ORGANIC REACTIONS IN THE SOLID STATE: ACCIDENT AND DESIGN

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Abstract - The factors that govern the nature and rate of
thermally-stimulated and photochemical reactions in organic
molecular crystals are reviewed. So far as thermal reac-
tions are concerned, reference is made to the general kinetic
patterns that prevail, to unusual dehydration and gas-solid
reactions, and to certain single-crystal ⇄ single-crystal
phase-transitions involving changes in the conformation of
molecular cations. The particular advantages of using sol-
vates and intercalates are also discussed. Radiation-induced
reactions are reviewed within the framework of topochemistry
and reference is made to temperature-independent polymeriza-
tions at cryogenic extremes, to (2+2) photopolymerizations at
room temperature, to the reactions of derivatives of cinnamic
acids, of poly-ynes (including diacetylenes), and of naphtha-
quinones. Recent progress in crystal engineering, assessing
the role of structural imperfections, site-selective photo-
chemistry, understanding the occurrence of stress-induced
reactions, as well as in computing the structure of reactive
crystals and the fine structure of imperfections, are also
reviewed. Future prospects, especially those relating to the
control of solid-state reactivity and the design of certain
desired materials, are outlined.

INTRODUCTION

For the physical chemist, much of the fascination of organic molecular crys-
tals arises because crystallographic and environmental factors hold sway.
Frequently, the intrinsic reactivity of a molecule is of secondary import-
ance - sometimes it is of no consequence - compared with factors such as the
crystal space group (and, therefore, site symmetry), nearest neighbour sep-
aration and other so-called topochemical considerations which we shall dis-
cuss below. It is appropriate to recall the compelling experimental
evidence upon which the veracity of the above statements is based (1-6).
(i)   The products of an organic solid-state reaction are almost invariably
fewer in number than, and frequently very different from, those produced
from the same starting materials in fluid phases. In other words, a given
progenitor yields different progeny depending upon whether the reaction
occurs in the solid or in solution.
(ii)   Some reactions proceed much more rapidly in the solid than in the
liquid state. Indeed there are several instances where a molecule, under
u.v. irradiation, suffers mere isomerization in the melt but freely reacts,
intermolecularly, in the solid.
(iii)   Organic molecular crystals generally display a rich diversity of
polymorphs (e.g. there are at least five forms of the bis-phenylurethan
derivative of diacetylene) yet only a few (in the case of the above diacet-
ylene only one) of these polymorphs are photopolymerizable, at least in a
topochemical sense. Likewise distyrylpyrazine is polymorphic, but only one
crystalline form yields a highly crystalline photopolymer.
(iv)   There are instances where two or more different polymorphs react to
yield (with 100 per cent efficiency) distinctive products, one polymorph

giving one product, the other another.

Striking illustrations of some of the processes encompassed by (i) to (iv) above are shown in figures 1 and 2.   Full details of the differences between the solid-state and solution behaviour of the three categories of monomers shown in figure 1 have been presented elsewhere (see Thomas, Morsi and Desvergne (6) and references therein).   The remarkably facile methyl-transfer process (7) involved in the solid-state conversion of the neutral methyl p-dimethylamino-benzenesulphonate to the corresponding zwitterion (figure 2) has been the subject of an illuminating semi-empirical M.O. cal-culation (8).   It was concluded that this reaction, which proceeds much more freely in the solid than in solution, entails a two-step mechanism involving a molecular ion-pair.   Enhancement of rate in the crystalline state is attributable to an entropic factor arising from the favourable orientation of neighbouring molecules.
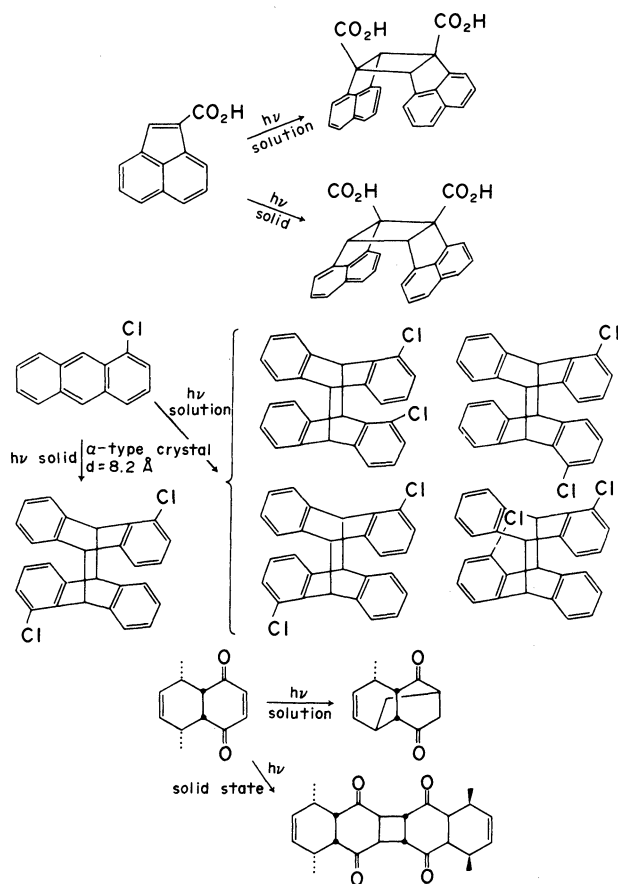

Fig. 1.

Examples where a given progenitor yields different progeny depending upon the phase in which the reaction proceeds (see (6) and references therein).
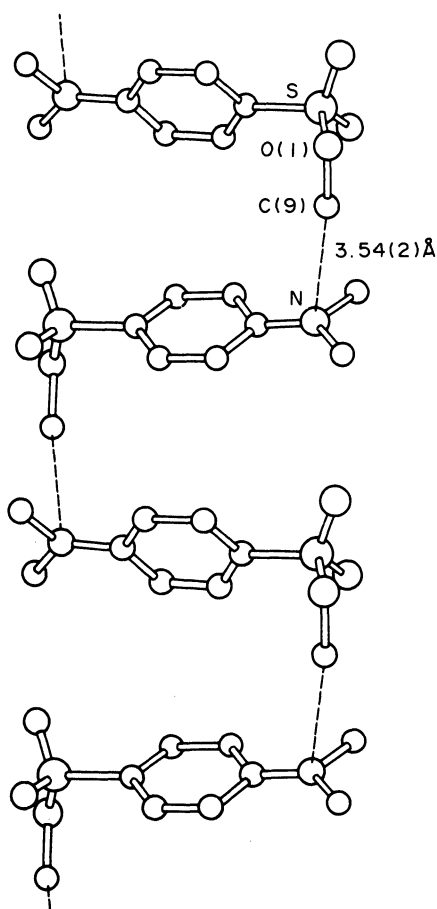
Fig. 2.

Facile methyl-transfer process in the solid state (7).

Apart from their intrinsic academic interest, organic reactions in the solid state are attractive for a variety of reasons. They are useful as means of synthesizing a host of novel products which may be very difficult, if not impossible, to prepare by other means. Thus, as is elaborated later, chiral molecules may be efficiently generated from achiral precursors; in addition, several regiospecific and stereospecific products may be efficiently prepared; materials of considerable practical potential (many of which are relevant in the context of prebiotic chemistry) such as pleochroic, electrically conducting and highly anisotropic polymers as well as phase-holographic and photochromic compounds may also be conveniently synthesized in the organic solid state. Moreover, in a general synthetic sense the solid state chemistry of organic molecules offers broad scope especially if further adventurous use is made of the concept of crystal engineering where, by various means (1,4-6), monomeric species bearing a reactive functional group are induced to crystallize in a space-group and structure which facilitate subsequent solid-state reactivity.

So far as predicting or controlling the photo- or thermally-induced reactivity of organic molecular crystals is concerned, post-event rationalization rather than inspired prognostication looms large (as in other sub-divisions of chemistry involving reactivity, such as heterogeneous catalysis). Nevertheless, important insights are obtained from X-ray crystallography, which yields the conformational characteristics of the reacting molecules, and sets on a quantitative footing the feasible reaction pathways and the precise inter- and intra-atomic distances involved in the chemical changes. X-ray diffraction yields, in other words, vital aspects of the topochemistry of the reactive crystal. But it must not be supposed that this technique, valuable as it is, is totally adequate. To be sure, the X-ray based structure is a spatially- and time-averaged result. This can be misleading when structural defects (which, in the course of structure refinement, are 'washed out') play, as they often do, a crucial role in solid-state reactivity. When, for example, excitation energy transfer is facile within an irradiated solid, the local structural characteristics at imperfections or traces of another coexistent phase, at which the excitations are ultimately trapped, and at which chemical relaxation duly occurs, is what dictates the nature and pathway of reaction. The idealized crystalline structure, under such circumstances, may, therefore, turn out to be supererogatory. When, however, there is very little excitation energy transfer, and reaction ensues at or close to the site of absorption, the idealized structure will, indeed, control the reactivity. It is important to appreciate that the minute traces of a coexistent phase which escapes detection by X-ray diffraction may often prove to be the locus of photochemical or thermal reaction. Another disadvantage, fortunately not in general a serious one, associated with X-ray diffraction is that it is not a suitable technique when the solid-state reactivity is considerable. Under such circumstances it may be possible to evaluate the crystal structure by computational methods, an approach which has also been used with profit to elucidate the local structure at various kinds of defects in organic solids (9-13). The final inadequacy of the X-ray structural method is that it is not surface sensitive; and it is vital to know the precise two-dimensional crystallography at the habit faces of certain crystals that undergo interesting gas-solid reactions. On general grounds, however, it seems safe to conclude that no major surface reconstruction, involving the creation of bizarre superlattices (as with certain metals), is likely to occur with organic molecular crystals. But it remains to be discovered whether significant conformational changes, which could influence reactivity, take place in the molecules situated at the exterior surfaces of molecular crystals.

At present two of the most powerful methods of attacking the ultrastructure, and therefore the topochemistry, of organic solids, are transmission electron microscopy (14) and the atom-atom (pairwise evaluation) computational (12) approach. The former yields from diffraction pattern the microscopic phase; from the bright-field and dark-field images, it also yields details of the structural imperfections at dislocations and planar faults. The latter offers additional insights such as the energetics of structural faults;

moreover, this approach may be employed under circumstances (e.g. for the analysis of point defects, such as a misoriented member (15) in a stack of otherwise properly oriented molecules) when other techniques, including electron microscopy, fail.

In proceeding to discuss organic reactions in the solid state, we shall first deal with thermal reactions before considering photostimulated ones.

THERMAL REACTIONS

The kinetics of most solid-state reactions that entail some kind of recon-struction at the molecular or sub-unit cell level generally conform to the classical, so-called sigmoid pattern (see Young (16)). The sigmoid refers to the shape of the curve describing the fraction converted as a function of time. After an induction period during which 'germ nuclei' are formed, there is an acceleration in reaction rate generally attributable to the 'branching' (i.e. further creation) of nuclei; this is followed by a linear rate ascribed to steady growth of the nuclei. Finally, as the nuclei begin to overlap, deceleration sets in and completion of reaction is reached asymptotically. There is no doubt that the vast majority of inorganic and very many organic solids decompose thermally according to this general pattern.
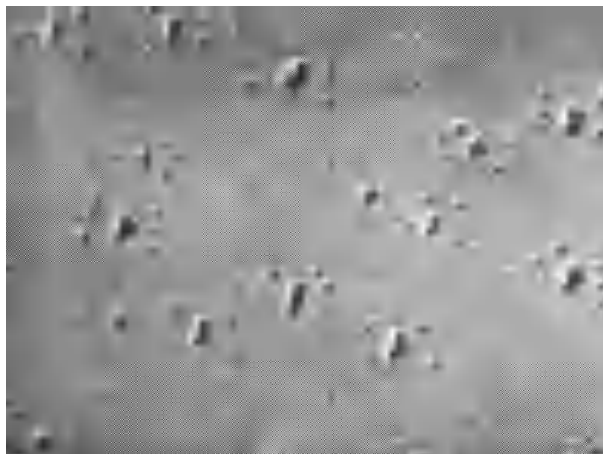

Fig. 3. Optical micrograph showing surface of a sucrose crystal in course of thermal carbonization. Reaction is preferred at emergent dislocations (17).

Figure 3 shows the surface of a sucrose crystal in course of thermal carbon-ization: the production of secondary nuclei as a result of the strain gen-erated by the product which has accumulated preferentially at the site of an emergent dislocation is clear (17). This micrograph represents the solid in its acceleratory phase of conversion. Often the dislocations at which reaction rate is enhanced (for a variety of kinetic and thermodynamic reasons, see (18-20)), are aligned in view of the fact that certain crys-tallographic planes favour their creation and passage. Such phenomena, for a range of solids, have been categorized elsewhere (20-22). An example, showing the crystallographic preference for the accumulation of the ammonium salt of acenaphthylene carboxylic acid, is shown in figure 4. The same pattern is obeyed for several other gas-solid reactions of organic solids, e.g. in the ozonolysis of trans-stilbene to benzaldehyde and of diethylstilb-oestrol to p-hydroxypropiophenone (16).

Fig. 4. Accumulation of reaction product at slip traces generated by the passage of dislocations on preferred planes within acenaphthylene carboxylic acid (23).

A. Dehydration

In the examples quoted above, clean, single-product reactions ensued largely as a result of the rigidly clamped positions of the reacting organic molecule. A striking example where prealignment of the reactant molecules leads to a specific dehydration process is summarized in the scheme shown below (taken from a recent review by Curtin et al. (24)).

R = H
R = Br
R = CH$_3$

R = H
R = Br
R = CH$_3$
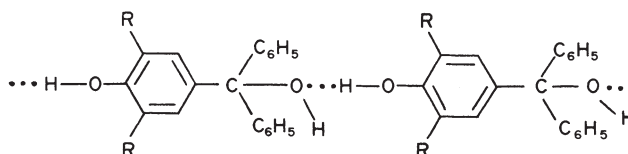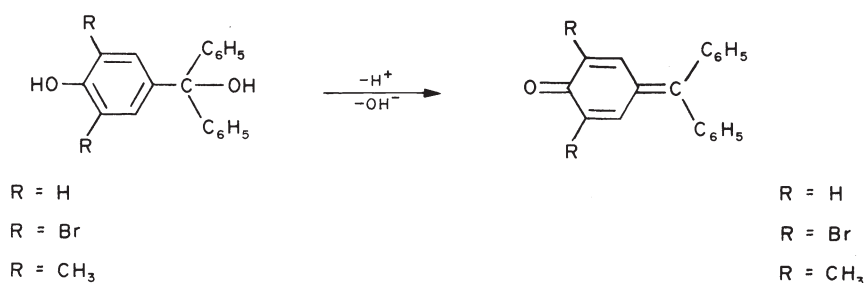
The phenolic proton of one molecule of the parent p-hydroxytriphenylmethanol can assist the loss of the alcoholic hydroxyl group of its neighbour in view of the nature of the hydrogen-bonded chains. The inference is drawn from the crystal structure (figure 5) of the dimethyl compound (24,25). Dehydration proceeds slowly at ca 110°C to yield fuchsone.

B. Phase Transitions (Single Crystal ⇌ Single Crystal).

For organic molecular crystals, processes such as solid → solid phase transitions, which would otherwise be regarded as simple physical events, take on a fuller chemical significance since the conformations of the constituent molecules are altered in going from one phase to the other. One remarkable example, which we shall now discuss, relates to the cyclooctane-based molecular-ion. The crystal structure of the perchlorate derivative of this thiaza derivative has been studied in detail both at 3° and 25°C by Paul and Go (26). The salient crystallographic data for the two phases are :

α-form: a = 9.87, b = 8.78, c = 13.26 Å; β = 97°54'; P2$_1$/c.

β-form: a = 20.10, b = 8.89, c = 6.77 Å; β = 97°48'; P2$_1$/a.

The β-form is stable at 25°C. It is to be noted that, in going from the lower to the higher temperature, the 'a' unit cell dimension doubles, whilst the c dimension halves with b remaining essentially unchanged. At the molecular level it is seen that there are, in both phases, two enantiomeric forms of the molecular cation, symbolized D and L in figure 6. Interconversion between D and L involves ring inversion and molecular rotation as schematized; but it is a moot point whether, in the actual phase change,
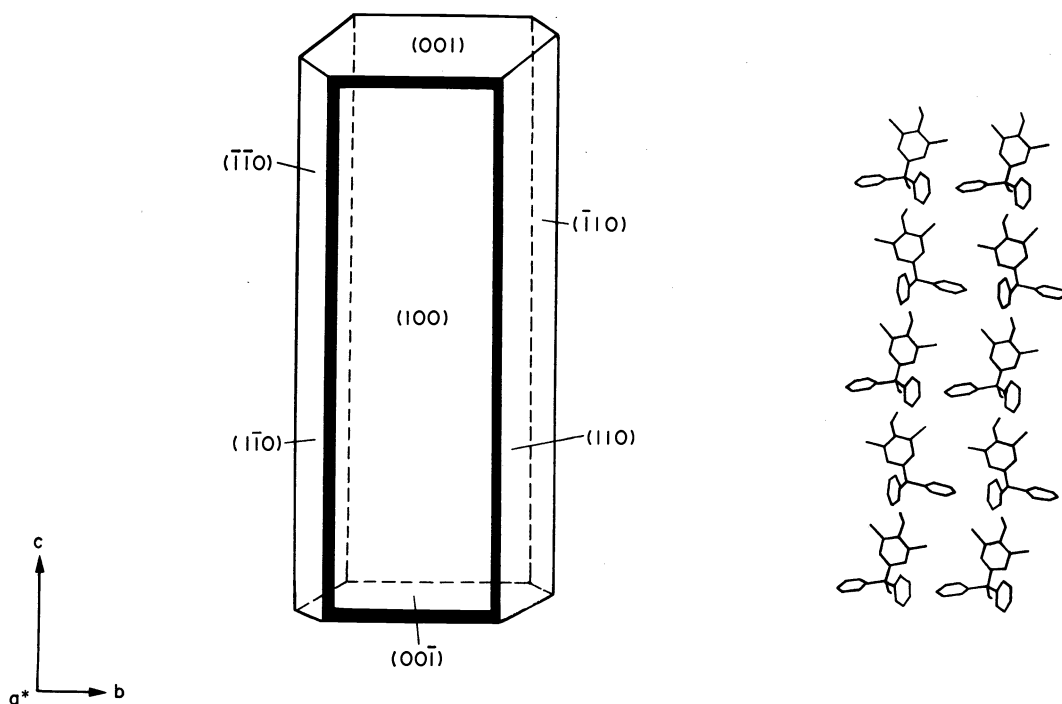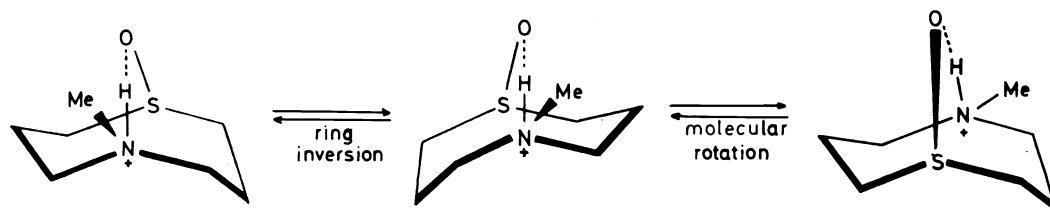
Fig. 5. A crystal of the dimethyl compound and a drawing of
the internal structure in the same orientation.
(After Curtin et al. (24)).

cooperative molecular D to L and L to D conversion take place in the manner
implied, with half the cations in each column and half the cations in each
row changing, in both senses of rotation, as implied.

There is an alternative method of envisaging this interconversion which
simply involves cooperative shear on alternate (102) crystallographic
planes (27). The degree of slip (to use the metallurgist's phrase) is
partial in the sense that the displacement vector is less (only half) the
unit repeat value on these planes. As shown in figure 7, when partial
dislocations sweep in opposite senses progressively on alternate planes,
single-crystal ⇄ single-crystal interconversion is secured. On this
model we see how, as is observed in practice, the morphology of the α and β
forms remains intact on the macroscopic scale. Although no direct vindica-
tion of this mechanism exists, it is likely to be correct in view of the
widespread dominance of strictly comparable solid-state processes in a range
of other, structurally simpler solids (the f.c.c. ⇄ h.c.p. conversion of
cobalt for example, and others discussed elsewhere - see refs (27,28)).
Paul and coworkers have recently found another organic molecular system which
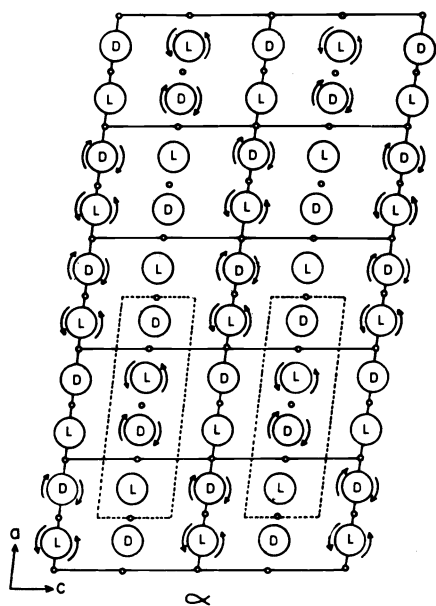seems to conform to this type of solid-state conversion (29).

Fig. 6.

Projection along [010] of the α-phase. The large circles represent the molecular cations (the D and L designating the appropriate enantiomorphs) and the small circles the perchlorate. The outline of two cells of the β-form are also superimposed in dotted lines. The particular mol-ions which, according to Paul and Go (26), are required to rotate and invert during the phase transition, are also represented, the direction of the arrows indicating the sense of the rotation.
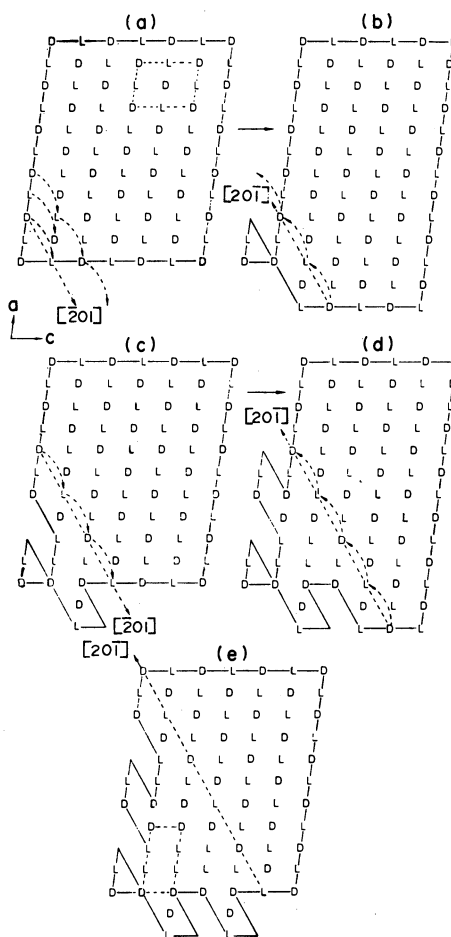
Fig. 7.

Schematic model (after Parkinson et al. (27)) of the progressive conversion of the α- to the β-form by the passage of partial dislocations. For simplicity only the cations are shown. In (a) the (102) plane on which the shear of ½ [$\bar{2}$01] leads to (b) is shown. In (b) the (102) plane in which the opposite shear of ½[20$\bar{1}$] operates is delineated. The arrows indicate some of the translations which result from the operation of (102) ½ [$\bar{2}$01] and (102) ½ [20$\bar{1}$]. By progressive opposite shear of ½ [$\bar{2}$01], ½ [20$\bar{1}$], ½ [$\bar{2}$01], etc., on adjacent planes the α- is converted into the β-phase. Note the outlined unit cells in (a) and (e).

C. Gas-solid Interactions

A full discussion of the importance of such reactions in the reactivity of
organic molecular crystals has been given recently.   Three examples will
suffice to indicate the scope of such reactions in organic syntheses.
First, the chlorination of _trans_-stilbene.   Miller et al. (30) observed that
the product of gas-solid reaction was exclusively dl-stilbene dichloride,
whereas in solution a 2:1 mixture of meso- and dl-stilbene dichloride
resulted.   Second, when single crystals of 2-methylphenol are chlorinated,
the amounts of 4-chloro- and 6-chloro-derivatives are a function of the crys-
tallographic identity of the exposed face (31).   Thus, crystallographic
faces parallel to (001) preferentially yield the _para_ chloro - whilst those
perpendicular to (001) the _ortho_-chloro product.   Third, chiral syntheses
may be effected by allowing an appropriate gas (e.g. bromine) to react with a
molecule (such as 4,4-dimethylchalcone) which is achiral but which, on crys-
tallizing, does so in a chiral group (1,32).   Addition of the halogen across
the central double bond thus converts all the achiral molecules in the R
crystal (pre -(+)) into an optically active product and likewise all the
achiral molecules in the S crystal (pre -(-)) into the opposite activity.
(Ways have been described of converting, via sequential gas-solid reaction,
dissolution and recrystallization, an achiral molecule into a single optic-
ally pure product.)   Dehydrohalogenations, another kind of gas-solid reac-
tion since it may be effected by ammonia or gaseous amines, also serve as a
means of effecting stereospecific conversions.   It has to be borne in mind,
however, that, occasionally, molecules situated at the exterior surface of,
or at structural defects in, the crystal "relax" to such an extent that fac-
ile stereo-conversion occurs during reaction, thereby generating products
which no longer exhibit optical enrichment.

D.   Solvates and Intercalates

Lahav and coworkers have recently drawn attention to the behaviour of certain
molecular complexes, possessing well-defined and favourable geometrical con-
tacts between reacting centres of guest and host, inside which one-step
regiospecific and stereospecific reactions may be effected, e.g. solid-state
functionalization of steroids, a class of organic compound which form com-
plexes - solvates - with a large number of guest molecules.   Lahav (33)
drew particular attention to the one-step regiospecific and stereospecific
hydroxylation at position 5 of desoxycholic acid when the molecular complex
of this acid and di-t-butyl diperoxymonocarbonate is either thermolysed at
90°C or photolysed at room temperature.   There are prospects that many
enzymic reactions may be mimicked in the solid state by adroit use of sol-
vates.   Technological as well as biological possibilities may be opened up
via these results, since it should be possible to synthesize one-dimensional
macromolecules (e.g. polyacetylenes) by placing an array of the acetylenic
precursor in, for example, the continuous open channels that molecules such
as urea and thiourea "create" for guest entities when the solvate crystall-
izes from solution.   If the radiative methods employed by Brown and White
(34) to effect one-dimensional polymerization in the solvate crystal could
be perfected, it should be possible to extract the extended-chain insoluble
products by dissolution of the water soluble host.   Such an approach is
currently being explored by Baughman (35).
Whereas the solvates generally involve guest molecules enclathrated in
pockets (or holes) or channels, the intercalates, by definition, refer to
layered solids which have expanded in the direction perpendicular to the
basal plane following assimilation of molecules into the interlamellar re-
gions.   Numerous layered solids display the phenomenon of intercalation;
though its nature is still incompletely understood.   The transition metal
chalcogenides and graphite take up intercalated guests when electron trans-
fer to or from the electronic bands of the host solid is facile.   The sheet
silicates, on the other hand, involve less extensive electron transfer which
is, in any case, localized at certain specific sites (36).   Numerous types
of sheet silicates, as well as a variety of other solids, which have been
discussed elsewhere, take up intercalated organic molecules which are often

quite rigidly clamped in the vicinity of interlamellar cations.   There is a
massive body of qualitative information pertaining to the sheet silicate
intercalates.   But relatively few studies have been devoted to the range of
highly specific organic chemical conversions that may be carried out through
the agency of sheet silicates.   Recently the author and his associates have
drawn attention to a variety of novel organic reactions that may be carried
out by the agency of sheet silicates, there being strong indications that
intercalation of the reagent is a prerequisite for reaction (36-41).   In
particular, it has been demonstrated (39) that diphenylethylene may be effi-
ciently converted to 1-methyl-1,3,3-triphenylindan using a cation-exchanged
montmorillonite that serves as a Brönsted acid.   By taking a synthesized
sheet silicate (a fluorohectorite prepared according to the procedure given
by Barrer) which is almost completely devoid of acidic hydroxyl groups, we
have shown (41) that diphenylethylene is converted, again with great effi-
ciency, into a totally different range of products.   Amongst these products
diphenylethane, diphenylmethane and benzophenone are dominant.   It is also
possible, with the agency of metal-exchanged, montmorillonoid sheet silicates,
to convert unsaturated cyclic carboxylic acids into 1,3- and 1,4-lactones,
the ratio of one to the other being 'tunable' by adjustment of the inter-
lamellar cation.   Yet a further remarkable reaction is the smooth conversion
of 1-alkenes to corresponding secondary ethers, the oxygen being taken from
the hydration shell of the interlamellar cation.   It has been shown that
there is an optimum degree of hydration (40) to secure quantitative conver-
sion to the ether: it has also been established that other layered solids
(e.g. the uranyl phosphates) which are architecturally similar to the sheet
silicates, are totally inactive in converting alkenes to ethers.
Numerous other categories of reaction that may be carried out via sheet
silicate intercalates have been described by Weiss (42), Thomas et al. (36),
and Barrer (43).   Transition metal chalcogenides also serve as important
hosts for reactions among intercalated organic molecules (see Hartless and
Trozzolo (44)).

RADIATION-INDUCED REACTIONS

Most photochemical and other radiation (e.g. γ-ray) induced reactions of
organic materials have been studied at room temperature or above.   A number
of studies describing conversions at ca 90 to 200 K have been reported, but
very few have been studied at the cryogenic extremes (4 K or less).   Very
recently, however, a number of temperature-independent reactions have come
to light as a result of kinetic studies carried out close to absolute zero.

A.   Temperature-independent Processes

In assessing factors relevant to the phenomenology of organic reactions at
cryogenic extremes, there are two important fundamental principles which
operate.   First, that reaction-rates should be zero close to 0 K as pre-
dicted by the Arrhenius equation.   Second, since $T \rightarrow 0$ and $\Delta G = \Delta H - T\Delta S$,
it follows that all exothermic reactions are thermodynamically feasible at
very low temperatures.   If bonds can form with liberation of heat, they will
be formed, provided kinetic factors permit them.
It has been known (45) for some time that electron transfer processes (e.g.
from cytochrome c to chlorophyll) are temperature-independent over quite a
broad range (in the above example from 130 to 4.2 K).   But it has recently
been established by Goldanskii and coworkers (46,47) that the polymerization
of formaldehyde, as well as certain reactions of olefinic double bonds, is
kinetically independent of temperature in the range 140 to 4 K.   Moreover,
it was shown that, following the initial act of bond scission (by γ- or
X-rays), subsequent events entailing sequential addition of monomer to the
growing chain takes place by quantum mechanical molecular tunnelling.
Powerful experimental evidence points to this conclusion.   It would be
interesting, in the light of Goldanskii's work, to set up monomers into
differently arranged sequences (in intercalates, e.g. where separation
distance and orientation may be modified), and then to investigate the low-
temperature reactivity of organic monomers.

Recent work in the U.S.S.R. has shown that certain ester derivatives of
phenylene diacrylic acids may, after photoinitiation, be polymerized to
completion in the temperature-independent regime.   This reaction is an
example of (2+2) photopolymerization which we discuss below.
Goldanskii has argued that temperature-independent processes could have
played a vital role in generating highly organized molecular structures in
the prebiotic environment.   Life, it seems, could just as readily have
emerged from frozen solids as from the warm liquids bearing the amino acids
generated from electrical discharges in reducing atmospheres.

B.   (2+2) Photopolymerizations

In 1962 Hasegawa made the chance discovery that one of the two known poly-
morphic forms of distyryl pyrazine (DSP) freely polymerizes at room tempera-
ture thereby generating a white, extended-chain compound from a yellow
monomeric crystal (48).   Much has been written about this fascinating re-
action which, inter alia, has been ingeniously utilized as a vehicle for the
production of a chiral polymer (perhaps oligomer is a more exact description)
by Lahav et al. (49) (see figure 8).   Hasegawa, Nakanishi and coworkers (50,
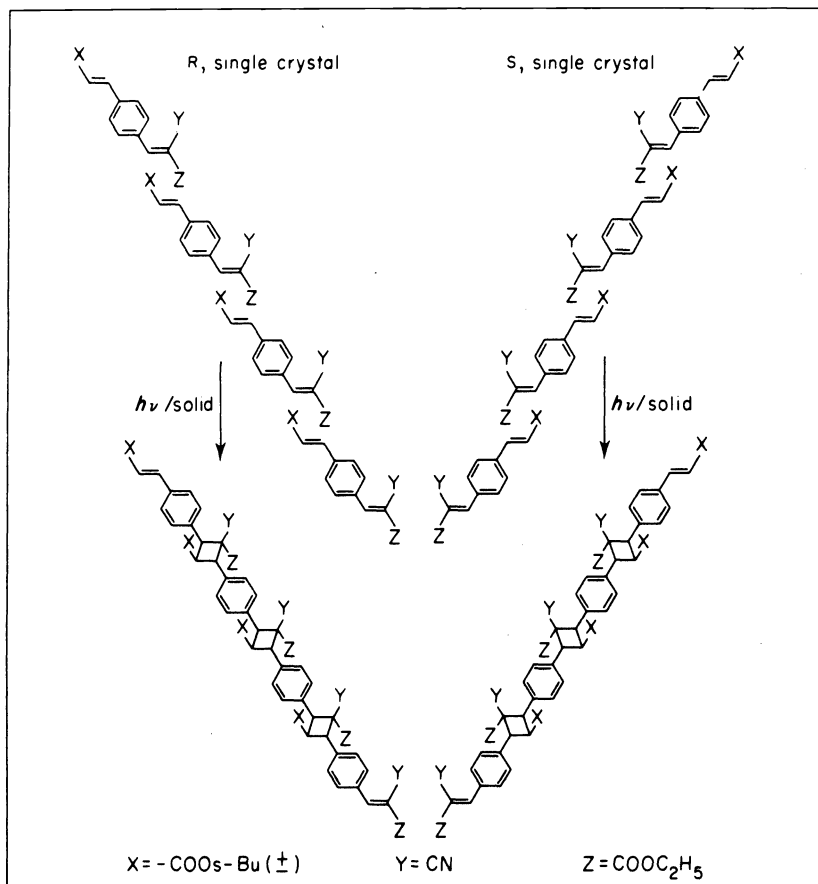51) have elegantly exploited this basic reaction type to produce an extensive

Fig. 8.   Schematic representation of the way Addadi et al.(49)
utilized the (2+2) photopolymerization process discovered by
Hasegawa et al. (48) to obtain chiral photoproducts.

range of polymerized diolefins.   All these reactions are topochemical in
the sense discussed elsewhere (1,4-6), i.e. the product is preformed within
the monomer matrix and reactive functional groups (the olefinic links) are
favourably located (≤ 4.0 to 4.2 Å) and disposed (collinear) to be photo-
polymerizable by means of a sequence of dimerizations leading to cyclobutane
rings as repeating units.   Hasegawa et al. (52) have shown that the thermal
depolymerization is also a topochemical process; and that the thermal sta-
bility of the rigid longer chain poly-DSP is less than that of shorter chain
analogues.   Arguments have been advanced by Wegner and coworkers (53) that
the four-centre polymerization first discovered by Hasegawa and coworkers is
not a homogeneous reaction, i.e. they argue that nuclei of a separated phase
are involved in the conversion right from the outset.   Careful electron
microscopy by Jones (54) using the powerful technique of real-space crys-
tallography (based on symmetric and crystallographically interpretable bend
extinction contours (55)) find no evidence for the operation of a hetero-
geneous reaction.   This is not altogether surprising (but not admittedly
inevitable) in view of the extent of change in the unit cell parameters and
other crystallographic identities.   Several divinyl derivatives have been
studied in detail, electron microscopically by Jones et al. (56).   Not only
was there no evidence for heterogeneity, there were no indications that dis-
locations, which are readily rendered visible by diffraction contrast, served
as preferential sites for the initiation of the photopolymerization or for
the separation of the polymer.   Whatever the outcome of the present debate
concerning the reaction mechanism, it is already obvious that the four-centre
photopolymerization in the crystalline state has already made a major impact
in optical device technology for Mizuno, Tawata and Hattori (57) have demon-
strated that a new dry-process phase-hologram material, offering attractive
prospects in real-time holographic interferometry, may be prepared from
m-phenylene diacrylic acid and an appropriate sensitizer.

C.   Reactions of Cinnamic Acids: Crystal Engineering

The photochemistry of trans-cinnamic acid derivatives has been discussed and
exploited for nearly a hundred years.   In solution or in the melt the mono-
mers merely isomerize under u.v. irradiation: in the solid state they are
apt to dimerize.   But here topochemical factors dominate.   If monomer pairs
are 'preformed' in a mirror-symmetric fashion, the head-to-head β-truxinic
acids product are generated, whereas the head-to-tail products (the so-called
α-truxillic acids) are formed from 'preformed' monomer pairs that are centro-
symmetric.   Exotic examples of how a given derivative (e.g. o-ethoxy-trans-
cinnamic acid) may separate from solution in three distinct crystallographic
forms have been cited (1,4,58).   The one yields the β-truxinic derivative on
u.v. irradiation, another forms the α-truxillic acid, and the third is light
stable (since the double bonds are not conducively situated for dimerization).
To 'engineer' overlap and appropriate juxtapositioning of dimerizable enti-
ties, various strategies have been adopted (for recent summaries see Cohen
(4,72), Thomas et al. (5,6)).   The dichlorophenyl substitution method,
through the agency of which it proved possible to synthesize an optically
active butadiene derivative from inactive precursors (see Elgavi et al. (59)),
still ranks amongst the most applicable.   Hydrogen-bonding, and the mutual
interaction of extended polymethylene chains are other devices which serve as
means of steering potential reactive groups into favourable disposition for
reaction: (see 'Future Prospects' below).

D.   Photo-reactivity of Poly-ynes

The idealized picture published (60) by Hirschfeld and Schmidt in 1964 en-
visaged monomeric entities draped on lattice sites in such a fashion as to be
readily converted by gentle stimulation (such as tilting of each entity con-
tingent upon the uptake of a photon), into a polymeric product.   Such a sys-
tem was discovered (61) by Wegner in 1969.   Wegner, as well as Baughman and
Chance, has shown that diacetylene monomers ($R-C\equiv C-C\equiv C-R$) typically polym-
erize in the solid state by a 1,4-addition reaction at the diacetylene group

to produce a polymer which can be alternately represented by the following
mesomeric structures :

$$(=(R)C-C \equiv C-C(R)=)_n \quad \longleftrightarrow \quad (-(R)C=C=C=C(R)-)_n$$
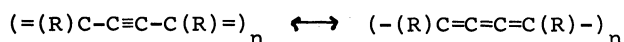
In some instances (depending upon R) the solid-state reaction transforms a
monomer crystal to a polymer crystal with similar dimensions and similar
structural perfection: the polymer chains enter the polymerizing phase as a
solid solution over the entire monomer-to-polymer conversion range.   In
others, phase separation occurs during polymerization.   When R is
$-CH_2OSO_2C_6H_5CH_3$ (i.e. p-toluenesulphonate, PTS) complete solid solution
occurs and the reaction rate exhibits a dramatic autocatalytic character -
the rate increases by about two orders of magnitude as the fraction converted
grows.   Baughman, in a penetrating analysis, has quantitatively explained
(62) this autocatalysis in terms of a strain-dependent rate of chain initia-
tion and propagation.   If the CH_3 group of the PTS is replaced by a $C\ell$ atom,
which occupies about the same volume as CH_3, the solid monomer loses all its
photoreactivity - a fact which the crystal analysis of Clarke and Myerle (63)
could rationalize.   Although the chlorosubstituted diacetylene monomer mol-
ecules pack in stacks in a manner similar to that which leads to polymeriza-
tion in the PTS monomer crystals and the arrangement within the stacks is
quite like that of the reactive PTS, there are quite strong attractive inter-
actions, probably dipolar, between the $C\ell$ atoms and the adjacent phenyl
rings.   Such interactions steer the molecules into a slightly more eclipsed
configuration than for the PTS monomer and, consequently, the potentially
reactive carbon atoms are too far apart for polymerization to occur.   1,4-
addition is simply not feasible.   This is a striking example of how solid-
state reactivity may be profoundly altered by introducing subtle changes in
the molecular framework which, in turn, modify the crystal packing charac-
teristics.   In the light of these comments, it is of great interest that
Wegner has recently reported (64) a photoreactive polymorph of the di-chloro-
substituted diacetylene which Clarke and Myerle found to be totally unreac-
tive.

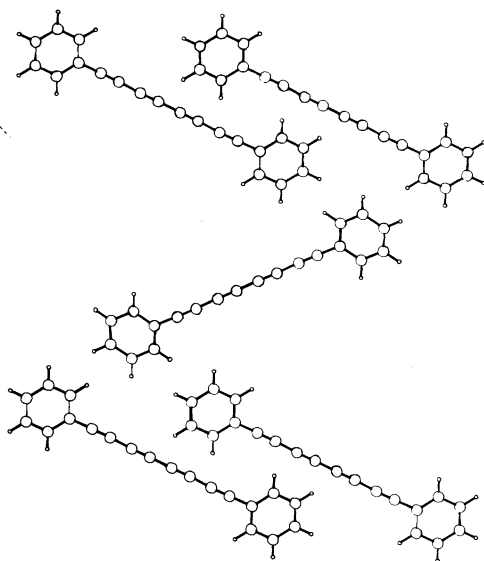Fig. 9. Computed crystal structure (after Ramdas et al.(65))
of the α,ω-diphenyltetrayne   (see text).

Another series of potentially interesting monomers which ought, on topochem-
ical grounds, to undergo solid-state photopolymerization, are the α,ω-di-
phenylpoly-ynes : $C_6H_5-(C \equiv C)_n-C_6H_5$.   Crystals of the homologous members
n = 1,2,3,4,5,6 and 8 are available, and the space-groups of most, and the

crystal structure of a few, are known.   Ramdas et al. (65) have recently
utilized the atom-atom procedure to compute the crystal structure of one of
the two known polymorphs of the diphenyltetrayne (n = 4).   The reliability
of the computational approach, along with the trustworthiness of the param-
eterized potentials used, was indicated by showing that the computed struc-
ture of α,ω-diphenyldiacetylene (n = 2) was identical with that of the ex-
perimentally determined structure (66).   It transpires that at least two
modes of topochemical solid-state polymerization (figure 9) are possible,
1,4 or 1,8.   Each mode would require the terminal phenyls to rotate upon
reaction.   The separation distances are different for the 1,4 and 1,8 modes,
but it remains to be discovered whether, in a situation of this kind where
both distances are well below the threshold value for reaction, the smaller
separation dominates.

E. Naphthoquinone Derivatives: Insights into Structure-Reactivity
     Relationships

Scheffer, Trotter and coworkers (67,68) have recently elucidated how the
ground state conformations influence the excited state reactivities of tetra-
hydro-1,4,naphthoquinones in the solid state.   In particular the photoreac-
tivity of substrates possessing the 4aβ,5,8,8aβ-tetrahydro-1,4-naphthoquinone
ring system, shown below, has been studied at wavelengths greater than 340nm.
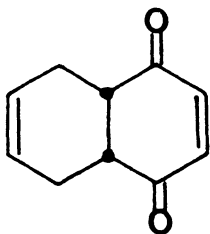
Although the X-ray crystal structures of these substrates revealed a common
ground state conformation irrespective of substitution, four different reac-
tivity patterns emerged.
Intermolecular [$\pi^2 + \pi^2$] cycloaddition to centrosymmetric dimers was the
reaction path for substrates which have crystal structures in which adjacent
pairs of molecules within a crystallographic cell are related by a centre of
symmetry with the reacting double bonds oriented parallel and at a centre-to-
centre separation of ≤ 4.04 Å.
Intramolecular hydrogen abstraction by an oxygen of an excited carbonyl moi-
ety proceeding via a five-membered cyclic transition state occurred in sub-
strates which lacked the intermolecular orientation necessary for dimeriza-
tion but which had the prerequisite β-hydrogen in the plane of the carbonyl
group and within a distance of ≤ 2.58 Å of the oxygen   The H_β-O-C angle in
all cases was very close to the optimum angle for efficient hydrogen abstrac-
tion by the n-orbital of oxygen.
Intramolecular γ-hydrogen abstraction by the β-carbon of an excited enone
system became the predominant reaction only in substrates which are believed
to have low-lying Π, Π* states.   The distance between the hydrogen and the
abstracting carbon was ≤ 2.89 Å.   Since the abstracting orbital in this
instance is the 2p orbital of carbon, the optimum geometry for efficient
abstraction differs from that which obtains for the β-process.
The fourth reaction type was intramolecular oxetane formation.   It occurred
only in one substrate which lacked the prerequisites for all the other three
processes.   There are indications that this process is the least preferred
photochemical reaction pathway for these compounds.
It is noteworthy that these results on photochemical hydrogen abstractions of
both the β- and γ- types suggest that, under favourable conditions, such
abstractions can occur over distances at least as great as the sum of the

van der Waals radii of hydrogen and the abstracting atom.
Scheffer and Trotter have recently reported (69) an elegant comparison of the
solid-state and solution behaviour of a β,γ-unsaturated ketone (see scheme).
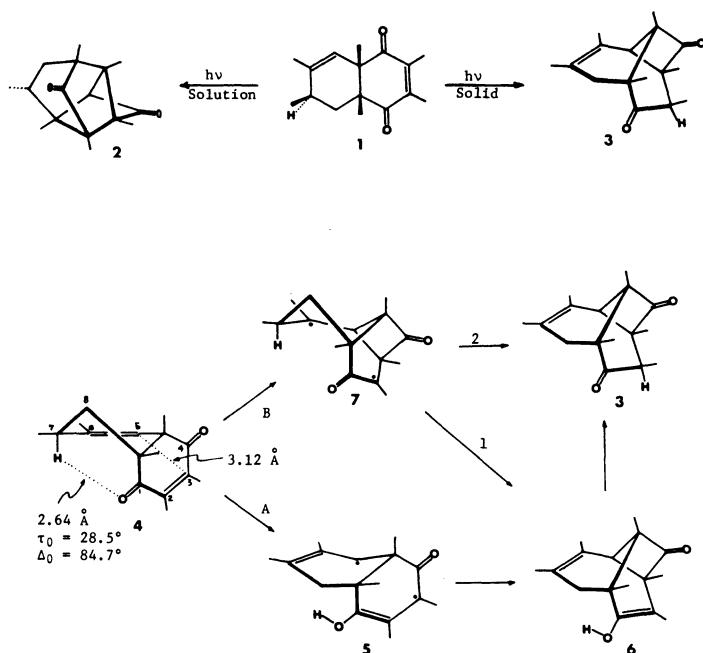
In solution the ketone is conformationally mobile: in the solid it is
'frozen' into a single conformation.   The photochemical consequences of this
simple fact, now to be summarized, illustrate well the unparalleled opportun-
ities that certain adroitly chosen organic solids offer for the construction
of detailed unimolecular structure-reactivity relationships.   Polycrystall-
ine samples of the diene-dione 1 are converted in 85% yield to the photo-
product 3.   It is to be noted that tetrahydronaphthoquinone 1 adopts a con-
formation in the solid in which the cyclohexane ring is half chair-like and
the methyl group at C_7 is pseudoequatorial rather than pseudoaxial.   A key
feature of this conformation (cf structure 4) is that the hydrogen atom at C_7
is pseudoaxial and in a position to be transferred to the ene-dione ring at
some stage in the formation of photoproduct 3.   The mechanistic possibilities
(which cannot at present be distinguished) include: initial γ-hydrogen ab-
straction of the C_7 hydrogen atom by oxygen to give biradical 5 which in turn
collapses to 6, the enol form of the final photoproduct 3.   The oxygen to
hydrogen distance involved in this case is 2.64 Å, somewhat greater than the
distance observed in Scheffer and Trotter's earlier work (67) on solid state
intramolecular hydrogen atom abstractions (2.26 to 2.58 Å), but still within
the limit, previously assessed, of the sum of the van der Waals radii for
oxygen and hydrogen (2.72 Å).   The angle τ_0 for 4, essentially the degree to
which the abstracted hydrogen is out of planarity with the mean plane of the
abstracting carbonyl group, is 28.5°, considerably greater than the near-
coplanar abstractions previously observed (68), and the C_1 to oxygen to H_7
angle, Δ_0, is 84.7°, close to the values found previously.
Note that, in terms of overall atomic motions, formation of 3 requires only
the relatively minor processes of rehybridization of carbon atoms 2,3,5 and 7
plus a decrease in the C_3 to C_5 contact: the basic molecular shape remains
constant throughout the transformation.   In contradistinction, the shape of
solution photoproduct 2 bears little resemblance to that of its progenitor 1,
and is formed via a sequence of steps each of which requires substantial
atomic motion and molecular deformation.   It would be interesting to carry
out reactions of the kind discussed here in more or less rigid glasses, as
was done by Trozzolo et al. in their study of aziridines and oxiranes (70,71).

ANOMALOUS BEHAVIOUR OF SOLIDS: ROLE OF STRUCTURAL IMPERFECTIONS

The general situation concerning the abnormalities displayed by certain crystalline solids, especially in regard to their photoreactivity, has been recently reviewed (6) - see also (72).   Suffice it to say that there are a number of instances where, on the basis of topochemical arguments, we would expect photostability, yet reaction does ensue.   The photodimerization of anthracene and of 1,8-dichloro-9-methylanthracene are in this category (73, 74).   There are other instances where topochemical principles lead us to expect a given photoproduct but another is, in fact, formed.   9-cyano-anthracene and 1,8-dichloro-10-methylanthracene are in this category.   It is now known, thanks largely to the application of electron and other micro-scopic techniques, that several factors may be responsible for this state of affairs.   So far as 1,8-dichloro-9-methylanthracene is concerned, planar faults, involving a stacking disorder and a misregistry that brings contig-uous molecules into an incipient head-to-tail arrangement, seems responsible for the photodimerization of the monomer (73,75).   For reasons amplified in the Introduction, excitation energy transfer is, in this case, facile and reaction ensues at the site of traps (i.e. at planar faults, the detailed structure of which may be arrived at computationally by the atom-atom approach (12,13)).   For anthracene itself, where energy transfer is again facile, it is now clear that the stable monoclinic phase, whose structure is inconducive for dimerization, readily converts, by application of external stress, to a triclinic phase (76) within which dimer formation freely pro-ceeds.   The atom-atom approach combined with low-temperature transmission electron microscopy enabled the crystal structure of the triclinic phase to be determined.   This phase has not yet been isolated in a pure state: it tends to coexist, topotactically (5), often as minute domains (volume de-fects), within the parent monoclinic matrix.   Other structural faults, not-ably an unexpected kind of coincidence boundary (77), have recently been dis-covered within anthracene and its analogues.   Their role in photochemical and cognate phenomena has yet to be explored.

One type of fault, an orientational defect, is worthy of special mention. It has no counterpart in the majority of inorganic solids and it consists of a lattice site at which the tenant molecule takes up an abnormal orientation. It is, in other words, a point defect of a kind not encompassed by the taxon-omy that applies to ionic or metallic solids.   Such a defect is believed to occur in the triclinic phase of 1,5-dichloroanthracene for reasons discussed by Ramdas et al. (78).   Briefly, this polymorph behaves abnormally upon u.v. irradiation in that 20% of the head-to-tail dimer as well as 80% of the head-to-head dimer forms.   The computed structure would lead one to expect 100% head-to-head dimer.   Ramdas et al. recognized that the space group to which the triclinic phase of the dichloroanthracene belongs does not generate pack-ing suitable for the 'preformation' of the head-to-tail dimer across any stacking fault within that phase.   A 'flipped' molecule (i.e. one that has been rotated through Π about an axis parallel to either the long or short molecular axis), on the other hand, does produce incipient head-to-tail pairs (78).

It can be seen from the foregoing that, as well as the experimental (prin-cipally electron microscopic) approach to the study of structure imperfections, computational procedure based on the pairwise evaluation of non-bonded inter-action are immensely powerful and versatile tools.   Potentials are better defined and fall off rather sharply with distance in molecular crystals - at least those that are composed of entities which are not too polar or too prone to form hydrogen bonds - than in covalent solids (silicon, germanium) or metallic and ionic crystals where truncation errors can be quite serious (12,79).   In addition to elucidating microstructural aspects of extended defects (planar and linear faults) the computational approach also throws light on the "relaxation" that takes place in the environment of both indi-vidual guest molecules (see Ramdas (79)) and misoriented host molecules. Knowledge of such "relaxation", about which we are still in the process of learning, should be of value in interpreting the phenomenon of site-selective photochemistry.   Site-selective heterodimer formation in anthracene has

recently been studied by several workers (80-82). In crystals of anthracene of the highest attainable purity, 2-hydroxyanthracene is invariably present as a trace impurity. These molecules occupy two sites in the anthracene crystal, and, in consequence, exhibit two fluorescence origins designated O_8 and O_9. The intriguing feature of this mixed photodimerization is that the O_8 site appears to be photostable, only the O_9 site being involved in dimer formation, though there has been one report which found O_8 also to be photo-active. There is little doubt (82) that, whenever heterodimer formation takes place, so-called X-traps (i.e. anthracene molecules dislodged from their regular lattice sites in the vicinity of guest molecules) are impli-cated.

FUTURE PROSPECTS

Abundant scope for subtle variation exists in organic solid state chemistry largely because of the almost infinite variety of structural type and pattern of substitution that is available at the molecular and sub-molecular level. The canvas is obviously large, but in painting the picture one must still decide on a specific pattern! Future progress will clearly depend on styles and strategies. And apart from those overtly discussed or tacitly assumed in the preceding paragraphs, we may safely identify others that are likely to loom large in the near future.
The use of cage or channel complexes is particularly appealing, especially since it offers an attractive route to optical resolution. Arad-Yellin _et al_. (83) have already capitalized on the ability displayed by tri-ortho-thymolide (TOT) to form complexes with a large variety of organic compounds. Both 'cage' and 'channel' inclusion complexes are formed, depending on the character, chiefly the dimension, of the enclathrated molecule. Moreover, because TOT adopts a propeller-like chiral conformation, its clathrate in-clusion complexes exhibit "spontaneous resolution" (84). Great rewards may, therefore, stem from future researches in the fields of solvates and, as stated earlier, intercalates.
So far as securing crystallographic and topochemical control, like compelling a molecule to separate out in chiral crystals, is concerned, much room for investigation remains in the strategy termed crystal engineering discussed earlier. Co-crystallization with inorganic or organic molecules, or uti-lizing non-trivial but rather delicate inter-molecular attractions (as ex-ists between a carbonyl group of one molecule and a bound chlorine atom in another) are but two examples. There are several others, see ref (6). In addition, the use of transition metal complexes bearing organic ligands offers promise, as may be gauged from the reported (85) topotactic and stereospecific polymerization of $NiBr_2[P(CH_2CH_2CN)_3]_2$. Conformational poly-morphism, as recently described by Bernstein and Hagler (86), merits further study, since it highlights the relationships between crystal forces and mol-ecular conformation. And stereospecific gas-solid reactions (87), espe-cially of olefins by simple gases which often preferentially yield _cis_ adducts. Finally, for the reasons cited earlier, we can expect to hear a great deal more about organic solid state reactions at very low (liquid helium) temperatures.

REFERENCES

1. G.M.J. Schmidt, _Pure Appl. Chem._ _27_, 647 (1971).
2. I.C. Paul and D.Y. Curtin, _Accounts Chem. Res._ _7_, 223 (1973).
3. H. Morawetz, _Science_, _152_, 705 (1966).
4. M.D. Cohen and B.S. Green, _Chem. in Britain_, _9_, 490 (1973).
5. J.M. Thomas, _Phil. Trans. Roy. Soc._, _277_, 251 (1974).

6. J.M. Thomas, S.E. Morsi and J.P. Desvergne, in _Advances in Physical Organic Chem_. Vol 15. (Ed. V. Gold and D. Bethell) Academic Press, London, 1977, 63.

7. C.N. Sukenik, J.A.P. Bonapace, N.S. Mandel, R.G. Bergman, P.Y. Lau and G. Wood, _J. Amer. Chem. Soc._ 97, 5290 (1975).

8. A. Gavezzotti and M. Simonetta, _Nouveau J. De Chimie_ 2, 69 (1977).

9. A.I. Kitaigorodskii, _Chem. Soc. Rev._ 7, 133 (1978), and A.I. Kitaigorodskii, _Molecular Crystals and Molecules_, Academic Press, New York (1973).

10. D.E. Williams, _Acta Cryst._ A27, 452 (1972).

11. S. Ramdas, J.M. Thomas and M.J. Goringe, _J.C.S. Faraday II_ 73, 551 (1977).

12. S. Ramdas and J.M. Thomas, in _Chemical Physics of Solids and Their Surfaces_ (Specialist Periodical Report, Chem. Soc.) (1978) (in press).

13. W. Jones, S. Ramdas and J.M. Thomas, _Chem. Phys. Lett._ 54, 490 (1978).

14. W. Jones and J.M. Thomas, in _Progress in Solid-State Chemistry_ (in press).

15. S. Ramdas, W. Jones, J.M. Thomas and J.P. Desvergne, _Chem. Phys. Lett._ 57, 468 (1978).

16. D.A. Young, _Decomposition of Solids_, Pergamon Press, London (1965).

17. J.M. Thomas, J.O. Williams, H. Marsh and B. Rand, _Carbon_ 4, 143 (1966).

18. J.M. Thomas, T.A. Clarke and E.L. Evans, _J. Chem. Soc.(A)_, 2338 (1971).

19. J.M. Thomas, E.L. Evans and J.O. Williams, _Proc. Roy. Soc._ A331, 417 (1972).

20. J.M. Thomas, _Advances in Catalysis_, 19, 293 (1969).

21. J.M. Thomas and J.O. Williams, _Progr. in Solid State Chemistry_ 6, 119, (1971).

22. J.M. Thomas, J.O. Williams, V.V. Boldyrev and Y.P. Savintsev, _J. Chem. Soc.(A)_, 1757 (1971).

23. J.P. Desvergne and J.M. Thomas, _Chem. Phys. Lett._ 23, 343 (1973).

24. D.Y. Curtin, I.C. Paul, E. Duesler, T.W. Lewis, B.J. Mann and Wen-I Shiau, paper presented at 5th Intl. Symp. on Chemistry of Organic Solid State (Brandeis Univ. June 1978). To be published in Molecular Crystals and Liquid Crystals.

25. S.A. Puckett, M.K. Greensley, I.C. Paul and D.Y. Curtin, _J. Chem. Soc. Perkin II_ 847 (1977).

26. I.C. Paul and K.T. Go, _J. Chem. Soc._ 33 (1969).

27. G.M. Parkinson, J.M. Thomas, J.O. Williams, M.J. Goringe and L.W. Hobbs, _J. Chem. Soc. Perkin II_ 836 (1976).

28. J.M. Thomas, J.O. Williams, C.F. Ng and D. Donati, _Disc. Faraday Soc._ 61, 118 (1976).

29. I.C. Paul _et al._ (to be published).

30. R.S. Miller, I.C. Paul, D.Y. Curtin, _J. Amer. Chem. Soc._ 94, 5117 (1972).

31. R. Lamartine and R. Perrin, _Compt. Rend. Acad. Sci._ C279, 367, 477 (1974).

32. K. Penzien and G.M.J. Schmidt, _Angew. Chem. Int. Ed. Eng._ 8, 608 (1969).

33. M. Lahav, G. Friedman, L. Leserowitz, R. Popovitz-Biro, C.P. Tang and Z.V.I. Zaretzkii, _J.C.S. Chem. Comm._ 864 (1975).

34. J.E. Brown and D.M. White, _J. Amer. Chem. Soc._ 82, 5671 (1960).

35. R.H. Baughman, private communication.

36. J.M. Thomas, J.M. Adams, S.H. Graham and D.T.B. Tennakoon, _Advances in Chem. Series_ (A.C.S.) 163, 298 (1977) ed. J.B. Goodenough and M.S. Whittingham.

37. D.T.B. Tennakoon, J.M. Thomas, M.J. Tricker and J.O. Williams, _J.C.S. Dalton Trans._ 2207 (1974).

38. M.J. Tricker, D.T.B. Tennakoon, J.M. Thomas and S.H. Graham, _Nature_ 253, 110 (1975).

39. J.M. Adams, S.H. Graham, P.I. Reid and J.M. Thomas, _J. Chem. Soc. Chem. Comm._ 67 (1977).

40. J.M. Adams, J.A. Ballantine, S.H. Graham, R.J. Laub, J.H. Purnell, P.I. Reid, W.Y.M. Shaman and J.M. Thomas, _Angew. Chemie_ 90, 290 (1978).

41. J.M. Adams, S.E. Davies, S.H. Graham and J.M. Thomas, _J. Chem. Soc. Chem. Comm._ (1978) (in press).

42. A. Weiss in _Organic Geochemistry_ (ed. G. Eglington and M.T.J. Murphy), Springer-Verlag, Berlin (1969).

43. R.M. Barrer in _Non Stoichiometric Compounds_ (ed. L. Mandelkern) Academic Press, 1964.

44. R.L. Hartless and A.M. Trozzolo, _ACS Symposium Series_ No.5, 23 (1974).

45. D. De Vault and B. Chance, _Biophys. J._ $\underline{6}$, 825 (1966).

46. V.I. Goldanskii, _Science_ 182, 1344 (1973); and V.I. Goldanskii in _Ann. Rev. Phys. Chem._ $\underline{27}$, 85 (1976).

47. V.I. Goldanskii in _Proc. Symp. on Tunnelling in Biology_ (Philadelphia, Nov. 1977).

48. M. Hasegawa, M. Iguchi and H. Nakanishi, _J. Polym. Sci._ A1 $\underline{6}$, 1054 (1968); also M. Hasegawa and Y. Suzuki, _J. Polymer Sci._ B-5, 813 (1967).

49. L. Addadi, M. Lahav and M.D. Cohen, _J. Chem. Soc. Chem. Comm._ 471 (1975).

50. H. Nakanishi, F. Nakanishi, Y. Suzuki, M. Hasegawa, _J. Polymer Sci.A-1_, $\underline{11}$, 2501 (1973).

51. F. Nakanishi, T. Tasai and M. Hasegawa, _Polymer_ 16, 218 (1975).

52. M. Hasegawa, H. Nakanishi and T. Yurugi, _26th IUPAC Congress_, Tokyo, 1977 (page 1246 of Abstracts).

53. W. Meyer, G. Lieser and G. Wegner, _Makromol. Chem._ $\underline{178}$, 631 (1977).

54. W. Jones, _J. Chem. Research (S)_, 142 (1978).

55. W. Jones, J.M. Thomas, J.O. Williams and L.W. Hobbs, _J. Chem. Soc. Faraday Trans. II_ $\underline{71}$, 138 (1975).

56. W. Jones, W.L. Rees, J.M. Thomas, H. Nakanishi and M. Hasegawa (in preparation).

57. T. Mizuno, M. Tawata and S. Hattori, _J. Opt. Soc. Amer._ (in press).

58. B.S. Green and M. Lahav, _J. Mol. Evol._ $\underline{6}$, 99 (1975).

59. A. Elgavi, B.S. Green and G.M.J. Schmidt, _J. Amer. Chem. Soc._ $\underline{95}$, 2058.

60. F.L. Hirschfeld and G.M.J. Schmidt, _J. Polymer Sci._ A2, 2181 (1964).

61. G. Wegner, _Z. Naturforsch. Teil_ B24, 824 (1969).

62. R.H. Baughman, _J. Chem. Phys._ $\underline{68}$, 3110 (1978).

63. J.J. Myerle and T.C. Clarke, _Acta Cryst._ B34, 143 (1978).

64. Private communication from G. Wegner.

65. S. Ramdas, R.H. Baughman and J.M. Thomas (in preparation).

66. E.H. Wiebenga, _Z. Kristallogr._ 102, 193 (1940).

67. A.A. Dzakpasu, S.E.V. Phillips, J.R. Scheffer and J. Trotter, _J. Amer. Chem. Soc._ $\underline{98}$, 6049 (1976).

68. J.R. Scheffer and A.A. Dzakpasu, _J. Amer. Chem. Soc._ $\underline{100}$, 2163 (1978); and _J. Photochemistry_ $\underline{9}$, 267 (1978).

69. W.K. Appel, T.J. Greenhough, J.R. Scheffer and J. Trotter (submitted for publication).

70. T. Do-Minh, A.M. Trozzolo and G.W. Griffin, _J. Amer. Chem. Soc._ $\underline{92}$, 1402 (1970).

71. A.M. Trozzolo, A.S. Sarpotdar, R.L. Hartless in _5th Intl. Symp. on Chemistry of Organic Solid State_ (Brandeis Univ. June 1978). To be published in Molecular Crystals, Liquid Crystals.

72. M.D. Cohen, _Angew. Chemie Intl. Ed._ $\underline{14}$, 386 (1975).

73. J.P. Desvergne, J.M. Thomas, J.O. Williams and H. Bouas-Laurent, _J.Chem. Soc. Perkin II_ 363 (1974).

74. J.P. Desvergne, H. Bouas-Laurent, R. Lapouyade, J.M. Thomas, J. Gaultier and C. Hauw, _Molecular Cryst. Liquid Cryst._ $\underline{32}$, 107 (1976).

75. S. Ramdas, J.M. Thomas and M.J. Goringe, _J. Chem. Soc. Faraday Trans. II_ $\underline{73}$, 551 (1977).

76. G.M. Parkinson, M.J. Goringe, S. Ramdas, J.O. Williams and J.M. Thomas, _J. Chem. Soc. Chem. Comm._ 134 (1978).

77. G.M. Parkinson, J.M. Thomas, D.A. Smith and M.J. Goringe (in preparation).

78. S. Ramdas, W. Jones, J.M. Thomas and J.P. Desvergne, _Chem. Phys. Lett._ $\underline{57}$, 468 (1978).

79. S. Ramdas and J.M. Thomas, _J. Chem. Soc. Faraday Trans. II_ $\underline{72}$, 1251 (1976) - see also R. Ramdas (to be published).