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Reactions in Organic Crystals

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Structural studies on the following types of chemical reactions in organic crystals published after 1977 are considered: dimerisation, redimerisation, polymerisation, asymmetric synthesis, chemical reactions in clathrate compounds, topotactic redox reactions in intercalation systems, and crystal-gas reactions. A common feature of all the processes examined is the influence of the crystal environment of the molecules of the initial substance on the mechanism of the reaction and the character of its product (the topochemical factor).
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I. INTRODUCTION

Solid-phase reactions are attracting increasing attention at the present time for a number of reasons. Firstly, the limited mobility of the reacting molecules in the crystal makes it possible to carry out a well-founded structural investigation of the entire chain of molecular transformations, i.e. of the reaction mechanism. Secondly, with the aid of solid-phase reactions, it is possible to obtain polymers with a regular structure, enantiomerically pure products with the configuration of the chiral centres specified beforehand, large defect-free single crystals, which are especially suitable for electrophysical measurements, etc. All these features have led to the appearance and development of a new field of scientific research—crystal engineering, whose aim is to investigate the principles and rules governing the construction of different types of packing of potentially reactive molecules and crystals such that favourable conditions are created for the involvement of the molecules in particular chemical reactions and rearrangements not requiring diffusion and accompanied by only a slight rearrangement when the process is subject to topochemical control.[1]

This review surveys the principal results of structural studies on chemical reactions in organic crystals published after 1977 and not included in our previous review,[1] which dealt with the intramolecular rearrangements and reactions involving the formation of low-molecular-weight products in the solid phase.

The dimerisation and polymerisation reactions, to which the greatest number of structural investigations have been devoted, are discussed in greatest detail. With the aid of these reactions, it is possible to obtain in some cases the final product in the form of a single crystal, which is nowadays of practical importance.

The reactions in clathrate compounds and topotactic redox reactions in intercalation systems, which are intermediates between topochemical transformations in organic crystals and charge-transfer processes in low-dimensional binary systems, are also fairly close to practical application. However, in view of the limited space available in the review, these processes are considered only briefly, although topochemical analysis of the charge-transfer conditions in organic systems, considered as a solid-phase chemical reaction, is fruitful.

The classification of solid-phase reactions employed in this review is somewhat arbitrary, but it makes it possible to differentiate the main types of processes and the directions of further development of this interesting field at the junction between organic chemistry, crystal chemistry, and physical chemistry.

II. DIMERISATION

Dimerisation belongs to one of the most thoroughly investigated types of solid-phase chemical reactions. In essence, the strategy used in crystal engineering†[2] has been developed in relation to the solid-phase synthesis of optically active olefin dimers (and polymers)[3-9] by cycloaddition with formation of cyclobutane derivatives.

It has been established that the occurrence of these processes requires the type of packing in the crystal where the reacting double bonds are parallel and separated from one another by not more than 4.1 Å.[2] If these conditions are met, the overall geometry of the atomic environment of the reacting double bonds persists in the cyclobutane product, i.e. these processes are subject to topochemical control.#

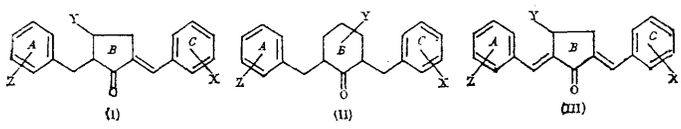
1. Benzylidene Derivatives of Cyclopentanones and Cyclohexanones

Compounds based on 2-benzyl-5-benzylidenecyclopentanone (I), 2-benzyl-6-benzylidenecyclohexanone (II), and 2,5-dibenzylidenecyclopentanone (III) are extremely promising for the study of solid-phase dimerisation and topotaxy of crystals as well as crystal engineering. Derivatives of these compounds (substituted in the *A*, *B*, and *C* rings) have been investigated in the dimerisation reaction in the crystalline state under UV irradiation.[11]

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†Solid-phase chemical reactions are controlled by specific types of organisation or by varying the character of the packing in the crystals of the initial compound.

#This rule agrees with a general topochemical principle, according to which reactions in organic crystals proceed with minimal atomic and molecular shifts.[10]



(I) (II) (III)

These systems are of considerable interest, because, in principle, it is possible to follow with their aid the non-diffusional rearrangement of atoms directly in the course of the chemical reaction.[5,12]

Table 1. The capacity for solid-phase dimerisation of the benzylidene derivatives of cyclopentanone and cyclohexanone whose structures have been investigated.[11]

Compound	X	Y	Z
(Ia)*	H	H	H
(Ib)	*p*-Br	H	H
(Ic)	*m*-Br	H	H
(Id)	*o*-Br	H	H
(Ie)	*p*-Cl	H	H
(If)	*o*-Cl	H	H
(Ig)	*p*-CH_3	H	H
(Ih)	*m*-CH_3	H	H
(Ii)*	H	H	*p*-Cl
(Ik)*	H	H	*p*-CH_3
(Il)*	*p*-Br	H	*p*-CH_3
(Im)	*p*-Br	H	*p*-Cl
(II)*	H	H	H
(IIIa)*	H	H	H
(IIIb)	H	Me	H
(IIIc)*	H	Me	H

*Has the ability to dimerise.

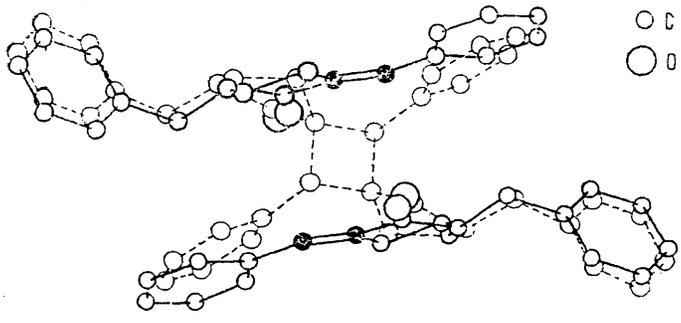


Figure 1. Schematic illustration of the dimerisation of compound (IIa) on irradiation with u.v. light in the crystal. The bold lines represent the monomer molecules and the dashed lines the centrosymmetric dimer molecule; the C atoms linked by a C=C bond are shown shaded. The insignificant shift of the benzene rings on dimerisation is worthy of note.[5]

The majority of reactive compounds of series (I), (II), and (III) (Table 1) crystallise in such a way that the nearest molecules are linked via their centres of symmetry and they therefore form centrosymmetric dimers in the solid-phase reaction (Fig.1). The double bonds in the crystals of compounds (Ia), (Ib), (Ii), and (II), whose structures have been investigated, are separated by distances of 4.2, 3.8, 4.0, and 3.8 Å respectively. The photostability of the remaining series (I) compounds can be accounted for by the larger distance between the double bonds [for example 6.2 and 4.7 Å in the crystal of compound (Ie) for molecules linked by glancing reflection planes]. The crystals of compounds (IIIb) and (IIIc), in which an asymmetric centre arises in the 3-position as a result of the introduction of the methyl substituent into the *B* ring constitutes an exception: the racemate (IIIb) is photostable and the crystals of the individual (IIIc) enantiomers are reactive. In the topotactic dimerisation of compound (Ia) (a single crystal–single crystal transition) the maximum change in the unit cell parameters is 0.7%.[5] However, by controlling carefully the rate of dimerisation, it is possible to achieve a homogeneous single crystal–single crystal transition for compound (Ib) and also for relatively large changes in the unit cell parameters (3.8, 5.6, and 6.5% for periods *a*, *b*, and *c* respectively).

Systems (I)–(III) open up completely new prospects in solid-state chemistry, namely the possibility of investigating the mechanism of a photochemical reaction in the crystal. The first step in this direction was the investigation of the variation of the unit cell parameters with increasing degree of conversion for a crystal of compound (Ia) in which the distance between the reacting double bonds is 4.166 Å, while the distance between the planes in which these bonds are located is 3.80 Å.[11]

The molecules in the crystal (Ii)[13] form around the centres of symmetry predimers in which the distance between the planes incorporating the C=O and C=C double bonds in each molecule is 4.036 Å, as well as the unsubstituted benzene ring. The intermolecular distance between the double bonds in such a predimer (4.027 Å) allows [2 + 2]-cyclodimerisation.[2] For this reason, on photoexcitation, these bonds can interact topochemically to form a cyclobutane ring, which has in fact been observed experimentally.

In order to elucidate the causes of the conversion of compound (II) into an amorphous form in its solid-phase photodimerisation reaction, its crystal structure was determined.[13] The molecules in the crystal of compound (II) also form predimers around the centres of symmetry with a distance of 3.028 Å between the planes incorporating (within each molecule) both double bonds and the unsubstituted benzene ring, which indicates a strong intermolecular interaction between the conjugated π-electron systems of the molecules. The shortest distance between the atoms involved in the C=C double bonds in the predimer is 3.792 Å. The loss of crystallinity by compound (II) as a result of photodimerisation[14] is probably associated with the necessity for an appreciable displacement of the dimer molecules due to the very close relative positions of the molecules in the predimer. In fact, in the crystal of compound (Ib), whose photodimerisation involves a single crystal–single crystal transition, the distance between the planes of the conjugated molecular systems in the predimer is 4.174 Å,[12] which is much greater than in compound (II). Furthermore, the decrease of crystallinity on photodimerisation can be caused by the low melting point of the product. The decrease of the melting point on formation of the new phase can induce the removal of the topochemical control over the solid phase reaction.[15]

Ideas concerning the possibility of topochemical interaction in crystals of types (I)–(III) have been developed[16] from an X-ray diffraction study of compounds (IIIa) and (IIIb) as well as the product of the solid-phase dimerisation of compound (IIIa).

The reactive C=C bonds of the neighbouring molecules in the photoactive crystal of compound (IIIa) and in the photostable crystal of compound (IIIb) have approached one another to distances of 3.720 and 3.871 Å respectively, permitting a topochemical interaction. However, these bonds

are not parallel, i.e. the condition necessary for topochemical interaction is infringed.[2,10,17] Nevertheless, photochemical dimerisation is observed in the crystal of compound (IIIa). The explanation is that, despite the lack of a parallel arrangement of the reacting double bonds (they form an angle of 56°), the axes of the p_z orbitals of the carbon atoms in compound (IIIa) are parallel. This is not observed in the crystal of compound (IIIb), which accounts for its photostability.

According to X-ray diffraction data,[16] the dimerisation of compound (IIIa) leads to the formation of precisely the isomer which should be obtained, i.e. the topochemical reaction proceeds via a defect-free mechanism. However, in contrast to the dimerisation of compound (Ia), the crystal structure of compound (IIIa) breaks down as a result of dimerisation and an amorphous product is formed. The transition to the amorphous state can be caused by the greater rigidity of the molecule of compound (IIIa) [i.e. its smaller ability, compared with compound (Ia), to "become adjusted" to the lattice of the new phase] and also by the necessity for the rotation of the molecules of compound (IIIa), because the formation of the dimer still requires that the double bonds of the interacting molecules be parallel.

The phenomenon of "structural mimicry" (the ability of molecules to change their conformation on becoming incorporated in the crystal lattice of the "host") has been used successfully[18] to ensure the reactivity of compound (Im), which is inert in the crystalline state, as a result of the formation of its solid solution with the reactive compound (II). The molecules of compound (II) have a planar conformation in the crystal, while those of compound (Im) have a bent conformation. This difference between the conformations, caused by the electronic and steric influence of the chloro-substituent,[18] changes the character of the molecular packing in these crystals. The mixed crystal having the composition (II) : (Im) = 7 : 3 is isostructural with the crystal of compound (II) and is photoactive, while the disposition of the double bonds satisfies the conditions for topochemical dimerisation. Whereas the distance between the double bonds in the photostable crystal of compound (Im) is 4.65 Å, in the photoactive crystal of compound (II) the C=C bonds of the molecules, linked via the centre of symmetry, are parallel and separated by 3.92 Å. In the mixed crystal the molecules of compound (Im) are forced to assume an extended conformation and the distance between the C=C bonds diminishes to 3.87 Å.[18] Thus Jones et al.[18] expanded the range of available tools in crystal engineering, previously restricted to the use of various "controlling" groups,[2,3,6,19] having used "structural mimicry" to convert the inactive molecules into a reactive form (conformation) by distributing them within a specified "active" packing.

2. Cyclohexylidenephenyl-5(4*H*)-oxazolones

In the course of the solid-phase photolysis of cyclohexylidenephenyl-5(4*H*)-oxazolones (IV), asymmetric dimers of three types, (V)–(VII), are formed.[20–23]

The structures of compounds of type (IV) with X = H[21] and Cl[22] the crystals are isomorphous), (V) (colourless main product with X = Cl[21]), and (VI) (yellow main product with X = H[20]) have been determined.

The crystal of compound (IV) has a layer structure with shortened distances between the molecules linked via the glancing reflection plane *b* (space group *Pbcn*). The formation of trispiropyrroloisoquinoline (V) in the crystal of compound (IV) not only as a result of asymmetric dimerisation but also due to the formation of two new C–N and C–C bonds between neighbouring molecules requires the transfer of one of the hydrogen atoms of the benzene ring to the nitrogen atom and the formation of a C–C bond between the benzene and cyclohexane rings. The geometry and relative orientations of the molecules in the predimer (IV) favour such a rearrangement.[21]

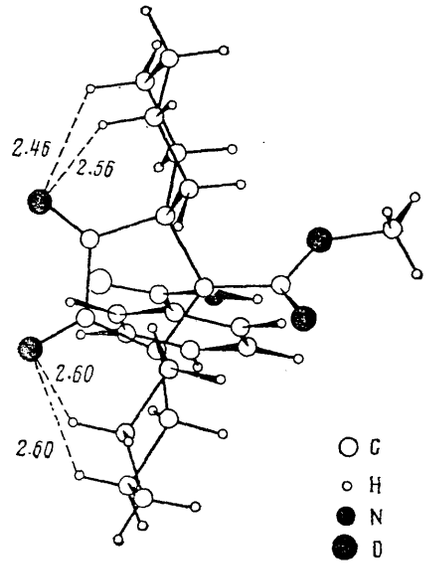
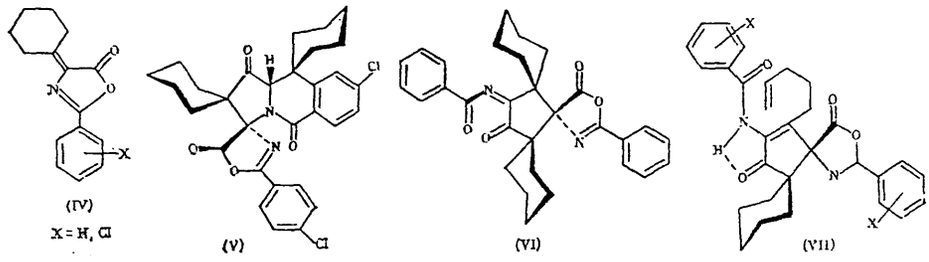
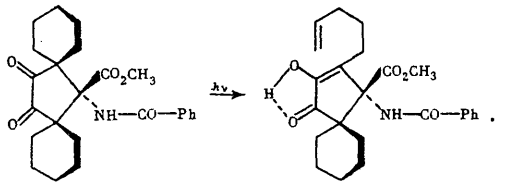


Figure 2. The structure of the diketoester (VIII) molecule. The short γ-H...O contacts are indicated by dashed lines.[20]

The formation of a dimer of type (VI) can be formally represented as asymmetric ($\pi^2 + \pi^2 + \pi^2 + \sigma^2$)-dimerisation of two molecules of the oxazolone (IV) linked by the plane *b*. The dimer having the presumed structure (VII) is not the primary solid-phase dimerisation product but is formed from the yellow dimer (VI) as a result of a Norrish fragmentation of the second type[20] with transfer of a H atom to the N atom.



Specific hypotheses concerning the mechanism of the γ-H transition are difficult to formulate in view of the disordered nature of the structure of compound (VI) in the region where the *N*-benzoylimino-group is located. However, fragmentation of the second type is characteristic not only of *N*-benzoyl-1,2-diketoimine (VI) but also of dispiro[5,1,5,2]pentadecane-14,15-diones obtained from the dimer (VI, X = H). For example, the yellow diketoester (VIII) gives rise to the colourless fragmentation product (IX).

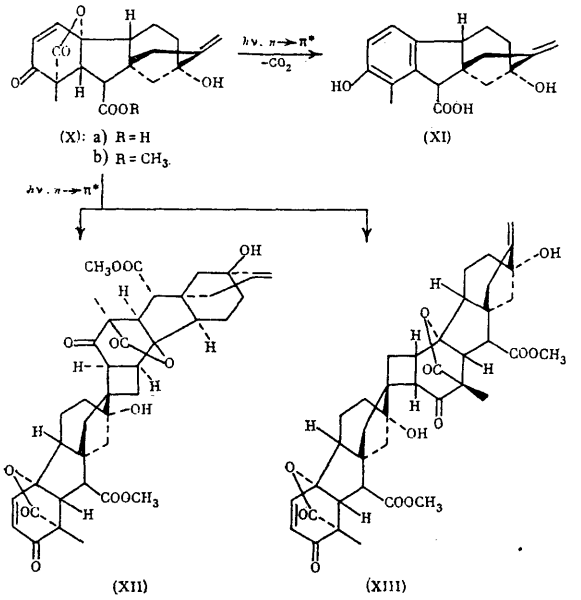


(VIII) (IX)

In the crystal of compound (VIII)[20] the four axial γ-hydrogen atoms are involved in intramolecular contact with the corresponding oxygen atoms of the keto-groups over distances of 2.46–2.60 Å, which favour the interaction (Fig. 2).

3. Derivatives of 3-Dehydrogibberellin A_3

The high photoactivity of 3-dehydrogibberellin A_3 (X) in the crystalline phase and the marked dependence of the pathway followed in this reaction on the character of the substituent R have been established.[24,25]



(X): a) R = H
b) R = CH_3

(XI)

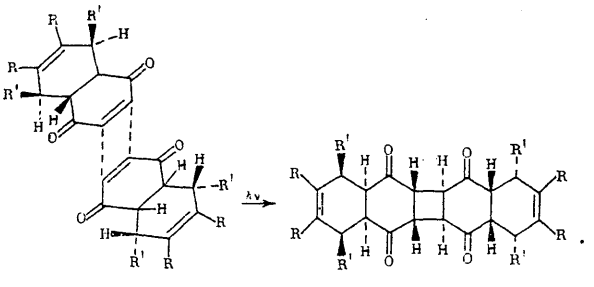
(XII) (XIII)

The enone acid (Xa) is decarboxylated as a result of the $n \rightarrow \pi^*$ excitation of the enone chromophore and is converted into the phenolic acid (XI) in a high yield,[26] while the corresponding methyl ester (Xb) dimerises with formation of compounds (XII) and (XIII) as a result of the intermolecular [2 + 2]-photocycloaddition of the C=C bond of the excited Δ^1-enone ring to the terminal double bond of a neighbouring molecule. The molecular geometries of the ester (Xb)[27] and the acid (Xa)[28] are very similar. Fig. 3 illustrates the relative dispositions of the molecules of compound (Xb), involved in the solid-phase dimerisation reaction, which are packed "head to tail" into infinite chains around the 4_1 axes (space group $P4_12_12_1$). The distance between the centres of the C(16)=C(17) and C(1′)=C(2′) double bonds in the neighbouring reacting molecules (3.71 Å) is favourable for topochemical reactions of this type.[2,29] The π orbitals of the double bonds of neighbouring molecules are located in approximately the same plane and are directed towards one another. The dihedral angle between the C(13)C(15)C(16)C(17) and C(1′)C(2′)C(3′)C(10′) planes is 19.7° and the torsional angle C(17)–[centre of C(16)–C(17) bond]–[centre of the C(1)–C(2) bond]–C(1) is 31.2°. Thus all the requirements for topochemical [2 + 2]-cycloaddition are met in the crystal of compound (Xb),[30] which makes it possible to predict the structure and stereochemistry of the main dimeric product (XIII) formed in 40% yield. The formation of the dimer (XII) as a side product is difficult to explain within the framework of the ideal topochemical model. Apparently this is a result of non-topochemical photodimerisation[29] caused by the imperfections of the initial crystal of compound (Xb).[2,30,31] It is believed[32,33] that the monomer molecules are able to rotate in the defective regions of this crystal in the intermediate excimeric state.

The different character of the solid-phase reactions on photoexcitation of compounds (Xa) and (Xb) has been explained by the different types of molecular packing in these crystals. In contrast to compound (Xa), in the crystal of compound (Xb)[28] the molecules are combined by hydrogen bonds into layers where the distance between the centres of the potentially active C(16)=C(17) and C(1)=C(2) double bonds is 4.5 Å and their π orbitals are oriented approximately at right angles, as a result of which only intramolecular photochemical reactions are possible.[27]

4. Derivatives of Naphthoquinone

Of the nine tetrahydronaphthoquinone systems whose structures have been investigated, only three [compounds (XVIa)–(XVIc)] are involved in topochemically controlled intermolecular reactions, forming the explosive dimers (XVIIa)–(XVIIc) via the [2 + 2]-photocycloaddition of the enedione double bonds of neighbouring molecules (the distances between the centres of their C=C double bonds are ≤4.04 Å).[34,35]

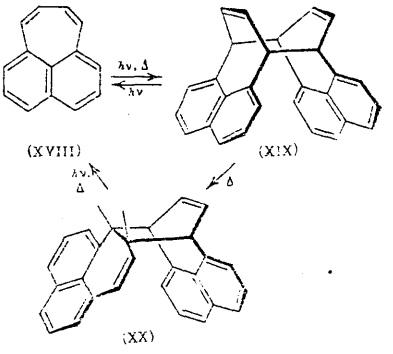


However, according to X-ray diffraction data, solid-phase intermolecular transfer of a hydrogen atom is also possible in compound (XVIb) (the H_β...O distances are 2.42 and 2.49 Å with the angles τ_O = 4° and 3° and Δ_O = 80.8° and

79.5°).§ Nevertheless, in the given instance the effect of the crystal packing, which favours a bimolecular reaction, predominates over the entropy factors, which usually promote a unimolecular reaction. This conclusion emphasises yet again how important it is to take into account the characteristics of the molecular packing in the crystal in formulating hypotheses about the course of photochemical reactions.[36]

5. 1,8-Naphthobicyclo[3.2.0]hepta-2,6-diene

Whereas prolonged irradiation of a solution of 1,8-naphthobicyclo[3.2.0]hepta-2,6-diene (XVIII) with ultraviolet light leads to the formation of a polymer and a small amount of naphthobicyclobutane, irradiation of the crystal with light in the visible region results in the appearance of the dimer (XIX):[37]



When the temperature is reduced to −195 °C, dimerisation ceases. On heating *in vacuo* to 150 °C, compound (XIX) isomerises quantitatively to the asymmetric dimer (XX), whose structure has been demonstrated by infrared spectroscopy and NMR. On irradiation with UV light at $\lambda = 313$ nm in solution, both dimers are readily converted into the initial monomer (XVIII).

In the crystal of compound (XVIII) at −196 °C the molecules are packed "head to tail" in pairs. On raising the temperature, the structure becomes disordered and the "head to head" arrangement appears within pairs of molecules, which leads to the formation of the dimer (XIX) for intermolecular distances permitting reaction in the solid phase. A decrease of temperature to −195 °C prevents the disordering and photodimerisation does not take place.

The molecule of compound (XIX) has a strained structure: the naphthalene fragments are not entirely non-planar, the valence angles at the peri-carbon atoms have been reduced to 113.2°, and the C–C bridging bonds have been extended on average to 1.626 Å. The strain energy of the molecule of compound (XIX), which was estimated by comparing the enthalpy of activation $\Delta H^{\neq}$ for the reaction (XIX) → (XX) with the enthalpy of dissociation of compound (XIX), is ~60 kJ mol^{-1}.[37]

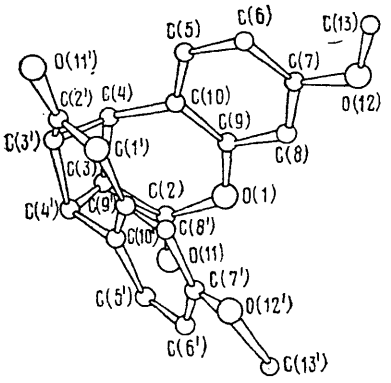


Figure 4. The structure of the 7-methoxycoumarin dimer (XXI); C(3)C(4)C(3′)C(4′) is the cyclobutane ring.[17]

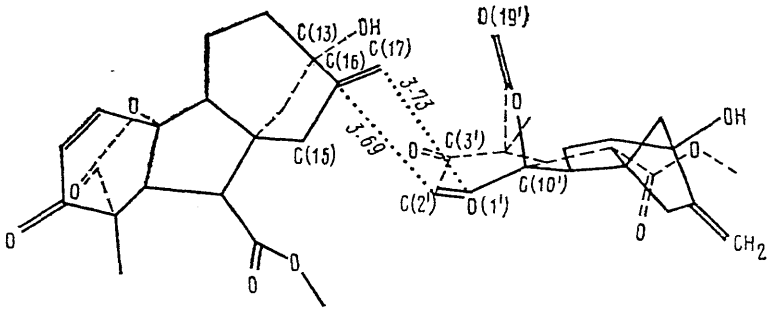


Figure 3. The relative disposition of the molecules linked by the 4_1 axis in the crystal of compound (Xb).[28]

§ The crystal of compound (XVIb) is constructed from two symmetrically independent molecules; τ_0 is the deviation of the atom H_β from the plane of the carbonyl group and Δ_0 is the $C(=O)H_\beta$ angle.

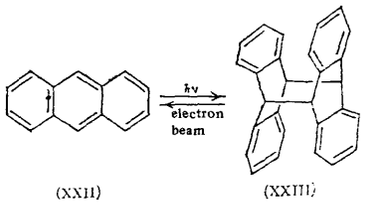
6. Coumarin Derivatives

Systematic crystallographic and photochemical studies have been made of the solid-phase dimerisation of ten coumarin derivatives.[17] The unsubstituted coumarin is photostable in the crystal, although it dimerises in solution.[38] On irradiation of the crystal with UV light, only 7- and 8-methoxycoumarins and 4-chlorocoumarin dimerise (the yields of the dimers are respectively 90, 50, and 40%). The dimer of 7-methoxycoumarin (XXI) has the *syn*-structure (head to tail arrangement, Fig.4), but in the crystal of the monomer the orientation of the double bonds of neighbouring molecules, forming an angle of 115°, is topochemically unfavourable. It is suggested that the rotation of the molecules of compound (XXI) essential for their transition to the reactive state is possible at the screw dislocations of the crystal of compound (XXI). The photostability of the non-dimerising crystalline coumarin derivatives is due to the unfavourable relative disposition of the molecules in the crystals[17] and not to their special electronic or steric properties.

7. Anthracene Derivatives

The solid-phase dimerisation and dimer dissociation reactions as well as the processes preceding the dimerisation of anthracene and its derivatives have been investigated quite comprehensively. Studies of the crystal structures of anthracene derivatives before dimerisation showed that the final products do not always correspond to compounds whose formation is predicted by the topochemical reaction mechanism. Calculations for the possible local rearrangements in the molecular packing (the appearance of defects and dislocations), responsible for the formation of the final products, are therefore essential in many instances for the modelling of the dimerisation processes.

The anthracene (XXII) dimerises on irradiation and the crystal structure of the monoclinic modification of compound (XXII) does not satisfy the requirements for the occurrence of a topochemical reaction.[39]



(XXII) (XXIII)

It has been suggested that the relative orientation of the molecules of (XXII) convenient for dimerisation can arise at structural defects. Calculation of the energy of the displacement of one half of the crystal relative to the other along the (001), (010), (0$\bar{1}$0), (100), and (20$\bar{1}$) planes (atom–atom approximation) showed[40] that the displacement along the (010) plane should take place most readily, which corresponds to the direction of the dislocations most frequently observed in the anthracene crystal.[41] Analysis of the intermolecular distances changing as a result of the displacement showed that local molecular arrangements, favourable for dimerisation, can arise at the interface. However, Mirsky and Cohen[40] failed to take into account the changes in the disposition of the molecules (relaxation) near the defect, which led to unduly high displacement energies and to clearly unduly low interatomic distances.

The stabilities of point defects arising on the surface and in the bulk of the crystal of compound (XXII) on the removal of one molecule or on replacement of five molecules in the lattice by the more "freely" distributed four molecules have been estimated.[42] This calculation, carried out taking into account the relaxation of the molecular environment around the defect, showed that a defect can be thermodynamically stable and favourable for the subsequent rearrangement with participation of excited molecules.

The metastable triclinic phase of the anthracene (XXII) is formed when the monoclinic crystal is compressed in the direction at right angles to the basal plane. Its structure has been determined by electronic transmission microscopy and has been confirmed by the calculation of the molecular packing by the method of atom–atom potentials. It was found that the atoms interacting on dimerisation in the triclinic structure of compound (XXII) are closer together than in the monoclinic phase (the distance between them has been reduced from 4.5 to 4.2 Å). Calculation for the possible rearrangement of the two modifications on excitation of their molecules[43] failed to reveal changes sufficient to ensure the topotactic formation of the dimer. Consequently the occurrence of the reaction at structural defects is extremely probable.

A similar picture has been observed also for anthracene derivatives. Thus, when 1,5-dichloroanthracene is irradiated in solution with UV light, it is converted into a mixture of "head to head" (HH) and "head to tail" (HT) isomers in proportions of 40:60.[32] The solid-phase dimerisation of the monoclinic form leads to the formation of a dimer of the HH type (the reacting atoms of neighbouring molecules are at a distance of 4.05 Å).[30] The crystalline structure of the triclinic modification formed on dimerisation of a mixture of 80% of the HH isomer and 20% of the HT isomer has been determined by the method of atom–atom potentials.[30] A distance of 4.0 Å between the translationally linked molecules in this structure corresponds to the topochemical mechanism of the formation of the HH isomer. The study of the planar or linear defects showed that the symmetry of the given lattice makes it impossible to find a displacement which would lead to the formation of a dimer of the HT type. Presumably some of the molecules acquired an orientation favouring the formation of the HT dimer on rotation during the crystallisation process, i.e. a point defect appeared. Calculation of the energy of such defects, which is defined as the difference between the energies of the interaction with the environment of the "defect" molecule and the molecule in the ideal lattice has shown[44] that it amounts to ~4 kJ mole^{-1} in the triclinic structure and ~100 kJ mol^{-1} in the monoclinic structure. These differences explain the ease of formation of defects and the appearance of two dimeric products in the triclinic structure.

Dimerisation in the crystals of 1,8-dichloro-9-methylanthracene (XXIV)[45] and 1,8-dichloro-10-methylanthracene (XXV)[30] entails the formation of *cis*-products which are not due to a topochemical reaction. Energy calculation for compound (XXIV)[45] has shown that the appearance of planar defects "preparing" for the formation of the *trans*-dimers is possible. Modelling and electron microscope study of the dislocations in the crystal of compound (XXV)[46] made it possible to explain analogously the formation of dimeric products in this case also. Processes involving the formation of excimers and rearrangements occurring in the crystal lattice under these conditions have been examined in fair detail for anthracene and its derivatives both experimentally and with the aid of computational models. The results of studies devoted to these questions are discussed in the next Section.

8. Excimers in Crystals

Excimers were first detected in concentrated pyrene solutions, which exhibited unusual spectroscopic properties on irradiation compared with dilute solutions.[47] Later excimers were found also in pyrene crystals.[48] Experiment showed that excimers are formed throughout the bulk of the crystal and not only at structural defects. The molecular planes are almost fully overlapped to the maximum extent and approach one another. The formation of excimers is most probable when such overlap obtains already in the initial crystal structure.

Various computational models have been used to describe the geometry and spectroscopic characteristics of excimers (excimer emission).[49-51] The interactions of the pair of molecules in the excimer are usually assessed semi-empirically by quantum-chemical methods, while the interactions with the environment in the crystal are assessed in terms of the atom–atom approximation. Other parameters, characterising the dispersion interactions, which change as a result of the polarisation or excitation of the molecule, are sometimes specified (within the framework of the atom–atom approximation) for the excited molecule.

In the free pyrene excimer the molecular planes overlap fully and the distance between them becomes 3.2 Å. For such mutual approach of the molecules in the crystal, it is essential to displace them by approximately 0.7 Å, which involves the overcoming of an energy barrier of ~15–20 kJ mole^{-1}.[50] Analogous results have also been obtained in the calculation for the α-form of perylene.[51]

Many compounds, in the crystals of which excimers arise on irradiation, tend to undergo photodimerisation reactions. Since the formation of the excimer involves the mutual approach of two molecules and an increase of the degree of overlap of their planes, the excimer can be regarded as a dimerisation intermediate. This has been demonstrated in relation to a series of anthracene derivatives[51-53] which have three types of characteristic packing in the crystal: (1) "herring bone" packing without the overlap of the planes of the nearest molecules (type A) (both anthracene modifications); (2) stacked packing with a "head to head" arrangement—type B1 (9-cyano-, 9-chloro-, 9,10-dichloro-, and 9-carboxy-anthracene); (3) packing with a "head to tail" arrangement of molecules in pairs—type B2 (9-methyl- and 9-amino-anthracene). Emission of the monomer type only is observed in type A crystals,[52] while in crystals of types B1 and B2 the overlap of the molecular planes is significantly greater, excimers and dimers being formed in them; the frequencies change to the greatest extent in type B2 compounds on transition to the excited state.

The possible changes in the relative disposition of the molecules in crystals following the appearance of an excited molecule in the latter have been calculated by the method of atom–atom potentials[54] for two modifications of anthracene and its derivatives—9-cyanoanthracene (XXVI) and 9-methylanthracene (XXVII), which are characterised by different types of packing. Following the appearance of an excited molecule in the crystal of compound (XXII), the disposition of the molecules surrounding it hardly changes, which agrees with the absence of excimer emission. Dimers apparently are not formed in the bulk of the crystal, which does not rule out dimerisation on the surface and on defects.[54] In crystals of compound (XXVI) the excited molecule approaches one of the neighbouring molecules in the stack and the surrounding molecules are "drawn" towards this pair. Since in the given instance the dimerisation products contain only the *trans*-dimer (and not the *cis*-dimer, which corresponds to a topochemical mechanism), presumably the excitation energy of the *cis*-excimers is transferred to structural defects, where the *trans*-dimer is formed. In crystals of compound (XXVII) (type B2), the excited molecules are appreciably displaced towards one of the molecules in its environment, while the positions of the remaining surrounding molecules change little. The absence of steric hindrance and the antiparallel directions of the molecular dipole moments, as in the second modification of 9-chloroanthracene (likewise type B2), permit dimerisation throughout the bulk of the crystal.[54]

The most striking examples of the intermediate formation of excimers are provided by the decomposition and redimerisation in the crystal of dianthracene (XXIII).[44] If a single crystal of compound (XXIII) is subjected to high-energy irradiation, some of the dimer molecules are cleaved into pairs of monomers. Exposure to low-energy irradiation leads to excimer emission and the redimerisation of the monomer molecules. The quantum yields of both processes depend on temperature. Thus, together with dimerisation, the excimer emission serves as a pathway leading to the deactivation of the excimer.

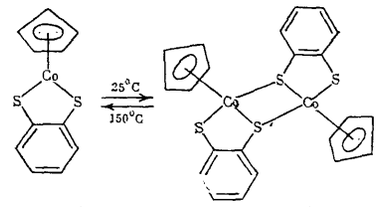
Calculations carried out in terms of the atom–atom approximation, which models the processes described above, have shown[55] that the formation of dianthracene crystals incorporating pairs of anthracene molecules is energetically more favourable than the formation of crystals of dianthracene alone as a result of the increase of the intensity of the non-valence interactions in pairs of molecules compared with the dimer.[55] In our view, a special physical significance should not be attributed to the energy differences observed, but it is clear that the dissociation of the dimer does not induce a significant steric hindrance in the lattice. According to the calculation, the disposition of a pair of molecules of compound (XXII) in the dianthracene matrix is such that their planes do not overlap fully. Hence one can understand the necessity for the expenditure of energy in order to overcome the barrier to the formation of the excimer or to redimerisation.[55]

Excimers are also formed in crystals made up of planar aromatic molecules. Thus excimer emission and photodimerisation are characteristic of two crystalline forms of 2,4-dichloro-3-methylstilbene.[56] In one of the modifications with a stacked molecular arrangement *cis*-excimers and dimers with *m* symmetry are formed. In the other modification, with molecules which have approached one another in pairs, *trans*-excimers and centrosymmetric dimers arise. Thus, in the given instance the structure of the dimer is determined by the same characteristics of the crystal packing as the structure of the excimer.

The formation of excimers in a crystal made up of non-rigid molecules (analogous to those mentioned above) is a more complex process than for rigid aromatic molecules. According to calculations, the photodimerisation of 1-(2,6-dichlorophenyl)-4-phenylbutadiene is accompanied not only by the mutual approach of the molecules but also by a change in their conformation.[57,58] It has been shown that the excimer can be obtained in two ways presupposing the approach to one of two neighbouring molecules in the stack, requiring approximately identical energy expenditures. At any rate, it follows from the results of the calculation taking into account the molecular relaxation that the excimer has an asymmetric environment. The real pathway followed in the dimerisation reaction can be deduced only by determining the structure of the monomer and the products formed by X-ray diffraction. Calculation for 1-(2,6-dichlorophenyl)-4-phenylbutadiene does not rule out the appearance in the crystal not only of excited dimers but also of trimers.

9. Cyclopentadienyl(*o*-phenylenedithio)cobalt

The dimerisation of cyclopentadienyl(*o*-phenylenedithio)-cobalt is an example of a rarely encountered reversible solid-phase process (XXVIII).[48]



(XXVIII) (XXIX)

In the crystal of compound (XXVIII) the molecules are arranged "head to tail" and, although the Co...S intermolecular distances [4.702 and 4.325(1), Å] are fairly large, the relative disposition of the "heavy" atoms (Co and S) resembles that observed in the crystal of the dimer (XXIX). In the course of the solid-phase transition the coordination of the cobalt atom changes from the "two-legged" type in compound (XXVIII) to the "three-legged" piano stool type in compound (XXIX). The slope of the plane of the η^5-C_5H_5 ring relative to the S–Co–S plane changes by 45° on passing from compound (XXIII) to compound (XXIX). Whereas the metal-containing ring in compound (XXVIII) is almost planar (the maximum deviation is 0.02 Å), in compound (XXIX) the ring is bent along the S...S line by 20.9°.

The solid-phase dimerisation of compound (XXVIII) takes place as a result of the mutual approach of its molecules (predominantly in the direction of the *b* axis) and increases the density of the crystal by 6%. The orientation of the axes in the crystals of compounds (XXVIII) and (XXIX) (which belong to the same space group $P2_1/c$) is not the same and the reaction is not topotactic. At 25 °C the dimerisation is fairly slow owing to the relatively high "rigidity" of the potential energy surface of the crystal. Furthermore, the development of the reaction requires defects—nucleation centres. The rate of the reverse reaction (XXIX) → (XXVIII), which depends on the particle size, is low at 150 °C but rapidly increases at higher temperatures. The small enthalpy of monomerisation (ΔH = 18.9 kJ mol^{-1} at 150–160 °C) found from data obtained by differential scanning calorimetry is consistent with data indicating the occurrence of conformational polymorphism and is insufficient for the occurrence of the reversible solid-phase reaction despite the considerable displacements of the atoms.[48]

The examples examined show that the combination of experiment (X-ray diffraction and spectroscopic methods) and calculation makes it possible to investigate various stages in the formation of dimers in the crystal. It may be that subsequently this approach will be applied also to the consideration of more complex solid-state reactions.

III. REDIMERISATION

The redimerisation process in the crystal has been most thoroughly investigated for anthracene derivatives (see also above). It has been shown that the *trans*-dimer (XXX) of 9-cyanoanthracene (XXXI), formed by the solid-phase dimerisation on irradiation with UV light,[59] is capable of being reconverted into the monomeric form in the crystal on thermal or photochemical initiation,[60] which imparts practical importance to this reversible process, for example, for the reversible absorption of solar energy.[61] The study of crystals by differential scanning calorimetry has revealed the presence of two exothermic peaks, the second of which corresponds to the complete conversion into the monomeric form and the first (at 152 °C) corresponds to a homogeneous topotactic single crystal → single crystal phase transition of the colourless triclinic crystal of compound (XXX) into the yellow, also triclinic, crystal of compound (XXX'). The driving force of this polymorphic transformation is partial conversion into the monomeric form [the admixture of the monomer (XXXI) in the crystal of compound (XXX') amounts to 8%].[60]

Pyrimidines and their *N*-methyl derivatives dimerise on UV irradiation in the solid phase via their double bonds in the 5- and 6-positions. Depending on the disposition of the dihydropyrimidine rings relative to the cyclobutane ring formed on dimerisation, four stereoisomeric forms of the dimer are possible: *cis, syn-*, *cis, anti-*, *trans, syn-*, and *trans, anti-*.[62] The structures of ten dimers of all four types have been determined,[63] including the *cis, syn*-form encountered in DNA[64] and two dimers (of the *trans, anti*-type) of thymine and 1-methylthymine.[65]

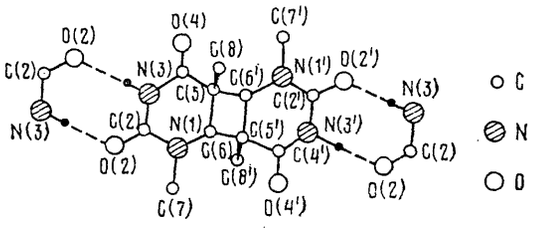


Figure 5. A fragment of the crystal structure of compound (XXXII); the N–H...O hydrogen bonds linking the molecules of compound (XXXII) into infinite chains in the [110] direction are shown dashed.[66]

The thymine dimers are cleaved in solution on irradiation with UV light[66] or X-rays.[67] The solid-phase conversion into the monomeric form on exposure to ^{60}Co γ-rays of the crystals of all four stereoisomers of the *NN*-dimethylthymine dimer[68] or in the course of X-ray measurements on three dimers of the *cis, syn*-type[69] is also possible. X-Ray diffraction study of the 1,1'-trimethylenethymine dimer revealed the presence of ~10% of monomeric molecules incorporated in the dimer crystal.[70] The possibility of the conversion into the monomeric form has been reported by the investigators of the structure of the 1,3-dimethylthymine dimer (a sharp increase in the length of one of the interpyrimidine bonds to 1.66 Å), but the monomeric molecules could not be located.[71] A third example is provided by the sodium salt of the thymine dimer, in the crystal of which monomer molecules were found.[72]

We shall consider the structure of the *trans, anti*-dimer of 1-methylthymine (XXXII).[66] The molecules of compound (XXXII), combined in the crystal into infinite chains along the [110] direction by N(3)–H...O(2) bonds (Fig.5), show no signs of the steric strain observed in the dimers of the *cis, syn*-type, which also associate in the crystal on irradiation with X-rays [the steric strain is shown by the shortened intramolecular distances between the methyl groups at the C(5) and C(5') atoms[70–72]]. Nevertheless the crystal of compound (XXXII) contains ~4% of the monomer molecules

formed as a result of the solid-phase dissociation on irradiation with X-rays in the course of the structural study. This result confirms data[64] indicating the possibility of the solid-phase dissociation on irradiation of unstrained stereoisomeric dimethylthymine dimers with X-rays.

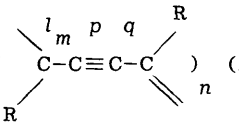
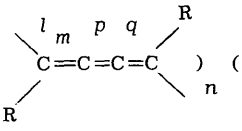
IV. POLYMERISATION

The greatest advances have been made in the field of topochemical solid-phase non-diffusional polymerisation of diacetylenes, which proceeds via 1,4-addition. Reports about these processes appeared a long time ago (the crystals of diacetylenedicarboxylic acid darken on illumination and irradiation with X-rays[73]), while the most important results were obtained approximately 15 years ago by Wegner[74-76] and Baughman.[77] The second field involved the study of solid-phase topochemical polymerisation reactions of diolefins. The investigations began after the report of the ability of the α-modification of 2,5-distyrylpyrazine to polymerise as a result of the photoinduced [2 + 2]-polycycloaddition[78,79] although data concerning the possibility of the occurrence of the process had appeared considerably earlier.[80]

A number of other systems which polymerise in the crystal subject to more or less vigorous topochemical control are also known.[80] Compared with the first two systems (diacetylenes and diolefins), they are less important. Among them, mention should be made in the first place of the cyclic oligomers of formaldehyde, which are capable of polymerisation with the opening of the ring. Although a distinct topotactic interrelation is observed between the starting materials and final product in this process, the latter is not topochemical. This reaction has been considered in detail in a review.[80]

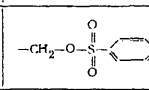
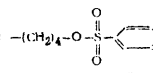
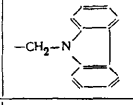
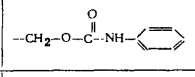
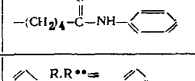
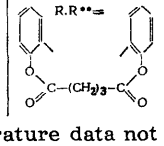
1. 1,4-Addition of Diacetylenes

The solid-phase polymerisation of diacetylenes (DA), which makes it possible to obtain large single crystals of polydiacetylenes (PDA), is a fairly thoroughly investigated reaction (see the relevant reviews[80-83]). Nevertheless studies in this field still remain timely, mainly in connection with the vigorous development of research in the field of conducting organic systems.

The solid-phase polymerisation of the diacetylene R–C≡C–C≡C–R, which is initiated either by heating to temperatures below the melting point, or by irradiation with γ-rays or UV light, or by other influences, constitutes poly-1,4-addition. The products of this reaction consist of quasi-one-dimensional macromolecules with a conjugated skeleton fully in the *trans*-configuration.[74-77] Two limiting structures of PDA are possible: the ene-yne (ethylene–acetylene structure  (A) and the butatriene (cumulene) structure  (B); in the real PDA, obtained by the solid-phase polymerisation of DA (Table 2), both structures have been detected, although structure (A) predominates.[78,84-88]

Numerous studies have been devoted to the physicochemical properties of PDA (see, for example, Yee and Chance[82]). The thermal stability of PDA can be both low [compound (XXXIIIp) decomposes at temperatures not

Table 2. Principal structural parameters of PDA obtained by the solid-phase polymerisation of R–C≡C–C≡C–R.

Compound	R	Structure	Bond length, Å				Space group, direction of chain	Refs.
			l	*m*	*p*	*q*		
(XXXIIIp)		(A)	1.356 (4)	1.428 (4)	1.191 (4)	1.428 (4)	$P2_1/c$, $Z = 2/n$; chain along $b = 4.910$ (3) Å	[83]
(XXXIVp)		(A)	*	*	*	*	$P\bar{1}$, $Z = 2/n$; chain along $c = 4.91$ (1) Å	[85]
(XXXVp)		(A)	1.33 (2)	1.44 (2)	1.21 (2)	1.44 (2)	$P2_1/c$, $Z = 2/n$; chain along $b = 4.907$ (4) Å	[86]
(XXXVIp)		(A)	1.36	1.41	1.21	1.42	$P\bar{1}$, $Z = 1/n$; chain along $a = 4.89$ (1) Å	[87]
(XXXVIIp)		(B)	*	*	*	*	*	[86]
(XXXVIIp)		(B)	1.42 (3)	1.38 (2)	1.29 (2)	1.38 (2)	$C2/c$, $Z = 8/n$; chain along $c = 9.69$ Å ***	[88]

*Literature data not available.

**The monomer unit has a cyclic structure.

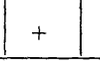
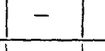
***The repeat period of the polymer chain is greater by a factor of approximately two than for (XXXIIIp)–(XXXVIp) in connection with the different (*trans*) disposition of the cyclic substituents relative to the PDA chain.

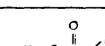
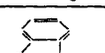
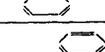
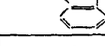
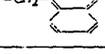
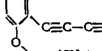
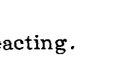
exceeding 70 °C[89]] and very high [the weight loss of compound (XXXVIIp) is 2.5% at 300 °C,[90] while compound (XXXVp) is stable up to 300 °C and at 400 °C its weight loss does not exceed 6.5%]. Whereas the thermal stability of compound (XXXVIIIp) has been accounted for by the stabilising effect of bisphenylglutaric chains forming a ring on the polymer chain, the thermal stability of compound (XXXVp) is associated with the stability of the carbazolyl substituent [furthermore, a high mechanical strength is characteristic of compound (XXXVp)[82]].

The electrophysical properties of PDA are of special interest. Although these polymers remain insulators under the usual conditions[91–95] [for example the average conductivity of compound (XXXIIIp) is $\sigma = 10^{-15}\ \Omega^{-1}\ cm^{-1}$ [82]], the PDA crystals exhibit anisotropic conductivity.[81] At the same time, by doping the DA crystals with iodine and by subsequent solid-phase polymerisation under the influence of γ-irradiation, it is possible to obtain PDA with metallic lustre and $\sigma = 10^{-4}\ \Omega^{-1}\ cm^{-1}$.[93] The photoconductivity of PDA has been investigated.[82,94] The lowest optical transition energy (1.89 eV) is that of the crystals of compound (XXXIIIp).[82] The appreciable hypsochromic shift of the photoconductivity spectra of PDA relative to the optical absorption spectra is consistent with the exciton mechanism of the optical transitions with the minimum energy in PDA.[82]

The study of the structure of PDA is of special interest for two reasons. Firstly, the polymerisation of DA is possible only under lattice control and is not observed in the melt, in the gas phase, or in solution.[81] Secondly, data for the structure of PDA are important in connection with the similarity of these polymers to polyacetylenes—an important class of organic metals, the elucidation of the structure of which (particularly in doped systems) is fairly difficult.[95]

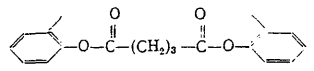
Table 3. The principal data on the reactivities in solid- phase polymerisation and molecular packing in crystals of the structurally investigated diacetylenes of the type R–C≡C–C≡C–R (for the significance of the parameters S_1, γ_1, and d_1, see Fig. 6).

Compound	R	Reactivity	Parameters of the relative disposition of the stacked DA molecules			Refs.
			S_1, Å	γ_1, deg	d_1, Å	
(XXXIX)	$-CH_2OH$	+*	3.94** 3.54	41.4 53.4	4.77 5.34	[96]
(XL) ***	$R^1 = -CH_2$; $R^2 = -CH_2OH$	+*	3.71	49.6	4.87	[97]
(XLI)	$-(CH_2)_2-OH$	+	3.65	—	—	[98]
(XLII)	$-Ph$	—	4.69	50.9	6.04	[99]
(XLIII)		—	—	—	—	[100]
(XLIV)	$-CH_2-O-Ph$ ***	—	—	73	7.47	[101]
(XLV)	$-C(OH)Ph_2$	—	—	—	—	[102]
(XLVI)		—	4.02 6.11	58.8 40	4.35 8.48	[103]
(XLVII)		+	—	—	—	[104]
(XLVIII)		—	—	—	—	[105]
(XLIX)		—	—	—	—	[106]
(L) ****		+	—	—	—	[107]

Compound	R	Reactivity	Parameters of the relative disposition of the stacked DA molecules			Refs.
			S_1, Å	γ_1, deg	d_1, Å	
(LI)		+	—	—	—	[106]
(LII)		+	—	44** 46	5.11	[108]
(LIII)		+	—	47.9	5.19	[85]
(LIV)		—	—	67.0	5.030 4.962*****	[109]
(LV)		—	—	90	5.977*****	[110]
(LVI)		+******	—	60	4.55	[111]
(LVII)		—	—	61.5	4.35	[111]
(LVIII)****		+* —	— —	46 90	4.93 5.42	[112]

*Incomplete conversion.
**There are two types of intermolecular contacts in the crystal with participation of diacetylene fragments.
***Asymmetric DA of the type $R^1-C\equiv C-C\equiv C-R^2$.
****Two polymorphic modifications have been investigated.
*****Intermolecular distance between atoms potentially capable of reacting.
******Phase transition on polymerisation.
*******Cyclic DA.

Apart from the linear DA (XXXIX)–(LVII), the solid-phase polymerisation of the cyclic DA (LVIII) (Table 3) with formation of a fully stereoregular polymer (XXXVIIIp), whose skeleton is threaded by ring-forming *oo*-bisphenylglutarate groups, has also been investigated:[90,112,113]



The capacity for solid-phase polymerisation of the even more complex macrocyclic DA $[-(CH_2)_2-C\equiv C-C\equiv C-(CH_2)_2-]_4$ (LIX) has been observed. As a result of the 1,4-addition via all four diacetylenic groups, this compound is converted into an ordered polymer with a "cylindrical" structure.[114]

The conditions governing the formation of large defect-free crystals of PDA by the solid-phase polymerisation of DA have been analysed.[115]

1. The free energy barrier to cooperative displacements of the DA molecules, necessary for their polymerisation, increases (i.e. the capacity for polymerisation diminishes) with increase of the displacement of the interacting molecules necessary for the reaction.

2. The polymeric molecules must be capable of forming solid solutions in the crystal of the polymerising matrix at any degree of conversion (single-phase or homogeneous polymerisation).

3. The symmetry of the crystal environment of the monomer molecules must correspond to the symmetry of the environment of the monomeric unit of the polymer molecule.

By varying the reaction conditions, it is in many instances possible to promote single-phase polymerisation, in particular, by imposing an external force field it is possible to alter the symmetry of the monomer crystal.[115] However, only polycrystalline PDA are formed in the polymerisation of certain DA. This happens in those cases where the nucleation of the new phase (the solid-phase polymerisation can be regarded as a special type of phase transition) occurs on defects, surfaces, or impurities in the monomer crystal.[81] In principle, such processes can lead to the formation of large PDA crystals (when the polymerisation and crystallisation take place simultaneously). On the other hand, the topotaxy in the initial and final phases does not necessarily indicate the topochemical character of the solid-phase transition.[81]

We shall consider the mechanism of chain propagation in the monomer crystal matrix. The following scheme has been proposed for this process: thermal (or radiation-induced) excitation of the conjugated triple bonds with transition to intermediates of the dicarbene type, combination of the dicarbenes with formation of double bonds, and growth of the macromolecule as a result of further addition of excited molecules to the carbene-like end of the chain.[81] The formation of biradical dimeric, trimeric, and tetrameric, etc. intermediate compounds has been detected by EPR[116–119] and optical spectroscopic[120,121] methods in the study of the solid-phase transition (LIII) → (XXXIVp). The most probable chain length of the PDA macromolecules in the polymerised crystal of compound (XXXIVp) has been estimated by gel-permeation chromatography. It amounts to 1600 monomeric units when the polymerisation is carried out at 7 °C and to 400 units at −263 °C. The difference is attributed to the different mechanisms of the polymer chain propagation.[85]

The condition governing the solid-phase reactivity (the Schmidt condition[2,10,122]), which has been extended in a general form to polymerisation by Kargin and Kabanov,[123] has been formulated by Wegner (see, for example, Shklover et al.[80]) and Baughman (see, for example, Ref.77) on the basis of the analysis of the crystal structures of DA active and inactive with respect to solid-phase polymerisation. This condition reduces to the following limiting values of the parameters S_1 and γ_1 of the molecular packing of DA, generating ladder (stacked) motifs in the crystals: $3.4 \leq S_1 \leq 4.0$ Å; $\gamma_1 \cong 45°$ (Fig.6). In the polymer, $d_2 = 4.9(1)$ Å and $\gamma_2 = 13.5°$.[77,80]

The rates of the solid-phase polymerisation of the chemically very similar compounds (XLVII) and (XLVIII) differ sharply: compound (XLIV) reacts much faster.[104,105] In the crystal of compound (XLIV), the values of S_1 (3.36 Å) and γ_1 (42.4°) satisfy the Wegner–Baughman conditions. In the crystal of compound (XLVIII) two types of relative dispositions of the molecules have been distinguished: the δ-type ($S_1 = 3.817$ Å and $\gamma_1 = 67.54°$) and the δ′-type ($S_1 = 4.643$ Å and $\gamma_1 = 63.44°$). In the former case the solid-phase interaction is significantly hindered, while in the latter case it is impossible.[104,105]

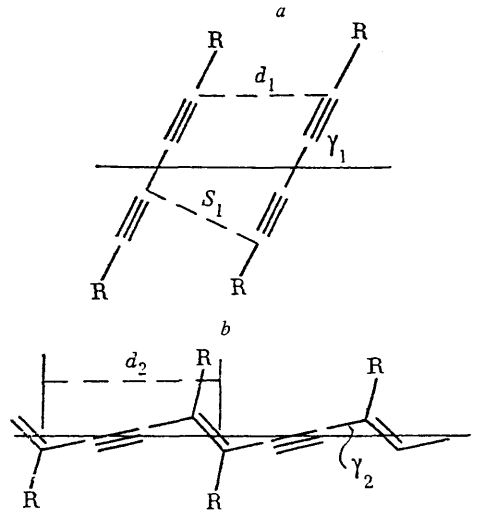


Figure 6. Schematic illustration of the packing of DA crystals with a ladder disposition of the molecules (*a*) and the structure (fragment) of the PDA molecules formed on polymerisation of DA via the "scissors" mechanism (*b*).[77,80]

It is of interest that an appreciable infringement of the "scissors" mechanism of the polymerisation of DA has been observed for the solid-phase reaction (LIII) → (XXXIVp) (Fig.6): the centre of gravity of the DA fragment shifts on polymerisation by 0.97 Å.[85] The possibility of such a shift without the breakdown of the crystal lattice structure can be explained by the fact that the toluene-β-sulphonate groups occupy pseudocentrosymmetric positions in the crystal, i.e. they retain their positions on transition to the centrosymmetric crystal of compound (XXXIVp).

The solid-phase polymerisation of the monomer (L), the only reactive DA in the crystal of which the DA "rods" are not parallel but are arranged at an angle of 72°, may constitute an exception to the "scissors" mechanism. The solid-phase transition of the monomer (L) on treatment with dioxan vapour to a very rapidly polymerising modification containing dioxan of crystallisation is also unusual.[106]

2. Polymerisation of Olefins

The topochemically controlled solid-phase polymerisation has found many applications in the past years. The synthesis from achiral precursors of chiral polymers, which are new materials for optical devices,[127] has been reported.[9,124–126] Goldanski[128] discovered reactions at extremely low temperatures whose rate is independent of temperature. However, the mechanism of the topochemical polymerisation has not so far been elucidated. In particular, it is not clear whether the crystal structure of the monomer controls all or only some of the three main processes: initiation of polymerisation, propagation of the polymer chain, and crystallisation. The role of the microstructure, in particular of the imperfections of the monomer crystal, has been inadequately investigated. A review[129] has been devoted to the discussion of these questions in terms of the results of X-ray diffraction and electron microscopy experiments. The crystallographic data for monomer–polymer pairs and the crystal structures of 11 diolefinic monomers are considered in this review.

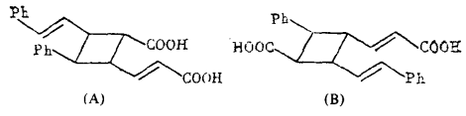
The main conclusion is that the principle of topochemical control formulated by Schmidt[2] plays a decisive role in the four-centre polymerisation of diolefins. In contrast to diacetylenes, many diolefins are available for X-ray diffraction study in both monomeric and polymeric states,[77,130] which makes it possible to determine the topotactic relation between the initial phase and the polymerisation product.[5] Three types of systems have been discovered: (a) all three crystallographic axes of the polymer and monomer crystals coincide (the difference between the volumes of the unit cells is small); (b) the directions of only one axis, along the polymer chain, coincide; (c) the directions of all three axes do not coincide. Although the changes in the unit cell parameters of all the systems investigated are fairly significant on polymerisation [up to 13% for 2,5-distyrylpyrazine (LIX)], the change in the unit cell is small [less than 2% for compound (LIX)].[129] The space group of the monomer crystal is as a rule retained on polymerisation. The solid-phase polymerisation of diolefins always occurs with topochemical control but the strains induced by this process in the lattice of the initial compound lead in all the cases investigated to the fragmentation of the monomer single crystal and the formation of a polycrystalline product.[129]

The role of the rigid lattice in solid-phase polymerisation has been confirmed by data for the reaction of diethyl *p*-phenylenebisacrylate (LX), whose polymerising centrosymmetric modification has a melting point of 96 °C. After the irradiation of crystals of compound (LX) at temperatures close to the melting point, an amorphous oligomer is formed; if the process is carried out at 0 °C, it is possible to obtain a crystalline polymer.[131] Thus, even if the initial reaction stages occur in the crystal lattice of the monomer, the topochemical control over the subsequent reaction stages is lost when the thermal energy evolved is comparable to the crystal lattice energy.[129]

Amorphous oligomers appear in the solid-phase reactions of diolefins in those cases where the translationally linked molecules react topochemically with formation of cyclobutane rings having the *m* symmetry. However, the primary products, the V-shaped dimers, disrupt the initial crystal lattice to such an extent that the distances between the reacting double bonds become too great. In other words, the monomer lattice breaks down at the dimerisation stage and the subsequent formation of the amorphous oligomer is not subject to rules of any kind.[130,131] It has been found that the solid-phase oligomerisation of dimethyl 4(2-carboxyvinyl)-α-cyanocinnamate (LXI) takes place in this way.[132]

The molecules in the crystal of compound (LXI) are packed in stacks along the $c = 3.956(1)$ Å axis, in contrast to the crystals of photo-diolefins, where the lattice period along the stacks, formed by molecules displaced by one half of the molecular length, is ~7 Å.[133] Thus the translation of *c* in the crystal of compound (LXI) corresponds to the shortest distance between the reactive double bonds, which is close to that found in photopolymerising crystals (on average 3.94 Å)[132] and differs from the crystals in photostable crystals (for example 4.187 and 4.369 Å[15]). The next distance in terms of magnitude between the double bonds of the molecules of different stacks in the crystal of compound (LXI) exceeds 5 Å. The molecules of compound (LXI) apparently interact within the stacks with formation of cyclobutane derivatives having the mirror symmetry. Such a reaction infringes the ordered arrangement of the molecules in the rest of the monomer crystal and for this reason only an amorphous oligomer is produced.[132]

Kashino and Haisa[134] investigated the geometrical conditions governing the solid-phase reactivity in crystals of two noncentrosymmetric diolefins: 5-phenylpenta-2,5-dienoic acid (LXII) and 1,5-diphenylpenta-2,4-dien-1-one (LXIII), of which the first exhibits solid-phase reactivity. The molecules in the crystal of compound (LXII) are combined via O–H...O hydrogen bonds into dimers whose axes are approximately parallel to the [0$\bar{1}$4] direction. The dimers are in their turn combined into broad strips. The distances between the approximately parallel double bonds (4.07 and 4.42 Å) are favourable for the formation of a type (A) dimer on irradiation of crystals of compound (LXII).[135]



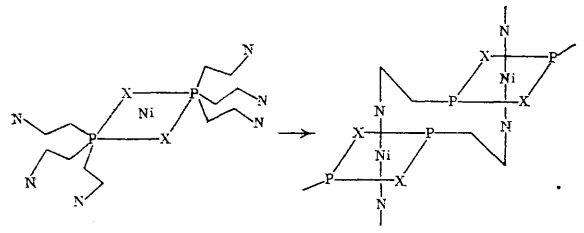
The angle between the interacting double bonds, which is 28°, can be reduced as a result of thermal movement. In the crystal of compound (LXII) it is also possible to distinguish pairs of molecules in which the mutual orientation of the double bonds promotes the preferential formation of the dimers (B).[135] However, in this case the distance between the double bonds (4.56 and 4.62 Å) is somewhat greater than in photopolymerising crystals.[2] On the other hand, it is possible to distinguish pairs of molecules in which the distance between the double bonds does in fact allow interaction (3.60 and 4.46 Å), but their inclination at an angle of 87° rules out the possibility of reaction in this direction according to the authors.[135]

In the crystal of compound (LXIII) the double bonds in neighbouring overlapping molecules have not approached one another and are not parallel, in contrast to, for example, the photopolymerising crystals of *trans*-cinnamic acid[136] and diphenyl *p*-phenylenediacrylate.[134] The gap of 5.31 Å between the nearest parallel C(4)...C(5) bonds greatly exceeds 4 Å, i.e. the distance necessary for dimerisation.[2]

An attempt has been made to interpret the solid-phase polymerisation process in relation to model crystals of ethylene[137–140] and formaldehyde.[141] Using quantum-chemical methods and the method of atom–atom potentials, calculations have been made of individual sections of the potential energy surface which suggested that the nuclei of the polymer chain are located in non-equilibrium positions between the crystal lattice sites; chain propagation takes place as a result of the migration of the chain nucleus in the crystal, which does not require an energy expenditure. Unfortunately, the alternative dislocation mechanism of the process was not considered in the above studies.

3. Thermal Polymerisation of the $NiHal_2L_2$ Complexes

The red square monomeric complexes $NiHal_2L_2$ [Hal = Cl or Br; L = $P(CH_2CH_2CN)_3$] are converted on standing into the blue polymers $(NiHal_2L_2)_x$ with the octahedral coordination of the Ni atom.[142]



Only one of the three cyanoethyl groups of each ligand L participates in the polymerisation. X-Ray diffraction study of the monomer, the polymer (its crystals were grown in solution), and also partly polymerised monomer crystals established that the volume of the unit cell of the complex $NiBr_2L_2$ changes only slightly on polymerisation (2459 and 2467 Å^3 for the monomer and polymer respectively) and the length of the lattice period *c* hardly changes at all (8.49 and 8.50 Å).[142] The reaction is heterogeneous and the monomer and polymer are not isomorphous. The topotactic relation between the crystal lattices of the monomer and polymer and the crystallographic direction of the propagation of the polymer chain, namely [101], have been determined. The identity of the polymers obtained by polymerisation in the crystal and in solution has been demonstrated.[142,143]

The monomer $NiCl_2L_2$ exhibits the lowest reactivity. Thermal depolymerisation before fusion is characteristic of the polymer formed. The volume of the monomer unit cell is smaller than that of the polymer (2386 and 2402 Å^3 respectively). The changes in the lattice identity period are somewhat greater than for the bromo-complex. Furthermore, not one direction of the propagation of the polymer chain, as in $NiBr_2L_2$, but two such directions, namely [101] and [10$\bar{1}$] have been observed for $NiCl_2L_2$ crystals, which leads to a different orientation of the polymer macromolecules in the crystal produced.[142]

The directions of growth of the macromolecules in the doped $NiBr_{1.84}I_{0.16}L_2$ {the [201] direction} and initial $NiBrL_2$ crystals are different, the difference being attributed,[142] in particular, to the character of the disposition of the dopant atoms and of the defects introduced by them approximately in planes perpendicular to the [201] direction.

The complexes $Ni(SCN)_2L_2$, $Ni(CN)_2L_2$, and NiI_2L_2 do not polymerise either in the solid phase or in solution. On the other hand, the $Ni(NCS)_2L_2$ crystals exhibit other interesting properties: conformational polymorphism and capacity for martensite-like phase transitions.[142]

V. ASYMMETRIC SYNTHESIS

Topochemically controlled reactions lead to new possibilities for asymmetric synthesis, frequently with a quantitative yield and in systems "convenient for control".[9,125,144] Furthermore, optically active compounds can be sometimes obtained as a result of the crystallisation of solutions of achiral starting materials and subsequent solid-phase reactions without any external asymmetric influence.[124,126] Studies on these lines, justly referred to as "absolute asymmetric synthesis", can bring us nearer to the solution of the more general problem of the appearance and spread of optically active compounds in biological systems.[124]

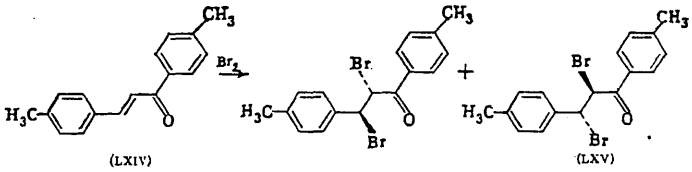
Asymmetric synthesis in the crystal has two aspects: the formation of chiral crystals and topochemically controlled solid-phase reactions with formation of chiral products. The very crystallisation process can be regarded as the simplest form of reaction, because the molecules in solution or in the melt usually assume an infinite number of conformations, while in crystallisation they have one or (more rarely) two conformations. Thus asymmetric induction is completed already in the crystallisation stage in the chiral structure; it only remains to transfer this chirality to the configurationally more stable form via a solid-phase reaction.[9]

Chiral crystal structures with definite intermolecular and intramolecular characteristics are essential for the systematic study of solid-phase asymmetric synthesis. This problem, which is part of the more general problem of crystal structure "engineering", so far has not had a general solution and studies on these lines are frequently heuristic.

A number of simple qualitative procedures for the synthesis of optically active products as a result of solid-phase reactions are known. For example, carboxylic acids and their primary and secondary amides tend to form centrosymmetric hydrogen-bonded dimers, i.e. they crystallise in centrosymmetric achiral space groups.[146,147] On the other hand, if the molecule contains a second functional group forming hydrogen bonds (–OH, >NH, S=O, etc), then, instead of centrosymmetric dimers, helical chains arise in the crystal, which increases the probability of the formation of crystals with a chiral structure.[148,149] Molecules with an intrinsic C_2 symmetry[150] and especially C_3 symmetry[9] tend to crystallise in chiral space groups. Clathrates, for example, those of urea and tri-*o*-thymotide, which form chiral crystals with incorporated achiral "guest" molecules, can be conveniently used to construct chiral crystal matrices.[151] The introduction of stable chiral groups into the molecule is believed nowadays to be the most reliable method for the synthesis of an achiral structure.[8]

We shall consider initially achiral or rapidly racemising molecules, which crystallise to give chiral crystals. If the inversion of the configuration is faster than crystallisation, there is a possibility of the formation of unequal amounts of enantiomorphic crystals with excess of one of the enantiomers. It is sometimes possible to obtain the entire substance in the form of a single enantiomorphic homochiral cyrstal.[152,156] The second case is one where the chirality of the crystal is determined by the molecular chirality. Asymmetric synthesis in such systems can be carried out in polycrystalline specimens, since asymmetric induction depends not only on the chirality of the molecules but also on the chirality of their environment in the crystal.

The first experimental confirmation of the possibility of the solid-phase asymmetric synthesis was provided by the interaction of the chiral 4,4′-dimethylchalcone single crystal with gaseous (or liquid) bromine.[157]



(LXIV) (LXV)

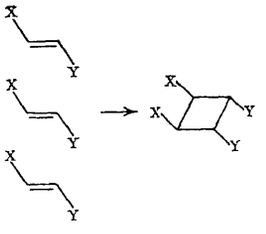
The choice of this particular system was made on the basis of earlier data for gas–crystal reactions and crystallographic studies on olefinic systems; 1,2-asymmetrically substituted crystalline *trans*-olefins interact with bromine vapour to form *erythro*-dibromides as a result of *anti*-addition.[158] Chalcones (αβ-unsaturated ketones) are capable of forming chiral crystals, because their molecules assume highly

twisted conformations in the crystalline state (i.e. the deviation from the achiral planar conformation is large).[159]

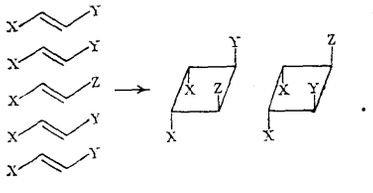
It has indeed been found that the molecules of compound (LXIV), which crystallises in the chiral space group $P2_12_12_1$ have a significantly non-planar structure in the crystal.[160] When ground (in order to increase the area of the exposed surface) crystals of compound (LXIV) are treated with bromine vapour, the dibromide (LXV) is formed with an excess of one of the enantiomers. The optical yield varies from 6 to 25%.[9,157] The determination of the absolute configuration of compound (LXIV)[161] makes it possible to relate the configuration of the initial molecule in the given single crystal to the configuration of the product (LXV) obtained in excess by brominating this single crystal.

It must be emphasised that the optical yield of these gas–crystal reactions depends on the degree of deviation of the molecular conformation from the planar form. This is confirmed by the formation of the racemic dibromide on interaction of bromine with the 4-methoxychalcone (LXVI).[9] Although the crystal of compound (LXVI) is chiral, in this case its molecules deviate less from planarity than in the crystal of compound (LXIV). Studies of the chemical properties and structures of the compounds involved in reactions where bromine adds to racemic crystalline cinnamoyl- and *o*-chlorocinnamoyl-alanines, and of the same compounds after resolution into the individual enantiomers, have also confirmed that the molecular conformation is the principal factor determining the course of these reactions.[9] The optically active dihalides have also been obtained by the addition of chlorine or bromine in the form of monohalogeno-derivatives to compound (LXIV).[9]

We shall consider in greater detail the mechanism of the solid-phase chemical reactions in olefin crystals. When a chiral crystalline olefin, whose molecules are separated by a distance of ~4 Å (β-structure), are irradiated, cyclobutane dimers with *m* symmetry are formed:

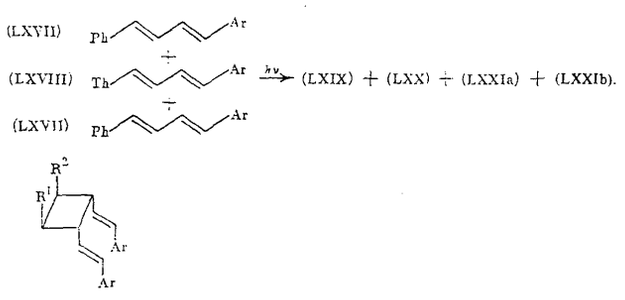


In order to disturb the mirror symmetry, suitable "guest" molecules can be introduced into the "host" lattice. When the correspondence between the molecular geometries of the two components is adequate (solid solutions, mixed crystals), irradiation results in the formation of two enantiomeric "heterodimers" in addition to the two "homodimers", which makes it possible to use these systems for asymmetric synthesis:[9]



To test these hypotheses, phenyl-substituted olefins (stilbenes, 1,4-diarylbutadienes), which form chiral structures, have been used. It has been noted that the necessary intermolecular distance of ~4 Å is attained by the introduction of two chlorosubstituents into the molecules.[3] It is also known that thienyl and phenyl derivatives frequently form mixed crystals.[162,164] In addition, the ability of the thiophen ring to undergo selective excitation in such mixed crystals has been established.[165]

Whereas the crystals of 4-aryl-1-phenylbutadienes (LXVII) and 4-aryl-1-thienylbutadienes (LXVIII) are converted on irradiation into the achiral cyclobutane dimers (LXIX) and (LXX) respectively, having the *m* symmetry, in the (LXVII) + (LXVIII) mixed crystal the enantiomeric heterodimers (LXXIa) and (LXXIb) are formed in addition to the meso-homodimers (LXIX) and (LXX):

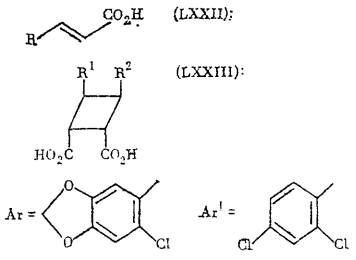


From the standpoint of the elucidation of the influence of the chirality of the crystal structure on the ratio of the enantiomers of compound (LXXI), it is important to excite selectively thienylbutadienes, which absorb in the region of longer wavelengths than the molecules of phenyl derivatives. For small ratios of the concentrations of the thienyl and phenyl derivatives, the selective excitation of the thienyl component suppresses the formation of the achiral dimers (LXIX) and (LXX).

When a light filter is used, irradiation of mixed crystals containing 15% of compound (LXVIII) and 85% of compound (LXVII) at a wavelength of 400 nm leads to a high yield of heterodimers; the filter reduces the absorption by the phenyl derivatives, which prevents the formation of compound (LXIX) and the homogeneous distribution of the thienyl monomer (LXVIII) in the mixed crystal inhibits the formation of the homodimer (LXX). When large homochiral single crystals are irradiated, an optically active dimer is obtained.[57] Dextrorotatory heterodimers are formed in some crystals, while laevorotatory heterodimers are produced in others; the optical yield of these reactions is ~70%. Irradiation at a shorter wavelength ($\lambda < 350$ nm) leads to a decrease of the optical yield, which might have been foreseen by assuming the possibility of absorption by phenyl fragments. This result confirms the preferential propagation of the reaction in stacks, where the distances between the active double bonds are 4 Å.

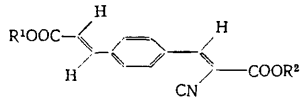
The optical yield of the reaction in the mixed crystal with the ratio (LXVII) : (LXVIII) ≅ 72 : 28[166] is determined by the rate of excitation of the thienyl derivative (LXVIII). Although the translational symmetry of the crystal has been infringed by the substitution of the phenyl group by the thienyl group, the extent of such infringement is slight, as can be seen from X-ray diffraction data, and the intermolecular distances between the olefinic groups in the direction of the ~4 Å translation, are almost identical. The photoexcitation of the thienyl groups can therefore lead to the formation of identical amounts of the enantiomers (LXXIa) and (LXXIb). However, the thiophen fragment is deformed on excitation and the different interactions of the photoexcited compounds (LXVIII) with two nearest neighbours occurring under these conditions induce the appearance of two diastereoisomeric transition states, which explains the observed asymmetry of the synthesis.

The solid-phase reactivity of alkoxyarylchloro-olefins, which also form β-structures, has been investigated.[167] For example, by irradiating at $\lambda \cong 350$ nm the substituted cinnamic acids (LXXIIa) and (LXXIIb), crystallising with formation of the β-structure, it is possible to obtain, as a result of topochemical solid-phase dimerisation, the β-truxillic acids (LXXIIIa) and (LXXIIIb) (with maximum yields of 70 and 90% respectively), compound (LXXIIIb) dimerising much more slowly.[168]



Cyclobutane derivatives of three types [compounds (LXXIIIa), (LXXIIIb), and the chiral compound (LXXIIIc)] are formed on dimerisation in the mixed crystal (LXXIV) made up of compounds (LXXIII) and (LXXII) (in proportions of 1 : 2). The ratios of these reaction products (4 : 1 : 4) agree with the statistical distribution of the molecules of compounds (LXXIIa) and (LXXIIb) in the stack of a (LXXIV) crystal.

Another method of asymmetric synthesis (see above—the chirality of the crystal is determined by the chirality of the molecules of the substance crystallising) requires that the molecules having two different optically active centres be stacked in the chiral crystal in a specific manner—the non-equivalent double bonds must have a favourable disposition (it is required that they be parallel and that the centre–centre distance be ~4 Å) for photocycloaddition with formation of only one of the two possible enantiomers. Among the large number of compounds investigated, 1,4-phenylene diacrylates [for example compounds (LXXV) and (LXXVI)] were selected, since these symmetrically disubstituted compounds are known to be capable of photopolymerisation,[169,170] while chiral s-butyl groups can induce the formation of chiral crystals and can then be readily removed from the product isolated:

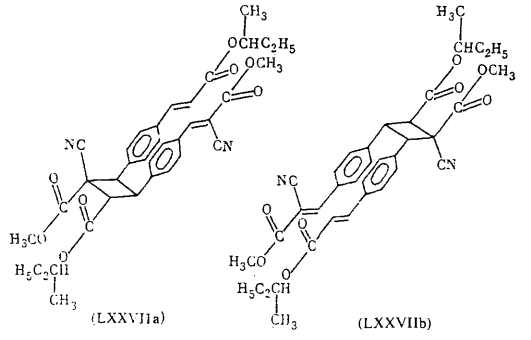


In addition, s-butyl groups ensure a relative disposition of the reacting double bonds at a distance of 4 Å, while the cyano-groups ensure the chirality of the product after the removal of the ester groups.

Two enantiomers of compound (LXXV) [the (*S*)-(+)- and (*R*)-(−)-forms] crystallise in two possible diastereoisomeric forms *A* and $\bar{A}$.[144] The reactions in these crystals lead to the formation of cyclobutane dimers, trimers, and oligomers with identical environments of the C_4 rings but with opposite chiralities. The absolute configuration of the molecules in the monomer crystal has been established by X-ray diffraction and the configurations of the dimer, trimer, and oligomers have been determined from the configurations of the molecules of the reacting crystal.

The molecular packing in the crystal of compound (LXXV) agrees with the mechanism of the synthesis examined above. The double bonds of neighbouring translationally linked molecules are separated by 4.04 Å. If one begins with the optically pure (*S*)-(+)-enantiomer of compound (LXXV), then the absolute configurations of its reaction product will be 1*S*, 2*S*, 3*S*, and 4*S*. According to the requirements for the packing of the initial enantiomer, under the conditions of topochemical control, only one diastereoisomer of the dimer, trimer, and the oligomers can be formed. Since the energy difference between structures *A* and $\bar{A}$ is not known beforehand, an independent determination of the diastereoisomeric yield of the products is necessary. Diastereoisomers of type $\bar{A}$ were specially synthesised for this purpose and it was shown that they are absent from the reaction mixture. The dimerising chromophoric groups in the racemate are distributed in the same way as in the enantiomeric crystal.

In the second example of asymmetric induction in an enantiomerically pure monomer, we shall consider the photochemical reaction in the crystal of compound (LXXVI) (space group $P2_1$).[144] The enantiomer of compound (LXXVI) is dimorphous: the α-form is stable under illumination, while irradiation of the (*S*)-(+)-monomer in the β-form, with $[\alpha]_D = +23°$, yields, as a result of the topochemical reaction, the dimer with $[\alpha]_D = +12°$ and the structure (LXXVII).



On the basis of the characteristic features of the packing in the crystal of compound (LXXVI), one may expect the formation of both diastereoisomers—(LXXVIIa) and (LXXVIIb).

It follows from the examples examined that the presence or absence of appreciable asymmetric induction depends on the chiral environment of the reaction centre in the crystal and not on the influence of the chiral s-butyl groups. The quantitative diastereoisomeric yield can be achieved even in the polymerisation of polycrystalline specimens of compound (LXXV) with a low optical purity.[144] The limiting case is the racemic mixture isomorphous with the pure enantiomer but made up of crystals of opposite chirality. Under certain conditions, one may expect the formation of a product having predominantly one chirality and specific rotations up to 30° have indeed been achieved in a number of experiments[126,172] by irradiating large crystals with racemic composition.

These considerations can be extended to any achiral compound belonging to the class of asymmetrically substituted dienes, which crystallise with the same chiral structure as compound (LXXV). The absolute configuration of the products must vary depending on which of the isoenergetic enantiomeric structures is formed on crystallisation. The absolute configuration of the product of the reaction of the enantiomerically enriched monomer (LXXV) is dictated by the chirality of the excess s-butyl groups. Since there is a possibility of the formation of solid solutions of enantiomers, it has been suggested[144] that the system investigated can be used as a solid matrix for the induction of crystallisation of other compounds of this class to give chiral structures.

Irradiation of a solution of 1,6-di-*trans*-cinnamate of (+)-2,3:4,5-di-*O*-methylene-D-mannitol (LXXVIII) leads to the formation of isomeric cyclobutane derivatives as a result of cycloaddition, which can be converted into the stereoisomeric truxillic esters on treatment with methanol. When a crystal of compound (LXXVIII) is irradiated, only intermolecular cycloaddition takes place and dimers, trimers, tetramers, pentamers, and higher oligomers with the α-truxillate cyclobutane unit are formed.[173,174]

The molecule of compound (LXXVIII) has a symmetry close to C_2 and the centre of gravity of the molecule has been displaced by 0.3 Å relative to that of the bicyclic fragment.[174] The distance of 3.98 Å between the centres of gravity of parallel C(13)=C(14) and C(17)=C(18) double bonds in the molecules linked by the *b* translation indicates that the condition governing topochemical reactivity is fulfilled for the crystal of compound (LXXVIII).[2]

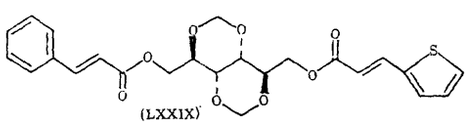
There are no distances permitting interaction between the molecules in the crystal of compound (LXXVIII) extended along the *b* axis, which means that the solid-phase oligomerisation of compound (LXXVIII) should lead to the formation of linear products.[174]

Before the study of Bernstein et al.,[174] the solid-phase di- and oligomerisation was observed only for molecules where two reactive olefinic groups are separated by strictly or approximately planar aromatic ester or amide groups and also by short aliphatic chains.[144,175,176] Bulky groups, such as the tetraoxa-*cis*-decalin group in compound (LXXVIII), had not been used earlier as "spacers" between the reaction centres of solid-phase oligomerisation, just as instances of the presence of 11 covalent bonds between two reactive groups (the distance between the centres of the active double bonds is 13.6 Å) had been unknown. The solid-phase reactivity of compound (LXXVIII) shows that photo-oligomerisation is possible for a much greater number of "spacers" than had been supposed previously. However, it is difficult to predict whether or not the conditions governing the presence of solid-phase reactivity will be maintained: among the six derivatives of D-mannitol with cinnamate end-groups, only compound (LXXVIII) proved to be reactive.[175]

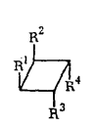
Oligomers (up to octamers) have been isolated chromatographically from the products of the solid-phase photo-oligomerisation of compound (LXXVIII). The proportions of the oligomers depend on the duration of the treatment: brief irradiation promotes the formation of a dimer and short oligomers, while more prolonged exposure entails the appearance of insoluble products, which contain (according to chromatographic data) ten and more monomer units.[174] There exist data indicating further intermolecular photocycloaddition in solutions of oligomers with five and more monomer units.[174,177,178]

In contrast to the crystal, where the molecules of compound (LXXVIII) have the approximate C_2 symmetry, in solution this type of symmetry is not characteristic of them according to NMR data and the cinnamate groups are structurally equivalent. Solid-phase photo-oligomerisation enhances the asymmetry and the signals of the cinnamate groups in the NMR spectra of the oligomers are different.[174]

In order to investigate the solid-phase asymmetric synthesis, an attempt has been made to carry out the photo-oligomerisation of compound (LXXIX) tentatively assumed to be isostructural with compound (LXXVIII):[57]



(LXXIX)



(LXXX).

Depending on the relative positions of the molecules in the crystal of compound (LXXIX), the formation of either the enantiomerically pure oligomer (LXXXa) or (LXXXb) [if the structure (LXXIX) is fully ordered] or of the (LXXXa) + (LXXXb) racemate and the achiral product (LXXXc) [for the statistical orientation of the molecules of compound (LXXIX)] might have been expected. However, although the crystals of compound (LXXIX) did exhibit solid-phase activity, they were found to be not isostructural with compound (LXXVIII) and the products of the reactions of compounds (LXXVIII) and (LXXIX) were different. Further work directed towards the investigation of solid-phase solutions of compounds (LXXVIII) and (LXXIX) is being continued.[174]

Racemic derivatives of anthracene frequently crystallise with formation of close-packed enantiomeric pairs of molecules manifesting a characteristic excimer emission and undergoing rapid photodimerisation. The crystals of individual enantiomers have a completely different type of packing, also exhibit a characteristic monomer emission, and are stable as regards the action of light. Esterification with 1-arylethanol of 9-anthroic acid, partly resolved into optical isomers, makes it possible to obtain a mixture of racemic and chiral crystals. On irradiation, the dimer is formed exclusively from racemic crystals. The soluble chiral monomer which failed to react is separated from the insoluble meso-dimer by extraction with hexane; the optical yield reaches 95%.[179]

Optically active products can be obtained from racemic single crystals with the aid of a solid-phase reaction. In principle, it is possible to carry out the reaction only on the upper (or lower) face of such a crystal. The reaction on one face results in the formation of one enantiomer, that on the other affording the other optical isomer. The usefulness of studies on these lines has been confirmed by the difference in the proportions of the reaction products obtained on different single crystal faces[180] and also by the anisotropy of the rate of reaction[181] observed in certain gas–crystal reactions.

The future of the chemistry of organic chiral crystals is associated with the progress in organic solid-state chemistry in general and also with a more profound investigation of the ways in which molecules are packed in crystals. Just as chiral groups are important in the study of many reactions of organic and inorganic compounds in solutions, chiral crystals make it possible to obtain detailed information about solid-phase reactions.

VI. OTHER REACTIONS

1. Chemical Reactions in Clathrate Compounds

Chemical reactions in clathrate compounds are well known (see, for example, Shklover et al.[80]). We shall consider several examples of such reactions. Alkylammonium cations can be incorporated in an inorganic matrix and can form hydrogen bonds with the latter.[182] For example, the intercalation in layer silicates[183] and the formation of mixed crystals by alkylammonium salts with transition metal halides MX_2, the so-called "layer perovskites" $(C_nH_{2n+1}NH_3)_2MX_4$, is known.[184,185] There exist numerous data on the magnetic properties and phase transitions in these systems.[186–188] However, until the study of Tieke and Wegner, the possibility of using them as matrices for chemical reactions in the crystal had not been investigated. Tieke and Wegner[182] demonstrated the ability of ω-aminoacids and n-alkylamines to crystallise in "layer perovskites" and also the ability of 6-aminohexa-2,4-dienoic acid, incorporated in $CoCl_2$, $MnCl_2$,

and $FeCl_3$, to polymerise to the *trans*-polyene structure (LXXXI) as a result of solid-phase reactions on irradiation with UV light (λ = 254 nm) or γ-rays:

$$n\,CHR^1{=}CH{-}CH{=}CHR^2 \rightarrow -(-CHR^1{-}CH{=}CH{-}CHR^2{-})_n\ ;$$
(LXXXI)

$R^1{=}CH_2NH_2$, $R^2{=}COOH$.

The polymerisation of *trans,trans*-dienes as a result of 1,4-additon had not been known previously either in the solid phase or in clathrate compounds.[189,190] According to NMR data, the *erythro*-diisotactic disposition of the substituents is postulated in the polymer (LXXXI), which is a racemate. On polymerisation in the clathrate compound in $CoCl_2$, the distance between the layers of metal ions (17.9 Å) increases only by 0.9 Å. The stereoregularity of the products, the insignificance of the structural changes, and the dependence of the reactivity of the monomer on the ionic character of the matrix indicate the possibility of the topochemical control of the reaction.[182] The polymer chains formed as a result of the 1,4-addition of diene groups are extended in the plane parallel to one of the crystallographic directions of the inorganic matrix. The separation of the polymer with an average molecular weight of ~35 000 from the matrix presents no difficulties.[182]

The use of chiral crystals as the medium for asymmetric synthesis is of great interest. This approach makes it possible to "convert" the chirality of the "host" crystal into the chirality of the reaction product.[129,192-195] Among the most successful attempts to carry out such reactions, mention may be made of the solid-phase asymmetric polymerisation of *trans*-penta-1,3-diene (LXXXII) incorporated in the chiral matrix of the crystal of (+)-perhydrotriphenylene.[196,197] γ-Irradiation results in the formation of an optically active pentadiene polymer, although the molecules of compound (LXXXII) are fixed in the matrix only via van der Waals forces. The same reaction has been carried out in the deoxyfolic acid matrix.[198]

2. Topotactic Redox Reactions in Intercalation Systems

Yet another important type of solid-phase reactions involves the formation of intercalation compounds (IC) as a result of the incorporation of "guest" molecules, atoms, and ions in the "host" crystal, which has a suitable structure.[199] Apart from the well known layer systems, for example, graphite, MoS_2, and others, both inorganic systems with a skeletal structure (for example WO_3) and organic molecular conducting crystals are used for intercalation.[200] The character of the intercalated "guest", ranging from small ions (H^+, transition and non-transition metal ions) to large molecular ions (metal complexions, dye, and heterocyclic ions), is also varied.[200]

Direct intercalation can be regarded as a reversible redox electron-ion transfer reaction, which makes it possible to treat from the general standpoint the intercalation processes involving both ions and neutral molecules of the "guest".[200]

Among the fairly varied topotactic redox intercalation processes,[200] the intercalation of organic compounds of the type of Lewis bases (hydrazines, amines, heterocycles, acid amides, *N*-oxides, etc.) in layer dichalcogenides on heating[201,202] as well as the formation of intercalation compounds with molecular "host" crystals[200] are relevant to the subject of the present review.

The interaction of the "host" lattice with the "guest" molecule is usually considered in terms of charge transfer from the donor "guest" molecule to the acceptor—the "host" lattice.[203-206] However, according to latest data, direct intercalation of Lewis bases takes place as a result of topotactic redox reactions with phases having an ionic structure.[207-209] This conclusion has been confirmed by a study of the mechanism of the intercalation of inorganic matrices by ammonia and pyridine. In contrast to the earlier model,[201,211] the ^1H NMR data for $TaS_2(NH_3)_x$ and $TiS_2(NH_3)_x$, where $x \cong 1$, indicate the parallel orientation of the C_3 axis of the NH_3 molecule in the interlayer space of the "host" crystal.[205,206] Such orientation is favourable for interaction with charge transfer between the unshared electron pair of nitrogen and the layers of the MX_2 crystal. The study of the mechanism of the intercalation of NH_3 has shown that the redox process accompanying this reaction involves the oxidation of some of the "guest" molecules with formation of N_2.[209] Electrons pass to the TaS_2 layers, while protons are bound to NH_3 molecules:

$$2NH_3 \rightarrow N_2 + 6H^+ + 6e^-\ ,$$
$$xe^- + TaS_2 \rightarrow [TaS_2]^{x-}\ ,$$
$$H^+ + NH_3 \rightarrow NH_4^+\ .$$

The intercalated compound $(NH_4^+)_x(NH_3)_{1-x}[TaS_2]^{x-}$ with $x \cong 0.1$ formed has an ionic structure; the NH_4^+ cations are "solvated" by neutral NH_3 molecules. This scheme accounts for the unusual orientation of the NH_3 molecules by the ion–dipole interaction. The thermal intercalation of pyridine (PyH) in TaS_2 also takes place as a result of a redox process involving the disproportionation of some of the "guest" molecules with formation of bipyridyl (Py–Py):

$$x\,PyH \rightarrow x/2(Py{-}Py) + xH^+ + xe^-\ ,$$
$$x\,PyH + xH^+ \rightarrow x(PyH_2^+)\ ,$$
$$xe^- + TaS_2 \rightarrow [TaS_2]^{x-}\ .$$

The reaction product also has an ionic structure, namely $(PyH)_{0.5-2x}(PyH_2^+)_x(Py{-}Py)_{x/2}[TaS_2]^{x-}$, where $x \cong 0.2$; the planes of the heterocycles are perpendicular to the six-fold *c* axis of the "host" crystal.[207,210,212]

In the case of compounds with a low ionisation potential, for example, aromatic Lewis bases capable of forming stable radical-cations, the reaction mechanism is simpler; indirect data for this intercalation process involving phenylenediamine have been published.[211] Direct ionisation has been postulated for the thermal intercalation of metallocenes[214,215] as a result of the cathodic reduction of MX_2 in electrolytes containing metallocenium cations.[216]

The low electrical conductivity and the low lattice energy prevent the occurrence of topotactic redox processes in molecular crystals. Three cases are exceptions: (a) appreciable intermolecular delocalisation of electrons, for example, as a result of charge transfer or the interaction of the *d* electrons of metals;[217,218] (b) the small size of the "guest" molecules, which leads to an insignificant steric change in the "host" lattice; (c) the presence of convenient ways for the intracrystal diffusion of "guest" ions with low activation energies. The electron-proton transfer is most probable in organic crystals.[200]

Oxygen-transferring metal chelates, for example, [2,2′-ethylenebis-(nitrilomethylidyne)diphenolato]cobalt(2+) and its derivatives have been investigated in greatest detail. These compounds form red-brown crystals, which blacken in air owing to reversible saturation by molecular oxygen.[219-222] Depending on the ligand environment of the cobalt atom, the $Co:O_2$ ratio may be 2:1 or 1:1. Planar chelate complex molecules are packed in such a way that in the crystal there exist large channels open to one-dimensional diffusion of O_2 molecules. The Co^{2+} ions are oxidised by oxygen, but the degree of their oxidation has not been established. The chelate complexes of cobalt are used in welding as a source of pure atmospheric oxygen.[200]

Numerous planar metal chelates having an analogous structure with a stacked arrangement of complex molecules are known; their conductivity along the stacks increases sharply on oxidation of the metal ions owing to the interaction with the partly filled *d* orbitals (one-dimensional metals and superconductors). The bis(benzil dioximato)-complexes of nickel(II) and palladium(II) are converted by oxidation with halogens into compounds having the composition $[MR_2]Y$ (Y = Br or I) and a tetragonal structure, characterised by a stacked packing and intermolecular metal–metal interactions; halide ions are distributed in channels parallel to the stack of complex molecules and apparently exist predominantly in the form of the anions Y_3^-. The halogen is partly eliminated from the bromo-derivatives, while the tetragonal structure persists over a wide non-stoichiometric range ($z_{max} = 0.8$):[223]

$$[MR_2]^{n+}(Y)^{n-} \rightleftarrows [MR_2]^{(n-x)+}(Y_{1-z})^{(n-x)-} + z/2Y_2\,Y_2 + Y^- \rightleftarrows Y_3^- .$$

Analogous processes are apparently characteristic of partly oxidised phthalocyanines.[224] Phthalocyanines and related metal chelates exhibit an appreciable electrocatalytic oxidative activity in the presence of oxygen,[225,226] which is apparently associated with topotactic redox processes.

Topotactic electron-proton transfer processes have been investigated for tantalum halide clusters and chloroammine-platinum complexes.[227] Reversible electron-proton transfer can occur in crystals of the quinolinium salts of tetracyanoquinodimethane (TCNQ):[228]

$$(C_9H_7NH)^+[(TCNQ)_2]^- + x\,e^- + x\,H^+ \rightleftarrows (C_9H_7NH)^+(H^+)_x[(TCNQ)_2]^{(1+x)-} .$$

Organic molecular crystals with semiconducting properties and an extensive system of π-interactions, for example, dyes and aromatic radical-cations, can be used as electrochromic materials for display purposes.[229–232] Since electron-proton transfer reactions are characteristic of these compounds in solutions,[233] it has been suggested[197] that such processes occur also in the crystalline state. Topotactic doping by oxidants leads to a sharp increase of the conductivity of crystalline polyacetylenes.[234,235]

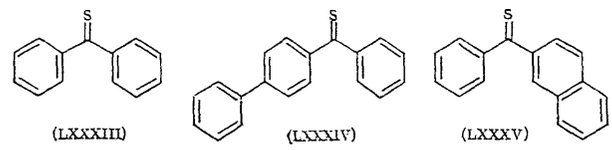
3. The Crystal–Gas Interaction

This extremely common type of solid-phase chemical reactions, which hinder the X-ray diffraction of hydrolysable or oxidisable compounds, has been inadequately investigated as regards structure.

One of the examples of the structural investigation of solid-phase reactions of this type, the interaction of chiral single crystals with gaseous bromine leading to chiral products, was examined above (Section V).

Another example of the chemical crystal–gas interaction is provided by topotactic redox reactions in the formation of intercalated systems (see above).

The ability of thioketones to be readily oxidised in solution to the corresponding *S*-oxides or ketones, the rate of oxidation and the proportions of the products being determined by the electronic and steric characteristics of the molecules, is also known.[236] The capacity of thioketones for oxidation in the solid phase is determined by the packing of their molecules in the crystals. The molecules of the aromatic thioketones (V)–(VII), which undergo solid-phase photochemical oxidation, are stacked in such a way that the thiocarbonyl chromophoric groups C=S are oriented in an antiparallel manner (the intermolecular S...S distances vary from 3.70 to 3.90 Å) and form channels along the shortest period of the unit cell.



(LXXXIII) (LXXXIV) (LXXXV)

The cross-sectional area of the channels is ~8.3 Å^2 in contrast to the crystals of stable diarylthioketones whose channels are much smaller (~2.3 Å^2).[237] The solid-phase reactivity of compounds (LXXXIII)–(LXXXV) can be accounted for by the diffusion of O_2 molecules in the channels and by the subsequent oxidation of the C=S groups.[238,239]

The C=S distances in compounds (LXXXIII)–(LXXXV) are 1.61–1.63 Å and are close to the standard C=S bond length in crystals which are stable as regards the photochemical oxidation of thioketones.[237] The solid-phase reactivity of thioketones is apparently not linked directly to changes in the C=S bond length.

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Thus the structural aspect of the solid-phase dimerisation, polymerisation, redimerisation, and other reactions has been investigated for a fairly wide variety of organic compounds. The dimerisation of certain derivatives of 2-benzyl-5-benzylidenecyclopentanone derivatives and the solid-phase polymerisation of diacetylene derivatives take place with rigorous topochemical control at all stages of the reaction with a single crystal → single crystal transition.

At the present time the ideas of crystal engineering have been developed in studies of crystalline low-dimensional semiconductors, metals, and superconductors.[240,241] Crystal engineering merits special consideration as a method of seeking and investigating the properties of this promising class of organic materials (the construction of molecular "corridors" for the preferential migration of electrons, the use of heteroatoms to ensure the overlap of neighbouring molecules, the elimination of the spatial modulation of charge density by altering intermolecular distances, etc.).

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