anthracene 1 (P2₁/a) and anthracene 2 (P1) is quite special because its nature enables the growth of one within the other in such a way that for every interplanar spacing within one there is an identical, correctly oriented spacing within the other; accordingly, coherent intergrowths between the two materials are quite feasible with very little or no strain involved (computations of interfacial energies between the two phases are currently being undertaken). Thus, not only do we have an example of the hybrid crystals mentioned earlier, but the situation is such that, certainly for small quantities, the presence of anthracene 2 growing topotactically within anthracene 1 would not be detectable by conventional, spatially averaging techniques such as x-ray diffraction: it is only as a result of investigation on the fine scale available to electron diffraction and microscopy that its existence has been revealed.

Further investigations in the electron microscope revealed a dramatic difference in the photochemical reactivity of the two phases. Previous investigations [31] had shown the chemical behaviour of anthracene to be very dependent upon sample purity and growth technique. Very thin crystals (approx. 200 nm thick, suitable for the T.E.M.) grown from the vapour from carefully purified material were found to photo-
Changes in diffraction patterns and chemical reactivity as a result of inducing the transformation anthracene 1 → anthracene 2, by compressing only one half of a single crystal of anthracene 1. (a) The (101) zone-axis of anthracene 1 (uncompressed half), (b) The (001) zone-axis of anthracene 2 brought into diffraction as a result of compressing the other half of the anthracene 1 crystal after photoreaction showing monomer and dimer reflections, (c) No detectable change produced by irradiation with U.V. light (bright-field image), (d) Topotactic crystallites of di-para anthracene rapidly form within the anthracene 2 crystal as a result of identical U.V. irradiation, images in the dark-field mode.

dimerize very slowly. Compression of such a sample to induce the phase transition, however, produced a very reactive crystal. Figure 9 shows micrographs of a single vapour-grown crystal of anthracene, only half of which has been transformed to anthracene 2 by compression. Irradiation of anthracene 2 (identified by its diffraction patterns) with 365 nm U.V. light produced extensive reaction to topotactic crystallites of dipara-anthracene within 5 hours. The uncompressed half (anthracene 1) remained apparently unaffected by identical irradiation for a prolonged period (150 hours). The photodimerization in anthracene 2 is apparently occurring homogeneously (Fig. 9d) and so we turn to the structure of a perfect crystal of this material, rather than to defects in it for an understanding of the increased reactivity.

Figure 11 shows space-filling models and projections of the unit cells and certain planes in anthracene 1 and anthracene 2. Inspection of the unit cell of anthracene 1 shows that the contacts between the molecule at (\( \frac{1}{2}, \frac{1}{2}, 0 \)) and the molecules at (0, 0, 0), (0, 1, 0), (1, 0, 0) and (1, 1, 0) are essentially similar, whereas in anthracene 2 the contacts between the molecule approximately at (\( \frac{1}{2}, \frac{1}{2}, 0 \)) and the ones at (0, 0, 0) and (1, 1, 0) are fundamentally different from
Thus, a cogent picture is beginning to emerge, enlarging our understanding of the solid state chemistry of anthracene, but also broadening our view of solid state chemical processes in general; the concept of coherent intergrowths of organic polymorphs providing appropriate intermolecular contacts for feasible reactions, either within individual phases or at interfaces, is likely to prove fruitful in the investigation of other anomalous crystalline materials. In this context, a brief mention of a related idea which may act as a unifying concept between crystal defects and polymorphs, is appropriate.

4. «Molecular defects»: a new family of crystal imperfections. — With the knowledge of the topotactic relation between the two phases of anthracene described above, on the basis of considerations akin to those undertaken concerning the cyclo-octane salt [30], it is possible to outline a feasible mechanistic route for this stress induced transformation. Inspection of figures 11c and d reveals that the change may be effected by partial slip of all the molecules of the type (0, 1, 0), (1, 2, 0), etc. with respect to those of the type (0, 0, 0), (1, 1, 0), etc. Although this process occurs throughout the bulk of the crystal, the slip between individual molecules is occurring on non-rational planes in non-crystallographic directions. Rather than try to express this motion in terms of the conventional Burgers vector notation, a far clearer understanding of the processes involved is gained if we turn away from the concept of the crystal lattice towards features of the molecules themselves: we thus find that the change from 2 : 3 to 3 : 3 type contacts is readily expressed in terms of a displacement $L/3$ $(L.M)$ which represents a movement of one molecule by one third along its $L$-axis across the plane of the other molecule $(L.M)$ (see Fig. 2). Atom-atom potential calculations have shown that the cohesive energies before and after such slip are very similar [32] which is indicative of the stability of the 3 : 3 type contact. We have, then, strong support for this concept of crystal defects (which are quite distinct from lattice defects), whereby polymorphic transformations and subtle changes in intermolecular contacts may be effected.

Further, direct, evidence has come from transmission electron microscopy studies, for example the directly related chemical transformation of di-para anthracene to anthracene which is induced by electron irradiation [31, 34]. At low temperatures, this transition commences by converting D.P.A. to the triclinic anthracene 2; further irradiation effects partial conversion of the (metastable) anthracene 2 crystals so produced to the monoclinic anthracene 1. This process is observed as occurring at the interface of moving boundaries along [110] and [110] directions (Fig. 12) in agreement with the mechanism mentioned above (concerning the reverse transformation), of crystal defects moving in these directions,

Fig. 11. — (a) and (b) Photographs of Van der Waals models of the contents of unit cells of anthracene 1 and anthracene 2, respectively. Computer drawings of the molecular packing (c) within (110) and (110) planes of anthracene 1 and (110) planes of anthracene 2 and (d) within (110) planes of anthracene 2.

those between the same molecule and those at (0, 1, 0) and (1, 0, 0). These different contacts are clearly illustrated in figures 11c and d. Considering the three hydrogen atoms of major importance in the packing between the corner and central molecules: $H_1$, $H_8$ and $H_9$ (see Fig. 2), figure 11c shows that two of these projections fit approximately into three of the hollows at the centre of each benzene ring; similarly, in figure 11d, three of these hydrogens fit approximately in to three hollows. A convenient terminology logically ensues, and these contacts are referred to as 2 : 3 and 3 : 3 type contacts respectively. Within this terminology, anthracene 1 (Fig. 11a) can be considered to consist of (110) and (110) planes all containing 2 : 3 type contacts; anthracene 2 (Fig. 11b) consisting of 2 : 3 contacts within (110) planes, and 3 : 3 contacts within (110) planes. It is the introduction of these 3 : 3 contacts in anthracene 2 (and their absence in anthracene 1) which is understood to account for their fundamental differences in chemical reactivity. Calculations on both structures show that the C9 ... C9' distance is 4.6 Å for 2 : 3 contacts and 3.9 Å for 3 : 3 contacts. This latter separation is well within that normally covered by the topochemical principle and is clearly pivotal in enabling the solid state photodimerization to occur; full details of this process are shortly to be described elsewhere [32].
although the rapidity of the transformation in the T.E.M. does not permit detailed characterization at this stage. However, independent evidence for crystal defects with molecular vector of the type $L/3$ in gently deformed crystals of anthracene 1, as detected by analysis of the diffracted intensities from these defects, is beginning to accumulate [31].

These, and other, crystal defects have no direct analogue in simple ionic and metallic systems where the repeat unit is the generally spherical atom or ion: the possibility of this new type of defect occurring is a direct consequence of the increased degrees of freedom (three translational, three rotational) available to a molecule over those of a spherical body (three translational); nonetheless, the potential extension of these ideas to the more complex ionic, particularly mineralogical, materials where repeat units are no longer spherical (e.g. octahedral) bears careful consideration. The full potential of crystal defects in organic solids where use is made of the rotational (molecular disclinations) and combined rotational and translational (molecular dispirations) degrees of freedom will be presented in full elsewhere [35]. Such considerations include standard crystallographic analyses (e.g. for anthracene six independent crystal structures may be postulated on the basis of 2 : 3 and 3 : 3 type contacts alone, for example, conversion of all the contacts to 3 : 3 type yields a pseudo-orthorhombic structure), but perhaps more far-reaching effects are to be felt in the biological realm. Because we have shied our dependence on the crystal lattice (the precision of which can become overly restrictive) in our description of these molecular defects we can extend their scope to the paracrystalline arrays which are of such paramount importance in innumerable living processes.

5. Conclusion. — This brief study is of necessity incomplete firstly because of the large areas of immense interest which it has not been feasible to include and secondly because many of the experimental observations and concepts sketched in the latter half are so recent as to be still incompletely understood even within their own framework. Partly as a result of the application of T.E.M. to this area, our understanding of the organic solid state is increasing rapidly in all directions; only time will assess the full implications of what is at present but seen as through a glass, darkly.

Acknowledgments. — It is a great pleasure to acknowledge the help and inspiration of many friends and colleagues, in particular Professor J. M. Thomas, F. R. S., Drs. W. Jones, S. Ramdas and J. O. Williams of the University College of Wales, Aberystwyth, and Professor Sir Peter Hirsch, F. R. S., Dr. M. J. Goringe and Mr. W. L. Rees of the University of Oxford.

References