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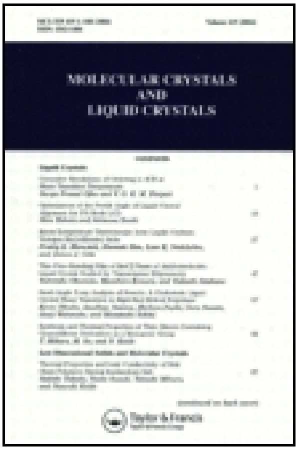

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Structural Factors in Some Solid State Photodimerizations

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Structural Factors in Some Solid State Photodimerizations

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Abstract—It has been reported previously that in the *trans*cinnamic acids and some substituted butadienes the crystal structure determines whether or not photodimerization occurs and the molecular structure of the dimer, if any. Similar results have been obtained also with chalcones. However, in anthracene and its 9-substituted derivatives the results are qualitatively different. Thus anthracene undergoes dimerization, if slowly, even though potentially combining atoms are 6 Å apart. 9-Cyano and 9-chloro-anthracenes, in structures with short axes of 4 Å, react to give head-to-tail dimers, whereas if structural effects were dominant the head-to-head dimers would be formed. It is concluded that in the last three examples, at least, the reaction does not occur in the bulk (i.e., at ordered sites). Two alternatives are suggested and discussed; the first is that reaction occurs in the vapor phase, the second that reaction occurs at defect sites, some of which are present initially, whereas others are produced during the dimerization. The factors which are responsible for the different behaviors of the anthracenes and of the other systems are discussed.

The work to be described is still in progress so that the interpretations of some of the phenomena involved are speculative. Nevertheless, the subject warrants discussion here since it impinges on a number of the disciplines represented at this meeting.

Some years ago we described our results with the *trans*cinnamic acids[1,2] and these results have been reviewed.[3,4] It will be recalled that three packing types have been identified amongst these acids: in two types the distance between neighboring double bonds is 4 Å or less. In one of the latter the nearest-neighbor molecules thus

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defined are translationally equivalent whereas in the second these molecules are related by a crystallographic center of symmetry. The first type gives rise to photodimers (cyclobutane derivatives) of mirror symmetry and the second to centric dimers. The third structure type has no close contacts (that is, less than about 4.8 Å) and materials of this type do not undergo photodimerization. These results are consistent with the hypothesis that nearest neighbor double bonds react with one another, that they do so only if they are within some critical distance of one another, and that reaction proceeds with retention of symmetry.

The products of these reactions are generally obtained in their own crystal lattices, i.e., the crystals of the starting materials are gradually replaced by crystalline powders of the products in their own phases. In many cases, however, considerable reaction (up to 50 *per cent* or more) occurs before X-ray reflections characteristic of the product can be observed. These results are adequately explained in terms of the following reaction steps:

1. Absorption of light.

2. Combination of an excited molecule with its nearest neighbor. This step may occur at the site of light absorption; it proceeds under the control of the lattice and determines the molecular structure of the dimer. The latter is formed in solid solution in the parent crystal.

3. As the concentration of dissolved dimer rises the stability of the solution drops and eventually recrystallization occurs. We may consider that there exist solid solutions of dimer in monomer and of monomer in dimer related by an immiscibility gap. These will be the two phases which separate from the recrystallization process.

We write 2. and 3. as follows:

$$\{M\}_M \rightarrow \{M + D\}_M \rightarrow \{M + D\}_M + \{M + D\}_D$$

where $\{\ \}_M$ and $\{\ \}_D$ denote in monomer and dimer crystal structures, respectively.

4. Reaction proceeds as long as there remain crystals having monomer crystal structure and with correct contacts between monomer molecules.

A number of other systems behave in ways similar to that of the cinnamic acids. Thus, the chalcones[5] (I) pack in structures similar

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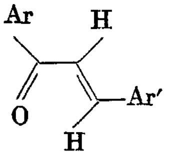
to those described above: crystals having translationally or centrically related close-packed molecules give high yields $(>50\%)$ of dimers of mirror- or centric-symmetry, respectively. In structures where there are no close contacts either no dimer is formed or low yields $(<10\%)$ of centric dimer are obtained. A series of butadienedicarboxylic acids and their derivatives (e.g., *cis, cis*muconic acid (II)) has also been investigated.[6] In this series the picture is more complicated since for a given double bond there is the possibility of short contacts with either or both of the double bonds of a neighboring molecule. However, it was possible here also to interpret the occurrence of dimerization, and the structures of dimers, in terms of the observed short contacts in the parent crystal structures.



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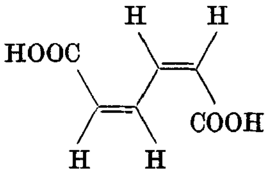

II

We recall that the cinnamic acids do not dimerize in solution or in the melt. The chalcones show a variety of behavior in solution: whereas some do not dimerize, others give very low yields of centric dimers, and yet others give moderate-to-high yields of the δ-dimer (C_2 symmetry). Little is known about the substituted dienes in solution except that some esters in the series dimerize efficiently when irradiated in benzene solution in the presence of benzophenone.[7]

We turn now to the anthracenes, limiting ourselves at this stage to anthracene itself and to its 9-substituted derivatives. These substances dimerize readily in solution by a mechanism which has been shown to involve[8] interaction of one molecule in its first singlet excited state with a second, ground state, molecule. The monomer molecules link at their 9 and 10 positions to give dianthracenes. We note that for anthracene itself there is only one possible dianthracene; for the 9-substituted monomers there are two possible structures for the dimer molecule, namely, the centric (head-to-tail) and mirror-symmetric (head-to-head) ones. In solution the centric dimers only

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have been found suggesting that steric repulsion between opposed substituents prevents the head-to-head approach.

The anthracenes have been obtained in a variety of crystal-structure types,[9,10] some analogous to those of the materials previously described:

(a) Structures having centrically related nearest neighbor molecules with strong overlap (9 to 10′ contact of less than 4 Å). These give excimer emission from 77 °K to near their melting points and react rapidly at room temperature to give head-to-tail dimers.[11] Examples are one each of the polymorphs of 9—CH_3— and 9—H_2NCO—anthracenes.

(b) Materials having nearest neighbor molecules strongly overlapped and translationally related (9 to 9′ contact of less than 4 Å). Of these substances, which also give excimer emission, some do not dimerize at all (9—COOH, 9—Br), whereas others (9—CN, 9—Cl) do so at moderate rates giving head-to-tail products. Thus, here the crystal structure of the monomer does not determine the molecular structure of dimer.[12] Further, in these materials reaction does not proceed uniformly throughout: observation of fluorescence under the microscope shows that the dimer-phase first separates at cracks and intergrain boundaries; in powders some grains become converted whereas others do not.

(c) Crystals having weakly overlapped molecules. These show structured emission and either do not dimerize or do so extremely slowly (anthracene, 9—CH_3O). Anthracene (short axis 6 Å) is an example of a material in which reaction occurs, albeit slowly, despite there being no short contact between potentially reactive sites. It has been shown that in this substance the dimer phase separates at dislocations.[13]

The totality of results can be summarized as follows: in the cinnamic acids, and possibly in the dienes, the lattice controls the reaction completely in that it determines both whether or not reaction occurs and also the molecular structure of the products, if any. In the " labile " chalcones, too, there is a unique correspondence between the structure of the parent phase and that of the molecules of dimer. However, amongst the other chalcones, which thus far have been found not to have short contacts, there are nevertheless some cases in which finite yields of dimer are obtained. Anthracene,

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too, undergoes slow dimerization in the absence of such contacts. Finally, in the 9-substituted anthracenes with suitable contacts it has not proved possible to predict the molecular structure of the dimer on the basis of crystal-structure considerations only.

These results raise numerous questions of which the first is whether in all systems we are indeed dealing with reactions in the solid. In the case of the unsubstituted chalcone, which has a low melting point, it is found that in fact the trace of product obtained on irradiation at room temperature is formed by reaction in the melt. Similarly, there is evidence[14] that a large proportion of the dimer obtained from acenaphthylene under similar conditions is the product of a gas phase reaction. In the anthracenes such a possibility is suggested by the fact that the same products are obtained by irradiation of solution and of solid, and it is conceivable that in the latter case reaction occurs in the vapour. Anthracene itself is known to dimerize in the gas phase,[15] and many of its derivatives have substantial sublimation pressures at room temperatures.

We are presently studying anthracene itself from this point of view. In the more rapidly dimerizing anthracenes, however, vapour-phase reaction is not dominant. Thus, for example, there is no apparent correlation between monomer melting point, which provides a rough indication of sublimation pressure, and rate of reaction. Further, the ratios of rates in different polymorphic forms are frequently extremely high whereas the ratios of the corresponding sublimation pressures must be relatively low. We have referred to the fact that some anthracenes do not react in the crystal, even though facile reaction occurs in solution. Finally we note the report of a case in which reaction occurs in the crystal but not in solution.[16]

We conclude that in the rapidly reacting anthracenes reaction proceeds in the solid. This is certainly true of the cinnamic acids, the dienes, and, amongst the chalcones, at least of the " labile " ones. Therefore comparison of the reactions in all these systems can be meaningful. We find that the products of the solid-state reactions are determined by the crystal structure in all systems except in the anthracenes of type *b* structure. In the latter, reaction either does not occur or leads to centric products. We ask how such products can arise from structures *b*, and why they should do so in the anthracenes only.

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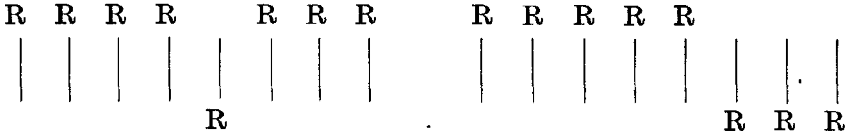
Reaction in the *b* type anthracenes to give centric dimers, if it involves nearest-neighbor molecules, requires that one of the two parallel monomer molecules rotates through 180°. Such a rotation of these large and anisotropic molecules cannot occur in the ordered crystal. There are several possible ways out of this dilemma. It is conceivable that after an induction period, during which the crystal becomes strained due to formation of a small concentration of head-to-head dimer, there occurs a polymorphic change. If this leads to a type *a* anathracene then the main product would be the centric dimer. Such a process occurs, for example, in β-*trans*cinnamic acid which on irradiation near 40° transforms to the α-acid, which in turn gives the centric α-truxillic acid. We find that polymorphism is widespread amongst the anthracenes and are presently investigating the possibility of such phase transformations. If no such transformations occur then we conclude that reaction must occur at disordered sites. Since this appears to be the more probable explanation it is worthwhile considering what types of sites would be effective.

Appropriate disorder centers are dislocations and surface sites. There are several other possibilities, however: it may be that no large scale rotation is involved but that reaction occurs at suitable built-in structural defects. These could be, for example, isolated inverted molecules (III) or micro-twinning planes (IV) in 4 Å structures, as shown schematically below.



III IV

The number of such sites is perforce small and therefore insufficient to explain the observed yields. Reaction could be initiated at such sites and then maintained because of the disorder engendered in the surrounding volume. If reaction occurs at specific sites only, then the excitation energy must migrate to these sites in order to be effective.

An alternative picture can be based on the interpretation given

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by Chandross and Ferguson[17] of the luminescence of the α-form of 9, 10—dichloroanthracene (non-dimerizing). These authors describe the emission as being of excimer type at 77 °K, but as exciton emission from " bulk " at 300 °K. They suggest that at low temperatures the excitation energy is trapped at a pair of parallel molecules which is misaligned in the lattice. This trapping allows time for the two molecules to approach and form a stable excimer. At higher temperatures the excimer is not stable and the energy can migrate into the ordered lattice. In this model the occurrence of excimer emission is an indication that the excitation energy has become localized. It is to be noted that such trapping would be equally effective if the pair is non-aligned from the start or becomes so after the arrival of the energy packet (as suggested for anthracene-trinitrobenzene[18]). In the latter case structural defects would be produced continuously; if this were true of dimerizing systems then the initial defect population need not limit the yield.

Whatever the exact nature of the effective sites we require of them two properties: they must trap the excitation energy absorbed by the crystal and they must allow the molecules to move as required for the formation of the appropriate dimer.

We have speculated above that in the *b* type anthracenes reaction occurs at certain defined sites in the crystal which are probably not the sites at which light is absorbed. This may or may not be true of the other series of compounds. Several factors may be responsible for this distinction:

1. The electronic states from which reaction proceeds may be of different types in the anthracenes and in the other series. There is some evidence for this. Thus only the anthracenes all undergo ready reaction in solution. This could imply that in the non-anthracenes the reaction proceeds through a long-lived excited state which is sensitive to collisional deactivation. Further, Kaufman and Sen Gupta[7] have shown that dimethyl *trans,trans*muconate dimerizes in solution in the presence of the triplet sensitizer benzophenone. However, our attempts at dimerization of *trans*cinnamic acid and of chalcone using acetone as sensitizer have been unsuccessful.

It is significant that the fluorescence yields of the anthracenes are very much higher than those of the non-anthracenes, both in the crystal and in solution. Yet in both series the longest-wavelength

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absorption band has an extinction coefficient of the order of 15,000. However, in the case of 4-methoxycinnamic acid crystal we have observed at low temperature a weak absorption band at the tail of the latter intense band.[19] This might be due to an $n\pi^*$ transition and it is possible that the other non-anthracenes also have $n\pi^*$ lowest singlet excited states.

These various observations on the non-anthracenes would be self-consistent if the lowest singlet excited state is an $n\pi^*$ one which readily crosses to the lowest triplet state in which the photo-reaction occurs.

2. The rates of excitation energy transfer may be much more rapid in the anthracenes than in the other compounds. There are no high-resolution data on the crystal spectra of the non-anthracenes which are interpretable in terms of energy transfer. Considering the crystal geometries and the intensities of the long-wavelength absorption bands the rates of transfer of pure electronic excitation should be similar in the two cases. However, if indeed the lowest singlet excited state of the non-anthracenes is an $n\pi^*$ one then the rate of transfer would be very low in these compounds.

3. Even if energy transfer occurs readily in both cases disorder sites may act as traps in one series and not in the other.

4. Finally, it is conceivable that in both systems trapping occurs but that different types of reactions occur at the trap sites in the various systems. That this may be so is suggested by the results with non-crystalline materials.

At this stage all these alternatives appear feasible. It will need careful experimentation to determine which effects are dominant.

Summary

In crystals of various families of organic materials the lattice determines whether or not photodimerization occurs and the structures of the dimers, if any. This is not true, however, of some anthracenes in which reaction appears to proceed at non-ordered sites and is not topochemically controlled. A variety of factors may be responsible for this distinction.

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