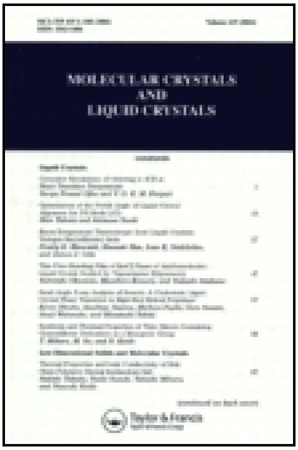

Molecular Crystals and Liquid Crystals

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Studies of Thermal Reactions in the Solid State

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Studies of Thermal Reactions in the Solid State

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In surveying reactions of molecular crystals it is instructive to consider them in the context of two hypothetical mechanisms illustrated in Figure 1. The first type which may be designated the "homogeneous mechanism" would involve conversion of "A" molecules of the starting material in the initial crystal lattice to "B" molecules, the B molecules remaining in place at the lattice sites previously occupied by the A molecules from which they were formed.[1] A single crystal of A would thus in the process of conversion to B pass through an essentially continuous series of solid solutions, first of B in A and later of A in B. The reaction would be topotactic, that is, the crystal structure of the product single crystal would be related to that of the parent crystal from which it was formed. The second hypothetical mechanism, the "heterogeneous mechanism", would involve initiation of reaction at a nucleation site (or sites) and spread of a reaction front (or fronts) through the crystal as A molecules were converted to B. There would be in this case no mixing of the A and B structures. The orientation of the lattice of the product crystal growing at the interface with the parent A crystal might be determined by the A lattice so that as with the homogeneous mechanism the reaction could be topotactic.

Because of the stringent requirements for solid solution formation, the search for reactions which might be expected to proceed by a mechanism approximating the homogeneous mechanism pictured above could reasonably focus on reactions which involve a minimum of structural change. Examples of reactions leading to interconversion of a low-temperature ordered structure to a room-temperature structure with specific disorder include fluoromalonic acid (carboxyl-proton transfer)[2] and terphenyl

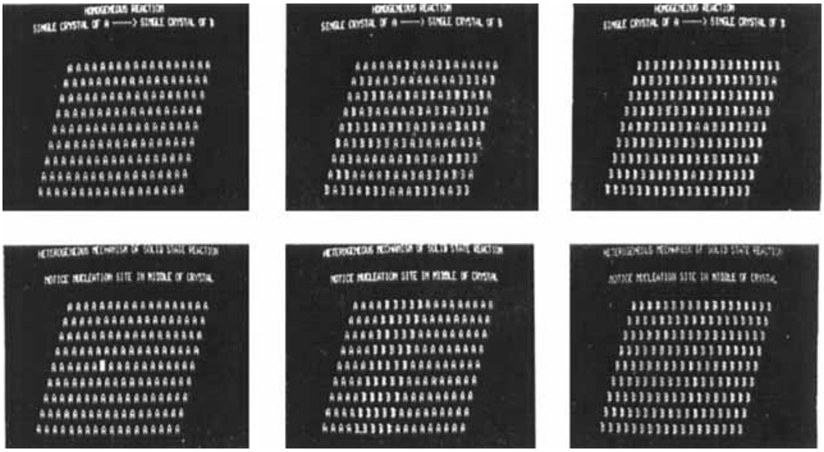
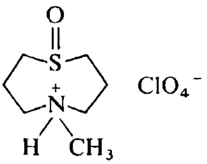


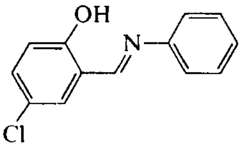
FIGURE 1 A computer simulation of two hypothetical mechanisms for solid state rearrangements. **1a** shows the starting crystal. In the homogeneous mechanism (**1a–1c**) product molecules (B) are produced randomly in the matrix of A molecules leading to an essentially continuous series of solid solutions with the eventual formation of a single crystal of B. The reaction is thus topotactic. **1c** shows the crystal after 95% reaction. In the heterogeneous mechanism (**1d–1e**) reaction begins at a nucleation site shown by the white rectangle in **1d** and spreads through the crystal in such a way that a reaction front (or fronts) develop. In **1e** two A–B fronts have developed and are gradually moving toward the left and right ultimately giving the crystal of B shown in **1f**. In this case the reaction is topotactic because the crystal of B has been oriented by the matrix of A from which it formed.

(rotation of central ring).[3] The ultimate example of an order-disorder transition appears in the change from an ordered to a plastic crystal.[4]

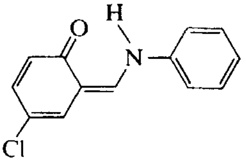
A phase transition of the perchlorate **1** is of interest as a candidate for the homogeneous mechanism since a crystal of the β-form, stable at 25°, after structure determination at that temperature gave on cooling to 3°C a single crystal of a second polymorph (α-form) which was used directly for x-ray structure determination at the lower temperature.[5] The polymorphic change could be explained in terms of molecular ring inversions and rotations in place. However, an alternative mechanism involving recurrent passage of glissile partial dislocations has been proposed.[6] The reversible change of crystals of the anil **2** from red at room temperature to colorless at the tem-



1



2a

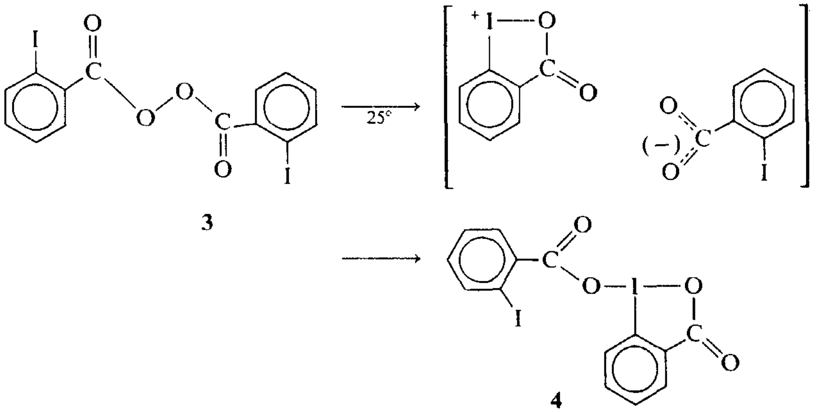


2b

perature of liquid air has been interpreted in terms of an equilibrium between **2a** and **2b**.[7] The red (room temperature) form appears to be a solid solution of a small amount of **2b** in crystalline **2a**. The equilibrium seems too far in favor of **2a**, however, to permit the reaction to be driven to **2b** by heating.

Among the most impressive candidates for a homogeneous mechanism somewhat related to that described above are the diacetylene polymerizations[8,9] in which single crystals of certain monomeric diacetylenes can be induced to undergo polymerization either thermally or by exposure to radiation, the products being single crystals of polymer.

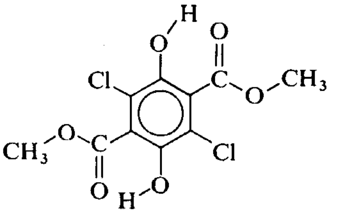
The thermal rearrangements of 2,2′-diiodobenzoyl peroxide (**3**) and a number of related compounds have been the subject of extensive investigation.[10,11] Single crystals of **3** are slowly transformed at room temperature to single crystals of **4** over a period of several weeks.[10] The reaction has been followed with x-ray diffraction and the relationship of the new axes to the old discussed.[12] The product crystal is opaque and has numerous defects. As has been pointed out[11] the change from **3** to **4** has steric requirements too great to be accommodated by the volume available at a molecular site in the crystal structure of **3**; the mechanism cannot be a simple one like the idealized homogeneous reaction of Figure 1 in spite of the observed topotaxy.



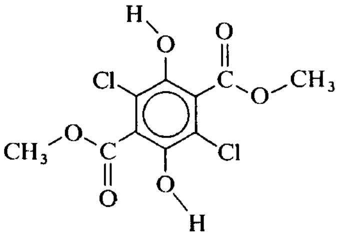
To summarize, the severe requirements (such as solid solution formation over an extended range) make candidates for reactions approaching the homogeneous mechanism extremely rare and in most cases further work is needed before it can be concluded that the mechanism is of this type.

In the heterogeneous mechanism (Figure 1) reaction begins at one or more nucleation sites and is characterized by the spread of well defined reaction fronts through the crystal. Microscopists have long been accustomed to seeing molecular polycrystalline films of a variety of organic compounds undergo phase transitions with the visible passage of a reaction front through the film.[13] Certain phase transitions involving little or no change in molecular shape have been studied in detail; that most carefully examined has been the interconversion of single crystals of α- and β-*p*-dichlorobenzene.[14–16]

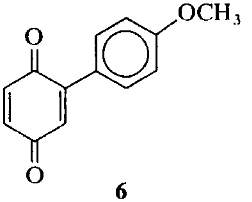
Over a number of years we have been interested in solid state changes on the borderline between "phase transitions" and "reactions"—changes in molecular conformation, hydrogen bonding, and color of the crystal have been involved. Previously published examples have been the conversion[17] of the yellow to the white form of dimethyl 3,6-dichloro-2,5-dihydroxyterephthalate (**5**) and the conversion[18] of the yellow to the red form of 2-(4′-methoxyphenyl)-1,4-benzoquinone (**6**). The first of these involved a rotation of phenolic hydroxylic protons from one side of an aromatic ring to the other together with an intramolecular change in hydrogen bonding and rotation of the carbomethoxyl groups some 70–80° out of the plane of the aromatic ring. In addition, every other molecule has to flip nearly 180° around an axis in the plane of the molecule.[17] The methoxyphenylquinone rearrangement involves an intramolecular rotation of one aromatic ring with respect to the other of nearly 110° as well as major reorientation of molecules with respect to each other and pi-complex formation in the red product.[18] Microscopic examination of single crystals undergoing these two reactions shows common features. Each begins at one or more nucleation sites and is characterized by passage of a reaction front (or fronts) through the crystal. There is a rather sharp demarcation (at least on the scale visible by microscopic examination) between the two phases. In each case the nucleation process is erratic but the rate of frontal motion seems to depend in a rather systematic way on reaction temperature; the higher the temperature the faster the front moves. Each of these changes thus seems, at least superficially, to occur by a process approximating the idealized "heterogeneous mechanism."



5Y



5W



6

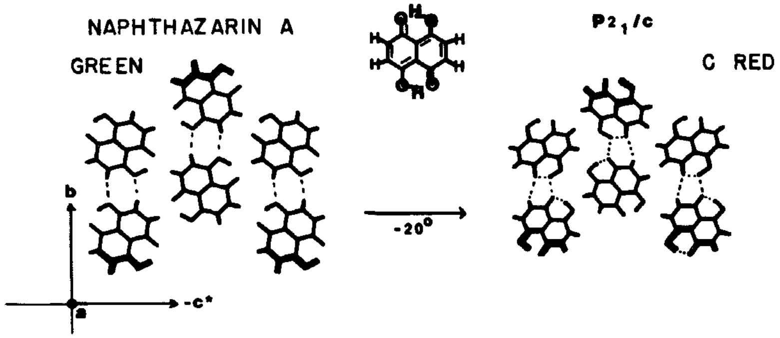
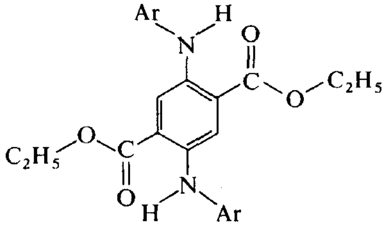


FIGURE 2 Crystal structures of the A and C forms of naphthazarin (7) transformed to space group $P2_1/c$ and viewed along the *a* axis.[19] Imagine each pair of molecules in approximately edge-to-edge contact as part of an essentially infinite lath as shown by the dotted lines. The first lath on the left side of the naphthazarin A drawing is tilted 64° above *a*. The structure of naphthazarin C is quite similar with the laths tilted 62° from the *a* axis. A very important difference, however, is that laths of the A form are produced by successive translations of a single type of molecule along [$\bar{1}$ 0 1] and [1 0 1]. (Note that the orientation of the oxygen atoms is the same for every molecule forming a lath.) The C form of naphthazarin has two half-molecules per asymmetric unit and a lath is composed of alternating molecules of type I and type II. Since the molecules occupy what appear to be crystallographic centers of symmetry hydroxylic protons have been located as shown. The question of their location will be discussed later in this paper.

We have examined some other reactions which follow a similar pattern although the structures and molecular changes are entirely different. Naphthazarin (7) is known to exist in three polymorphic forms: a green one called A, dark red called B, and light red, or C.[19] Although the B form and C form are stable when cooled, the green A form changes to the red C form when cooled to −20°.[20] The structural change is shown in Figure 2. Although the two structures are remarkably similar it will be noted that the edge-to-edge contacts of molecules adjacent at the points indicated by dotted lines in the figure are very different in the C structure from those in the A structure. The volume per molecule of C is only 1 % less than that of A. In spite of the fact that the change of the A to the C form could be formulated as involving a relatively uncomplicated rotation of molecules at their lattice sites accompanied by some other "minor" adjustments the reaction clearly begins at one or more nucleation sites and a reaction front then spreads down the needle axis (*a*-axis) of the crystal.[20] The crystal after passage of the front becomes opaque. The structure of the product was established by comparison of its powder patterns (from a pseudomorph either mounted directly in the powder camera without grinding or after grinding) with those of the three polymorphs of 7. The reaction clearly belongs in the heterogeneous class with a mechanism at least approximately like the idealized one discussed above. The speed of the reaction is noteworthy; the reaction front moved the length of a crystal about two millimeters long in a little more than 1 hr at a temperature below 0°C.

A family of compounds, with the formula below and first described in 1914, attracted our attention because each compound in the series occurs in two polymorphic forms, one series absorbing at lower wavelengths and one at



8 Ar = H
9 Ar = C_6H_5

higher in the visible spectrum.[21] The parent compound, **8**, was reported to exist in a metastable yellow, **8-Y**, and in a stable orange modification **8-O**; the yellow form could be transformed to orange by recrystallization or by heating to 100°.[21] X-ray crystal structures of the two forms of **8** were determined by Dr. Barbara Mann.[22] The structural change involved in the transformation of **8-Y** to **8-O** is shown in Figure 3. Extensive changes in both molecular orientation and in intermolecular hydrogen bonding are involved. When

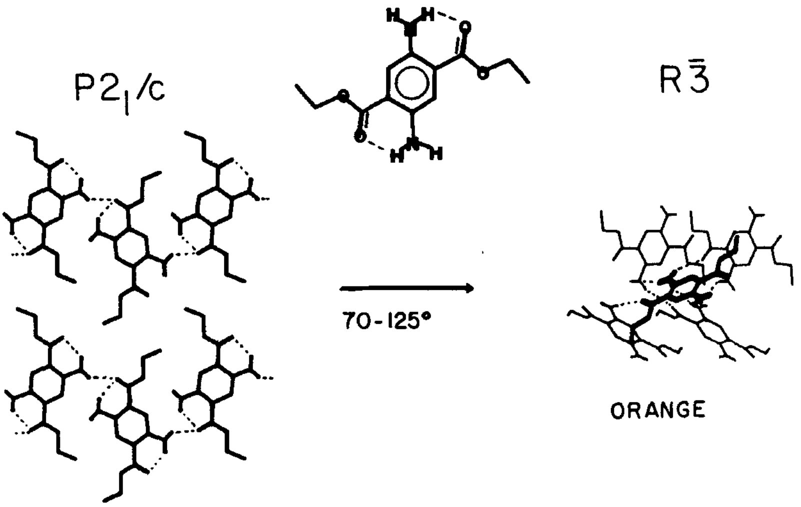


FIGURE 3 Structures of (left) the yellow metastable form **8-Y** and (right) the orange stable form **8-O** of the diaminoterephthalate ester **8**.[22] Note the relatively simple packing of **8-Y** whose molecules are held together by hydrogen bonds only along the *b* direction and have only two molecular orientations. Molecules of product **8-O** on the other hand have three orientations with the rings almost mutually orthogonal and with much more complex hydrogen bonding.

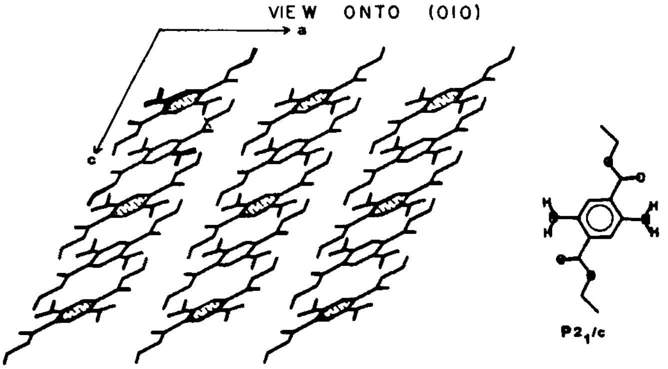


FIGURE 4 The crystal structure of the metastable yellow compound looking down on its major face.[22] Two layers of molecules deep (into the page) are shown—the upper layer consists of the molecules with cross-hatching in the rings. Note that in spite of a considerable difference in the forces holding the crystal together in the *a* direction as compared to *c* no pronounced anisotropy is seen in the migration of reaction fronts in those two directions.

single crystals were heated reaction began at one or more nucleation sites at temperatures of 70–125°.[22] Fronts developed and passed through the crystal at a rate which was dependent on the temperature. Reaction times varied from 10 sec to 1 hr or longer. Reaction started preferentially at an edge of the crystal. Two crystals were found to be nucleated at room temperature but, in general, prolonged heating below 70° (24 hr at 55–70°) failed to induce reaction. Figure 4 shows the structure of a crystal of **8-Y** as viewed looking down on the major crystal face. Although the crystal shows a highly layered structure with significant isolation of one layer from the next along the *a* axis there seemed during reaction to be no particular anisotropy of frontal migration in the *a* direction as compared to *c*.

The related compound **9** was of particular interest because it crystallized as a yellow benzene solvate which was stable in an atmosphere saturated with benzene or when stored below 0°C. At room temperature the single crystals showed development of a front beginning at one or more nucleation sites as solvent was lost to form a yellow phase which was disordered as shown by its scattering of visible light and also by its failure to undergo extinction between crossed polarizing filters. Behind the fronts separating yellow benzene solvate from the yellow disordered solvent-free region a second front quickly developed behind which was the red product **9-R**. Reaction normally began at a side face of the crystal but was influenced to occur elsewhere by defects occurring naturally in the crystal or induced by pricking with a pin.

The examples of rearrangements of **5** to **8**, although they differ greatly from each other in the change in molecular shape and extent of reorganization of the crystal required to go from starting crystal to product, have certain

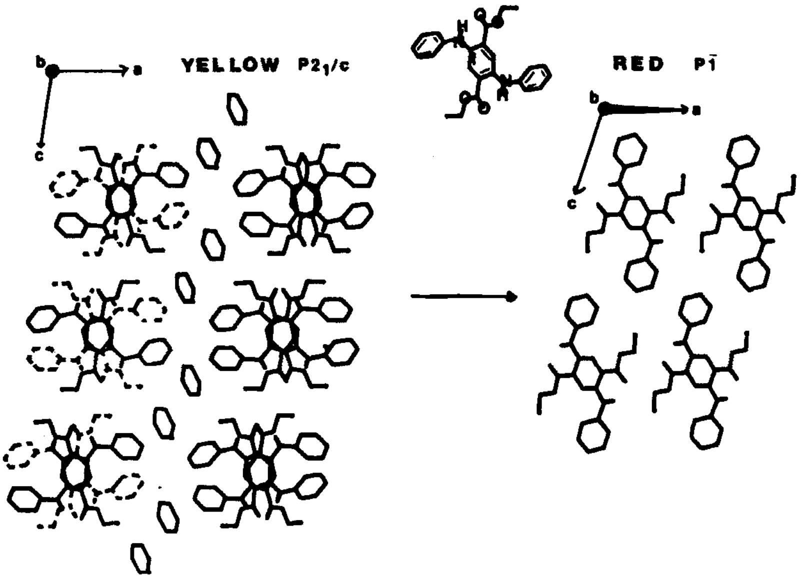
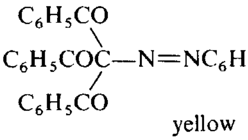


FIGURE 5 The crystal structures of the benzene solvate (9-Y) (left) and the stable red form (9-R) (right).[22] To analyze the left hand drawing compare the parent structure at the top in the middle of the page. The yellow structure contains stacks of such molecules (into the page) adjacent members in a stack being turned nearly 180° from each other. Note the channel between layers where the benzene molecules are located. The change from 9-Y to 9-R clearly involves very extensive repacking of the crystal.

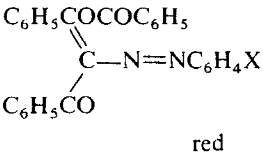
features in common. They all begin at nucleation sites with the formation of sharply defined reaction fronts and no indication of mixing of the two structures on a scale detectable by microscopic examination. They all involve changes which if they were to occur in an isolated molecule or small aggregate (such as a pair or triplet) would be very rapid processes ($\Delta G^{\ddagger} < \sim 12$ kcal). In each case the product is disordered but is microcrystalline (often with signs of streaking indicating some net orientation in "powder photographs" of unground product "crystals"). These together with other examples which have been observed suggest that this kind of heterogeneous mechanism has considerable generality among crystals whose transformation requires a change no more drastic than one which would be expected to be rapid with half-time measured in fractions of a second.

A crucial goal in the control of reactions of the type just discussed is to control the nucleation process. In this challenge we have been generally unsuccessful. The transformations of compounds **5–8** have been quite unresponsive to such measures as mechanical deformation, seeding, treating a spot on the crystal with acid and exposure to ultraviolet radiation. A successful example of photochemical nucleation of a thermal reaction will be discussed later in this paper, however.

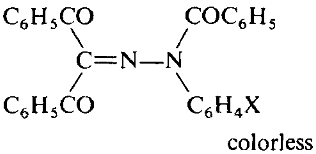
At this point we discuss a group of four reactions which involve a much more substantial molecular change. The azotriketone **10** undergoes parallel rearrangements in solution or in the solid state to the two products **11**, and **12**.[23,24] Unlike the examples above where the molecular changes were



10 X = Br
13 X = H



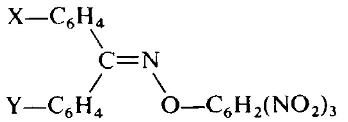
11 X = Br



12 X = Br

simpler these reactions fail to follow strictly the nucleation-followed-by-frontal-migration behavior. However, there is evidence of the rudiments of such a mechanism since nuclei of the red product **11** accompanied by scattering of light from behind the crystal appear at first (non-uniformly distributed over the crystal) and these regions containing reaction centers gradually spread throughout the crystal. Various individual crystals differed greatly in the time required for both initiation and completion of reaction. Similar behavior is found with the related compound **13**. The implication of these observations is that reaction nuclei are more apt to be generated near regions of the crystal where other nuclei are concentrated. The most obvious possibility suggested is that mechanical stress introduced by formation of **11** and **12** from **10** can help form additional nuclei and thus catalyze development of additional reaction centers. The role of defects in promoting chemical reactivity has been studied in other cases.[25]

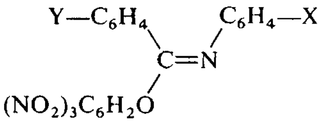
Even more dramatic evidence of the effects of mechanical properties of crystals on chemical reactivity has been found in the study[26] of the highly exothermic rearrangement of the oxime picryl ether **14** by way of intermediate **15** to the yellowish amide **16**. The behavior of single crystals of **14** and its monobromo derivatives **17** and **18** is quite different from that of the examples mentioned earlier. Regions of the crystal undergoing reaction remain clear but develop the yellow color of the reaction product and continue to show extinction of the starting crystal between crossed polarizing filters. A crystal



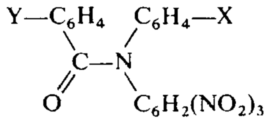
14 X = Y = H

17 X = Br, Y = H

18 X = H, Y = Br



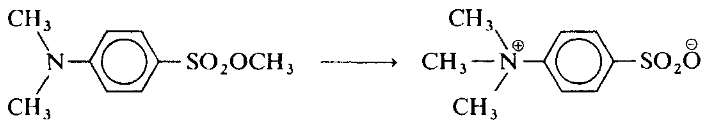
15 X = Y = H



16 X = Y = H

could be heated at 60–90° until such regions containing a solid solution of product were formed and then allowed to stand at room temperature. After some days microcrystallites of the product could be seen to crystallize from the solid solution on examination under crossed polarizing filters. Color pictures of this phenomenon are shown in ref. 26. Characteristically rather sharply defined V-shaped regions of reaction developed side-by-side with regions where no visible reaction was occurring, although after sufficient time the entire crystal did undergo reaction. In the regions where solid solution was developing there was often visible cracking of the crystal. Very thin crystals show solid-solution formation and separation of microcrystalline product without the V-shaped regions and cracking. Although, as has been pointed out, the molecular shapes of starting material **14** and product **16** are more similar than might be anticipated (if the most favorable conformations are compared) the complexity and steric requirements of the change required for these rearrangements is such that a "homogeneous mechanism" of the idealized sort is precluded.

An approach to designing solid state reactions which shows some promise involves choosing a substrate which can be expected to crystallize with reactive atoms fixed during the crystallization process in proper positions for reaction. An impressive example of such a reaction is the solid state conversion of **17** to **18**, studied by Sukenik, Bonapace, Mandel, Lau, Wood, and Bergman.[27] An x-ray structure determination of **17** showed that the methyl group of one molecule was in approximately the correct position for nucleo-



17 **18**

philic attack by the amine nitrogen of an adjacent molecule. Microscopic examination of single crystals undergoing reaction led to the conclusion that there "was no distinguishable pattern of change relative to crystal morphology." They proposed a mechanism in which reaction was "initiated at random points throughout the crystal . . . propagated over microscopically short chains interrupted by random molecular dislocations." The most interesting result of this work was the observation that the rate of the solid state reaction was 25–40 times that of reaction in solution.

For many years it was the consensus that solid state reactions should be orders of magnitude slower than comparable reactions in solution. In Table I is a condensed and up-dated version of a Table of 1973 vintage[23a] comparing rates in solution and in the solid state for a few reactions. Although the difficulty of defining a meaningful rate constant for solid state reactions of this kind is apparent, the data in the table at least indicate the wide variation which can be expected in the rate in solution compared to the rate in the solid over a series of reactions. The last entry in the table is of particular interest. The diisocyanate shown is more reactive in the solid state than liquid just over the melting point. A patent assigned to the DuPont Company claims

TABLE I

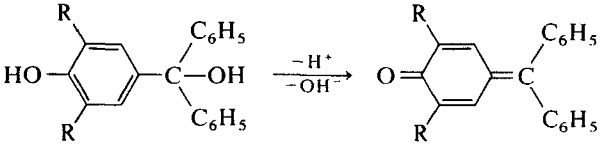
Rates of Solid-State Reaction

Reaction	Temperature °C	Reaction Order Assumed	$k_{soln.}/k_{solid}$	Ref.
Yellow to white[a] Dihydroxyterephthalate **5Y** → **5W**	90	?	$>10^3$	17
Phenylazotribenzoylmethane (**13**) to the enol benzoate and hydrazone	75	1	100	23, 24
Beckmann–Chapman rearrangement of oxime picrates (**14**) → (**16**)	60	1	5–14	26
Isomerization of exo- and endo-norbornenedicarboxylic anhydrides	120	1	5, 1	29
Racemization of (+)-bicyclo-[2.2.1]heptene-*trans*-dicarboxylic acid	131–152	1	2–2.5	28
Methyl dimethylaminobenzenesulfonate to zwitterion (**17**) → (**18**)	85		1/25–1/40	27
$(-CH_2C_6H_4N{=}C{=}O)_2$ to polymer	20–40		<1	30

[a] Since a sufficiently perfect crystal lacking a nucleation site can remain indefinitely at this temperature without reaction this estimate of $k_{soln.}/k_{solid}$ is quite arbitrary.

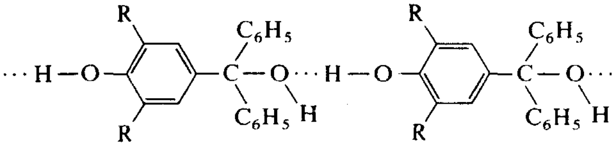
storage of the diisocyanate just over its melting point at 40° as a method of preventing its premature polymerization which occurs when it is stored in the solid state.[30]

Another example of the utilization of the prealignment of reactants into positions appropriate for reaction was the dehydration of *p*-hydroxytriphenylmethanol (**19**) to fuchsone (**20**)[31,32] suggested by early work of Gomberg. The first requirement for a mechanism in which the phenolic proton of one molecule can assist the loss of the alcoholic hydroxyl group of its neighbor is that the compound crystallize in a structure with appropriate hydrogen-bonded chains. The crystal structure of the dibromo compound has been determined by Stora[32] and x-ray structure determinations[33] of the unsubstituted compound **19** and the dimethyl compound **23** suggest that this packing feature has some generality. A sketch of a crystal of one of the two habits of the dimethyl compound **23** is shown in Figure 6 together with a drawing of part of the internal structure of a crystal in that orientation. When heated at 110° there is a very slow dehydration reaction. The appearance of crystals of this habit is surprisingly similar to that of reacting crystals of the picryl oxime **14** mentioned earlier; reaction begins in V-shaped regions which develop the color of the product fuchsone. Reactions of **19**–**23** can be made to occur photochemically as well as thermally. Exposure to the mild radiation of a Minerallight UVSL25 TLC indicator lamp for 48 hr caused the yellow or orange color of fuchsone **24** or **22** to appear. This experiment has interesting implications with respect to attempts which have been made to carry out excited-state-acid-catalyzed reactions.[34] The most intriguing aspect of this work, however, has been the demonstration that the photochemical reactions of **21** or **23** could be used to nucleate the thermal reactions. Thus a crystal of which one-half was exposed to ultraviolet light (just to the point at which the induced reaction could be detected) when heated to 110°



19 $R = H$
21 $R = Br$
23 $R = CH_3$

20 $R = H$
22 $R = Br$
24 $R = CH_3$



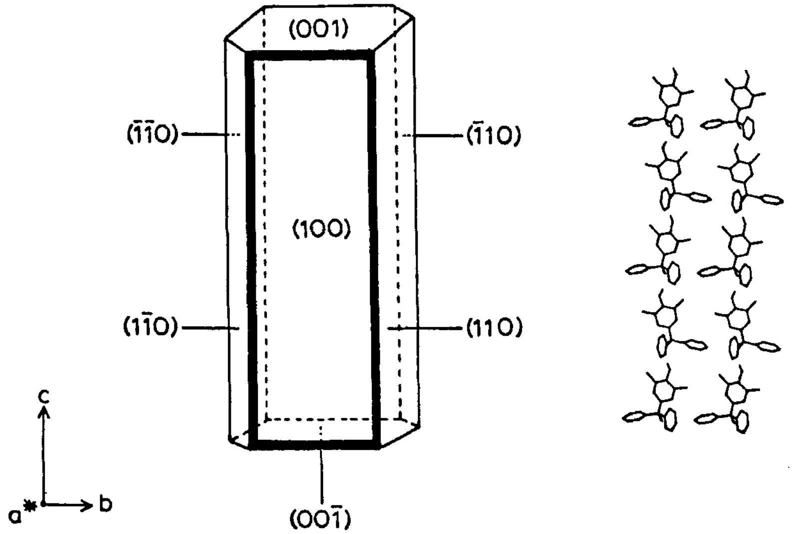
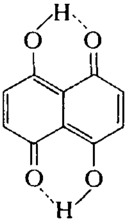


FIGURE 6 A crystal of the dimethyl compound **23** and a drawing of the internal structure in the same orientation. Note the hydrogen-bonded chains (the actual hydrogen bonds are not shown) running parallel to the long morphological direction of the crystal.

for a short time underwent thermal reaction selectively on the side which had been irradiated. A difficulty with this system, however, is that it could be shown that the photochemical reaction occurs in a thin layer at the surface of the crystal.

In bringing to a close this discussion of solid state reactions of molecular crystals we describe two structural problems which may hint in a vague way at some possibilities for the future. To return to an earlier topic, naphthazarin (**7**), whose polymorphic conversion of the *A* to the *C* form was discussed, has presented a puzzling structural problem. All three forms of naphthazarin have been shown to crystallize with the molecule at a crystallographic center of symmetry and this has led to the conclusion that in the crystal the molecular structure is the centrosymmetric one (**25**) rather than that found in solution (**26**).[19] Contrary evidence has included the observation that the two



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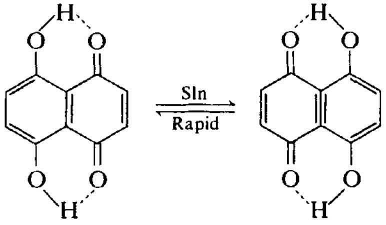

26 **27**

independent C–O distances are found to be essentially equal[35,19] that the 1,5-quinone structure in solution is highly unstable with respect to the 1,4-quinone (calculations have suggested that the difference in heats of formation between **25** and **26** may be as much as 14 kcal/mole),[36] and the fact that the x-ray structure of methylnaphthazarin is **26** (with the methyl group on the quinone ring).[37] A disordered structure composed of **26** and **27** should also be considered. The relationship of the positions of the hydroxyl hydrogen atoms to crystal symmetry is the point of particular interest in the present discussion and is shown in Figure 7. Three hypothetical drawings of the B naphthazarin structure with the heavy atoms in positions determined by x-ray crystallography are shown. The question arises whether the proton

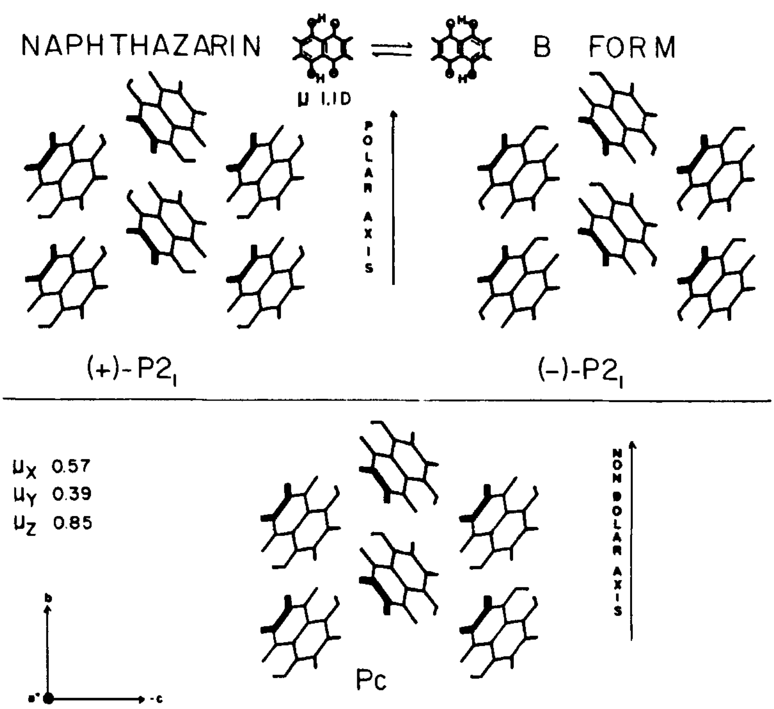

FIGURE 7 Hypothetical ordered structures of naphthazarin B showing how proton switching can, in principle, change the crystal symmetry. The structure of the B form is quite different from structures of A and C—laths of nearly coplanar molecules are absent in the B structure.[40] Note that the edges with heavy lines in the drawing are toward the viewer. Three crystals having approximately the same heavy atom arrangement are (upper left and upper right) a pair of chiral crystals and a meso (achiral) form (bottom). Note that the polar axis in the $P2_1$ crystals becomes the only non-polar direction in the Pc case. The dipole moment of naphthazarin in solution has been found to be 1.1D.[39] The u_x, u_y, and u_z show how such a moment would be partitioned along the three crystal axes. The drawing is over-simplified since clearly switching protons also requires small readjustments of the positions of the heavy atoms.

positions are related to and might be controlled by taking advantage of the change in direction of the polar axes in going from one of these states to the other. The structural differences here are subtle and x-ray crystallography is perhaps not the ideal technique for analyzing such differences. Thus we have found that refinement of the structure in space groups $P2_1/c$, Pc, or $P2_1$ with data collected at either room temperature or −60°C gives equally satisfactory R values of about 5%.[40] Phenomena such as second harmonic generation[41] may provide information about crystal symmetry. Of course, a question of great importance is how fast is the proton switching in the solid state in this kind of situation? An example, of a substance whose symmetry situation is similar and where proton-switching is clearly very slow, if it can be made to occur at all, has been found in the quinhydrones.[42]

As a final somewhat related example we return to the anil (**2**) which was mentioned near the beginning of the article. In Figure 8 is shown a sketch of a crystal[43] together with the structures of the two tautomeric anil structures.

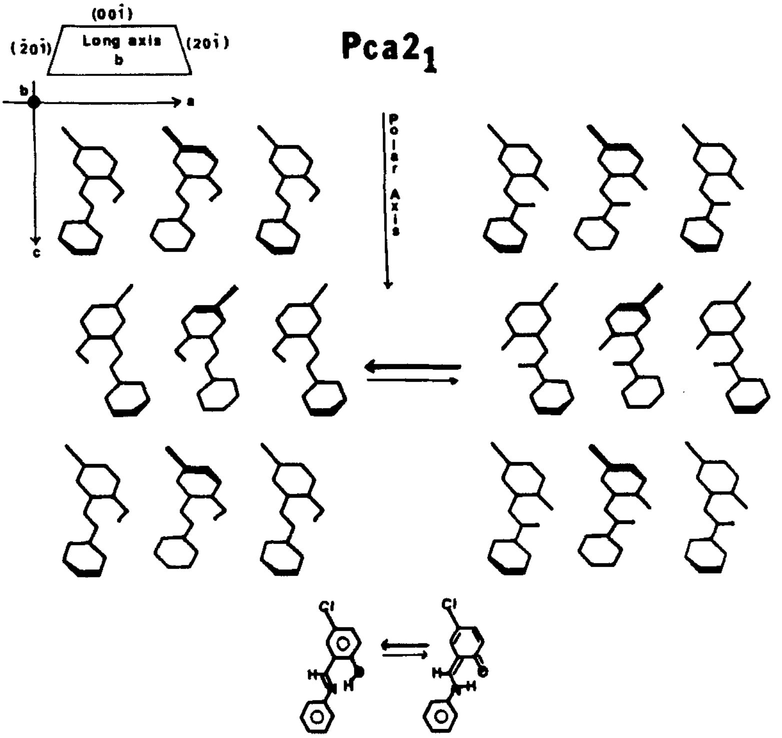

FIGURE 8 Drawing showing the tautomerism of the anil **2** based on the crystal structures of Bregman, Leiserowitz, and Schmidt.[7] The OH position in the left hand structure is based on the coordinates of ref. 7. The N*H* position in the right hand structure was estimated by the present authors. Note that the angle between the O-N vector and the polar c axis is 70°.

We have been intrigued by the possibility that it might be possible to influence the tautomeric equilibrium (and thus the color) by application of an external field. However, a crude experiment in which 2 Kv dc electric field was applied across a 2-mm gap containing the crystal and a dielectric layer to prevent arcing failed to produce an obvious color change. This substance **2** has a crystal structure of such interest that its behavior deserves more careful study.

In conclusion if may be said that solid state reactions of the type discussed here have much more generality than was assumed at one time. Although reactions of synthetic importance might be developed it seems possible that, in view of the highly unusual and specialized characteristics of the solid state, their greatest usefulness and interest may lie in quite unexpected directions.

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