©*Proc. Indian natn. Sci. Acad.*, **52**, A, No. 1, 1986, pp. 363–378
Printed in India

TRENDS AND PROSPECTS IN ORGANIC SOLID STATE CHEMISTRY*

WILLIAM JONES* *and* JOHN M THOMAS

Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, UK

(*Received 28 January 1986*)

Recent progress in the area of diffusionless reactions in organic crystals is reviewed, with particular emphasis upon : single-crystal to single-crystal transformations; morphology control and absolute configuration determination; and the reactivity of guest molecules incorporated in clathrates and zeolites.

Key Words : Organic Solid State Chemistry; Diffusionless Reactions: Single-Crystal-Single-Crystal Transformation; Morphology Control; Absolute Configuration; Guest Molecules in Clathrates and Zeolites

INTRODUCTION

INTEREST in the various transformations (both chemical and physical) which may occur within an organic solid continues to increase. In part, this interest arises from the potential of utilizing the restrictive environment and limited motion available to the reacting molecules towards the synthesis of new and novel materials. At the same time the exploitation of these constrained systems for studying in detail the mechanism of certain reactions has also been pursued. Indeed the range of topics which have been studied is impressive and covers amongst other things; an analysis of the influence of structure on the perfection with which a reaction proceeds;[1,2] the control of crystal morphology by addition of tailor-made impurities,[3] an area of key industrial importance; the determination of absolute configuration;[4] monitoring the course and identifying the small changes in molecular packing associated with the onset of photoinduced decomposition and abstraction reactions;[5,6] the influence of the surrounding matrix on the reaction of guest molecules in both clathrates and inclusion compounds[2] and in inorganic matrices such as zeolites.[7]

Associated with these wide ranging interests a concommitant development of techniques aimed at probing slight changes in structure have also emerged; *in situ* X-ray diffractometry[1]—whereby the exact orientation of product molecules within reactant may be determined; Fourier transform infrared—so sensitive that isotopes of very low natural abundance may be studied;[8] electron spin resonance—giving

*Lecture delivered at the INSA Golden Jubilee Symposium in Solid State Chemistry held at INSA, New Delhi during 4-6 December 1985.

the relative orientation and separation of free radical pairs;[9] and most recently, and with considerable future potential, solid state nuclear magnetic resonance[10] emerging primarily as a result of the realisation that the inherent difficulties associated with the application of NMR to solids may be removed by so-called magic-angle-spinning techniques and with the low natural abundance of ^{13}C overcome by cross-polarization procedures.

This article will briefly review some of the key areas which are currently being studied in the area of organic solid state chemistry. We shall, in particular, refer to :

(1) Single-crystal → single-crystal transformations, which have been extensively studied in our own laboratory and elsewhere.

(2) Recent trends in the area of so-called "crystal engineering."

(3) The control of crystal morphology by the addition of small amounts of selected (tailor-made) additives, and the possibility of determining absolute configuration by selective uptake of impurities by particular crystal surfaces.

(4) Recent developments in the area of polydiacetylene chemistry, in particular a method of enhancing the conductivity of such polymers by incorporating dopant molecules into the monomer structure prior to polymerization. The manner in which one may locate these impurity molecules within the lattice is also considered.

(5) The nature of the reactions which occur when organic molecules are converted to product-either thermally or photochemically-within rigid host matrices such as clathrates and zeolites.

1. Single-Crystal-Single-Crystal Transformations and Topochemical Requirements in [2 + 2] Dimerizations

Few examples of perfect single-crystal-single-crystal photoinduced reactions are known. In the course of a solid state reaction there is generally a significant change in bond distance and geometry.[11–15] In the case of the [2 + 2] photodimerization reactions, for example, there is generally either considerable fracture of the crystal during reaction, or else a loss in crystallinity. In both cases the marked change in local geometry results in a loss of lattice control. One particular system, however, which yields highly perfect single-crystal product is based upon[14] 2-benzyl-5-benzylidenecyclopentanone (BBCP), see Fig. 1, and several of its derivatives—see Table I.

The crystallographic features associated with this reaction and the associated changes in cell parameters which occur during the transformation have been carefully monitored.[1] A gradual change in cell parameter is observed, suggesting that the reaction proceeds smoothly throughout the entire crystal lattice, an observation which may be readily understood by comparing the monomer structure with that

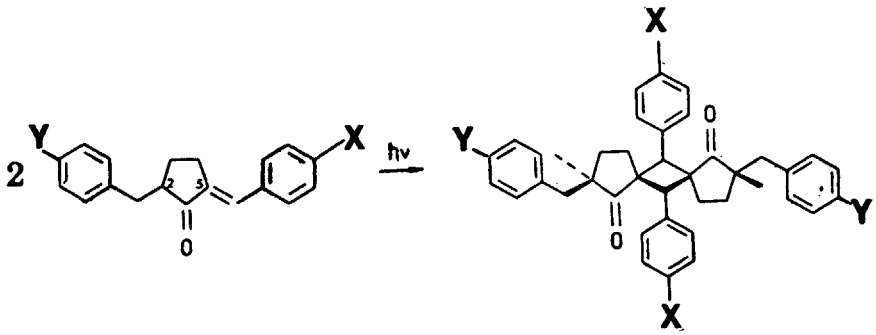

FIG 1 Schematic illustration of the dimerization of BBCP and its derivatives to yield the centrosymmetric product. The changes in cell parameter and space group for various *X* and *Y* substituents are given in Table I.

TABLE I

Unit cell values for monomer and dimer crystals for various derivatives of 2-benzyl-5-benzylidenecyclopentanone

X	Y			Space Group	*a*/Å	*b*/Å;β(°)	*c*/Å	*V*/Å3
H	H	BBCP	monomer	Pbca	31.302(11)	10.784(3)	8.687(3)	2932
			dimer	Pbca	31.321(4)	10.811(4)	8.629(3)	2922
Br	H	BpBrBCP	monomer	Pbca	34.222(6)	10.923(1)	8.427(1)	3150
H	Cl	pClBBCP	monomer	$P2_1/c$	17.175(4)	10.587(3) 76.33(9)	8.796(5)	1554
H	Me	pMeBBCP	monomer	$P2_1/c$	17.341(2)	10.675(1) 102.54(1)	8.736(1)	1579
Br	Cl	pClBpBr-BCP	monomer	$P2_1/c$	17.522(4)	7.906(2) 91.19(1)	11.888(2)	1646
Br	Me	pMeBpBr-BCP	monomer	$P2_1/c$	18.381(2)	11.209(2) 94.46(1)	8.285(2)	1702
		A	monomer	$P2_1/c$	17.314(2)	10.667(1) 77.39(2)	8.747(2)	1577
			dimeric	$P2_1/c$	17.306(3)	10.667(2) 76.64(2)	8.768(2)	1575

see Fig. 1 for position of substituents X and Y within the molecule.

of the product dimer—the space group and crystal packing of the product dimer is identical to that of one of the dimer polymorphs obtained by recrystallization. Fig. 2 illustrates the crystal structure of the BBCP monomer viewed along [001]; a comparable view of the dimer structure is shown below it. There is clearly little movement associated with the reaction. Indeed, because of the perfection with which the reaction proceeds it transpires that it is possible to obtain full structural

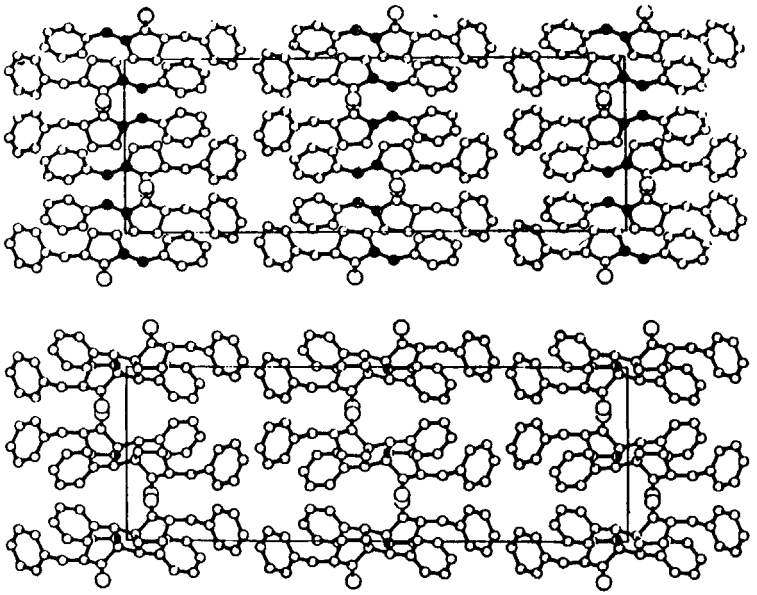

FIG 2 Packing diagram of the monomer of BBCP viewed along [001], upper; and the corresponding view of the dimer product—again along [001] after reaction, lower : carbon atoms C5 and C13 in individual incipient dimer pairs are highlighted.

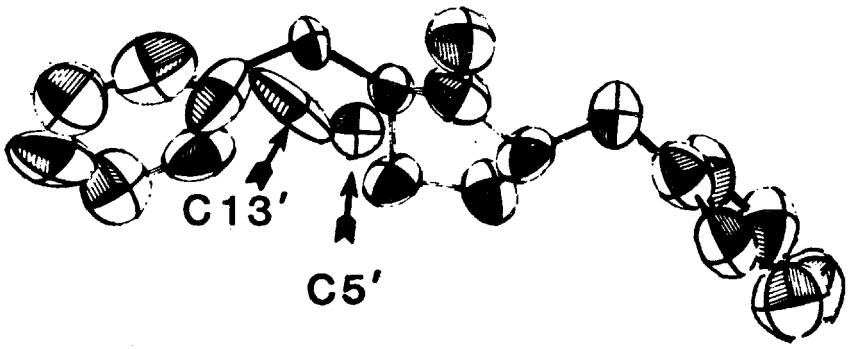

FIG 3 ORTEP plot illustrating the monomer and half-dimer equivalent fragments at approximately 70 per cent conversion-conversions estimated from the refined occupancies of the respective atoms. The thermal elipsoids are drawn at a 50 per cent probability level; the elipsoids marked C13′ and C5′ correspond to the residual monomer within the crystal.

data at various stages of the conversion. Fig. 3 shows the situation when 70 per cent of the material has reacted. The structural refinement reveals two locations for the C5 and C13 carbon atoms. One is associated with that component of the crystal which is unreacted, whilst the other corresponds to the dimeric product. Various derivatives, and indeed mixed crystals, have been shown to follow this rather

ideal reaction pathway. In most cases the product yield of dimer is, as expected, very close to 100 per cent.

For BBCP the photoreactivity may be correlated with the presence, in the monomer structure, of incipient dimer pairs in which the two benzylidene C = C bonds are related by a center of symmetry, Fig. 4. Intuitively, one might except this particular arrangement to be a prerequisite for photoreactivity, and loss of such reactivity to arise when the packing mode does not allow either a close-enough approach of the double bonds, or perhaps presents a rather unhelpful relative orientational relationship. This requirement for a particular arrangement was the basis of the ideas first formulated earlier by Schmidt and his colleagues,[11] when they outlined the principles of topochemical reactions in organic solids.

In certain crystals non-reactivity is understood as arising either because the reaction centres are too far apart or because the required symmetry relationship is absent. Indeed, where reactivity under inappropriate circumstances has occurred, the reaction has frequently been considered to occur at certain crystalline imperfections.

It might usefully be asked, therefore, what is the flexibility in the parameters defining the geometry of a reactive double-bond configuration?

A system which has thrown considerable light on this question has been described by Theocharis *et al.* using dibenzylidenecyclopentanone as the parent compound.[16]

DBCP crystallises in the space group $C222_1$ with cell parameters of $a = 11.803(2)$, $b = 5.698(4)$ and $c = 20.872(2)$Å; there are 4 molecules per unit cell. The molecules are arranged in stacks along [010]—see Fig. 5—in such a way that nearest neighbour molecules are related by translation along [010], such that C(2)...C(13′) is 3.714(5) and C(6)...C(5′) is 3.725Å; the primes indicate symmetry related molecules. The dimer obtained from the solid state reaction packs into the tetragonal space group $P4_12_12$ with $a = b = 10.860$ and $c = 23.979$Å; $z = 4$.

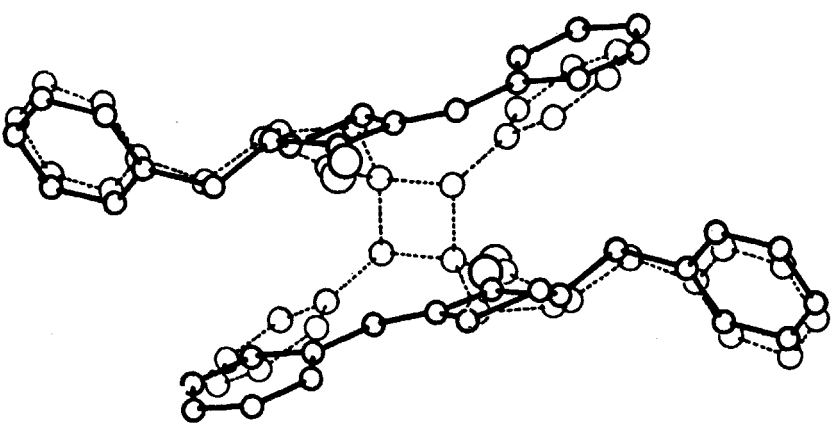

FIG 4 Composite diagram of 'incipient' dimer and 'product' dimer illustrating the relative positions of the monomer and dimer molecules.

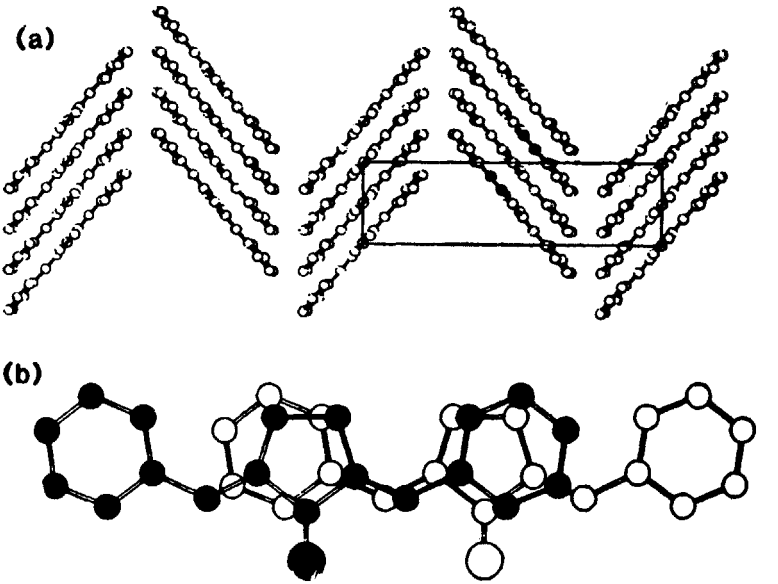

FIG 5 (*a*) DBCP structure viewed along the *a*-axis (*b*) A view along a direction perpendicular to the mean molecular plane of the 'incipient' dimer pair; the angle between the reactive is 56°.

Close inspection of the monomer structure reveals that the two bonds which react to give the cyclobutane ring belong to benzyl groups which are parallel, but not themselves colinear; there is a rotation of 56° between them. It is argued that although this is not the geometry generally considered conducive for a topochemical reaction, given that the mean distance separating the potentially reactive centres is well within the limits previously deduced to be necessary for such reactions, upon photoexcitation, there is sufficient overlap and interaction of the p_z-orbitals of the double bonds involved in the reaction, for reaction to occur.

In the case of DBCP—and in contrast to BBCP—reaction yields an amorphous product. This most likely results from the intrinsic rigidity of the rather large molecular framework, with the product dimer not being readily accommodated within the monomer lattice.

Other photo-induced phase transformations have been observed. For example, the solid-state photochemical behaviour of trans-stilbenes has long been of interest and in particular the fact that, in contrast to the cinnamic acids, when crystals of the parent material are irradiated with u.v. light *cis-trans* isomerization occurs without [2 + 2] cycloaddition of the exocyclic double bond. When the dichloro derivative is irradiated, however, reaction ensues.[17] The *p*-methoxy derivative was studied because there was some possibility that the methoxy group might "steer", see later, the structure into a reactive arrangement, and indeed irradiation of single crystals resulted in significant changes in the infra-red pattern.

Further study, however, confirmed that no chemical reaction had occurred, but rather that a novel photoinduced phase change had taken place with substantial changes in molecular conformation.[18] *p*-Methoxy stilbene packs in the space-group Pbca, the asymmetric unit comprising half the molecule; the centre of the exocyclic double bond is located on a crystallographic centre of symmetry and the molecule is flat. The view along the *c*-axis of the crystal structure is shown in Fig. (6*a*). Irradiation of a single crystal results in a change in space group, but significantly the single crystal character of the specimen is retained.

The irradiated material packs in the space group $P2_1/n$. Within the asymmetric unit the methyl carbon, as well as part of the phenyl group were refined at two different positions, each with a refined occupancy of 0.5. The carbon atoms of the phenyl group bonded to the two substituents (double bond and methoxy), the oxygen, and the double bond carbon refined to a single position. Rotation around the single bonds linking the double bonds to the phenyl rings resulted in a structure which was no longer planar, Fig. 6(*b*).

The transformation has been suggested to take place through an excimeric intermediate. Ordinarily the excimer may relax back to the ground state allowing the

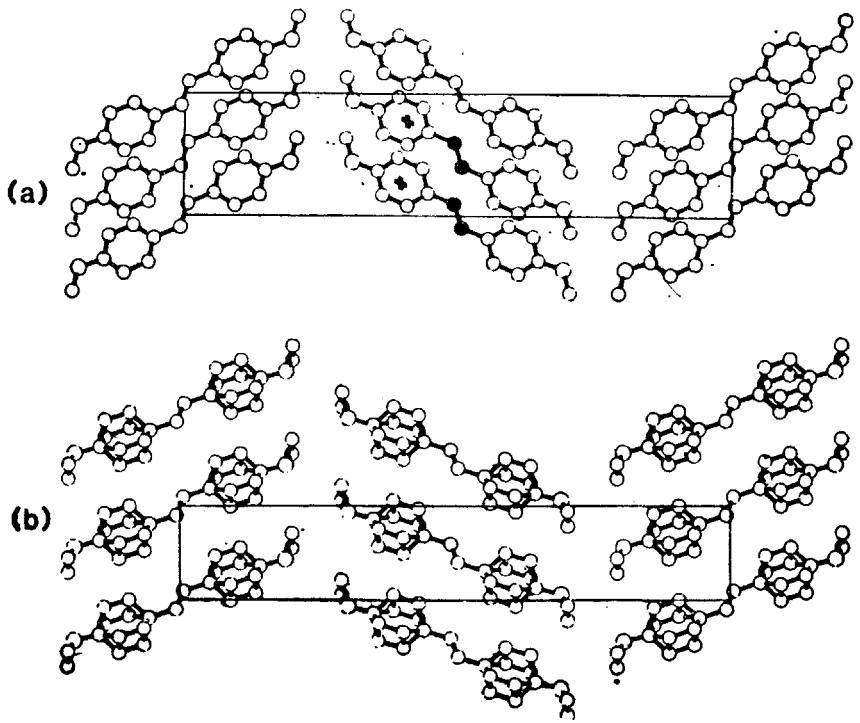

FIG 6 (*a*) Crystal structure of *p*-methoxystilbene viewed along the *c*-axis. (*b*) After irradiation of a single crystal the centre of the exocyclic double bond coincides with a crystallographic centre of symmetry. The phenyl rings adopt two positions within the crystal—*see* text.

constituent monomers to revert to their original positions. Because of the rather crowded nature of the packing in this case, however, it seems that this may not be possible and instead the ground state molecules take up new positions resulting in a new structure. It is notewothy that the whole process is however accommodated within the single crystal structure.

2. Recent Trends and Developments in Crystal Engineering

Crystal engineering, a concept[11] first introduced to organic solids by Schmidt in 1971, still generates considerable interest and study. Ideally it may be considered as the deliberate modification of a molecule by, for example, the addition of specific functional groups, such that packing into a desired crystallographic array occurs. As a consequence, the solid state properties of the crystal, including solid-state reacvity, may be controlled. Specific pair interactions which have been identified include: C = 0 . Cl, C = 0...Ph and Cl...Cl, and in general the identification of dominant interactions within a series of compounds requires a systematic study in which gradual changes in molecular structure are made.[12,13]

One previously held view was that chloro-methyl interchange is possible. Consideration of Table I reveals that the pClBBCP and pMeBBCP derivatives are isostructural, as indeed are the BpClBCP and BpMeBCP derivatives. It was expected therefore that both groups of compounds should be capable of forming solid solutions of varying composition, with isotonic changes in cell parameters and melting points. Such was indeed the case.

Interestingly, however, this strict chloro-methyl interchange does not exist for the compounds pClBpBrBCP and pMeBpBrBCP. The principal differences in molecular structure may be appreciated from an examination of the structures projected along, approximately, the C(2)-C(6) bond, see Fig. 7. The pMeBpBrBCP derivative, which is photoactive, has an essentially linear geometry whilst the stable modification of PClBpBrBCP consists of molecules with a substantially 'bent' geometry.[19] The nature of the interactions in these and similar crystals which gives rise to this rather pronounced change in geometry has been investigated using semi-empirical methods as well as more quantitative methods.[20,21]

The idea of structural mimicry—whereby a molecule may be induced to adopt a new conformation different to the one it adopts in its own pure lattice—has been explored using these derivatives. Theocharis *et al.* have shown, *see* Fig. 7, that when mixed crystals of pClBpBrBCP and pMeBpBrBCP are grown the conformation taken by the pClBpBrBCP derivative is very similar to that of pMeBpBrBCP, and that both components are able to react.[22]

3. Morphology Control and the Determination of Absolute Configuration

In the context of generating optically active product from a solid state reaction—see reference 23 for full details of the ways in which this may be achived—a key question

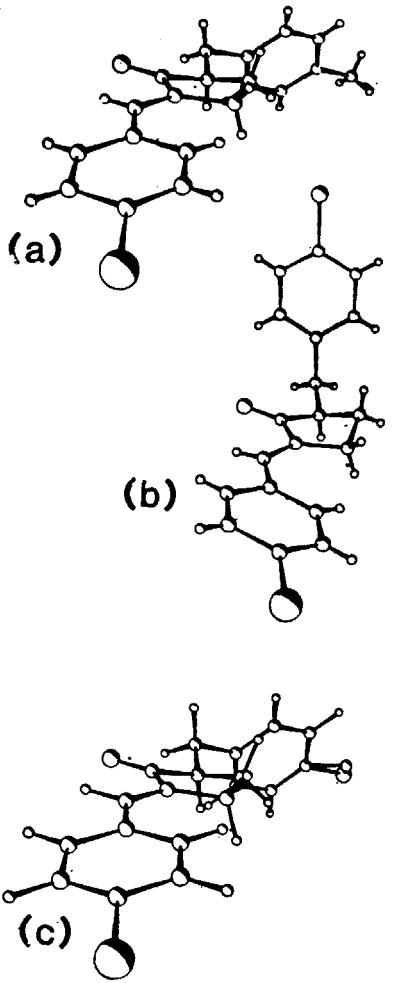

FIG 7 Molecular conformations viewed approximately along the C(2)-C(6) bond for (*a*) pMeBpBrBCP; (*b*) pClBpBrBCP and (*c*) mixed crystal of pMeBpBrBCP and pClBpBrBCP. In the latter case the chloro-derivative adopts a very similar conformation to that of the methyl-derivative.

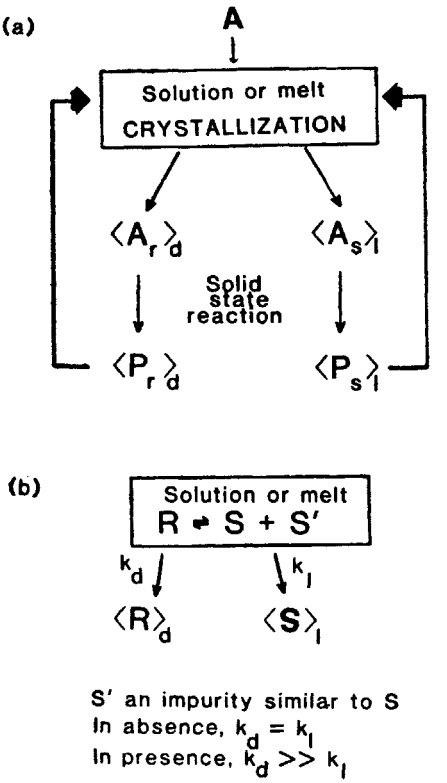

FIG 8(*a*) Amplification of subsequent product chirality as a result of feedback from addition of initial product. The "inversion rule" relates to the fact that, as shown in the lower part of the figure, crystals of opposite handedness are produced. A = reactants and P = products (*b*) Spontaneous crystallization to give a $< R >_d$ and $< S >_l$ conglomerate, with the growth of $< S >_l$ crystals being retarded a result of the presence of *S* impurity—*see* text.[3,24,25]

is whether significant activity may be obtained from a single crystal reaction. In general it would be advantageous if the generation step which introduces asymmetry could be followed by an efficient feedback mechanism.

Green and Heller[24] proposed a cyclic process, see Fig. 8, in which the products of the solid state reaction might, by incorporation into the melt or the solution, drive the crystallization step preferentially towards one of the two enantiomorphous phases.

The proposal was tested using the reaction of bromine and 4, 4′-dimethylchalcone—a gas solid reaction which yields a slight excess of optically active product when a single crystal of the chalcone is used; see Fig. 9. It transpires, however, that in such an experiment the product obtained from a crystal of, say, right handed character repeatedly caused preferential crystallization of the reagent into a crystal of the left-handed form. The term "inversion rule" was coined to describe this effect.[25] The explanation rests in the selective adsorption of small amounts of impurities at the growing sites of a specific face of a crystal,[26] with this adsorption drastically reducing the relative growth of this particular face with respect to other faces of the same crystal. Two consequences are forseen : firstly, a decrease in the overall growth rate, Fig. 8(*b*), and secondly, a pronounced change in crystal morphology.[25] Lahav, Leiserowitz and their co-workers have now demonstrated that numerous examples of enhanced growth of selected configurations in the presence of impurities could be expected using this approach. When (R, S)-threonine is crystallised in the presence of various impurities (typically 900mg of threonine and 100mg

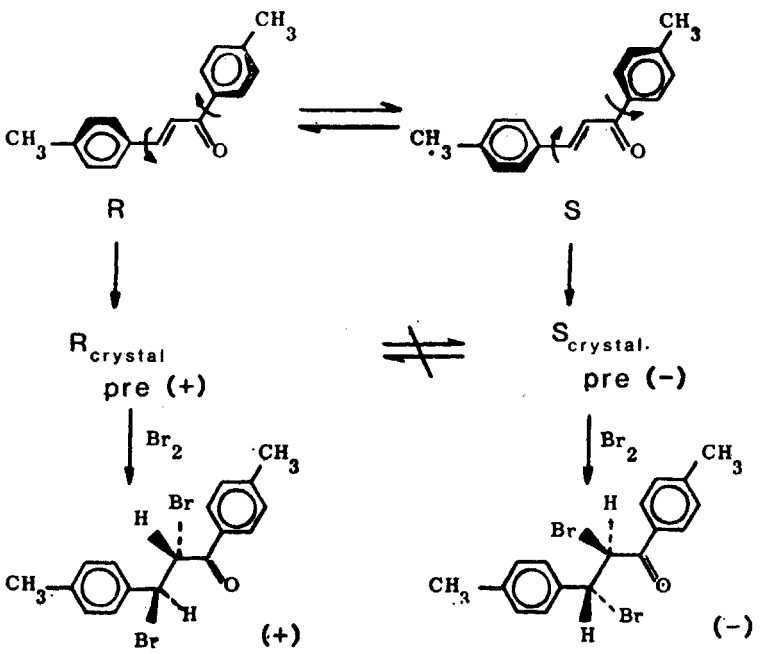

FIG 9 Schematic diagram of the bromination of crystals of dimethylchalcone (with crystailizes into the space group $P2_12_12_1$) illustrating how either (+) or (−) dibromide may result from the reaction of a single crystal.[24]

impurity), the event of the enantiomeric excess within the first crop of crystals is, in some cases, in excess of 95 per cent. Futhermore, in extending their work to amino acids and related materials a particularly important aspect of this selective adsorption has been developed.[27]

These observations may be viewed in a different way and the question asked as to whether it is possible, knowing the absolute configuration of the material produced in enantiomeric excess, to determine the absolute configuration of the additive molecule. The answer is a resounding yes, and several examples has now appeared which demonstrate this important extension.[28]

Consider the case of a polar crystal. We may schematically represent the arrangement of the molecules within the crystal as shown in Fig. 10. The unique axis of the crystal is parallel to the *X-A* molecular axis. Impurity molecules of the type *X-Y* will be accepted at f_1 and f_2; but not at f_3, f_4 or f_5. The adsorption will then lead to retarded growth along one direction of the crystal and either an increase in area of the inhibited faces with respect to the unaffected ones, or to the development of new faces on the affected side of the crystal.

In principle it should be possible to determine on which of the polar faces the impurity has been adsorbed, and hence determine the absolute chirality of the crystal. This has been demonstrated, for example, for enantiomerically pure tr-cinnamoyl-(*S*)-alanine which crystallizes in the polar space group $P2_1$. The principal question upon which the assignment of an absolute configuration rests is whether the —OH groups of the acid point along — *b* or + *b*; once this is known the configuration is known.[28] This question of orientation may be answered if, by selective adsorption, the orientation of the particular functional groups within the polar crystal with respect to the crystal axis is determined.

Indeed this method is not limited to polar crystals, but has been applied to effect morphological changes in achiral crystals composed of, for example, racemic mixtures.[3] Whilst X-ray analysis will not distinguish between the enantiomeric crystal structures $\langle R \rangle_1$ and $\langle S \rangle_1$, it establishes unambiguously the sites occupied by the *R* and *S* moieties with respect to the crystal axis in the centrosymmetric crystal. If the structural information contained in the racemic crystal is transferred to a third chiral molecule interacting stereospecifically with the racemic system through

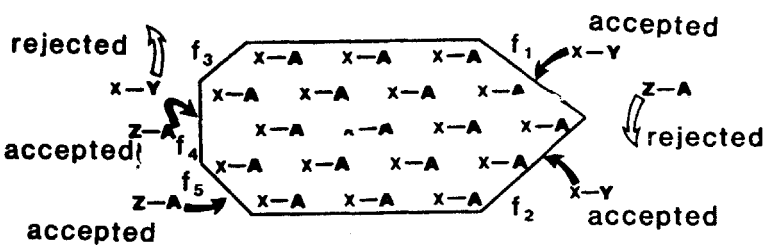

FIG 10 Rejection and acceptance of specific molecules at the different faces of a polar crystal—after Addadi *et al.*[3]

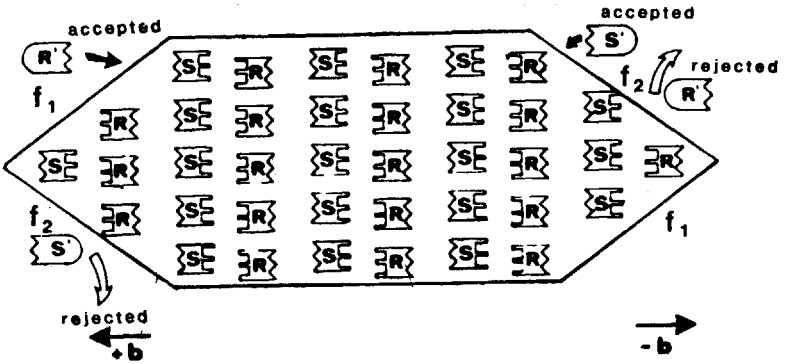

FIG 11 Schematic illustration of how chirial molecules may induce changes in the morophology of a centrosymmetric crystal, composed of a racemic mixture—after Addadi *et al.*[3]

a well-defined mechanism, then the absolute configuration of the resolved impurities may be obtained, Fig. 11.

The importance of this point can be best appreciated when it is realised that until 1951, (when the utilization of the anomolous dispersion of X-rays by J M Bijvoet was first used) the assignment of an absolute configuration to a molecule was not possible– and to this date the method of anomolous dispersion remains in isolation.

4. POLYMERIZATION OF DIACETYLENES

There is considerable interest in developing conjugated organic polymers which may be made conducting upon doping with various electron donor or acceptor compounds. To date success has been achieved with systems of the type polyacetylene, polyphenyl and polypyrrole.[29]

Diacetylene derivatives[30] represent an important group of materials with interesting electrical properties. They also represent an important class of materials for which the monomer phase acts as a three-dimensional template for the growth of polymer product. This 1,4-addition reaction, where polymerization occurs in the solid state as a result of successive tilting of monomer molecules, allows the synthesis of fully conjugated essentially defect-free crystalline polymer of high molecular weight. Large single crystals of conjugated polymer, as a result of topochemical polymerization, may result. In general, however, the polydiacetylenes insulators and the conversion to conducting material has not been possible by normal doping methods. Such is generally not the case for less well ordered samples e.g. multilayer samples, where iodine doping has resulted in conductivities approaching 10^{-6} S/cm.

Recently, however, Nakanishi and his colleagues[31] have attempted to prepare a doped monomer crystal such that the dopant is locked into the lattice during polymerization, see Fig. 12, and it is of interest in these systems to know where the

dopant is located—both in the monomer and in the polymer. This would allow a greater understanding of the nature of the dopant-organic interaction which govern the conductivity of the polymer.

Theocharis *et al.*[32] have obtained structural data on a *p*-toluene-sulphonate diacetylene derivative in which the dopant was $AgClO_4$. The tosyl derivative was chosen for a variety of reasons, particularly that the incorporation of sufficient dopant does not result in a new polymorph or hinder the polymerization process. It is also an advantage that the material—unlike many diacetylenes—is not readily polymerized by the X-ray beam. The unit cell of the doped and pure diacetylenes are very similar so that polymerization proceeds in the normal manner. Fig. 13 illustrates the molecular structure of the perchlorate doped *p*-TS. The Ag^+ is located—as expected—near an electron rich part of the sidechain.

5. Reactivity in Inclusion Compounds and Zeolite Matrices

The photodecomposition of alkanones included within urea complexes has been studied by Casal *et al.*[33] Urea, when crystallized in the hexagonal lattice, possesses long channels of approximately 5Å diameter into which guest molecules are incorporated. For 5-nonanone the possible reactions which may occur are shown in Fig. 14. In solution photodecomposition occurs principally *via* the Norrish Type II reaction, leading to 2-hexanone, propylene and two isomeric cyclobutanols, *see* scheme. The crystalline hexagonal urea complex gave, on the other hand, essentally only one cyclobutanol isomer—the cis. The formation of the cis isomer may be rationalised in so far as formation of this product requires less stringent rotational requirements. The generation of the cyclobutanol occurs without significant loss of integrity of the crystal lattice.

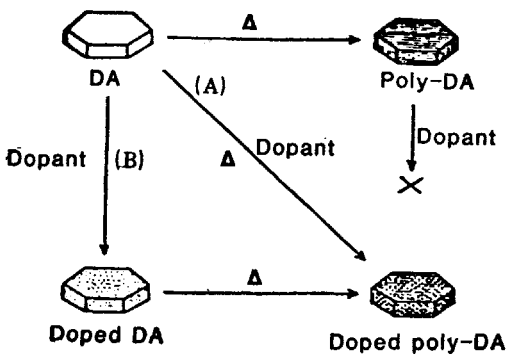

Fig 12 Schematic illustration of two approaches to the production of conducting polymer crystals. Path (*A*) involves polymerization in an atmosphere of dopant whilst path (*B*) requires the growth of monomer crystals *containing* dopant molecules. For the case of (*B*) the dopant molecules should not modify the usual packing arrangement of the monomeric material—after Nakanshi *et al.*[31]

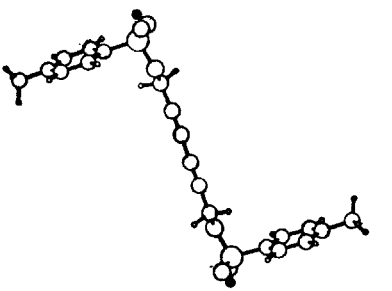

Fig 13 Molecular structure of the hexadiynelene toluene-*p*-sulphonate (*p*TS). The filled circles represent the position of the Ag^+ component of the $AgClO_4$ dopant.

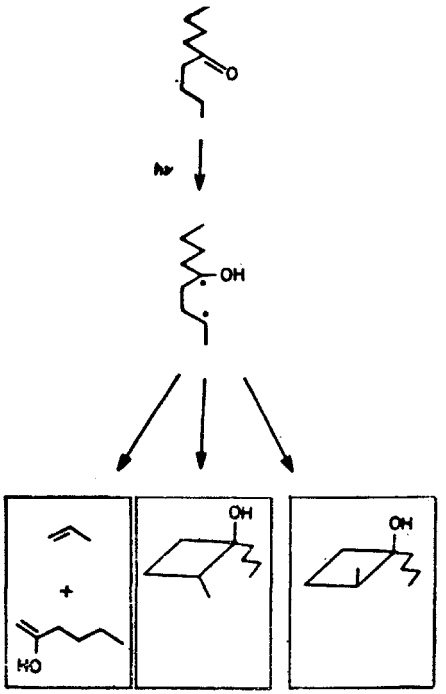

FIG 14 Schematic illustration of the possible reactions—via the Norrish Type II reaction—of 5-nonanone—after Casal *et al.*[33]

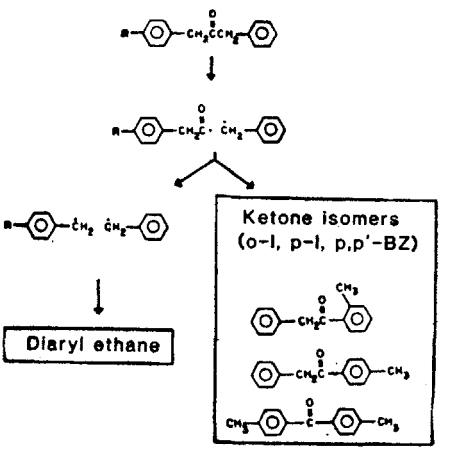

FIG 15 Possible photolysis steps for dibenzylketone (DBK) and *p*-methyldibenzylketone ($R = CH_3$).

When dibenzylketones are adsorbed on to zeolitic materials[7] the products which are obtained upon photolysis are very sensitive to both zeolite structure and to the presence of adsorbed additives, such as water, benzene, cyclohexane and hexane. For example in the case of dibenzylketone (DBK) and its *p*-methyl derivative (pMeDBK) the possible photolysis steps are shown in Fig. 15. In zeolite Na-A, where the entrance pores are too small (ca 4Å) to allow entry of DBK or pMeDBK into the cavities, the products of photolysis are completely analogous to those from reaction in a homogeneous solution. In thoroughly dehydrated Na-X or -Y, however, where the pore openings are ca 8 Å in diameter the yields of DPE* are 60 and 85 per cent, respectively : for pMeDBK the corresponding values are 18 and 19 per cent. When exposed to benzene vapour the yield of DPE is only 37 per cent for Na-Y, with isomers of DBK becoming the major products. When water is added to Na-Y only traces of isomers were observed.

It appears that the additives shroud the walls of the zeolite, thus presenting a rather more confined volume in which decomposition may take place, Fig. 16. The restricted motion then leads to an increased cage effect, with enhanced recombination of the generated radicals.[34]

*Diphenylethane.

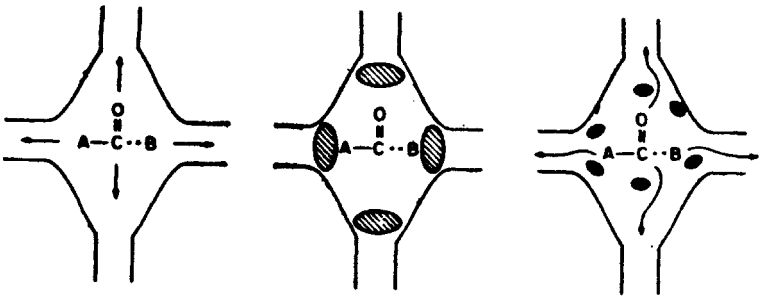

FIG 16 Schematic illustration of the influence of secondary guest molecules upon the reaction of primary radical pairs. Without additives (case (*a*)) there is rapid diffusion and rotation of the radicals. When an organic reagent is present (case (*b*)) it is postulated that both diffusion and rotation are inhibited, whilst in case (*c*) water modifies the rotation but not the diffusion of the radicals—after Turro *et al.*[7]

Adsorption of molecules onto other types of surfaces has also been investigated with a view to modifying reactivity. Thus photocatalysed olefin cis-trans isomerization has been observed for substituted styrenes[35] when exposed to the semiconducting material CdS and subsequently excited by light of wavelength shorter than its band gap of 2.4eV, approximately 520nm. A possible mechanism for the reaction is that electron transfer from the olefin to the photogenerated 'hole' in the semiconductor occurs, with the generation of a radical-cation. When dianthracene is adsorbed, the CdS serves as a heterogeneous photocatalyst for monomerization.[35] When the dimer is irradiated in methylene chloride with light of wavelength greater than 450nm no monomerization takes place. In the presence of CdS anthracene results in high yield.

ACKNOWLEDGEMENTS

We are grateful to the SERC and the University of Cambridge for support. Numerous discussions with our colleagues are appreciated.

REFERENCES

1. H Nakanishi W Jones J M Thomas M Motevalli and M B Hursthouse *J phys Chem* **85** (1981) 8636
2. C P Tang H C Chang R Popovich-Biro F Frolow M Lahav L Leiserovitz and R K McMullan *J Am chem Soc* **107** (1985) 4058
3. L Addadi Z Berkovich-Yellin I Weissbuch J Van Mil J W Shimon M Lahav and L Leiserowitz *Angew Chem int Edn (Engl)* **24** (1985) 466
4. Z Berkovich-Yellin L Addadi M Idelson L Leiserovitz and M Lahav *Nature* **296** (1982) 27
5. J R Scheffer *Accts chem Res* **13** (1980) 283; S Ariel S Askari J R Scheffer J Trotter and L Walsh In : *Organic Transformations in Nonhomogeneons Media* (*Ed* M A Fox) ACS Symposium Series No 278 (1985) 243

6. J M McBride *Accts chem Res* **16** (1983) 304
7. N J Turro C-C Cheng and X-G Lei *J Am chem Soc* **107** (1985) 3739
8. J M McBride and M D Hollingsworth *private communication*
9 D W Walter and J M McBride *J Am chem Soc* **101** (1981) 7074
10. C A Fyfe *et al* *Phil Trans R Soc London* **A305** (1982) 591; J R Lyerla C S Yannoni C A Fyfe *Accts chem Res* **15** (1982) 208
11. G M J Schmidt *Pure appl Chem* **27** (1971) 647
12. M D Cohen *Angew Chem int Edn (Engl)* **14** (1975) 386
13. J M Thomas *Phil Trans R Soc London* **A277** (1974) 251
14. J M Thomas S E Morsi and J P Desvergne *Progr phys Org Chem* (*Ed* V I Gold and D Bethele) **15** (1977) 63
15. W Jones H Nakanishi C R Theocharis and J M Thomas *J chem Soc Chem Commun* (1980) 610
16. C R Theocharis W Jones J M Thomas M Motevalli and M B Hursthouse *J chem Soc Perkin Trans* **II** (1984) 71
17. M D Cohen B S Green Z Ludmer and G M J Schmidt *Chem Phys Lett* **7** (1970) 486
18. C R Theocharis W Jones and C N R Rao *J chem Soc Chem Commun* (1984) 1291
19. C R Theocharis W Jones M Motevalli and M B Hursthouse *J cryst spectrosc Res* **12** (1982) 377
20. W Jones S Ramdas C R Theocharis J M Thomas and N W Thomas *J phys Chem* **85** (1981) 2594
21. N W Thomas S Romdas and J M Thomas *Proc R Soc London* **A400** (1985) 291
22. C R Theocharis G R Desiraju and W Jones *J Am chem Soc* **106** (1984) 3606
23. L Addadi S Ariel M Lahav L Leiserovitz R Popovitz-Biro and C P Tang *Chem Phys Solids and their Solid Surfaces* **8** (1980) 202 B S Green M Lahav and D Rabinovich *Accts chem Res* 12 (1979) 191
24. B S Green and L Heller *Science* **185** (1974) 527
25. L Addadi J van Mil E Gati and M Lahav In : *Symposium on the Origin of Life* (*Ed* I Walman) Reidel Dordrecht (1981)
26. H E Buckley In : *Crystal Growth* Chapman and Hall London (1951)
27. Z Berkovich-Yellin L Addadi M Idelson L Leiserovitz and M Lahav *Nature* **296** (1982) 21; L Addadi S Weinstein E Gati I Weissbuch and M Lahav *J Am chem Soc* **104** (1982) 4610; I Weissbuch L Addadi Z Berkovich-Yellin E Gati S Weinstein M Lahav and L Leiserovitz *J Am chem Soc* **105** (1983) 6615
28. D Y Curtin and I C Paul *Chem Rev* **81** (1981) 525; L Addadi Z Berkovich-Yellin I Wissbuch M Lahav and L Leiserovitz *Mol Cryst Liq Cryst* **96** (1983) 1
29. K J Wynne and G B Street *Ind Engng Chem Prod Res Dev* **21** (1982) 23
30. G Wegner *Makromol Chem* **154** (1972) 35
31. H Nakanishi H Matsuda and M Kato *Mol Cryst Liq Cryst* **105** (1984) 77
32. C R Theocharis H Nakanishi H Matsuda W Jones J M Thomas and M Kato *J chem Soc Chem Commun* (1985) 1334
33. H L Casal P de Mayo J F Miranda and J C Scaiano *J Am chem Soc* **105** (1983) 5155
34. H Al-Ekabi and P de Mayo *J chem Soc Chem Commun* (1982) 1073
35. R A Barber P de Mayo and K Okada *J chem Soc Chem Commun* (1982) 1073