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Reactions in Organic Crystals

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Structural investigations of two types of chemical reactions occurring in organic crystals on heating and irradiation are examined, namely intermolecular rearrangements (including the rearrangement of molecules via the transfer of individual atoms and groups of atoms, isomerisation, stereo-isomerisation, etc.) and reactions with elimination of small molecules (N_2, CO_2, H_2O, HHal). Solid-phase processes are discussed in terms of topochemical reactions and reactions in non-crystalline (amorphous) regions.
The bibliography includes 195 references.

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I. INTRODUCTION

Reactions occurring in the solid phase have been known for a long time but they have attracted increasing attention recently, because of two main factors. The first of these is that the occurrence of reactions in the solid phase imposes significant limitations on the mobility of the reacting molecules. This not only facilitates the experimental and theoretical study of chemical reactions in the crystal but frequently creates completely new (compared with traditional liquid-phase reactions) possibilities for their investigation. The combined use of various techniques for the investigation of solid-phase reactions makes it possible to follow the entire chain of molecular transformations taking place and in a number of instances to achieve a well-founded characterisation of their mechanism. The first advances on these lines have already been made as regards the mechanisms of intramolecular rearrangements, reactions with elimination of small molecules, etc. The second factor is that the practical use of the possibilities of solid-phase synthesis which cannot be achieved in liquid- or gas-phase reactions (for example, the preparation of crystalline polymers with chains having a regular structure, the formation of enantiomerically pure products with the configuration of asymmetric centres specified beforehand, etc.) was initiated in recent years.

It is possible to differentiate two main types of solid-phase reactions: topochemical reactions and reactions in non-crystalline regions.[1,2]† The topochemical character of the

†Topochemical reactions consist in the conversion of the molecules of the initial substance into those of the product without the disturbance of the crystal lattice and without the formation of non-crystalline intermediates.[1-4] The relation between the crystallographic directions of the product of the solid-phase process and the initial substance is then referred to as topotaxy.[1]

process makes it possible to predict the structure of the product formed, which is by no means possible in all non-topochemical reactions.

The essential condition for the occurrence of intermolecular solid-phase topochemical reactions is that the shifts in the equilibrium positions of the atoms in the interacting molecules are small, while the thermal vibrations of the molecules themselves are fairly strong. This general principle, formulated by Schmidt,[5-7] can be specified in a more concrete form for solid-phase reactions of the most varied types. For example, it has been established empirically that, in the photochemical interaction of unsaturated molecules in the crystal via their C=C π bonds, topochemical control requires that these bonds should be oriented in parallel and that the atoms formed should be separated from one another by not more than 4.0 Å.[8] In order to stimulate chemical reactions in the solid phase, one employs nowadays virtually all the procedures for the usual chemical reactions, but it is entirely clear that the maximum topochemical control is possible when the solid-phase reactions are carried out with photoirradiation, which makes it possible to create the optimum conditions for the realisation of the principle indicated above. Schmidt's principle has been somewhat modified.[9] The preferred reaction in the crystal is that which requires the minimum change in the form of the "reaction cavity" (the space incorporating the reacting molecule before the reaction and the molecule of the reaction product). The principle of the conservation of the shape of the reaction cavity is especially useful for the explanation of chemical reactions in clathrates and for the description of the reactivities of excimers in crystals.

It must be emphasised that topochemical factors operate also in solid-phase intramolecular reactions, creating in this instance a kind of external limitation to the atomic shift necessary for the occurrence of the reaction (when the internal limitations are defined as those caused by the structure of the molecule itself).[10]

A disposition of the molecules suitable for the reaction is sometimes not inherent in the periodic lattice of the crystal but arises only when defects or dislocations are formed in the latter. However, in this instance too, as in topochemical reactions, the process actually occurs under the control of the lattice, since its direction and mechanism are determined by the fixed disposition of the interacting molecules.

The most important method for the investigation of solid-phase reactions is X-ray diffraction analysis, since it enables one to establish vigorously and quantitatively all the structural and geometrical parameters of the starting materials and final products (the valence and dihedral angles and the bond lengths), so that the process occurring can be adequately characterised when a topochemical mechanism operates. Under the conditions of a non-topochemical mechanism, information about the defects and dislocations and about their number and the principal reaction pathways can be obtained with the aid of electron microscopy. However, this is insufficient for the establishment of the orientation of the molecules at the dislocation boundaries. Computational methods, whereby one can model both the character of the relative disposition of the molecules and the possibility of their displacements in the course of a reaction, are frequently employed in such instances.

An important characteristic of solid-phase processes is their homogeneity or heterogeneity. By a homogeneous process one understands in this instance one whose product forms a solid solution in the lattice of the initial compound. In the corresponding heterogeneous process the product forms its own lattice and does not give rise to solid solutions in the initial compound. In a homogeneous mechanism a transition of the single crystal → single crystal type takes place, while in a heterogeneous mechanism the single crystal of the initial compound disintegrates. One must note that in a number of instances solid-phase reactions are investigated in polycrystalline specimens, which hinders their X-ray diffraction study. Since data concerning the structure of the crystal obtained from an X-ray diffraction study are averaged both in space (throughout the crystal) and in time, it is difficult to characterise by this method the homogeneity and heterogeneity of the process (with the exception of cases of the so-called dynamic X-ray diffraction analysis used for comparatively slow processes). Important additional information about the character of solid-phase processes and about the movement of the molecules involved in the reaction can be obtained from Raman phonon spectra. Thus a sufficiently complete picture of solid-phase processes can be obtained solely by a combined study of the structure and reactivity of the organic crystals using the entire set of the methods indicated above.

Investigation of chemical reactions in solid crystals (see the relevant reviews[1,9-17]) led to the development of a new scientific discipline, which arose recently at the frontier between organic chemistry and organic crystal chemistry (crystal engineering). The aim of this new discipline is to understand and formulate the main rules and principles governing the structure of the packing of potentially reactive molecules in crystals such that the most favourable conditions are created for the participation of the molecules in particular chemical reactions and rearrangements without the need for diffusion and requiring only a slight rearrangement of the crystal packing with topochemical control of the process.[17]

This paper represents a review of the structural investigations of chemical reactions in organic crystals published mainly after the appearance in 1977 of our previous review on this topic.[1] The review includes various types of thermal and photochemical intramolecular rearrangements and reactions involving the elimination of small molecules in crystals of organic compounds. In order to demonstrate the wide-scale occurrence of solid-phase reactions, several types of solid-phase processes in molecular crystals formed by complex compounds have also been examined.

The proposed subdivision of the reactions considered in the review into intramolecular rearrangements and reactions involving the elimination of small molecules is to some extent arbitrary. The first of the above two types includes processes in which the overall composition of the molecules of the initial substances and final products is the same. The character of the rearrangements taking place under these conditions is fairly varied. They can be intramolecular, whereupon only proton transfer can lead to a significantly different result: for example, it can lead to a significant alteration of the molecular skeleton, which entails a change in the chemical properties of the compound or to insignificant geometrical changes (the transfer of a hydrogen atom via a hydrogen bond and small conformational changes), as a consequence of which a significant alteration of the physical characteristics of the specimen, particularly its colour, takes place.

The rearrangements of molecules can also take place via the transfer of larger atomic fragments, in particular, methyl or phenyl groups. Together with the instances of intramolecular mechanism, such as, for example, that operating in the stereoisomerisation of metal complexes, there is also a possibility in this case of intermolecular processes. It must be emphasised that all the processes involving the transfer of atoms or groups of atoms mentioned above take place in the manner stated only by virtue of their suitable disposition in the crystal and such disposition can be both inherent in the structure of the crystal itself and can be "created" at its defects or dislocations.

The character of reactions of the second type (with elimination of small molecules) is in most cases predetermined not only by the very disposition of the molecules but also by their interactions in the crystal, in particular, by the existence of a system of intermolecular hydrogen bonds whose chains provide a pathway for the reaction. A striking manifestation of the role of such interactions is provided by the differences between the reactions on different faces and along different directions in crystals.

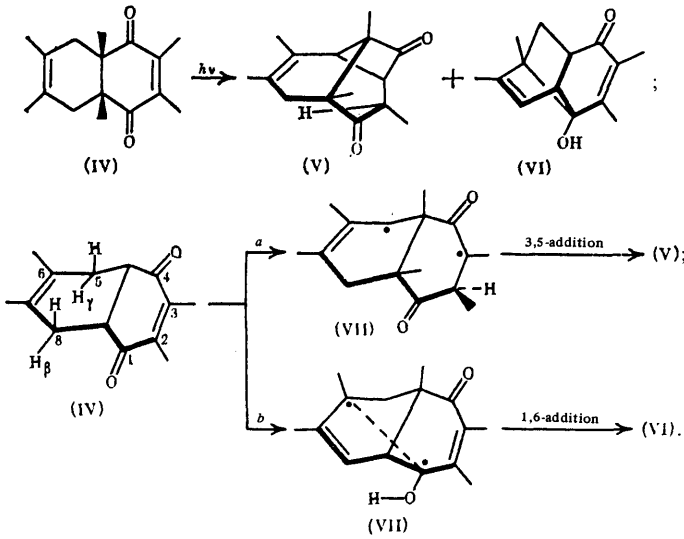
II. INTERMOLECULAR REARRANGEMENTS

The study of the controlling influence of molecular packing in the crystal and the photochemical behaviour of organic systems undergoing unimolecular photo-rearrangements in solution was initiated, according to Scheffer,[10] by investigations of the photoreactions of santonin (I) in the solid phase. It was observed that the photolysis of crystalline santonin results in the formation of a product whose appearance can be accounted for by the formation and subsequent dimerisation of cyclopentadienone (III) and not of luminosanton (II), as in solution (scheme 1). However, the relation between the structure and reactivity remained unelucidated in this instance and required further study.

1. Isomerisation of Naphthoquinone Derivatives

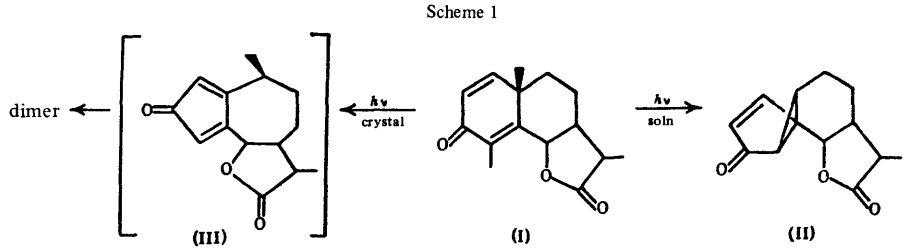
Studies of the photochemical reactions of solutions of Diels-Alder adducts of non-cyclic 1,3-dienes with *p*-quinones have shown that two main types of reactions, which depend on the character of the substituents in the initial adduct, are characteristic of these systems.[18,19] The interaction of a quinone and 1,3-dienes [for example, of the 2,3-dimethylbutadiene adduct (IV) (Scheme 2)] on irradiation of the solution, leads to the formation of cyclobutanones of type (V) as the main product, while compound (VI) has been detected as the side product [with the ratio (V):(VI) = 2:1]. The formation of these photoproducts requires at first sight a very major molecular rearrangement of compound (IV), but it was found that irradiation of crystals of compound (IV) yields the same products and in the same proportions (2:1) as in solution.[20,21]

Scheme 2



The cyclohexane ring of the molecule of compound (IV) has the half-chair conformation in the crystal and has a *cis*-junction with the approximately planar enedione ring. The formation of cyclobutanone (V) (reactions *a* in Scheme 2) takes place as a result of the transfer of the allyl hydrogen atom H_γ to the C(2) atom of the enedione chromophore and the subsequent formation of a bond between the C(3) and C(5) atoms in the biradical (VII) produced. The mechanism of the formation of the dienol (VI) (reaction *b* in Scheme 2) should include the initial excitation of the molecule with subsequent transfer of the H_β atom to the O atom of the carbonyl group at C(1) with formation of the intermediate biradical (VIII). The occurrence of these two competing solid-phase

Scheme 1



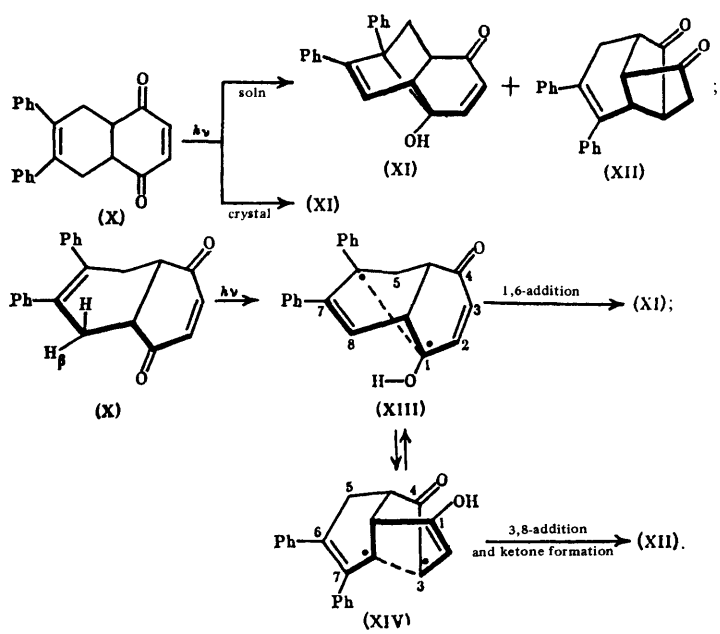
photoprocesses is determined by two factors: (1) the geometry of the initial molecules is extremely favourable for intramolecular transfers of hydrogen atoms; (2) the intermediate states arising in the transfer of H atoms are ideally suitable for the subsequent intramolecular interaction of the biradicals produced. The form of the molecules of the photo-products (V) and (VI) is then extremely similar to that of the initial molecule of compound (IV).[6] Analogous data have also been obtained for the adducts produced in the Diels-Alder reaction between duroquinone and *trans,trans*-hexa-2,4-diene (IX).[10]

Photolysis of the Diels-Alder adduct of *p*-benzoquinone with 2,3-diphenylbutadiene (X) in solution affords the products (XI) and (XII) in proportions of 3:1 (Scheme 3);[10] in this case photoproducts of the type of cyclobutanone are not formed. Photolysis of compound (X) in the solid phase leads to the unsaturated alcohol (XI), which can be regarded as an analogue of compound (VI); the diketone (XII) is not formed. An answer to the question of the causes of the differences between the reaction products in different media was provided by an X-ray diffraction study of compound (X).[22] Since the overall twist-conformation of the molecule of compound (X) found in the crystal apparently predominates also in solution, presumably the reaction in both liquid and solid phases begins with the same conformation as that of the initial molecule of compound (X) and the differences between the reaction products are determined by the conformational flexibility of the biradical intermediate (XIII) produced when a β-hydrogen atom is transferred. In fact the biradical (XIII) has the same conformation as its precursor (X) and can undergo biradical condensation to the dienone alcohol (XI) both in solution and in the solid phase. The direct formation of the diketone (XII) and the biradical (XIII) is sterically impossible[10] and requires a conformational rearrangement of the rings with transition to the biradical (XIV). Naturally, such a transition, which is permissible in solution, is no longer possible in a crystal, so that the photoproduct (XII) is formed only when the reaction is carried out in the liquid phase.

Another example of the different course of a chemical reaction in the crystal and in solution, due to the different possibilities for the necessary conformational rearrangements of the reacting molecules in the liquid and solid phases, is provided by the intramolecular rearrangement in the crystals of 1,3-diphenylindan-2-dione and *NN*-dialkyl-α-oxoamide.[23,24] If the molecular structure limits the possible conformational rearrangements, then the reaction products in solution and in the crystal are as a rule identical; for example, the presence of the axial CH_3 group in the molecule of compound (IV) prevents the rearrangement of the intermediates (VII) and (VIII) and leads to identical products of the photochemical reaction of compound (IV) in both phases investigated.

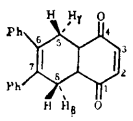
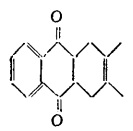
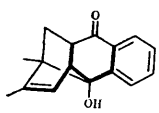
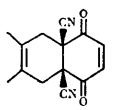
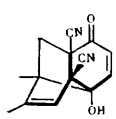
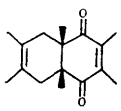
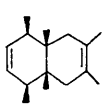
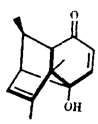
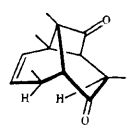
All the photochemical reactions considered begin with the intramolecular abstraction of a hydrogen atom. Table 1 presents data for the geometry of five compounds, in which photoinitiated solid phase abstraction of a β-hydrogen atom by the carbonyl oxygen atom (leading to the formation of an enone alcohol) has been observed, as well as two adducts produced by the Diels-Alder reaction in which a γ-hydrogen atom is abstracted by the enone carbon atom with formation of photoproducts of the cyclobutane type. Although the data in Table 1 do not refer to the real geometry of the molecule at the instant of photochemical reaction (X-ray diffraction study has yielded the parameters for only the ground electronic state), they nevertheless can reveal the factors which favour such reactions. This applies particularly to the transfer of a β-hydrogen atom to oxygen, since it is quite likely[25-32] that the carbonyl fragment in enones (and apparently also in enediones) retains the geometry of

Scheme 3



its ground state on photochemical excitation. Even when a H_β atom is transferred to the enone C atom, the X-ray diffraction data for the relative positions of the H_γ and C(2) atoms reproduce fairly exactly the geometry of the excited state, because the twisting of the enone C=C π-bond on formation of the activated state alters mainly the parameter τ_C [25–32] (data concerning the possible planarity of the enone molecules in the activated state are quoted by Dyxtra[33] and Jones and Kearns[34]). We may note that such twisting can facilitate the abstraction as a result of the more exact alignment of the 2*p* orbital of the C(2) atom with the direction of the H_γ atom, i.e. as a result of the increase of the angle τ_C in the direction of the ideal value of 90°.[10]

Table 1. Intramolecular solid-phase reactions accompanied by the transfer of a hydrogen atom.[15]

Initial compound	Product containing the enone fragment	$R(H_\beta\ldots O(1))$, Å	τ_O, deg	Δ_O, deg	Product containing the enedione fragment*	$R(H_\gamma\ldots C(2))$, Å	τ_C, deg	Δ_C, deg
	(XI)	2.46	3	81.3	*	—	—	—
		2.57	5	80.7	*	—	—	—
		2.58	8	83.6	*	—	—	—
	(VI)	2.47	0	85.1	(V)	2.89	52	72.6
		2.26	1	86.4		2.66	50	74.4

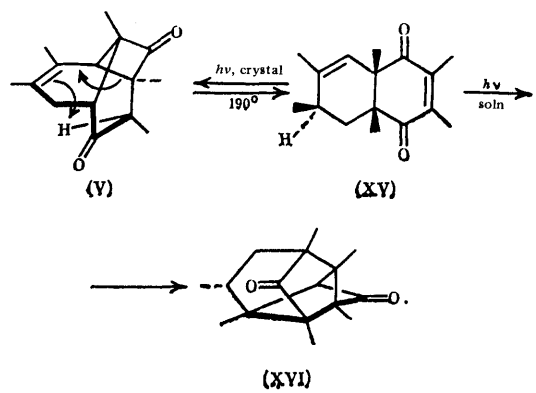
Notation: τ_O is the deviation of the H_β atom from the plane of the carbonyl group at the C(1) atom, Δ_O is the angle $C(1)O(1)H_\beta$, τ_C is the deviation of the H_γ atom from the plane of the C(2)=C(3) double bond, and Δ_C is the angle $C(3)C(2)H_\gamma$.

*Does not form.

The distances between the hydrogen atom and the "abstracting" atom over which the transfer of a hydrogen atom is observed vary from 2.26 to 2.58 Å for abstraction by oxygen and from 2.66 to 2.89 Å for abstraction by carbon, which agrees with the difference between the van der Waals radii of the oxygen and carbon atoms (1.52 and 1.70 Å).[35,36] It is believed[10] that the intramolecular transfer of a hydrogen atom is feasible over distances comparable to the sum of the van der Waals radii of the interacting atoms. If one begins with the postulate that the radius of the hydrogen atom is 1.20 Å,[36] these sums are 2.72 Å for the H and O atoms and 2.90 Å for the H and C atoms. These values are appreciably higher than those proposed earlier on the basis of calculations and/or molecular models. For example, a spherical "activated volume" of the carbonyl group, whose radius has been estimated as 1.7–2.1 Å, has been proposed[37] for the intramolecular photochemical hydrogen atom transfer reactions.

The relative orientation of the orbitals of the "abstracting" atom and the hydrogen atom is no less important. Table 1 shows that the β-hydrogen atom is located in all cases (within the limits of several degrees) in the mean-square plane of the "abstracting" carbonyl group, which favours the thoroughly investigated[38] transfer of a hydrogen atom to the excited carbonyl fragment located in the same plane. The values of Δ_O for these systems are close to 90° (Table 1) and are almost ideal for the transfer considered.[10]

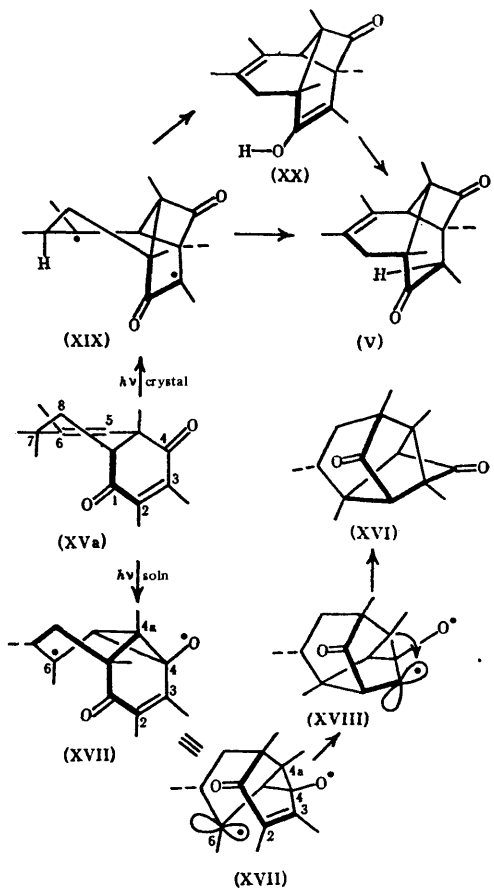
Scheme 4



In the course of thermolysis at 190 °C cyclobutanone undergoes the retroene reaction (Scheme 4), giving a satisfactory yield of the crystalline β,γ-unsaturated ketone (XV),[18] whose further photochemical reactions in solution and in the crystal proceed in entirely different ways. Whereas the explosive photoproduct (XVI) is formed in solution, the initial cyclobutanone (V) is regenerated almost quantitatively in the crystal.[39] According to X-ray diffraction data, the ketone (XV) has the conformation (XVa) in the crystal (Scheme 5) and the bulky CH_3 substituent at the C(7) atom occupies a pseudoequatorial position in this instance. If it is assumed that compound (XVa) behaves as a typical $^3(\pi,\pi^*)$-excited βγ-unsaturated ketone, then in the first stage it should undergo the well known oxadi-π-methane rearrangement[40–43] consisting in the formation of a bridge between the carbonyl carbon atom and the vinyl group, which leads to the product (XVII). The transition to compound

(XVI) requires then the rupture of the C(4)–C(4a) bond with formation of the C(4a)–C(3) and C(6)–C(2) bonds (Scheme 5).

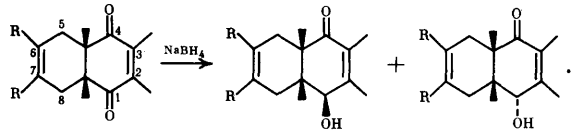
Scheme 5



It has been noted[10] that each stage of the transition (XV) → (XVI) involves a significant displacement of the atoms and deformation of the molecule and leads ultimately to a product, the form of the molecule of which has very little in common with that of the initial molecule. This is not observed in the solid-phase rearrangement, which constitutes a radical difference between the reactivities of compound (XV) in the two different phase states examined.

A detailed comparison has shown that the molecular shapes of compound (XV) and of its photoproduct (V) are very similar. Compound (V) is formed as a result of the appearance of the C(3)–C(5) bond [the 2*p* orbitals of the C(3) and C(5) atoms are directed towards one another; the C(3)...C(5) distance is 3.12 Å, which is less than twice the van der Waals radius of the C atom (3.40 Å)[20]] via the intermediate compound (XIX), which is followed by the intramolecular transfer of the pseudoaxial hydrogen atom from the C(7) atom to the C(2) atom, which takes place either directly or via the enol (XX). The configuration of the C(7) atom in compound (XVa) is extremely favourable for such transfer: the H(7)...O(1) distance is 2.64 Å and we have the angles $\tau_C = 28.5°$ and $\Delta_O = 84.7°$. The mechanism of the solid-phase transition described requires a minimum displacement of the atoms from the initial positions: the C(2), C(3), C(5), and C(7) atoms are rehybridised and the C(3) and C(5) atoms approach one another, but the overall molecular shape is retained. Another mechanism of the (XV) → (V) transformation, differing from the foregoing by the sequence of stages, has also been proposed.[15]

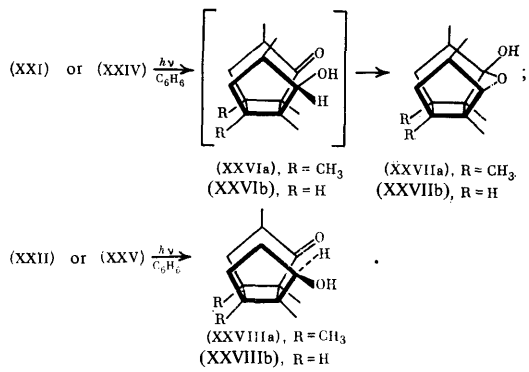
Scheme 6



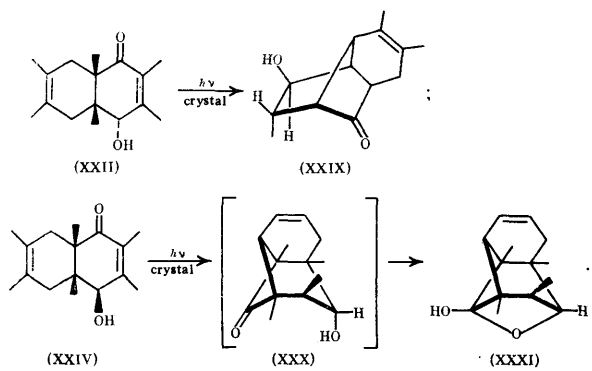
(IV), R = CH_3 (XXIII), R = H (XXI), R = CH_3 (XXIV), R = H (XXII), R = CH_3 (XXV), R = H

The reduction of the duroquinone–butadiene Diels-Alder adduct (IV) leads to a mixture of the alcohols (XXI) (50%) and (XXII) (35%) (Scheme 6). Analogously, the reduction of the duroquinone–butadiene adduct (XXIII) affords the products (XXIV) (63%) and (XXV) (31%). The photochemical behaviour of these products in the solid phase differs sharply from that observed in solution.[44,45] Irradiation at $\lambda > 330$ nm of benzene solutions of all four tetrahydronaphthoquinones (Scheme 7) leads to products of the intramolecular [2 + 2]-cycloaddition having the tetracyclo[5.3.0.$0^{2,6}$.$0^{4,9}$] decane skeleton. In compounds (XXI) and (XXIV) the configuration of the carbon atom to which the OH group is attached is such that the ketoalcohols (XXVIa) and (XXVIb) formed initially cyclise to the internal hemiacetals (XXVIIa) and (XXVIIb). At the same time the formation of similar acetals from the photoproducts (XXVIIIa) and (XXVIIIb) is not observed.

Scheme 7



Scheme 8

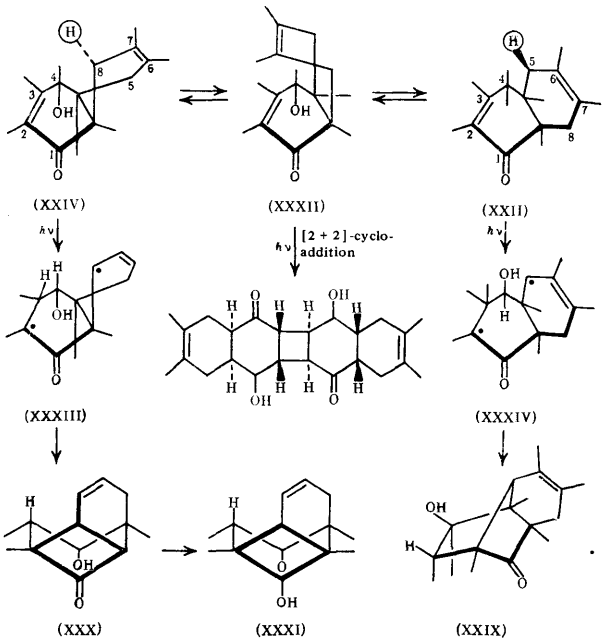


Irradiation of the same substances in the solid phase does not lead to the formation of products with a skeletal structure. The character of the photoproducts formed in the

solid phase is determined, as in solution, by the disposition of the hydroxy-groups in the substrate molecule; a typical picture is presented in Scheme 8. We may note that irradiation of the polycrystalline specimens of compound (XXII) is used to obtain the ketoalcohol (XXIX); the photolysis of the polycrystalline compound (XXIV) is used in exactly the same way for the quantitative formation of the hemiacetals (XXXI) (a structural scheme for this process has been published[31]).

Scheme 9 illustrates the conformation of the molecules of the cyclohexenones (XXII) and (XXIV) in the crystal;[46] the cyclohexenone ring in the half-chair conformation has a *cis*-junction with the cyclohexene fragment (also in the half-chair conformation). Since the carbon atoms attached to the OH substituents have the opposite configurations in compounds (XXII) and (XXIV), these molecules are characterised by the opposite directions of the twist of the second ring. The photoproduct (XXXI) is formed from the conformer (XXIV) as a result of the transfer of the allyl hydrogen atom from C(8) to C(3) and the subsequent formation of the C(2)–C(8) bond in the biradical (XXXIII). The photoproduct (XXIX) is formed via the conformer (XXII) as a result of the C(5) → C(3) transfer of the allyl hydrogen atom and subsequent formation of the C(2)–C(5) bond in the biradical (XXXIV) produced.

Scheme 9



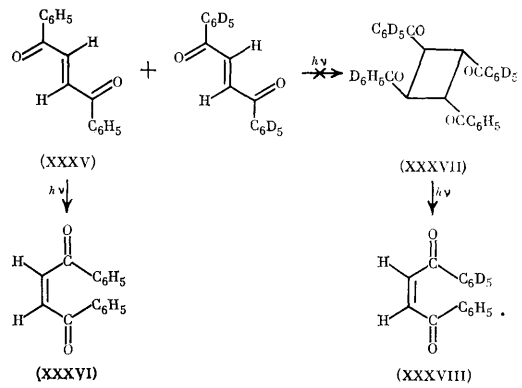
As in the other cases described above, the reactions of compounds (XXII) and (XXIV) proceed with minimal deformations of the molecules. The transfer of a hydrogen atom is achieved over a distance of 2.72 Å in compound (XXII) and 2.84 Å in compound (XXIV), which is less than the limiting distance of 2.90 Å required for the transfer to a carbon atom. The conformational similarity of the biradicals (XXXIII) and (XXXIV) with the products (XXXI) and (XXIX) is also significant.

Comparative analysis of the reactivities of the isomers (XXI) and XXII) in the solid phase, carried out on the basis of their X-ray diffraction study,[47] has shown that the molecules have different conformations in the crystal and the distances from the H_γ atoms to the C(2) and C(3) atoms in compound (XXII) are somewhat smaller than in compound (XXI) (2.78 and 2.72 Å in the former case and 2.88 and 2.92 Å in the latter), which accounts for the reactivity of compound (XXII) [and the lack of reactivity of compound (XXI)] in a solid-phase reaction proceeding via the transfer of a H_γ atom to the β-enone C(3) atom. We may note that the angles Δ_C and τ_C (Table 1) in compounds (XXI) and (XXII) proved to be similar: 75.2° and 78.5° in the former case and 49.3° and 53.2° in the latter.

2. Isomerisation of 1,2-Dibenzoylethylene

Crystalline *trans*-1,2-dibenzoylethylene (XXXV) is gradually converted into the *cis*-isomer (XXXVI) in the light.[48] Since the corresponding cross-product, namely benzoyl(pentadeuteriobenzoyl)ethylene (XXXVIII), was not detected by the mass spectrometry of a solid solution of the bispentadeuteriated analogue of compound (XXXV) and the non-deuteriated compound (XXXV) was used in this reaction, it is suggested that the above isomerisation does not include a stage involving the intermediate formation of the cyclobutane derivative (XXXVII) (Scheme 10).[49]

Scheme 10



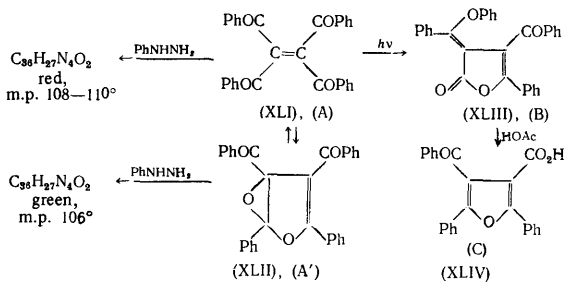
In order to investigate the factors influencing the solid-phase *cis–trans* transformations of compounds of the class considered, the structures of compound (XXXV), *trans*-1,2-ditolylethylene (XXXIX),[48] compound (XXXVI), and *cis*-1,2-bis(*p*-chlorobenzoyl)ethylene (XL)[50] were determined. Analysis of the molecular parameters indicates an appreciable loss of conjugation between the carbonyl and phenyl groups in compound (XXXV) compared with compound (XXXIX). The molecular packing in the crystals of compounds (XXXV) and (XXXIX) is of the stacked type and is not determined by the mutual contacts of the carbonyl group as in the *cis*-isomers (XXXVI) and (XL). The large distances between the centres of the double bonds [5.0 Å in compound (XXXV) and 5.4 Å in compound (XXXIX)] preclude the occurrence in this instance of solid-phase dimerisation reactions with formation of cyclobutane derivatives, which agrees with the data of Griffin et al.[49] The mutual orientation of the crystallographic axes of the phases (XXXV) and (XXXVI) has been determined from the X-ray diffraction pattern of compound (XXXV), on which reflections characteristic of compound (XXXVI) appear.[49] The packing density in the *cis*-isomer is somewhat smaller (the unit cell volumes are V_{cis} = 608.9 A^3 and V_{trans} = 596.1 A^3). The transition (XXXV) → (XXXVI) is accompanied by the loss of the centre of symmetry and leads to a change in the space group ($P2_1/c \rightarrow P2_1$). Even in the imperfect crystals of compound (XXXV)

the rate of rearrangement is low, i.e. the photoisomerisation apparently takes place in defective regions and is propagated via the dislocations formed around the nuclei of the *cis*-isomer.[48]

3. Isomerisation of Tetrabenzoylethylene

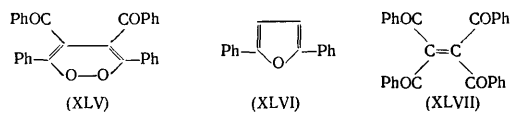
Tetrabenzoylethylene exists in three crystalline forms: two colourless forms (A) and (A') and in the yellow form (B), to which structures (XLI), (XLII), and (XLIII) respectively have been ascribed (Scheme 11).[51–55]

Scheme 11



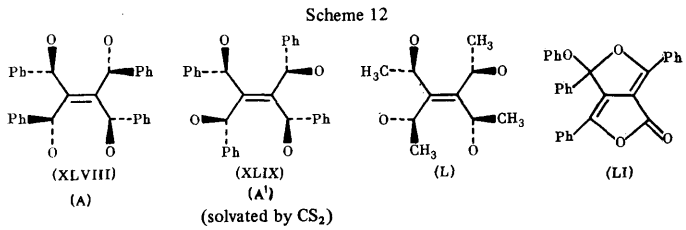
In daylight form (A), produced on crystallisation from a large amount of organic solvents, is irreversibly converted into form (B), whose treatment with acetic acid affords the product (C), to which the structure (XLIV) has been attributed. Crystals of compound (A') are obtained by crystallisation from CS_2 and are resistant to the action of light.

In addition, the structure (XLV) has been proposed[54] for compound (A'). The structure (XLIV) of the product (C) has been confirmed[55] by the formation of 2,5-diphenylfuran (XLVI) on its decomposition. Data for the tetra-acetyl derivative (XLVII) have been used in the analysis of the possible structure of tetrabenzoylethylene.[51–55]



It has been established by X-ray diffraction studies[56] that compounds (A) and (A') do indeed represent different crystalline modifications of tetrabenzoylethylene, the different types of behaviour of which on irradiation with visible light being explained by the difference between the conformations of their molecules and in their packing in the crystals. The conformations (XLVIII) and (XLIX) correspond to forms (A) and (A') respectively (Scheme 12). The related tetra-acetylethylene molecule has the conformation (L) in the crystal. In addition, X-ray diffraction study[57] has shown that the product (B) of the photolysis of (A) has the structure (LI) and not the structure (XLIII) proposed previously.[52]

Scheme 12

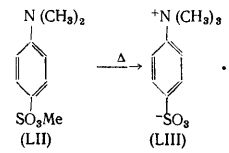


Intermolecular contact between the carbonyl oxygen atom and the hydrogen atoms in the *o*-positions in the ring has been observed in the crystal (A), its length being 2.62(8) Å, which is close to the sum of their van der Waals radii (2.72 Å).[35,36] A series of fairly short contacts involving the hydrogen atoms in the *m*-positions in the same ring have also been found. It may be that the intermolecular interaction in the direction of this O...H contact leads to the formation of a phenyl radical whose attack on a neighbouring molecule gives rise to the product (B); the generation of the next phenyl radical then leads to the propagation of reaction via chain mechanism along the *a* crystallographic axis.[42]

At the same time the authors[57] do not rule out the possibility of an intramolecular rearrangement of compound (XLVIII) to compound (LI). As a consequence of the alternation of the deviations of the parallel groups from the plane of the ethylene fragment in the molecule of compound (XLVIII), there is a possibility of forming hydrogen bonds between the carbonyl oxygen atoms and the *o*-hydrogen atoms of the neighbouring benzoyl groups. In addition, the alternating disposition of the benzoyl groups in compound (XLVIII) relative to the plane of the ethylene group prevents a concerted intramolecular movement of the phenyl groups. The disposition of the oxygen atoms in compound (XLVIII) favours the formation of the condensed furo[3,4-c]furan system (LI).

4. Rearrangement of Methyl *p*-Dimethylaminobenzenesulphonate

Methyl *p*-dimethylaminobenzenesulphonate (LII) rearranges in the solid phase to the betaine (LIII), the rate of reaction increasing with temperature until the attainment of the melting point, after which it falls sharply:[58]



An X-ray diffraction study showed[58] that the crystals of compound (LII) is made up of stacks of molecules, whose arrangement is convenient for the transfer of the CH_3 group along the molecular chain. The impossibility of an intramolecular rearrangement has been demonstrated experimentally using the corresponding deuterio-derivatives.

The CH_3 transfer process has been modelled by calculating the energy of the interaction of the molecule of compound (LII) with the CH_3 group approaching it,[59] using the extended Hückel method. The initial molecular geometry was taken from X-ray diffraction data. The extent to which the CH_3 and $(CH_3)_2N$ groups are pyramidal was varied as a function of the increasing distance from the N and O atoms; it was assumed that the CH_3 group is planar and is located between the N and O atoms at equal distances from the latter.

Fig.1 presents the dependence of the energy of the system described on the O—CH_3 and N—CH_3 distances and the extent to which the CH_3 group has been withdrawn (λ_1 and λ_2). The energy surface was of the kind usual for reactions of the type X + YZ = XY + Z, but the presence of a minimum in the lower left-hand region, where a saddle point is normally present, is striking. The dashed line indicates the path corresponding to the formation of an adduct with subsequent abstraction of the ether CH_3 group. The mechanism of the formation of a new bond with simultaneous dissociation of the old one would correspond to a diagonal path on the energy surface. The need to overcome a significant energy barrier

in this path suggests a two-stage process mechanism involving the formation of the corresponding intermediate compound. The total activation energy for the process along this reaction path is low and the relative thermodynamic advantage of the product molecule compared with the initial molecule is equivalent to ~12 kcal mol^{-1}.

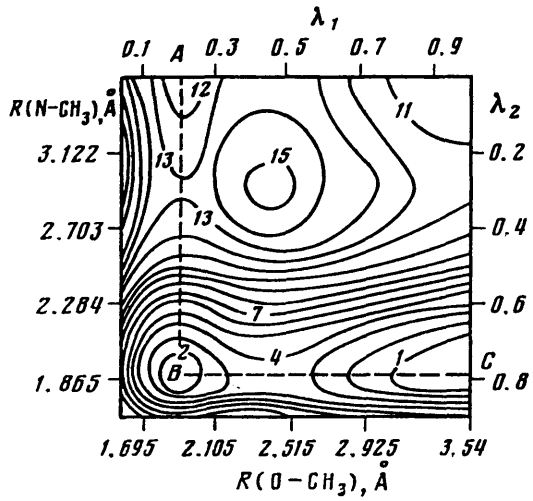


Figure 1. The energy surface for the reaction as a function of the distance to which the CH_3 groups are removed (λ_1 and λ_2) on dissociation of the O–CH_3 and N–CH_3 bonds. The energy contours are drawn at 1 kcal mol^{-1} intervals. Stage *A* corresponds to $^{+}CH_3 + (CH_3)_2NC_6H_4SO_3CH_3$, stage *B* corresponds to $(CH_3)_3\overset{+}{N}C_6H_4SO_3CH_3$, and stage *C* corresponds to $(CH_3)_3NC_6H_4SO_3^{-} + \dot{C}H_3$.[59]

The charges on the atoms and the Mulliken bond orders have been calculated for the molecules of the initial compound and the product. The CH_3 group abstracted has a large positive charge, which is partly transferred to the remaining CH_3 group. In the course of this rearrangement the negative charge on the N atoms becomes smaller and that on the O atom increases. The migrating CH_3 group leaves behind a bonding electron on the O atom, but at the same time it captures an electron from the N atom, which is used to form a new bond, so that the total change in the charge of the CH_3 groups should be small. The reaction involving the formation of methyl radicals does not then occur, since such a pathway would have involved a greater activation energy.

The change in the energy of the crystal structure as the CH_3 group moves towards a neighbouring molecule (and also as the character of the coordination of the N atoms is altered) in the course of the migration of the CH_3 group in the crystal was estimated by the method of atom–atom potentials,[68] taking into account the electrostatic component. The calculation showed that the displacement of the CH_3 group by 1 Å changes the energy of the crystal structure by only 7 kcal mol^{-1}. For the $(CH_3)_2N$ group, the deviation of the substituents towards the approaching CH_3 group is unfavourable, while that in the opposite direction is free (within the limits of 40°).

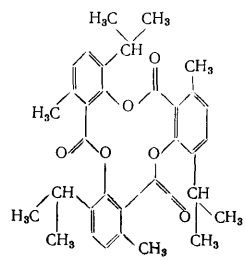
In order to elucidate the character of the changes in the molecular packing energy in the crystal on passing from compound (LII) to compound (LIII), the energy of the structure of compound (LII) was also calculated using the coordinates taken from the results of its X-ray diffraction study[58] together with the energy of a model crystal made up of molecules of compound (LIII) but packed in the (LII) lattice.[59] It was found that this hypothetical structure is significantly less favourable than the real structure of compound (LII). This is apparently in fact one of the reasons why the transformation described above does not proceed via a single crystal–single crystal mechanism.

Additional information about the mechanism of the reaction considered has been obtained from Raman phonon spectra,[60–62] which yield information both about the structure and the dynamics of the lattice, by means of which it is possible to obtain the characteristics of the homogeneity or heterogeneity of the solid-phase processes. The dynamics of the crystal lattice in which solid-phase reactions take place can favour their occurrence (the so-called "phonon enhancement"). In order to detect the possibility of such an enhancement, one considers the temperature dependence of the phonon spectra, where it is possible to observe a softening of certain modes, which indicates an increase in the amplitudes of the molecular movements precisely in the crystallographic directions along which solid-phase reactions can occur.

Analysis of the phonon spectra of crystals of compound (LII)[61] led to the conclusion that in this instance the solid-phase reaction is heterogeneous, which is consistent with the conclusions of Gavezzotti and Simonetta.[59] A study of the temperature dependence of the phonon spectrum revealed a softening of one of the modes (27 cm^{-1}), which indicates the possibility of the phonon enhancement of the reaction considered.

5. Geometrical Isomerisation of *cis*-Stilbene in Clathrate Complexes

The intramolecular solid-phase rearrangements in crystals made up of identical molecules were discussed above. Naturally, such reactions are possible also in clathrate compounds, where the reacting molecules are enclosed within cavities of the crystal lattice of the "host" molecules. Among the numerous known clathrate-forming compounds, the one which attracts most attention as regards the topic of the present review is tri-o-thymotide (TOT), which forms clathrates of different type,[63] a common feature of which is their chiral structure.[64] In particular, this gives rise to the possibility of the asymmetric synthesis in the reactions of prochiral "guest" molecules enclosed in the chiral TOT crystals.[65]



The first example of the photoinduced stereoisomerisation in crystals of TOT clathrates is the solid-phase rearrangement *cis*-stilbene.TOT–*trans*-stilbene.TOT under the influence of ultraviolet irradiation.[63] The reverse transition

in the crystal has not so far been observed, although in solution both processes are possible.[66] The quantitative *cis–trans* photoisomerisation has been thoroughly investigated also for crystalline olefins (for example, for cinnamic acid derivatives) in the absence of clathrate-forming compounds[7,67] and a common feature of all these processes is the absence of the reverse conversion of the *trans*-isomers into the *cis*-isomers. This constitutes the fundamental difference between the solid-phase processes of this kind and liquid-phase processes, although the rearrangements can take place in both directions.[63]

The conformations of the TOT molecules in crystals of the *cis*-stilbene.TOT (LIV) and *trans*-stilbene.TOT (LV) clathrates are very similar.[63] In the crystal of compound (LV) two symmetrically independent (i.e. not linked by the symmetry elements of the space group) stilbene molecules are located at the centre of symmetry, fill the non-intersecting channels parallel to the *a* and *b* crystallographic axes respectively, and are disordered (statistically or dynamically), which is manifested by high thermal parameters of their atoms. The characteristic features of the molecules incorporated in various inclusion complexes are in general either complete orientational disorder, which can be detected in certain cases by NMR in the solid state,[64] or a fairly high order, the extent of which, for example in the case of compound (XL), can be reliably determined by X-ray diffraction.

The packing of symmetrically independent *trans*-stilbene molecules in the above two types of channels of one (LV) crystal differs as regards the C...C distances between neighbouring molecules in the channel of each given type (4.60 and 3.83 Å) and the distances between the planes passing through the aromatic rings of neighbouring molecules (0.6 and 2.0 Å). The *cis*-stilbene molecules in the crystal of compound (LIV) are disordered with respect to two positions (linked by a centre of symmetry), the overall population of which is lower than that of the populations of the positions of the *trans*-stilbene in the crystal of compound (LV).

Table 2. The volume of the channels in the clathrates (LIV) and (LV).[63]

Channel	V_f, Å^3	V_u, Å^3
a-Channel (LV)	570	94
a-Channel (LIV)	570	72
b-Channel (LV)	826	56
b-Channel (LIV)	887	103

Notation: V_f is the free volume in the TOT matrix and V_u the useful volume (accessible to the "guest" molecules).

The reactions of the occluded molecules in clathrates require a preliminary alteration of the shape and volume of the channels; the very similar densities and unit cell parameters of the clathrates (LIV) and (LV) indicate an insignificant alteration of the free volume in the TOT matrix. Table 2 shows that, whereas the overall volume of all the cavities (the free volume) in the TOT matrix changes insignificantly in the (LIV) → (LV) transition, its component in which the "guest" molecules can be accommodated (the useful volume) undergoes an appreciable change (namely there is a sharp alteration in the *b* channels and a smaller alteration in the *a* channels), which can be accounted for by a change in the shape of the channels, while the volume remains unaltered.

The reason why *trans*-stilbene is preferentially incorporated in TOT may be associated with the mutual correspondence of the symmetries of the "guest" molecule and of the cavity in the matrix of the "host" molecule. The absence of a centre of symmetry in the *cis*-stilbene molecules creates less favourable conditions for their packing in a centrosymmetrical cavity, as a result of which the corresponding clathrate is less stable. It is useful to take this into account in seeking suitable molecules for inclusion in the lattice of the given "host". For example, one may expect that, for a "host" forming centrosymmetrical cavities, the *meso*-(*R*,*S*)-diastereoisomers are preferable to the D- or L-(*RR* or *SS*)-stereoisomers, while the inclusion of molecules of the second type will be preferable in cavities having the C_2 symmetry.

When any solid-phase chemical reaction is considered, provided that it differs from the corresponding reaction in solution, the question arises in what way and at what stages does the crystalline medium exert its influence on the course of the reaction. Thermal solid-phase reactions can therefore be usefully subdivided into four stages: the initial "loosening" of the molecular packing in the "reaction centre" of the crystal, their subsequent intra- or inter-molecular chemical transformation, then the formation of a solid solution of the product in the initial substrate, and finally the concluding separation of the product phase.[10] In photochemical solid-phase reactions the first stage as such is naturally absent, its role being assumed by the photoexcitation of the crystal system.

The photoisomerisation reactions in TOT clathrates can be regarded as processes occurring in the closed volume of the "reaction cavity" of the clathrate. An alternative explanation is that the molecules can diffuse from the closed cavities of the clathrate into its less "constrained" positions, in which they initially undergo chemical transformations and this is followed by the recrystallisation of TOT and the reaction product (*trans*-stilbene) with formation of the final clathrate. Although the second pathway cannot in fact be fully ruled out, preference has been given[63] to the process in the "reaction cavity".

As regards the solid-phase transition (LIV) → (LV), it has been concluded[63] that the transformation of a molecule with C_1 symmetry into one with a C_i point group within the cavity having the same C_i symmetry is the main factor which determines the observed photochemical reaction. Since the *cis–trans* isomerisation of stilbene requires the internal rotation of one fragment of the molecule relative to the other by 180° and therefore presupposes a definite deformation of the reaction cavity, it has been suggested that this kind of deformation takes place readily in TOT clathrates, which has been confirmed, in particular, by the wide variety of molecules which can be incorporated in such clathrates.[63,67] The manifestation in the crystal of compound (LV) of a temperature dependence of the rate of the *cis–trans* isomerisation of stilbene, is apparently associated with a kind of activation of the "loosening" of the molecular packing in the corresponding cavity,[10,63] which promotes a freer internal rotation, necessary for the *cis–trans* isomerisation indicated. The breakdown of the ordered disposition of the molecules in TOT clathrates following this kind of loosening of the packing is not always reversible and, when the molecules do not return to their initial positions or when the concerted nature of their migration in various parts of the crystal is disturbed, then a transition of the single crystal–single crystal type does not take place and individual crystallites of the new phase are formed.

6. Isomerisation of the Monoadduct of 11-Cyano-1,6-Methano[10]Annulene and 4-Methyl-1,2,4-Triazoline-3,5-Dione

In the study of the liquid-phase Diels–Alder reactions between bridge [10]annulenes and *N*-methyl- and *N*-phenyltriazoindolines,[69] isomers of the *exo*-type [compounds (LVI)] and the *endo*-type [compounds (LVII)] of the monoadducts of 11-cyano-1,6-methano[10]annulene with 4-methyl-1,2,4-triazoline-3,5-dione were isolated (Fig. 2).[70] It was found that the interaction of compounds (LVI) and (LVII) with a second mole of 4-methyl-1,2,4-triazoline-3,5-dione leads to only one isomer of the bisadduct (LVIII), namely one having the *endo,endo*-configuration. Thus the initial monoadduct of the *exo*-type undergoes the configurational transformation (LVI) → (LVII) into the isomer of the *endo*-type before or in the course of the reaction with the dienophile.[69,71]

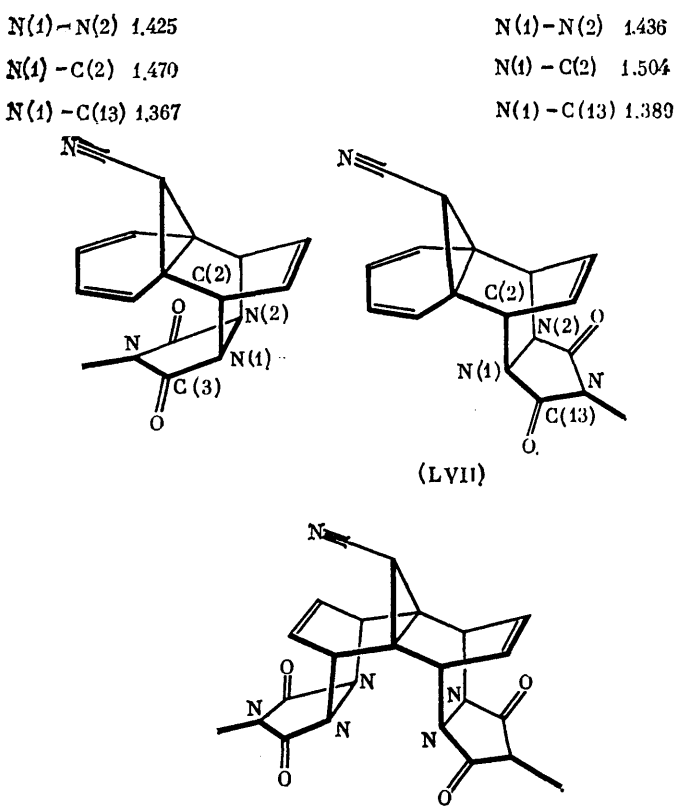


Figure 2. The structures of the *exo*- and *endo*-isomers (LVI) and (LVII) of the monoadduct and also of the *endo,endo*-isomer of the bisadduct (LVIII) of 11-cyano-1,6-methano-[10]annulene and 4-methyl-1,2,4-triazoline-3,5-dione.[71]

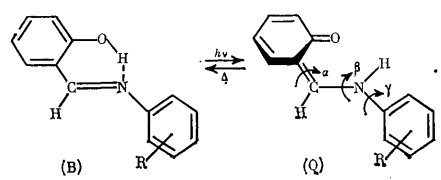
A similar study of the analogous solid-phase rearrangement (LVI) → (LVII) showed[71] that, on heating to 75 °C, dark bands appear within the (LVI) single crystal, although its outer form does not change. The complete transition (LVI) → (LVII) takes place at a temperature close to 175 °C: the X-ray diffraction patterns of compounds (LVI) and (LVII) become identical (when the powder method is used), and the reaction in the single crystal leads to the polycrystalline product (LVII). Of the two possible mechanisms of this process proposed for the solution, namely the Diels–Alder retro-reaction or or inversion relative to the N–N bridge in the primary adduct, the latter appears more probable. The barrier to the Diels–Alder retro-reaction of the model adduct of cyclopentadiene and maleic anhydride is 37.5 kcal mol^{-1}.[72] Since the C–N bond present in the molecule of compound (LVI) is only slightly weaker than the C–C bond in the model adduct, for compound (LVI) this barrier should be not less than 30 kcal mol^{-1}. In the case of double inversion the barrier should in its turn be only approximately 7 kcal mol^{-1} [for the (LVI) → (LVII) inversion] and ~9 kcal mol^{-1} [for the inversion (LVII) → (LVI)].[71] The experimental value is ~11.9 kcal mol^{-1},[71,73] which thus confirms the double N-inversion mechanism of the process under consideration.

Comparison of the geometrical parameters of the isomers (LVI) and (LVII) also confirms that the observed rearrangement proceeds via the mechanism involving the inversion of the N–N bridge. The less stable *exo*-isomer has a geometry closer to the flattened transition state of the isomerisation reaction considered. In fact, the dihedral angle between the planar fragments intersecting along the N–N bond in compound (LVI) (152.1°) is greater than in compound (LVII) (137.0°). The shortening of the bond between the hydrazine N atom and the C atom of the carbonyl group in the *exo*-isomer (LVI) thus also confirms the hypothesis that the planar transition state is stabilised by the conjugation of the diazo-group with the carbonyl group, which lowers the barrier to the inversion process.[71]

7. Chromotropic Reactions

Yet another large class of organic reactions which differ fundamentally when they are carried out in the liquid and crystalline phases comprises chromotropic transformations, in which the rearrangement is accompanied by a change in the colour of the reacting compounds. The arylimines of substituted salicylaldehydes are the most thoroughly investigated organic photochromic compounds in relation to this reaction (Scheme 13):[74,75]

Scheme 13



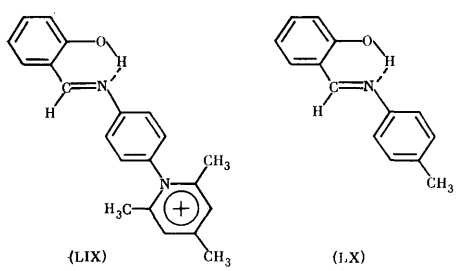
In solutions they are almost all photochromic, which is due to their ability to undergo on irradiation ($\lambda \cong 340–360$ nm) a rearrangement with phototransfer of a proton via the hydrogen bond from the O atom of the hydroxy-group to the imine N atom with transition of the planar benzenoid structure (B) into the quinonoid NH form (Q). As a consequence of the easier internal rotation of the fragments in the resulting (Q) molecule (with a change in the angles α and β and the rupture of the NH...O hydrogen bond), it now has a non-planar structure and is characterised by the appearance of the so-called "photochromic" absorption bands due to the different angles of rotation of the aldehyde ring in different molecules (λ = 480 nm, $\alpha \cong 50–55°$; λ = 540 nm, $\alpha \cong 65–70°$).[75–78]

The extremely short lifetimes of such (Q) structures in condensed phases ($\tau_{1/2} \cong 10^{-6}$ s) significantly hinder their study in solutions. However, in polymer matrices, frozen solutions, and in the crystalline phase, their lifetime is significantly increased, which explains the special advantages of the solid-phase methods for the investigation of chromotropic reactions compared with the liquid-phase methods.

Crystalline salicylidenearylamines (which are photochromic in solution) have been subdivided into two classes, which differ from one another as regards the character of physical influences inducing a change in their colour:[75] (1) photochromic non-fluorescent crystals which are coloured like the solutions, with the appearance in the absorption spectrum of bands at 485 and 540 nm, and which do not change colour when the temperature is altered; (2) thermochromic crystals which do not exhibit photochromic properties on irradiation but do fluoresce with a large Stokes shift at 77 K and are capable of acquiring a colour only on raising the temperature, whereupon a broad absorption band appears in their spectrum with a somewhat shorter wavelength in the range 400–470 nm.

Different types of behaviour of the compounds considered in solution and in the crystal justify the assumption that their photochromic and thermochromic properties in the crystalline state should be determined to a large extent by the influence of the packing.[75,79,80] This is confirmed by the formation of polymorphic photochromic and thermochromic modifications of salicylideneaniline[81] and salicylidene-*m*-chloroaniline[82] (depending on the rate of cooling of the solution on crystallisation) and also the photochromic and thermochromic solid solutions of compounds of this class, whose properties are determined exclusively by the crystal lattice of the "host".[83]

In order to elucidate the influence of intermolecular interactions and the nature of the phenomenon of chromotropism, the crystal structures of the photochromic (compound (LIX)] and thermochromic [compound (LX)] salicylidenearylamines have been compared.[75]



In the molecule of compound (LIX) $\alpha = 4°$, $\gamma = 51°$, and the angle of rotation of the trimethylpyridinium ring relative to the aniline ring is 87.2°. The molecules of compound (LX) in the crystal are planar and are packed in stacks along the c axis; the interplanar distance is ~3.4 Å. These data agree well with the results of other structural studies on compounds of this class[79,80,84–87] and show that the stacked close packing of the planar molecules is characteristic of thermochromic crystals and its absence and a non-planar molecular structure are characteristic of photochromic crystals.[75] Quantum-chemical calculation by the CNDO/2 method for the planar and non-planar ($\gamma = 60°$) molecules showed that the non-planar structure is preferable to the planar-structure only to the extent of ~2.5 kcal mol^{-1} [75] and the conformation of the molecules of compound (LIX) in the crystal can be fully determined by the packing effects.

The increased electron density at the N atom in the planar structure, which follows from the above calculation, strengthens the N...H–O hydrogen bonds, lowers the activation energy for the transfer of a proton from the O atom to the N atom in the ground state, and leads to the formation of the quinonoid form on raising the temperature. The formation of non-planar (in terms of the angles α and β) quinonoid forms of thermochromic compounds can be hindered by the stacked close packing of the planar molecules. Indeed calculation of the intermolecular interaction in the crystal of compound (LXX) by the method of atom–atom potentials yields 10.0 kcal mol^{-1} as the energy of the interaction between the molecules in the stacks, while the energy of interaction between the stacks does not exceed 2.5 kcal mol^{-1}.[75]

The non-planar photochromic molecules do not form close-packed stacks in the crystals, because the intermolecular interaction energy in such stacks does not exceed 1–3 kcal mol^{-1}. The non-planar molecular structure resulting from the decreased electron density at an N atom leads to an increased activation energy for the proton transfer in the ground state and the absence of thermochromism. However, on photoexcitation to the S_1 state, adiabatic proton transfer does occur.[75] In contrast to thermochromic crystals, in the photochromic structures the absence of a stacked structure in the latter entails the occurrence of an adiabatic non-coplanarisation process (with respect to the angles α and β), after the proton transfer, which no longer leads to fluorescence but to the formation of coloured forms with long-wavelength absorption at ~480 and 540 nm. The additional appearance in the spectra of thermochromic crystals of a long-wavelength absorption band at ~470 nm on raising the temperature can be associated with the formation of a certain amount of non-planar quinonoid forms, for example, on the surface of the crystal, as a result of an increase in the thermal vibrations of the atoms.

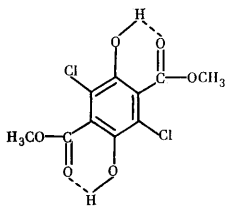
According to Aldoshin et al.,[75] the difference between the energies of the planar and non-planar forms of the free molecules of salicylidenearylamines is insignificant and is close to the intermolecular interaction energy in the crystal. If the gain in the crystal lattice energy is greater than the gain in the energy of the free molecule in one or other of the possible conformations, a structure arises in the crystal whose conformation ensures a minimum crystal lattice energy. Thus, by altering the ratio between the free energy of the molecule and the crystal lattice energy (by introducing various substituents), it is possible to regulate the structure and properties of the crystals.

A structural study[88] of the photochromic α_1- and α_2-forms of *N*-salicylidenepentafluoroaniline [compounds (LXI) and (LXII)], the α-form of *N*-salicylidene-4-bromoaniline (LXIII), and the thermochromic β-form of *N*-salicylidene-4-chloroaniline (LXIV) [the molecules of compounds (LXI)–(LXIII) are non-planar while those of compound (LXIV) are planar and packed in stacks] led to a mechanism of both types of chromotropic transitions based on the idea of the formation of intermolecular charge-transfer complexes (IRCTC). Thermochromic crystals are regarded in this case as an equilibrium mixture of tautomers, forming the corresponding IRCTC (the rate of equilibration depends on temperature). As regards photochromic crystals, their irradiation with ultraviolet light induces tautomerisation with formation of IRCTC [the crystals of compounds (LXI) and (LXII) have structures of the IRCTC type].

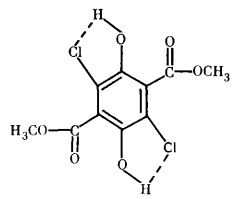
Investigations of solid-phase processes, which are close to phase transitions and in particular are close to the so-called conformational polymorphism in which a change in the conformation of the molecules in the crystal is accompanied by the

simultaneous alteration of structural and/or electronic characteristics of the system (intra- and inter-molecular hydrogen bonds, the colour of the crystal, etc.), can also be included among studies of intramolecular rearrangements.

The transition of the yellow form (LXV) of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate into the colourless form or, in the terminology of Curtin et al.,[89] the white form (LXVI), occurring on heating compound (LXV) to 140°, which is significantly below the melting point of compound (LXVI), is an example of this kind. The difference between the yellow and white forms, established by X-ray diffraction,[89] consists in the different dispositions of the intermolecular hydrogen bonds and also in the different orientations of the methoxycarbonyl groups relative to the plane of the benzene ring—in the yellow form these groups are in the plane of the benzene ring, while in the white form they are almost at right angles to it.



(LXV) yellow form



(LXVI) white form

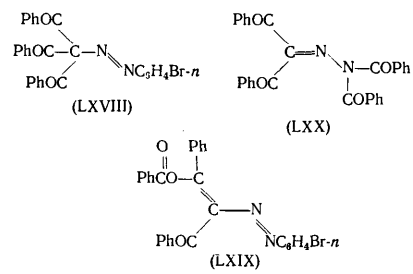
The difference between the characters of the intermolecular hydrogen bonds makes it possible to classify the molecules of the above two forms as isomers. Although the two forms crystallise in the same space group $P\bar{1}$, in the yellow form $Z = 1$ (one system of centres is occupied), while in the white form $Z = 2$ (two systems of centres are occupied), as a result of which the volume of the unit cell increases by a factor of two. The packing in the crystals of the yellow form consists of stacks of translationally linked molecules; the rearrangement of the packing occurring on transition to the white form can be described as the rotation of alternate molecules in the stack by 180° about the axis joining the Cl atom.

The rate of transformation of one form into the other depends significantly in this instance on temperature. Thus, whereas at room temperature both forms can coexist indefinitely, at 140° the transition takes place in several minutes. The transition can begin over a wide temperature range. Having been initiated at any point in the crystal, the new phase spreads in the [110] direction. When viewed through an optical microscope, this process appears to be a transition of the single crystal–single crystal type, but X-ray diffraction data show that the specimen obtained is polycrystalline, although it can consist of fine single crystals having similar orientations.

For a more complete investigation of the kind of processes occurring in the transition considered, the recently proposed technique of Ramon phonon spectroscopy in the solid state was used.[60–62] The Raman spectra confirmed the presence of different systems of hydrogen bonds in compounds (LXV) and (LXVI).[62] It was observed that only in the initial stages, when the content of the white form is low, does the process proceed as a homogeneous reaction, after which it acquires a heterogeneous character. The study of the temperature dependence of the phonon spectrum did not reveal a soft mode in the latter, which might have indicated the occurrence of lattice vibrations favouring the process via a topochemical mechanism. It was therefore concluded[62] that the thermal rearrangement is of a dislocation type although its mechanism at the molecular level still remains obscure.

Other examples of solid-phase conformational transformations are the transition of 2-(4-methoxyphenyl)-1,4-benzoquinone (LXVII) from the yellow to the red form (in which the rings undergo a mutual rotation by 110° and an overall reorientation of the molecule takes place with appearance of an intermolecular donor–acceptor interaction[90]) and the thermochromic polymorphic transitions of naphthazarine[91–93] and diaminoterephthalic acid esters.[94]

The structural rearrangement in the thermochromic transitions (observed both in solution and in the crystal) of the yellow azotriketone [compound (LXVIII)] to the red (compound (LXIX)] and colourless [compound (LXX)] products is more significant.[95] These processes consist in the competing migration of the acyl group from the C atom to the O atom [the (LXVIII) → (LXIX) transition] and from the C atom to the N atom [the (LXVIII) → (LXX) transition].



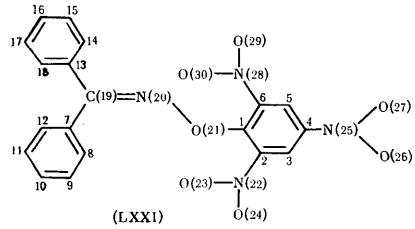
(LXVIII)

(LXX)

(LXIX)

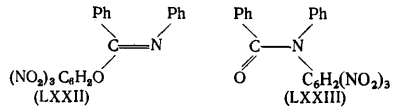
The ratio of the isomerisation products in the crystal and in the solution (dioxan) should then be fairly similar [(LXIX):(LXX) is 0.85 and 1.05 respectively]. The rate of reaction in the crystal is 100–400 times lower than in solution and diminishes as the quality of the crystals of compound (LXVIII) improves. If a more volatile solvent ($CHCl_3$) is used for crystallisation, then, when the resulting crystal of compound (LXVIII) is allowed to stand, the solvent diffuses from it and the rate of the thermochromic rearrangement increases (although the ratio of the red and white products is also altered).[96] Analysis of the non-valence contacts in the molecule of compound (LXVIII) did not reveal a structural preference for the migration of any particular acyl groups to the O or N atoms. At the same time the absence of intermolecular contacts from the crystal of compound (LXVIII) and the corresponding N, O, and C atoms in neighbouring molecules makes it impossible to attribute an intermolecular mechanism to the observed solid-phase thermochromism.[96]

An appreciable rearrangement of the molecule is observed also in the solid-phase thermochromic (≤70 °C) transformation of the colourless picryloxime (LXXI):



(LXXI)

and of its derivatives via the intermediate (LXXII) into the yellow amide (LXXIII):[96,97]

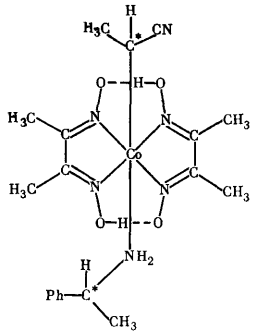


Steric strain is observed in the molecule of compound (LXXI) in the region of the O–Ph bond [C(1–6)], where the O(21), N(22), and N(28) atoms deviate from the plane of the benzene ring by −0.095, 0.144, and −0.134 Å respectively, while the N(25) atom in the *p*-position is located exactly in this plane. The C(6)C(1)O(21) and C(2)C(1)O(21) valence angles differ markedly (129.0° and 114.5°). The above geometrical distortions are caused by the intramolecular steric interaction of the N(20) atom and the nitro-group at the N(28) atom, on the one hand, and between the O(21) atom and the nitro-group at the N(22) atom, on the other [the N(20)...N(28), N(20)...O(30), O(21)...N(22), and O(21)...O(23) distances are 2.668, 2.859, 2.676, and 2.766 Å]. The aromatic C(7–12) ring in the *syn*-position relative to the picryl group has been rotated by a larger angle in the plane of the $C_2C{=}N(-O)$ group compared with the C(13–18) ring (60.5° and 18.6° respectively). The distance between the O(21) atom and the C(19) atom to which it migrates is 2.213 Å. Intermolecular distances less than 4 Å between the potentially reactive atoms in the crystal compound (LXXI) were not observed.[97]

8. Rearrangements of Metal Complexes

A structural study of *R*-α-cyanoethyl-(*S*-α-methylbenzylamino)cobaloxime (LXXIV) revealed a change in the unit cell parameters in the course of the X-ray diffraction which was not accompanied by the disruption of the single crystal.[98] After exposure for 22 days, a crystal of compound (LXXIV) [a = 8.665(2) Å, b = 13.485(3) Å, c = 9.584(3) Å, β = 96.95(3)°, V = 1111.6(5) Å^3; space group $P2_1$] is converted into a crystal of compound (LXXV) [a = 8.637(2) Å, b = 13.833(3) Å, c = 9.539(2) Å, β = 99.07(3)°, and V = 1125.5(4) Å^3]. A similar change in the unit cell parameters in the formation of a crystal of compound (LXXV) in the course of irradiation with X-rays has been established also for crystals of the second enantiomorphic form of compound (LXXIV).

Despite the retention of the non-centrosymmetric space group $P2_1$ of the initial compound for both types of crystals of compound (LXXV) formed, the two processes investigated represent the racemisation of the enantiomorphic forms of compound (LXXIV). An X-ray diffraction study[98] showed that, after the transition, the CH_3 groups of the cyanoethyl ligand occupy with equal probabilities two positions corresponding to the *R*- and *S*-configurations. It has been suggested[98] that this process proceeds via the dissociation of the Co–C bond and the appearance of the planar cyanoethyl radical capable of further recombination to reform the initial structures with equally probable attack on both sides in this reaction. This hypothesis has been confirmed by direct EPR observations of the homolytic cleavage of the Co–C bond in alkylaminocobaloximes when they are irradiated with visible light (λ > 420 nm).[99,100] The energy liberated on dissociation of the bonds can induce the formation of local zones consisting of the melt. The appearance of the racemic structure on re-formation of the bonds is apparently to be explained by its greater thermodynamic stability. The retention of the single crystal structure can be accounted for by the identity of the crystal-structure parameters of both enantiomers.



(LXXIV) and (LXXV)

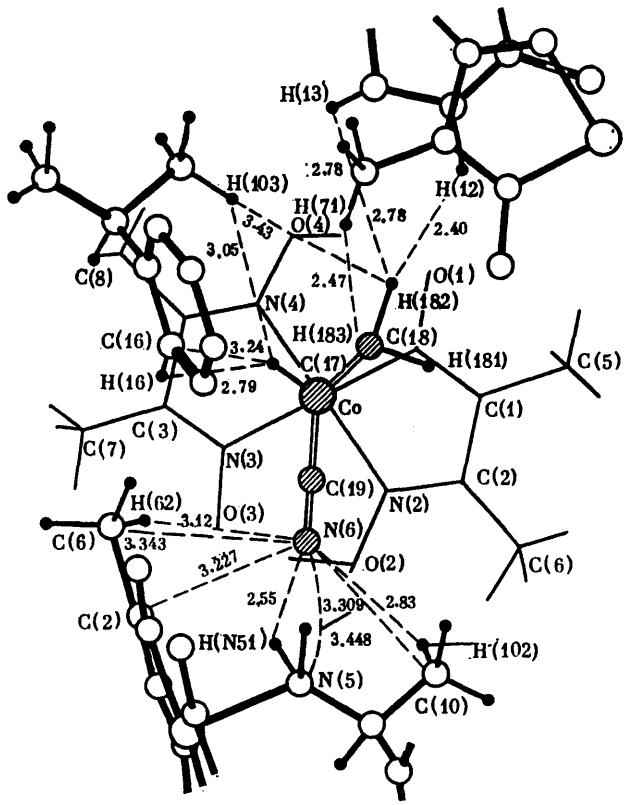


Figure 3. The environment of the atoms of the α-cyanoethyl group (shaded circles) in a crystal of compound (LXXIV); the C(17) atom is projected on to the Co atom.[98]

In order to investigate the dependence of the rate of the solid-phase racemisation of compound (LXXIV) on temperature, measurements have been made of the unit cell parameters of this compound at 133 K [a = 8.791(2) Å, b = 13.516(2) Å, c = 9.161(2) Å, and β = 98.31(3)°] and also their variation with increase of temperature to 293 K.[101] The difference between the parameters at 133 and 293 K is

unusual; on the one hand, it does not indicate the occurrence the (LXXIV) → (LXXV) transition, while, on the other hand, the explanation cannot be reduced to the thermal expansion of the crystals of compound (LXXIV) (the linear thermal expansion coefficients are -1.00×10^{-4}, -0.10×10^{4}, and 2.95×10^{-4} K^{-1} along the *a*, *b*, and *c* axes respectively). For the crystal of the racemate (LXXII) under the same conditions, the linear expansion coefficients are similar (-1.00×10^{-4}, 0.25×10^{-4}, and 2.50×10^{-4} K^{-1}), whence it follows that the thermal expansion of compound (LXXIV) [and possibly also of compound (LXXII)] is reversible.

Comparison of the crystal structures of compound (LXXIV) at 173 and 293 K has shown that cooling leads to the contraction of the crystal owing to the compaction of the structure in the region of the H(17) atom (Fig. 3). The most significant changes are in the H(17)...H(103) = 3.05 Å, H(17)...H(16) = 2.79 Å, and H(182)...H(103) = 3.43 Å, distances which diminish to 2.47, 2.53, and 2.56 Å respectively, i.e. the values corresponding to the normal van der Waals contacts. This compaction does in fact explain the retardation of the racemisation of compound (LXXI) at low temperatures.

Racemisation in the course of X-ray irradiation and its retardation on reducing the temperature to 133 K are also characteristic of crystals of the diastereoisomeric [in relation to compound (LXXIV)] complex *S*-α-cyanoethyl(*S*-α-methylbenzylamine)cobaloxime (LXXVI).[102] The crystals of compounds (LXXIV) and (LXXVI) have two features in common: (1) the molecules in the crystal have a bond which is sensitive to irradiation by X-rays and to exposure to electromagnetic radiation with a higher wavelength; (2) this bond is located in the region of loose packing (with increased intermolecular distances). However, in the case of the crystals of *R*-α-(methoxycarbonyl)ethyl(*R*-α-methylbenzylamine)bis(dimethylglyoximato(cobalt(III) racemisation is no longer observed, which is caused by the failure of the second of the conditions indicated in this instance.[103] Nevertheless, it is believed[101,103] that the number of crystalline complexes which satisfy both conditions should be large and that varied solid-phase reactions should be observed in them.

In contrast to compounds (LXXIV) and (LXXVI), the racemisation which takes place on irradiation of crystals of [(*S*)-1-cyanoethyl](pyridine)cobaloxime (LXXVII)[104] and [(*R*)-1-cyanoethyl](pyridine-4-carbonitrile)cobaloxime (LXXVIII),[105] which proceeds via the inversion of the configuration of the cyanoethyl group in one of the two [(A) and (B)] symmetrically independent molecules (in both cases the space group is P_1 with $Z = 2$), gives rise to the racemate (A'), whose molecules are characterised by an ordered disposition of the cyanoethyl groups (with a centrosymmetric space group $P\bar{1}$, Z = 1).

The volumes of the reaction cavities of the cyanoethyl groups in the enantiomorphic crystals of compounds (LXXVII) and (LXXVIII) and the crystals of the corresponding racemates are compared in Table 3 with the rate constants for racemisation in the crystal. The cyanoethyl group of the molecule (B), which undergoes inversion in racemisation, occupies a larger volume than the cyanoethyl group in the molecule (A). Evidently the greater the volume of such cavities, the higher the reaction rate. The retardation of the racemisation of the crystal of compound (LXXIV) at 173 K can also be attributed to a decrease of the volume of the cavity of the cyanoethyl group from 14.53 $Å^3$ at 273 K to 12.95 $Å^3$ at 173 K.[105] In the crystal of [(*R*)-1-cyanoethyl]-(4-methylpyridine)cobaltoxime, for which racemisation is also observed on irradiation, the cavities occupied by the reactive groups have a larger volume than those incorporating inactive groups.[105]

Yet another example of racemisation in the crystal has been described for the solid-phase transition on irradiation with X-rays of [(*R*)-1-methoxycarbonylethyl](pyridine)cobaloxime (LXXIX) containing the methoxycarbonylethyl groups $CH(CH_3)CO_2CH$ instead of the cyanoethyl groups.[106] The rate of racemisation of compound (LXXIX) (space group $P2_1$) is in this case so high that it has been possible to investigate by X-ray diffraction only the racemates of compound (LXXX) (space group $P2_1/n$).[105]

Table 3. The volume v of the cavities occupied by the cyanoethyl groups before (A and B) and after (A') the racemisation of compounds (LXXVII) and (LXXVIII) together with the rate constants *k* for the racemisation.[105]

Parameter	(LXXVII)	(LXXVIII)
v(A), Å³	7.97	8.89
v(B), Å³	10.37	11.34
v(A'), Å³	10.52	10.52
v(A+B), Å³	27.95	25.58
v(2A'), Å³	26.41	26.49
k, s^{-1}	$1.65 \cdot 10^{-6}$	$2.83 \cdot 10^{-6}$

9. Spin Isomerism

Many chemically and biologically important processes involving iron(II) and iron(III) complexes are accompanied by a change in the spin state of the metal atom. Such changes cause a sharp alteration in the strength of the donor ligand–metal ion bond and hence in the chemical properties of the complex; however, compounds manifesting the properties of "spin equilibrium", i.e. capable of existing in the form of an equilibrium mixture of spin isomers, have so far been little investigated.[107–112]

The crystallographic approach to the description of spin transitions both in the crystal and in solution involves the measurement at room temperature of the geometrical parameters of complexes with similar structures but with different spin states. For example, a study at room temperature of the low-spin complexes $[Fe(sal)_2trien]Cl.2H_2O$ and $[Fe(sal)_2.trien]NO_3.H_2O$ and the high-spin complexes $[Fe(acac)_2Cl_2.trien]PF_6$ and $[Fe(acac)_2trien]PF_6$(sal = salicylaldehyde, trien = triethylenetetramine, and acac = acetylacetone) revealed a difference of 0.12 Å between the average metal–ligand bond lengths.[113]

A more complete structural description of the spin isomers is provided by the X-ray diffraction study of the same object at high and low temperatures. Thus investigation of $Fe(2,2'\text{-bipy})_2.(NCS)_2$ (β-modification) at temperatures above and below the spin transition established a change in the Fe–N bond length from 2.02 Å in the state $^1A_1$ to 2.14 Å in the state $^5T_2$.[114] For the iron(II) complex with the hexadentate [4-(6-*R*)-2,2'-bipyridyl]-3-aza-3-butenylamine ligand,[115] the expected increase (by ~0.12 Å) of the average of the six Fe–N distances was observed on passing from the high-spin state at 300 K to a mixture of the high- and low-spin states at 205 K. The structure of iron(III) trisdithiocarbamate was determined at 79 K, where the complex exists predominantly in the low-spin state, and at room temperature, where there are approximately equal contents of iron in the high- and low-spin states.[116]

When the investigations are carried out at temperatures such that two or more isomers are present in large amounts, in all cases it is possible to observe only the "average" structure, i.e. the spin isomers are crystallographically indistinguishable. Crystallographic studies carried out at several temperatures, where the disorder caused by the presence of spin isomers can be experimentally differentiated, are therefore of greatest interest. We shall consider the X-ray diffraction study of the methanol solvate of tris(2-picolinylamine)iron(II) dichloride (LXXXI) carried out at five temperatures (115, 148, 171, 199, and 227 K).[117] The high- and low-spin isomers of this compound are well resolved at four temperatures in the range 148–227 K. The differences between the spin isomers are evident also from a comparison of the structural parameters of compound (LXXXI) at 148–171 K (where both spin isomers are present in appreciable amounts) with the parameters obtained at the highest and lowest of the selected temperatures of their measurements. The average distances between the low-spin iron atom and the nitrogen atom at 148 and 171 K are 2.01(1) and 2.02(2) Å respectively, whereas at 115 K, when the substance consists of 98% of the low-spin isomer, the difference is 2.016(3) Å. The average distances between the high-spin iron atom and the nitrogen atom at 148 and 171 K are in their turn 2.18(1) and 2.19(1) Å, while at 227 K, where compound (LXXXI) consists of 84% of the high-spin complex, the average distance is 2.198(6) Å.

Another criterion which makes it possible to distinguish the spin isomers is the presence of correlations between the thermal parameters of the corresponding ligand atoms in the low- and high-spin forms. The structure of compound (LXXXI) (at 148 and 171 K)[117] was refined on the assumption that the isotropic thermal parameters of all the atoms are independent. The physically reasonable values of these parameters even in those cases where the distances between the atoms of the low- and high-spin isomers are small is remarkable. In the crystal of compound (LXXXI) there exists a two-dimensional system of the Cl...H–N and Cl...H–O hydrogen bonds. Although it has been remarked that the nature of the hydrogen bonds in the spin-isomeric compounds can influence appreciably the spin equilibrium, a detailed analysis of the change in the system of hydrogen bonds in the crystal of compound (LXXXI) at different temperatures has not been carried out.[117]

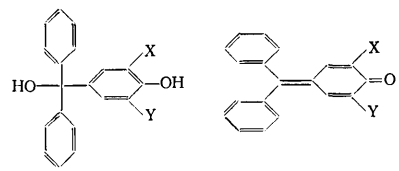
Estimates of the equilibrium constants for the spin transitions, obtained for compound (LXXXI) by X-ray diffraction[117] and by studying the Mössbauer effect,[118,119] have shown that the spin transitions in compound (LXXXI) are significantly non-cooperative; ΔH and ΔS are then 2.35(8) kcal mol^{-1} and 15.3(8) e.u. respectively, which may be compared, for example, with 4 kcal mol^{-1} and 10 e.u. for the spin transition in the complex tris [4-(6-*R*-2,2-bipyridyl)-3-azabutenylamine]iron(II) in the solid phase and in solution.[115] The above enthalpy change is apparently associated with the proximity of the spin transition temperature in these complexes to room temperature. In general the enthalpy change in the spin transition in the crystal is very sensitive to "specific" intermolecular interactions. On the other hand, one may expect that a change in entropy will not greatly influence the change in the crystal lattice observed during the course of the spin transition.[117]

III. REACTIONS WITH ELIMINATION OF SMALL MOLECULES

Chemical reactions in organic crystals accompanied by the liberation of low-molecular-weight products (in particular gaseous products) are well known. They include the desolvation of crystalline solvates (see, for example, Byrn and Lin[120] and Curtin and Paul[121]), controlled decomposition of explosive substances[122] and solid aza-compounds,[123] decarboxylation of diacyl peroxide,[124,125] and also the decarboxylation of *p*-aminosalicylic[126–129] and benzoic[130] acids.

1. Dehydration of *p*-Hydroxytriarylmethanols

The solid-phase thermal dehydration to the fuchsones (LXXXIII) of certain *p*-hydroxytriarylmethanols (LXXXII),[131,132] whose molecules have functional groups ensuring the presence in the crystal of a system of hydrogen bonds between the phenolic OH group (the proton donor) and the OH group at the sp^3 carbon atom (proton acceptor) in a neighbouring molecule, is well known. The presence of such hydrogen bonds, which link up the molecules into infinite chains, has been demonstrated by an X-ray diffraction study of compound (LXXXIIa) and also by the investigation of the isostructural crystals of compounds (LXXXIIb) and (LXXXIIc)[132,133]



(LXXXII): (a) X, Y=H; (b) X, Y=Br; (c) X, Y=CH_3; (d) X=CH_3, Y=H; (e) X=CH_3, Y=Br.

(LXXXIII): (a) X, Y=H; (b) X, Y=Br; (c) X, Y=CH_3

The thermal solid-phase dehydration of compound (LXXXII) in crystals having two different habits [(LXXXIIc′) and (LXXXIIc″) (Fig. 4)] has been investigated.[133] The reactions in crystals of compound (LXXXIIc) proceeds in the same way as in crystals of compounds of a completely different type, namely certain oximes of picryl esters.[134–135] The reaction begins with the development at opposite end-faces of the crystal, namely (001) and (00$\bar{1}$), of readily distinguishable opaque triangular yellow regions, which consist of a solid solution of the reaction product in the initial crystal. The regions which have reacted crack and are then separated from the specimen. The [001] direction, in which the reaction is preferentially propagated, corresponds to the orientation of the hydrogen bond chains in the crystal of compound (LXXXIIc′).

The thermal dehydration of crystals of compound (LXXXIIc″) proceeds in a completely different way and begins immediately throughout the bulk of the crystal. It is striking that the crystal becomes yellow and turbid already at a low degree of conversion. Despite its identical structure, the thermal dehydration of compound (LXXXIIb) is approximately an order of magnitude faster than that of compound (LXXXIIc),[133] which can be attributed to the sharp (by a factor of 10^4) increase of acidity after the substitution of the CH_3 groups in 2,6-dimethylphenol by Br atoms.[136] However, the study of the rate of evolution of water vapour on heating the crystal showed that the monomethyl derivative (LXXXIId) is dehydrated much faster than the monobromo-derivative (LXXXIIe).[137] Unfortunately there are no structural data for compounds (LXXXIId) and (LXXXIIe).

The study of the photochemical dehydration of compound (LXXXII) (under ultraviolet irradiation) demonstrated that the reaction in both the single crystal and in polycrystalline

specimens (its visible manifestation consists in the appearance of a yellow colour and turbidity in the specimen) is observed only in thin surface layers.[133,136]

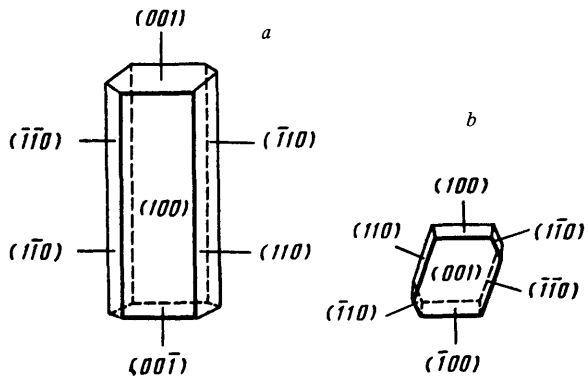


Figure 4. Two habits, (*a*) and (*b*), of crystals of compound (LXXXII).[133]

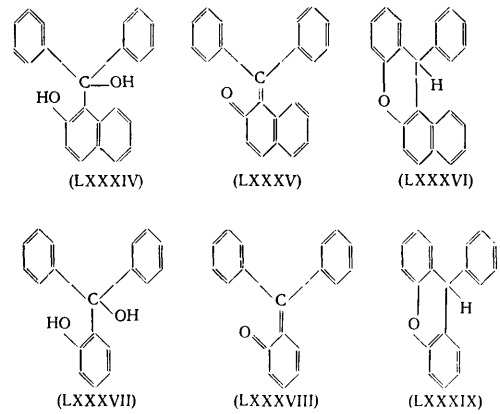
We may note that the crystal of (LXXXIIc) subjected to preliminary ultraviolet irradiation undergoes thermal dehydration much faster.[133] This is apparently caused by the photolytic formation in the crystal of the carbinol (LXXXII) of the nuclei of the fuchsone (LXXXIII) phase. It remains obscure how the fuchsone phase is propagated in the carbinol crystal: chemically, i.e. by transfer of the phenolic proton along the lattice defects, or in some other way.

As already stated, thermal solid-phase reactions in organic crystals have come to be described in terms of two limiting mechanisms, "heterogeneous" and "homogeneous", which have been used by Wegner et al. in the study of the solid-phase polymerisation of diacetylenes.[139] The heterogeneous reaction is characterised by an initial nucleation stage and subsequent migration of the reaction front through the crystal. The stage which determines the operation of one of the two reaction mechanisms is in fact nucleation. Both homogeneous and heterogeneous mechanisms are characteristic of the nucleation of the thermal dehydration of the carbinols (LXXXII), i.e. the process is the first example of a solid-phase reaction where the nucleation stage is under a kind of double control.[133]

The molecules of type (LXXXIII) can acquire chirality as a consequence of the internal rotation of their groups about single bonds. In the liquid phase the rapid interconversion of enantiomers should lead to the disappearance of chirality. However, in the solid phase, where the molecular conformation is frozen, there is a possibility of crystallisation in enantiomorphic space groups, as has been observed for binaphthyl (see, for example, Pincock and coworkers[140,141]).

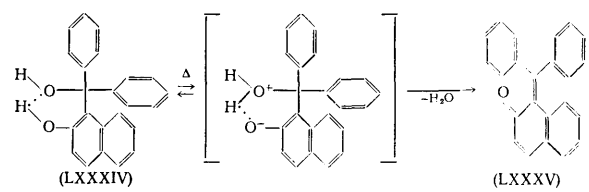
Three polymorphic modifications (α, β, and γ) have been observed for compound (LXXXIIIc), one of which, namely β-(LXXXIIIc), crystallises in the enantiomorphic space group $P2_12_12_1$.[142,143] X-Ray diffraction study revealed three types of deformations of the molecules of compound (LXXXIIc) in the crystals relative to the planar form: distortion of the quinone ring, breakdown of the planarity of the exocyclic double bond, and rotation of the aromatic rings relative to this bond. The crystals of α-(LXXXIIIc) and β-(LXXXIIIc) are made up of layers having similar structures but linked symmetrically to one another in different ways: via the 2_1 axes in β-(LXXXIIIc) and via the slip reflection planes and symmetry centres in α-(LXXXIIIc). The possibility of the thermal solid-phase transition α → β has been demonstrated[142] (by means of a powder diffraction pattern recorded at 383 K) and the changes in the geometry and packing of the molecules of compound (LXXXIIIc) required for this transition have been analysed.

In contrast to compound (LXXXVII), the solid-phase thermal dehydration of compounds (LXXXIV) and (LXXXVII) can proceed both intramolecularly [with formation of the fuchsones (LXXXV) and (LXXXVIII)] and intermolecularly [with formation of the xanthenes (LXXXVI) and (LXXXIX).[144,145]



Later investigations[146] of the thermal dehydration of compounds (LXXXIV) and (LXXXVII) by infrared spectroscopy and NMR confirmed only the occurrence of the transitions (LXXXIV) → (LXXXV) and (LXXXVII) → (LXXXIX). X-Ray diffraction study[146] demonstrated the existence of intramolecular hydrogen bonds in crystals of compounds (LXXXIV) and (LXXXVII); thus the thermal dehydration in the crystals of compound (LXXXIV) probably proceeds via Scheme 14:

Scheme 14



An analogous mechanism of the intermolecular transfer of a hydrogen atom has been used to account for the thermochromic and photochromic transitions in crystals of salicylideneanilines (see, for example, Aldoshin and Atovmyan[147] and Cohen et al.[148]).

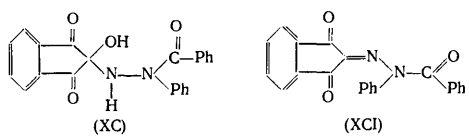
However, the discrepancy between the molecular geometries in the crystals of compounds (LXXXIV) and (LXXXVI) conflicts with the above description of the thermal dehydration of crystals of compound (LXXXIV). In fact the dihedral angle relative to the C(sp^3)–C(naphth.) bond in compound (LXXXIV) [as well as the corresponding angle in compound (LXXXVII)] is close to 80°, while an angle close to 0° (or 180°) would have been ideal for the rearrangement in accordance with Scheme 14. In a molecule of compound (LXXXV) the dihedral angles relative to the central double bond are 10.4° and 13.5° (two values are given in view of the breakdown of the planarity of the two central carbon atoms.[149] It has therefore been suggested[146] that the difference between

the solid-phase reactivities of compounds (LXXXIV) and (LXXXIIb) [the process (LXXXIIb) → (LXXXIIIb) is much faster than (LXXXIV) → (LXXXVI)] cannot be accounted for solely by the difference between the crystal structures of compounds (LXXXIV) and (LXXXVII).

The similarity of the crystal structures and hydrogen bond systems in compounds (LXXXIV) and (LXXXVII) makes it difficult to account for the difference between the products of their solid-phase thermal dehydration. It has been postulated[146] that the greater bulk of the naphthalene ring in the molecule of compound (LXXXIV) compared with that of the phenyl substituent in compound (LXXXVII) results in some flattening of the tetrahedron at the central sp^3-hybridised carbon atom, i.e. leads to a greater amount of sp^2-character in the latter. It may be that this difference between the geometries of the ground states of compounds (LXXXIV) and (LXXXVII) actually determines the difference between their reactivities in solid-phase dehydration processes.

2. Dehydration of (β-Benzoyl-β-Phenylhydrazyl)-2-Hydroxyindan-1,3-Dione

The solid-phase thermal dehydration of the hydrazinocarbinol (XC) proceeds anisotropically:[150] the appearance of the reaction product (XCI) [the acquisition of a red colour by the initial crystal of compound (XC)] begins at the $(10\bar{1})$ and $(\bar{1}01)$ faces and is propagated in the [001] direction.



After 17 days at 65 °C, the degree of conversion in the process (XC) → (XCI) is 10%. The possible sequence of stages in the solid-phase reactions of this type (nucleation, the formation of a solid solution, initiation of the new phase, and its separation) have been examined.[151]

The hydroxy-group O(4)–H in the molecule of compound (XC) in the crystal forms intramolecular hydrogen bonds with the carbonyl O(3) atom (Fig.5). The N(1)–H...O(2) hydrogen bonds between the molecules of compound (XC), linked by 2_1 axes, combine them into chains along the *b* axis of the crystal. Attack by a proton from the outer side of the chain (Fig.6) leads to the elimination of the OH group from the molecule of (A), which promotes also the subsequent abstraction of the OH group from a neighbouring molecule of (B) by the H(N) group. However, the H(N) atom forms a hydrogen bond with the O(1) carbonyl group of the molecule of (B) and not with the OH group; the H(N)...O(2) distance is 3.01 Å. The low rate of the reaction (XC) → (XCI) is apparently due precisely to the complexity of the rearrangement of the hydrogen bond formed by the N–H group. This hypothesis has been confirmed by the initiation of the reaction when a thin layer of the hydrate of toluene-*p*-sulphonic acid is deposited on the faces of the crystal of compound (XC),[151] the acceleration effect diminishing as the reaction front moves away from the region where the crystal is in contact with the acid. Fig.5 shows that the conformation of the molecule of compound (XC) is close to that necessary for the elimination of the H_2O molecule. During the reaction, there is an appreciable change in the geometry of the molecule of compound (XC), because its (H)OC(2)N(1)H(N) torsional angle is 36°, while in the indandione molecule the >C(2)=N(1) fragment should be planar.

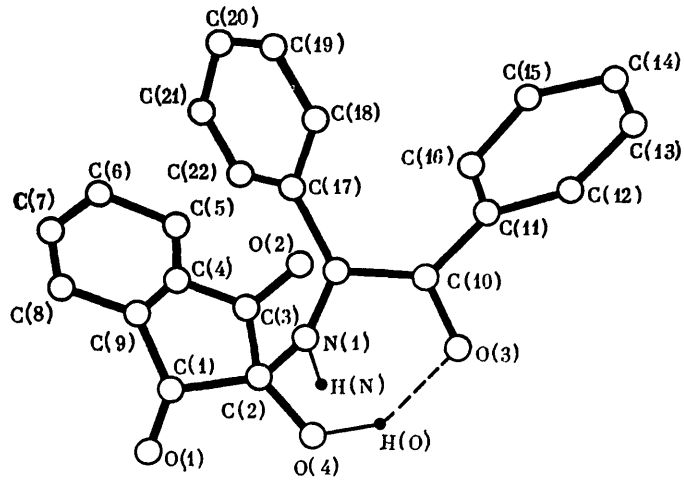


Figure 5. The structure of the molecule of compound (XC).[150]

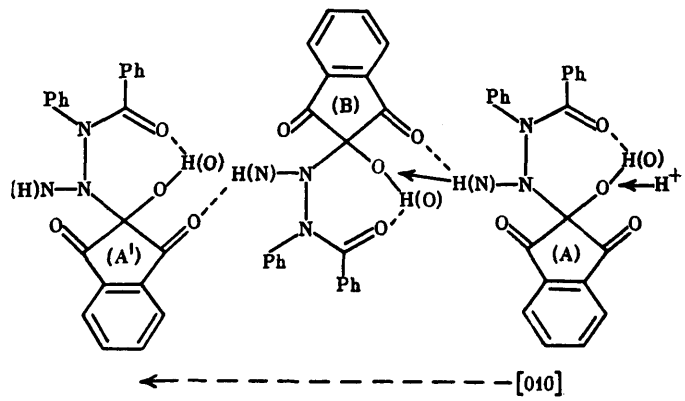
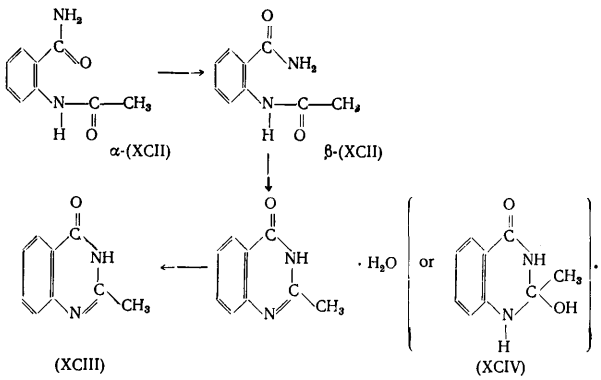


Figure 6. The possible mechanism of the solid-phase dehydration of compound (XC); the preferred direction [010] of dehydration is shown by a dashed line.[150]

3. Dehydration of *o*-Acetamidobenzamide

o-Acetamidobenzamide crystallises in two polymorphic modifications, α-(XCII) and β-(XCII), the solid-phase thermal transformation of which leads to anhydro-2-methyl-4-quinazolinone (XCIII).[152] Spectroscopic data and differential

scanning calorimetry indicate the following sequence of stages in the reaction (XCII) → (XCIII):



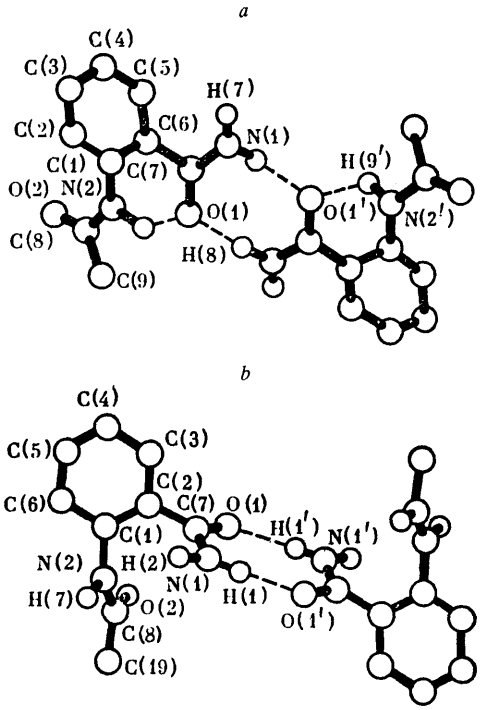


Figure 7. The structure of the centrosymmetric dimers in the crystals of α-(XCII) (*a*) and β-(XCII) (*b*).[152]

The crystals of α-(XCII) and β-(XCII) are made up of centrosymmetric molecular dimers (Fig.7) formed via a hydrogen bond with participation of the primary amido-group, the plane of the amide fragment in the structure β-(XCII) being inclined at 52° relative to the plane of the benzene ring, while in α-(XCII) the angle of inclination is only 8°. The appreciable difference of these angles from the energetically optimum value of 25° [152] has been explained by the simultaneous involvement of secondary *o*-amido-substituents in hydrogen bonds: the secondary amido-group in α-(XCII) participates in the intramolecular hydrogen bond with the primary amido-group, while in β-(XCII) it is involved in the intermolecular hydrogen bond between molecules linked only via the 2_1 axis. Fig.8 illustrates schematically the conformational transition α-(XCII) → β-(XCII) which is necessary for the formation of the system of hydrogen bonds observed in β-(XCII) crystals. Primary structural data for compound (XCIII) and the postulated structure of compound (XCIV) permit the conclusion that the main role in the destabilisation of the structure of β-(XCII), which leads to the solid-phase dehydration and the formation of compound (XCIII), is due to the hydrogen bonds combining the molecules of compound β-(XCII) into dimers.[151]

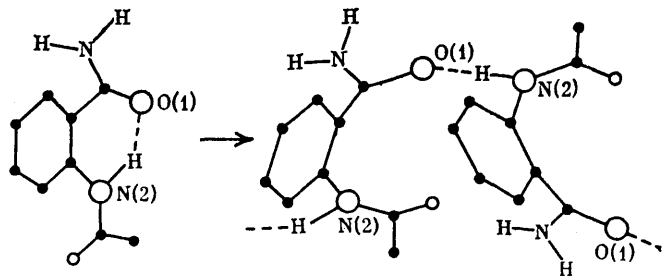


Figure 8. Schematic illustration of the conformational changes in the transition α-(XCII) → β-(XCII).[152]

X-Ray diffraction study of compound (XCIII) permitted hypotheses concerning the mechanism of its solid-phase hydrolysis with formation of compound (XCII).[153] The crystal structures of compounds (XCII) and (XCIII) are similar—the carbonyl groups in the molecules of compound (XCIII), linked via the 2_1 axis, form hydrophilic cavities parallel to the (001) plane. It has been suggested that the solid-phase hydrolysis of compound (XLIV) takes place precisely in the hydrophilic cavities along the *a* axis.

4. Dehydration of Copper Formate Hydrates

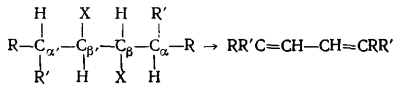
Crystals of copper(II) formate hydrates are known to be capable of thermal dehydration.[154–157] The structural treatment of this process, which is topotactic in character and leads to well oriented pseudomorphic anhydrous phases as products,[154,155,157] has been held back by the lack of structural data for such phases although the crystal structures of the initial copper(II) formate hydrates are known.[158–161]

The pale-blue crystals of copper(II) formate tetrahydrate $Cu(HCOO)_2.4H_2O$ (XCV) lose the water of crystallisation on drying in air and become opaque, being converted into the anhydrous phase $Cu(HCOO)_2$.[162] Comparison of the crystallographic parameters of compounds (XCV) and (XCVI) indicates the similarity of the structures in the *ab* planes and considerable differences between them in the direction of the *c* axis, which suggests the topotactic character of the dehydration of compound (XCV). A crystal of this compound is made up of layers, parallel to the (001) face, in which the copper atoms have a square planar environment consisting of four formate anions, each of which links two copper atoms. The H_2O molecules are distributed between these layers, half of them augmenting the coordination of the copper atoms to the octahedral coordination; the remaining water molecules are not coordinated at the metal atoms but form hydrogen

bonds with the H_2O molecules coordinated to the copper atoms.[162] The crystal of compound (XCVI) is also made up of layers of tetracoordinate copper atoms, analogous to those found in compound (XCV); the fifth and sixth coordination sites of the copper atom are occupied by the O atoms of the formate groups. Both types of molecules of water of crystallisation in the crystal of compound (XCV) have a relatively large amount of freedom as regards diffusion parallel to the layers. The removal of water should alter the coordination of the copper atoms and should lead to the mutual approach of the layers. Some structural rearrangement should occur also within the layers themselves.

5. Dehydrobromination of *meso*-dibromobutane Derivatives

Crystalline *meso*-dibromobutanes undergo double dehydrobromination on treatment with gaseous ammonia or amines, giving rise to quantitative yields of the corresponding buta-1,3-dienes[163]

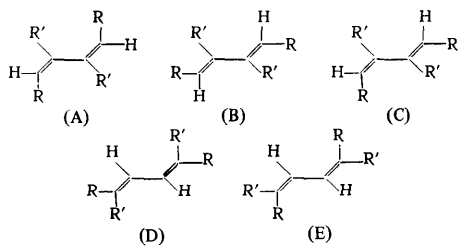


(XCVII)–(CI)

where (XCVII) = *meso*-β β′-dibromoadiponitrile, (XCVIII) = (*R*, *S*, *R*, *S*)-αα′-dimethyl-ββ′-dibromoadiponitrile, (XCIXa), (XCIXb) = (*R*, *R*, *S*, *S*)-αα′-dimethyl-ββ′-dibromoadiponitrile, (C) = dimethyl (*R*, *S*, *R*, *S*)-αα′-dimethyl-ββ′-dibromoadipate, and (CI) = dimethyl (*R*, *R*, *S*, *S*)-αα′-dimethyl-ββ′-dibromoadipate.

Apart from the van der Waals interactions, the molecular packing in crystals of compounds (XCVII)–(CI) is determined by the Br...N≡C and C...N≡C donor acceptor interactions.[164,165] The Br...N distances in the crystals of compounds (XCVII), (XCVIII), and (XCIXb) (3.20, 3.26, 3.22 Å respectively), which are significantly smaller than the sum of the van der Waals radii (3.45 Å),[35,36] can be regarded as corresponding to weak interactions between a Lewis acid and a Lewis base.[166] A weak interaction of the type C...N≡C is observed also in the crystal of compound (XCVII) (the corresponding C...N distance is 3.27 Å).

The solid-phase dehydrobromination of compound (XCVII) gives rise to a mixture of the isomeric butadienes (A)–(C) in the proportions 2:3:5, while the dehydrobromination of crystals of compounds (XCVIII), (XCIX), (C), and (CI) yields the pure products (B), (A), (D), and (E) respectively.[164,167]

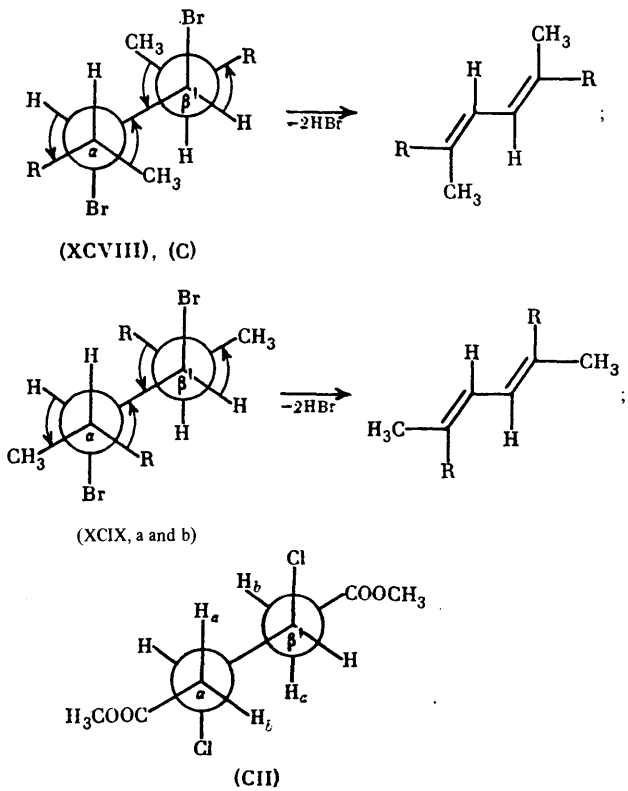


(A) (B) (C) (D) (E)

The reaction of the crystals of compound (XCIXa) is faster than in another polymorphic modification (XCIXb) of this compound.

In the crystals of the αα′-dimethyl derivatives of compounds (XCVIII), (XCIXa), (XCIXb), (C), and (CI), in which there is a possibility of the elimination of only one hydrogen atom from each C_α atom, all the H_α atoms are in the antiperiplanar positions relative to the Br atom. Assuming an *anti*-elimination mechanism, which requires a minimal rearrangement of the geometry of the carbon atoms for transition to the sp^2-hybridised state, one should expect the formation of the corresponding *trans,trans*-butadienes from the molecules of compounds (XCVIII) and (C) having the *R*, *S*, *R*, *S*-configuration and of *cis*-butadienes from the molecules of compounds (XCIX, a and b) and (CI) having the *R*, *R*, *S*, *S*-configuration (Scheme 15). This hypothesis has been confirmed experimentally[164,167] and it has demonstrated that the *anti*-elimination processes and the configuration of the products under the conditions of the heterogeneous gas–crystal reaction are controlled by the conformation of the initial molecules.

Scheme 15



(XCVIII), (C)

(XCIX, a and b)

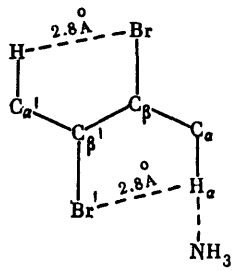
(CII)

The mechanism for the elimination reaction in molecules with two hydrogen atoms at each C_α atom is more complex. In the nitrile (XCVII) and the ester (CII) the H_a atom is antiperiplanar relative to the Br atom, while the H_b atom has a *gauche*-orientation. Since the *anti*-elimination mechanism applies also to the nitriles and esters, presumably the *cis,cis*-butadiene and the *trans,trans*-butadiene are formed respectively from compounds (XCVII) and (C). This course for the elimination process is consistent with the experimental data for compound (C),[164] but has not been confirmed for compound (XCVII). The formation in the latter case of a mixture of butadiene isomers shows that the elimination was preceded by rotation about the C_α–C_β bond in some of the molecules of compound (XCVII). Such rotation, which requires an energy expenditure of 5 kcal mol^{-1} according to conformational calculations,[168] is impossible in the crystal matrix, but, on the crystal surface and at the dislocations, where the reaction is initiated, the lattice is somewhat "staggered" and this barrier can be overcome.

We shall consider how, within the framework of the steric control of the *anti*-elimination in the crystal, the NH_4^+ ion is formed on one side of the molecule and a halide ion is

removed on the other (charge separation). It may be that, by virtue of the relatively short distance between the H_α and Br atom (~2.8 Å), the NH_4^+ ion, formed on the side of the C_α atom, induces the elimination of the Br′ atom linked to the C'_β atom, while the non-solvated Br^- anion, formed at the C_β atom, behaves as a strong base capable of abstracting the hydrogen atom linked to the C'_α atom (Scheme 16). The closeness of the oppositely charged ions leads to the subsequent rapid interaction.

Scheme 16



The induction period, frequently observed in reactions of the gas–crystal type,[169] as well as the influence of defects on the rate of these solid-phase processes[168,169] have shown that they begin with the diffusion of gas molecules to the existing nucleation centres (for example, to dislocations and impurities) at which the reaction is initiated and is then propagated throughout the bulk of the crystal.

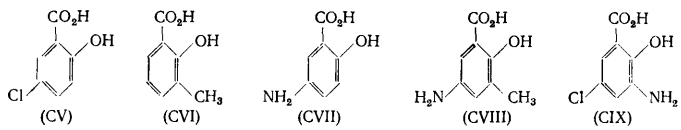
The difference between the types of packing should lead to a difference between the rates of diffusion and it is to be expected that the reaction should be faster in the less dense crystalline forms where the crystal field hindering diffusion is usually weaker. Apparently this is the explanation of the higher rate of dehydrobromination in crystals of compound (XCIXa) compared with (XCIXb), since the density of compound (XCIXa) is less than that of (XCIXb) (d = 1.84 and 1.90 g cm^{-3} respectively), while the intermolecular forces in the former case are weaker, which can be seen from the greater intensity of the thermal movement of atoms in the crystals of compound (XCIXa) at room temperature. The difference between the rates of diffusion of Br atoms, which is a consequence of the anisotropy of the crystal packing, has also been invoked to account for the different rates of bromination reactions of the gas–crystal type of the polymorphic forms of mesaconic acid.[169]

According to microscopic studies, reactions of the gas–crystal type are heterogeneous,[168,170,171] beginning on the surface of the crystal, while the process determining their rate is the "unpacking" of the layer formed, which hinders the movement of gas to the next layer. The observed difference between the rates of reaction in different crystallographic directions is usually interpreted on the basis of the idea that the reacting groups are unequally accessible to the diffusing gas molecules on different crystal faces. The anisotropy of the propagation of the reaction front is also observed in solid-phase rearrangements with thermal initiation.

We shall consider the possibilities of access to the potentially reactive hydrogen atoms on different faces of (XCIXa) and (XCIXb) crystals. The approach of NH_3 molecules to the H_α atoms can be blocked by the CH_3, CN, and C_β groups. The molecules in the crystal of compound (XCIXa) form layers perpendicular to the *b* axis and in each layer they are linked solely by *a* and *c* translations. The C_α–H bonds are perpendicular to the plane of the layer, while all the remaining bonds of the tetrahedral C_α atom are located approximately in the plane of the layer. In such a structure of the crystal, the neighbouring molecules located in a single layer do not hinder the approach of NH_3 molecules to the H_α atoms. The initial elimination of one H_α atom, which leads to the formation of NH_4^+ and Br^-, induces the elimination of a second H_α atom and results in a weakening of the fixation of the reacting molecule within the plane of the layer. The rate of the second process depends on the crystal forces, which are weaker in compound (XCIXa) than in (XCIXb). The partial "unpacking" of the layer ensures the access of NH_3 molecules to the next molecular layer. The H_α atoms of the molecular layer in compound (XCIXb) are much less accessible than in (XCIXa), which explains the lower rate of dehydrohalogenation of this crystalline modification.

6. Dehydrochlorination and Decarboxylation of *p*-Substituted Derivatives of Salicylic Acid

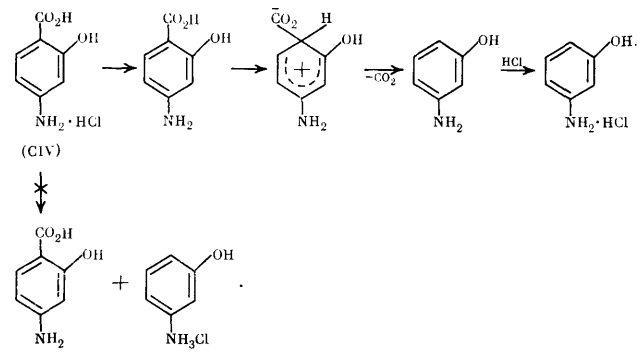
The kinetics and mechanism of the decarboxylation of *p*-substituted derivatives of salicylic acid in solution have been thoroughly investigated.[126–129] Solid *p*-aminosalicylic acid (CIII) decomposes at 70 °C, while its hydrochloride (CIV) decomposes at 100 °C. On heating to 100 °C, compound (CIV) is fully converted into *m*-aminophenol in 10 h. The salicylic acids (CV)–(CIX) did not decompose appreciably on heating to 100 °C for a week.



On the basis of kinetic data, a carbanionic mechanism of the decarboxylation reaction, similar to that observed for the decarboxylation of trinitrobenzoic acid, has been suggested.[172]

The decarboxylation of compound (CIV) involves the initial loss of HCl, which is followed by the decarboxylation, the sublimation of *m*-aminophenol, and finally its reverse interaction with HCl (Scheme 17). This sequence of stages agrees with the absence of a reaction of the crystal–crystal type between *m*-aminophenol and compound (CIV) when they come into direct contact.

Scheme 17



It has been stated[172] that this mechanism agrees with the characteristic features of the molecular packing in the crystals of compound (CIV). In conformity with the idea that solid-phase photochemical interaction between C=C bonds separated by a distance of ~4 Å is possible,[173] there exist four intermolecular contacts in the crystals of compound (CIV) between the acid proton and the unco-atom of the carbon ring attached to the carboxy-group, whose lengths are 3.98, 4.99, 4.60, and 4.42(3) Å, which gives rise to the possibility

of the propagation of the reaction in the crystal in several directions. The reaction is initiated on the $(10\bar{2})$ faces. Layers of polar carboxy-groups and non-polar aromatic groups, arranged parallel to the (100) face, are approximately perpendicular to the $(10\bar{2})$ faces. Thus the evolution of the CO_2 formed is to be expected from the side of the $(10\bar{2})$ face and not the (100) face.[169]

The solid-phase thermal (at 95 °C) decarboxylation of crystals of compound (CIV) having different habits (A, B, and C) has been investigated;[174] for this purpose, the development of the region of turbidity in the crystal (which corresponds to the disordering induced by the loss of HCl preceding the decarboxylation) was observed. In a crystal of compound (CIV) having the A habit, HCl is evolved along the *b* axis. The reaction along the *c* axis is slower. The loss of HCl by crystals of compound (CIV) having the B habit takes place in the direction of the *a* axis. If we now turn to the molecular packing in the crystal of compound (CIV), it is found that the HCl molecules can leave the crystal along the *a* and *b* directions without involving the non-polar functional groups and interacting only with the amino- and carboxy-groups. The evolution of HCl along the *c* direction is also possible, although in this case Cl^- ions and OH and NH_2 groups as well as hydrocarbon radicals may be encountered in the path of the HCl molecules.

Thus, the characteristics of the molecular packing suggest that the dehydrochlorination reaction should proceed along the *a* and *b* directions. The authors[174] were unable to explain the observed course of the reaction, which started from the $(0\bar{1}1)$, (011), and $(10\bar{2})$ faces of the form A of the (CIV) crystal. The attempts to explain the characteristic directions of propagation of the solid-phase reaction in a crystal of compound (CIV) having the B habit on the basis of the characteristic features of the molecular packing in the crystal were also unsuccessful.# Apparently the anisotropic loss of HCl by (CIII) and (CIV) crystals is associated with the characteristic features of the initiation of the reaction. The zone of the reaction initiated on a certain face of the crystal (having the A or B habit) migrates to its centre, and HCl is most easily removed via the regions which have reacted or been disrupted.[174]§

According to microscopic observations, the reaction in the *a* direction of the (CIV) crystal is faster than in the *b* direction, in conformity with the calculated cross-section of the tunnel for the release of HCl, which amounts to 3.23 $Å^2$ along the *a* axis and to 1.60 $Å^2$ along the *b* axis. The distance between the rings in the direction of the *a* axis is also smaller than in the direction of the *b* axis (5.316 and 4.232 Å respectively).[174]

The interaction of (CIV) crystals having the A and B habits with gaseous primary, secondary, and tertiary amines has been investigated.[174] The interaction with primary and secondary amines proceeds rapidly and leads to liquid products. However, hexamethylenetetramine reacts at the (001) face in the A crystal habit (in the course of 30 min), while crystals having the B habit [with (001) and (100) faces having a large area] do not decompose even after 72 h. Different rates of reaction with hexamethylenetetramine are also characteristic of the different faces of the acetylsalicylic acid crystal. There exist data demonstrating different rates of interaction of crystalline aminoacid enantiomers with optically active amines.[177]

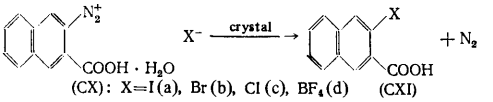
Crystals of compound (CIV) with all three habits are involved in an interaction of the crystal–crystal type with Na_2CO_3. This reaction always begins at the site of contact between the crystals of the acid and the carbonate and is fairly slow (it is completed after 40 days at 60 °C).[174] If the reaction occurs at room temperature, drops of water are formed. Compound (CIII) is formed as the product and *p*-aminosalicylate anions have also been detected. The low rate of reactions of the crystal–crystal type compared with those in solution can be accounted for by the low rates of diffusion of ions in the crystal lattice in compound (CIV).[178–182] If the solid-phase thermal decomposition of compound (CIV) in the absence of contact with Na_2CO_3 involves the loss of HCl by diffusion, then the reaction of the crystal–crystal type (acid–base) considered above consists either in the diffusion of HCl to Na_2CO_3 or in the counterdiffusion of H^+ or Na^+ ions with formation of H_2CO_3 in the lattice of the base and of NaCl in the lattice of the acid.

Reactions of the crystal–crystal type are relatively rare and have been thoroughly investigated only in relation to the formation of spinels from metal oxides (for example, Al_2O_3 and MgO) at high temperatures.[178–182] The most probable mechanism of these reactions is based precisely on the counterdiffusion of cations.

7. Decomposition of 3-Carboxynaphthalene-2-Diazonium Halides with Evolution of Nitrogen

Studies of the solid-phase reactions of aromatic diazonium salts began with the investigation of the thermal decomposition of solid benzenediazonium fluoroborate.[183] Aromatic diazonium salts readily explode and are isolated only rarely; nevertheless, a series of diazonium salts with weakly nucleophilic anions have been investigated by X-ray diffraction.[184–192]

We shall consider the mechanism of the decomposition of these salts in relation to the monohydrate (CX). The orange crystals of compound (CXa) rapidly acquire a blue colour on standing at room temperature, evolve nitrogen as a result of the substitution of its diazo-group by an I atom, and are converted into the polycrystalline acid (CXIa).[193–195] The intensity of the 2250 cm^{-1} band of the RN_2^+ group in the infrared spectrum diminishes rapidly. The topotaxy of crystals of compounds (CXa) and (CXIa) has not been observed.



(CX): X=I(a), Br(b), Cl(c), BF_4(d) (CXI)

The crystals of compounds (CXb) and (CXc) are isostructural and, like compound (CXd), crystallise as monohydrates. Data obtained by differential scanning calorimetry, thermogravimetric analysis, and X-ray diffraction indicate the ability of the triclinic crystals of compound (CXb) to lose water topotactically on heating about 65 °C and to be converted into an intermediate α-phase which is in itself then converted into the β-phase at 90 °C. The thermal decomposition of the β-phase (at ~100 °C) is accompanied by the evolution of nitrogen and the formation of 3-bromo-3-naphthoic acid (CXIb).[193–195]

#An analogous description of the propagation of a solid-phase reaction has also been resorted to to explain the loss of the water of solvation from the crystalline hydrates when the latter are cut by a razor blade[175] and in the solid-phase reaction of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate,[176] which begins at one end of the crystal and passes through the entire crystal in a direction which cannot be accounted for by the character of the molecular packing.

§Crystals of compound (XXIII) having the C habit have not been investigated by X-ray diffraction.

Although the molecular packing of the molecules in crystals of compounds (CXIa) and (CXIb) is of different types, the direct environment of the diazonium group in these compounds is similar: all the 15 C, N, and O atoms in the cations are approximately coplanar and there exists one shorter intramolecular O(13)...N(14) contact, whose length is 2.5 Å. The shortest intermolecular contact (2.9 Å) has been observed between the "outer" N(15) atom and the O(13) atom of the carbonyl group. The shortest contacts involving the halogen atom, namely I...N(15), which is 3.4 Å long in compound (CXIa), and Br...N(15), which is 3.27 Å long in compound (CXIb), also involve the outer N atom and are significantly shorter than the sum of the van der Waals radii (3.53 and 3.40 Å respectively[35,36]). The distances between the halogen atom and the "inner" N atom are 3.80 Å for compound (CXIa) and 3.50 Å for compound (CXb).

Each halogen atom is coordinated via two diazonium groups and is also involved in hydrogen bonds with the two solvating H_2O molecules [the Hal...OH_2 distances are 3.4 and 3.6 Å in compound (CXa) and 3.27 and 3.29 Å in compound (CXb)]. In addition, the H_2O molecule [O(16)] forms hydrogen bonds with carboxy-groups over O(12)...O(16) distances of 2.6 Å in compound (CXa) and 2.54 Å in compound (CXb) and is located opposite the C(2)–N(1) bond at a distance of 3.3 Å in compound (CXa) and 3.39 Å in compound (CXb) from the C(2) atom [the shortest intermolecular contact involving the C(2) atom].

The difference between the immediate environments of the diazonium groups in compounds (CXa) and (CXb) is determined by the van der Waals radii of the halogen atoms whose non-identity is manifested by the small differences between the corresponding Hal...N distances and also by the different intermolecular coordinations of the carbonyl O(13) atom.[193–195]

One may assume that the reactivity of compounds (CXa) and (CXb) is determined by the initial disposition of the halide and diazonium ions; N_2 is then evolved by a mechanism involving substitution as a result of attack by the halide ion. However, the discrepancy between the similarity of the environments of the diazonium group and the different stabilities of compounds (CXa) and (CXb) conflicts with this mechanism. The stability of the diazonium group in the β-phase (CXb) (~2 h at 95 °C) also conflicts with the alternative unimolecular mechanism involving the reversible loss of molecular nitrogen and the formation of aryl cations and relatively rapid cooling of compound (CXa) at 30–60 °C. The difference between the stabilities of the diazonium group combined with the similar environments in compounds (CXa) and (CXb) probably reflects the greater ease of oxidation of I^- ions compared with Br^- ions when an electron is transferred to the diazonium cation.[193–195]

The difference indicated between compounds (CXa) and (CXb) is intensified by virtue of the different character of the hydrogen bonds in the two structures, which link each halide ion to two molecules of water of crystallisation and also each water molecule to two halide ions. In the crystals of compounds (CXb) two bromide ions and two H_2O molecules are linked into rings around the centres of symmetry, while in compound (CXa) the hydrogen bonds form chains along the *c* axis made up of alternating iodide ions and H_2O molecules. The disruptions in the structure due to the absence of an H_2O molecule or the removal of a halide ion transmitted along the chain of hydrogen bonds [although it had not been possible to isolate the preferred direction of the disruption of the crystal of compound (CXa)]. When compound (CXb) is subjected to analogous disruption, there is a greater probability of the localisation of point defects, i.e. they do not spread throughout the bulk of the crystal.

The O–H...O hydrogen bonds and the short N(15)...O(13) intermolecular contacts in the crystals of compound (CXb) combine the cations into layers parallel to the $(1\bar{1}1)$ face; the shortest Br...N contacts are between the layers. The cracks appearing in the crystal of compound (CXb) in the transition (CXb) → α-(CXb) are perpendicular to the (001) face of the initial crystal of compound (CXb). It has been possible to establish a topotactic relation only with the fairly well ordered β-(CXb) phase, the volume of the unit cell of which proved to be smaller than for its hydrated precursor (CXb) (570 and 593 A^3). The $(\bar{1}1\bar{1})$ plane of the β-(CXb) crystal is inclined only at an angle of 14° to the $(1\bar{1}1)$ plane of the layers in the crystal of compound (CXb) and they both determine the direction of the cracks on dehydration of compound (CXb). It has therefore been suggested[190] that the layer structure of the crystals of compound (CXb) is preserved in the dehydration process and that the change (the disruption of the hydrogen bond system) takes place between the layers.

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Thus the intramolecular rearrangements and reactions with evolution of a low-molecular-weight product are characteristic of crystals of organic and complex compounds of a fairly wide variety of types. The degree of control of the course of these solid-phase reactions by the crystal lattices of the initial compounds in different reaction stages can be various.

The high selectivity of the majority of the reactions considered and the possibility of regulating them, at least in some cases, by altering the character of the molecular packing of the crystals of the initial compounds (crystal engineering) leads to extensive prospects for specific synthesis under the control of the lattice.

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