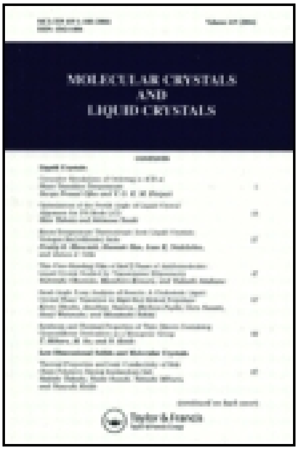

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Excimers in Crystals

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Excimers in Crystals

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The concept of the reaction cavity is used to indicate what types of reaction are allowed in the crystal state. Application is made to the formation of excimers in the crystal. The lattice determines whether or not the excimer is formed. There are two types of excimer-forming structures, stack and pair ones; it appears that the former forms *cis*-excimers, the latter *trans*- ones.

In the anthracenes, and probably generally, the excimer is an intermediate on the route to photodimer. The crystal constraints which determine the geometry of the excimer determine the stereochemistry of the product. However, the geometry of the product and of the precursor excimer may differ between bulk phase and structural defects.

Reactions in chiral crystals may yield optically active products. In an example of photodimerization the chirality of the dominant product appears to be determined by the chirality of the dominant excimer precursor.

In this talk I will consider the rudimentary and simple reaction of excimer formation in a crystal and discuss to what extent we can understand the lattice constraint of this reaction.

Consider a hypothetical reaction $A + B \rightarrow C + D$, taking place in a crystal. On the molecular scale this reaction takes place in a certain volume, which we call the reaction cavity:[1] this is the space which contains the reactant molecules prior to reaction, and the product molecules after the product-determining step. The total energy at every point along the reaction coordinate will be the sum of the energy of the contents of the cavity and the energy of interaction of the contents with the surroundings. In general both these terms will vary as the reaction proceeds.

Now consider that there is a competing reaction $A + B \rightarrow E$. The change in shape of the reaction cavity, and therefore the change in energy of interaction with the surroundings, will be different for the two reactions (Fig. 1). In particular, the transition state for II is energetically very unfavorable because of the bulges and voids formed. In other words, because of the interactions across the face of the reaction cavity, reaction II involves a high

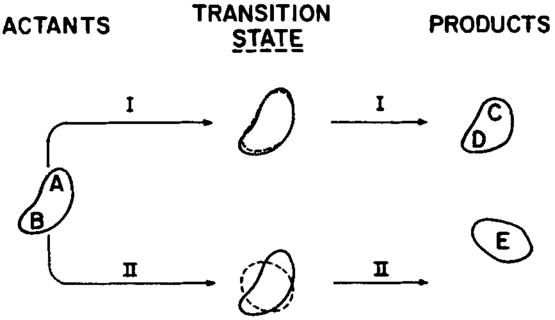


FIGURE 1 The reaction cavity for reactions (I) $A + B \rightarrow C + D$, and (II) $A + B \rightarrow E$.

activation energy. On the other hand, for reaction I the shape of the cavity remains practically unchanged during reaction, so that interactions with the surroundings add little to the activation energy. Thus the surroundings constrain the system to act by path I rather than by path II. *In general, the preferred reaction will be that which involves minimal change in the shape of the reaction cavity.* Note that this picture says nothing about the atomic movement *within* the cavity, and to that extent is a refinement of our earlier postulate[2] that reactions in the solid state involve minimal atomic movement.

A macroscopic sample will contain a very large number of potential reaction cavities. In most cases, however, these are all related to one another by the symmetry operations of the space group. Therefore the macroscopic specificity, resulting from reaction in a large number of cavities, will be the same as the microscopic specificity, resulting from reaction in a single cavity.

One should realize that the product of reaction is an impurity in the parent crystal, and tends to be rejected. As a result, solid-state reactions frequently go in two stages: the first is the actual reaction stage, with the product formed in solid solution in the parent crystal. In the second stage the product molecules crystallize out in their own crystal structures. The type of crystal-imposed specificity of which I speak here applies generally only to the first of these stages.

The reaction which provides the theme of this talk is the formation of excimers in crystals. First, a little history: about twenty-five years ago Förster and Kasper found the fluorescence of pyrene in solution to be anomalous.[3] At low concentrations pyrene shows "normal" monomer emission. However, at high concentrations there is observed an additional emission band at lower energy. Förster and Kasper correctly assigned the anomalous, red-shifted emission to a bimolecular complex carrying one quantum of excitation energy. This complex has been given the name excimer, short for excited dimer.

Since this pioneering work excimer formation has been found in many materials, particularly where the molecules are planar aromatic ones. Both theory and experiment suggest that in solution the two molecules in the complex lie parallel, completely overlapped and about 3.2 Å apart. However, from crystal structure data we know that aromatic molecules in the ground state tend to have interplanar spacings of about 3.5 Å and are not completely overlapped. Thus emission from the excimer leads to a pair of molecules in a repulsive ground-state configuration, and the emission is diffuse. Apart from its low energy and diffuseness, the emission is characterized by its large bandwidth and long decay time.

A few years after the work of Förster and Kasper, Ferguson found[4] that pyrene also in the crystal shows excimer emission—in fact, without any monomer component. All the evidence presently available indicates that in the crystal the excimer is formed in the bulk phase, and not at any specific structural defects. We can therefore consider excimer formation in terms of the known crystal structure (Fig. 2). Since in excimer formation the molecules move towards total overlap, we conclude that it is the two close-spaced,

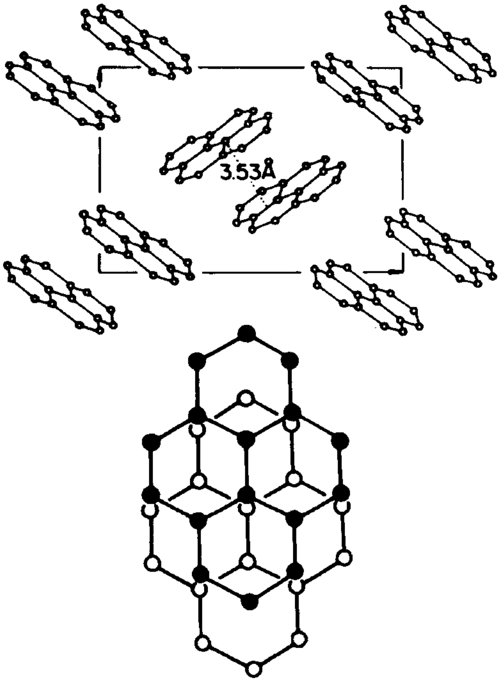


FIGURE 2 The crystal structure of and molecular overlap diagram for pyrene [based on J. M. Robinson and J. G. White, *J. Chem. Soc.*, 358 (1947)].

centrically related, and highly overlapped molecules which combine to give the complex. Thus we have defined the reaction cavity at the start of reaction.

When a pyrene molecule in the crystal absorbs excitation energy, the pair of molecules will move towards one another and towards complete overlap. These movements are resisted by the environment; in other words, the reaction cavity changes its shape and this leads to unfavorable interactions with the neighboring molecules. As a result the excimer cannot attain the geometry which it would in solution. Rather, some compromise is achieved between the driving force for excimer formation and the restraints imposed by the crystal.

An example of this is provided by the calculations of Warshel and Huler[5] on the pyrene excimer, both "free" and in the crystal. This calculation treats the delocalized π electrons by a quantum mechanical scheme while describing the hard core interaction between the σ electrons by empirical atom–atom nonbonded functions. The minimum-energy configuration of the free excimer has the molecules completely overlapped and about 3.2 Å apart. On the other hand, for the excimer in the crystal, while the interplanar

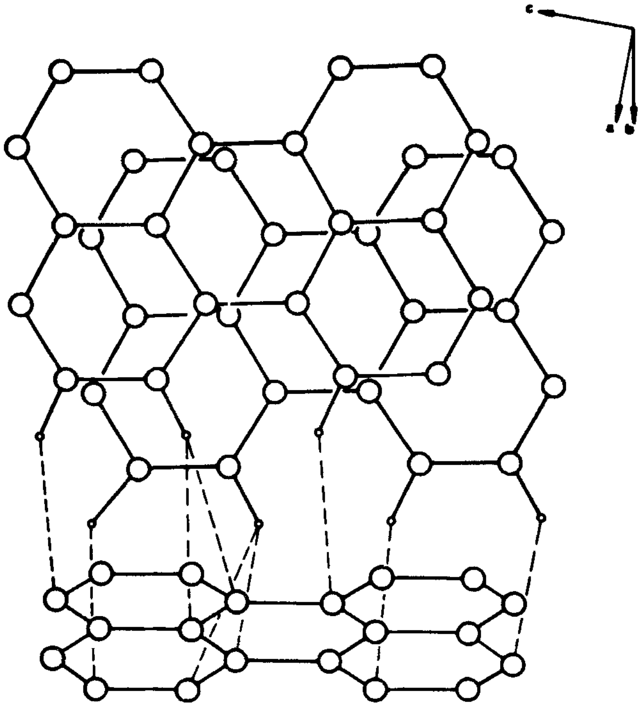


FIGURE 3 View normal to the molecules in the reaction cavity in α-perylene (from Ref. 6, by permission of the editors of *Chemical Physics*).

distance remains 3.2 Å, the two molecules are displaced by 0.7 Å relative to one another, in the direction of the long molecular axis. There is an energy barrier of 4–5 kcals/mole preventing total overlap in the crystal.

A similar calculation was carried out by Cohen *et al.*[6] on the α-crystal form of perylene, with similar results for room temperature. Figure 3 shows in projection the two perylene molecules in the reaction cavity, and the short contacts to one neighboring molecule. It is clear that some of these contacts will resist the movement of the reference pair towards complete overlap. It is of interest that the agreement of calculated and measured data is much improved by allowing the environment to relax; this will probably be true of all calculations of the energetics of crystal-phase reactions.

When we move from the pyrene and perylene type structure, choosing materials where the intermolecular overlap is smaller and smaller, the driving force for excimer formation will decrease whilst the resistance to the required movement will increase. We expect that eventually, when the overlap is small enough, the excimer will not be formed. In keeping with this we find[7] that the anthracenes crystallize in three structure types. In the first two, which we call "pair" (Fig. 4) and "stack" (Fig. 5) structures, there is

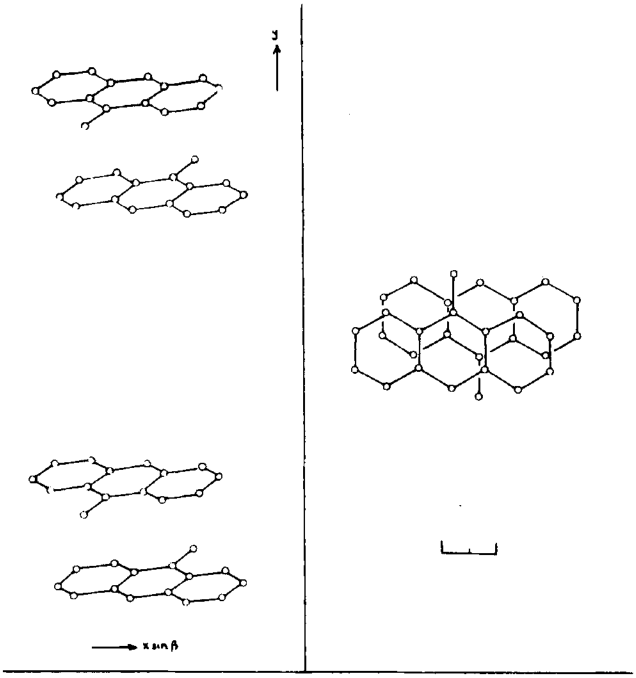


FIGURE 4 An example of a pair-structured material. The crystal structure of and molecular overlap diagram for 9-methylanthracene [based on J. C. J. Bart and G. M. J. Schmidt, *Israel J. Chem.*, **9**, 429 (1971)].

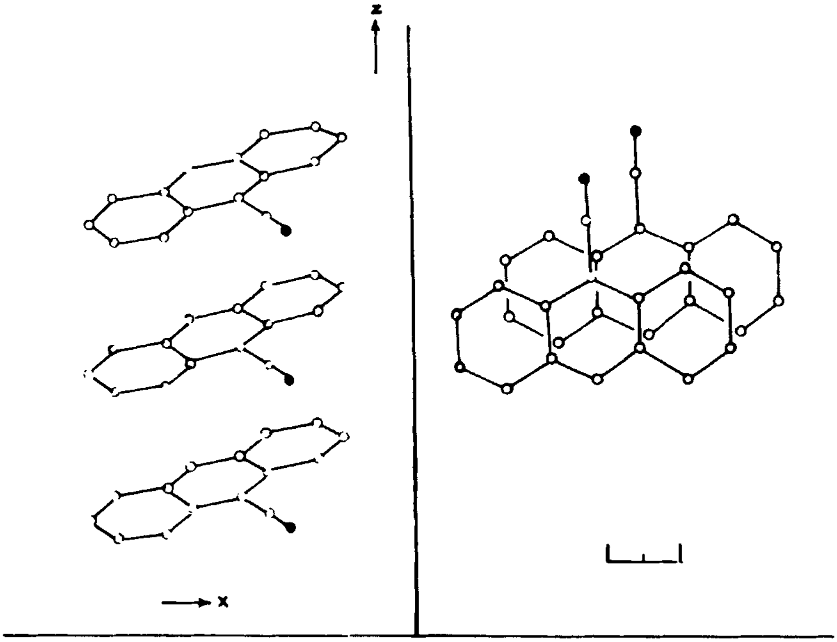


FIGURE 5 An example of a stack-structured material. The crystal structure of and molecular overlap diagram for 9-cyanoanthracene [based on H. Rabaud and J. Clastre, *Acta Cryst.*, **12**, 911 (1959)].

appreciable overlap between nearest-neighbor molecules; materials of these structures give rise to excimer emission. In the third type (Fig. 6) there is negligible overlap, and the emission is of monomer, not excimer, type.

The excimer emissions from stack and pair structures are distinguishable. In both cases the emission moves to higher energy with increasing temperature, but the sensitivity to temperature is much larger for stack than for pair materials.[7] A theoretical analysis of this effect led to the prediction that for a given molecule at low temperature the emission should be of higher energy in a stack than in a pair structure. The materials we have checked in this connection gave results[7,8] in keeping with this prediction. This leads us to conclude that the two types of structure give rise to geometrically different excimers. It is reasonable to assume that the stack structures give *cis*-excimers and the pair structures give *trans*-excimers. It is clear that interconversion of these two species in the crystal would require appreciable activation energy.

Many excimer-emitting crystals undergo photodimerization. Since excimer formation involves approach and increased overlap of the two molecules, it seems plausible that the pair of molecules passes through the excimer state

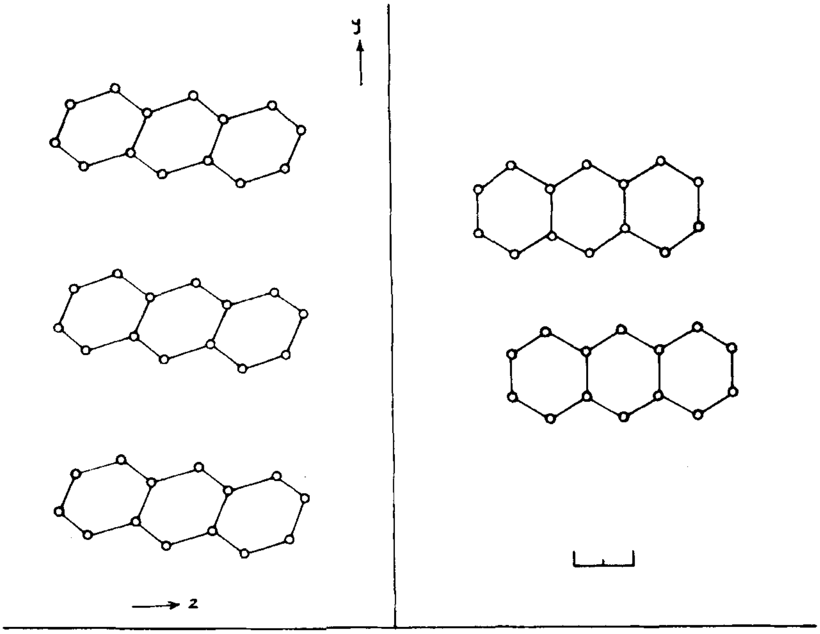


FIGURE 6 An example of a material with negligible intermolecular overlap. The crystal structure of and molecular overlap diagram for anthracene [based on D. W. J. Cruickshank, *Acta Cryst.*, 9, 915 (1956)].

on its way to dimer. That this is indeed so for anthracene and some of its derivatives was established by Ferguson and Mau.[9] Their experiment utilized a single crystal of di-anthracene (anthracene photodimer); this crystal was photolyzed with high-energy light so that some of the dimer molecules were split into pairs of monomers. The crystal was then irradiated with low-energy light which gave rise to both excimer emission from and redimerization of the monomer pairs. The quantum yields of these two processes were determined as functions of temperature. The results show that excimer emission and dimerization are the only two processes deactivating the excimer, and they are in direct competition. Thus, the excimer is an intermediate on the route to photodimer.

An interesting system was studied by R. Cohen *et al.*,[8] the dimorphic 2,4-dichloro-3′-methylstilbene. Both crystal forms give rise to excimer emission and both undergo photodimerization. Spectroscopic analysis shows that the two excimers are different, and the two photodimers are also found to differ. It seems that:

stack structure → *cis*-excimer → mirror-symmetric dimer, and
pair structure → *trans*-excimer → centro-symmetric dimer.

Thus the structure of the dimer is determined by those crystal constraints which determine the structure of the excimer.

A different case is provided by 9-chloroanthracene, which is also dimorphic. The two forms give rise to different excimer emissions,[7] but both give the same photodimer[10] (the centro-symmetric one). Since we consider excimer formation to be a bulk phenomenon, and since it seems that *cis* and *trans* excimers do not equilibrate in the crystal, we conclude that at least in the stack structure photodimerization does not occur in the bulk crystal. The most plausible alternative is that it takes place at certain structural faults.

The stack-structured 9-chloroanthracene and 9-cyano-anthracene are examples of anthracenes in which photodimerization does not appear to be under topochemical control. In both materials it seems probable that the dimerization reaction occurs only at specific sites in the crystal. We believe that *cis*-excimers are formed in the bulk crystal, but *trans*-excimers at the photodimerizable sites. Then the overall process involves the following steps: absorption of light in the bulk crystal; formation of *cis*-excimer; energy transfer at the *cis*-excimer level; trapping at a site giving *trans*-excimer; photodimerization. Several steps are in competition with radiative deactivation.

A second type of non-topochemical behavior is shown by anthracene itself. As we have seen, in this structure there is negligible intermolecular overlap, and the emission is of monomer type. Nevertheless, anthracene undergoes photodimerization. There is much evidence that, in this system too, reaction occurs preferentially at certain defect sites. There has been considerable speculation as to the exact nature of these sites, but this question appears to have been settled by the recent work of Parkinson *et al.*[11] These sites are excimer emitting. Thus the overall process is much as for the materials of the previous paragraph, except that there is no excimer formation in the bulk phase, and the energy is transferred at the monomer-exciton level.

I finally turn to another type of lattice control, that leading to asymmetric reactions. To introduce this subject consider a reaction cavity which lies on a crystallographic plane of mirror symmetry (Figure 7, top). Then, whatever

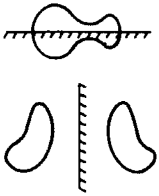
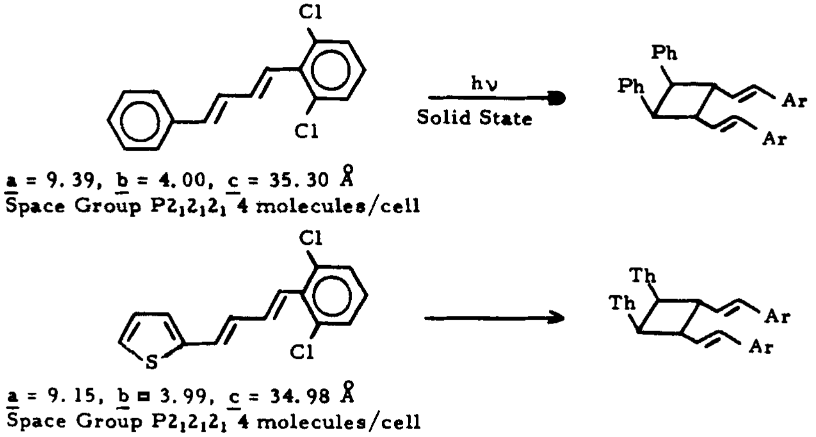


FIGURE 7 Top: reaction cavity lying on a crystallographic mirror plane. Bottom: two reaction cavities related by a crystallographic mirror plane.

the reaction, the product molecules cannot show optical activity: they must either be internally compensated or must form a racemic mixture. A second possibility (Figure 7, bottom) is that pairs of reaction cavities are related by mirror symmetry. Then if the products in one cavity are optically active, with a certain sign of rotation, then the products in the second cavity must have the same value of optical activity, but of opposite sign. Thus the total product is a racemic mixture, and we conclude that when the symmetry operations of the space group include mirroring ones, the product of reaction must be optically inactive. On the other hand, if the crystal is chiral, which means that the symmetry operations do not include mirroring ones, this is no longer so. For then the contents of every cavity must be chiral, the constraints on every cavity are asymmetric, and there is no symmetry imposed compensation between cavities. Thus, even starting with optically inactive molecules, if they crystallize in a chiral structure we may be able to produce optically active products by solid-state reaction.



SCHEME 1

Consider the diphenylbutadiene shown at the top of Scheme 1. It crystallizes in a chiral structure and photodimerizes. However, the dimer is mirror-symmetric and therefore optically inactive. The corresponding thiophene derivative (bottom of Scheme) crystallizes in an isomorphous structure and also gives a mirror-symmetric dimer. The two monomers are mutually soluble in all proportions; irradiation of such a solid solution yields, in addition to the two homodimers shown in the Scheme, the two enantiomeric hetero-dimers. Elgavi, Green and Schmidt[12] performed the following experiment: They grew a large single mixed crystal of the two monomers containing 15% of the thiophene derivative. They irradiated this crystal with monochromatic light which was absorbed only by the thiophene derivative. The experimental parameters were such that essentially the sole products were the two heterodimers. It was found that these products were formed with an enantiomeric excess of 70%.

The above reactant mixed crystal is of stack structure, and one can conclude from the experimental conditions that the large enantiomeric excess results from differences of the rates of attack of an excited thiophene molecule on its upper and lower phenyl neighbors in the stack. The crystal is excimer emitting. Calculations by Warshel and Shakked[13] suggest that the asymmetric induction occurs during the formation of the enantiomeric excimers; in other words, the chirality of the product dimer is determined during the formation of the chiral excimer intermediate.

Acknowledgments

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