Photochemical Reactions of Organic Crystals

V. RAMAMURTHY* and K. VENKATESAN*

Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, India

Received April 3, 1986 (Revised Manuscript Received October 13, 1986)

Contents

I. Introduction

Organic photoreactions in the crystalline state have been studied widely and date back to the end of the last century.[1-3] Early organic chemists frequently worked with solid materials because of the unavailability or expense of suitable solvents. But growth came to a halt because not much was known at that time of the nature and structure of crystals. However, as the years passed, synthetic and mechanistic organic chemists have concentrated on reactions in fluid media and solid-state reactivity did not enjoy in these years the popularity of solution reaction studies. The main experimental obstacle was probably the difficulty of identifying reactive crystals. In order to control and exploit organic reactions in crystals, chemists must develop the same sort of intution about these processes that they have developed for fluid-phase reactions.

The science of solid-state organic chemistry, and particularly the area of lattice control over reaction pathways, now seems to be entering a period of flowering and growth. There is no doubt that with deeper understanding of packing effects and of topochemistry, solid-state organic reactions could be planned and exploited in organic chemistry. The combination of organic solid-state chemistry and X-ray crystallography has proved to be invaluable for structure–reactivity correlation studies. Techniques such as X-ray crystallography, high-resolution electron microscopy, and solid-state magic angle spinning NMR spectroscopy have opened up entirely new dimensions in organic solid-state chemistry. Although considerable progress has been made in this multi-disciplinary field in the last two decades, much chemistry still remains to be done. It seems appropriate at this stage of development in this field to review in depth the existing literature as it stands in 1986. This review is primarily aimed at the practicing organic chemist.

The article is primarily concerned with *organic photoreactions* in the *crystalline state*. Photopolymerization in the crystalline state is not covered. It is important to note that tremendous progress has been made in this area during the last decade.[5-7] Studies on inclusion complexes and on surfaces have not been included although interesting results have been reported;[4] further, photophysical studies of organic crystals have also been excluded. Photodimerization of cinnamic acid and its derivatives in polymer matrix

0009-2665/87/0787-0433$06.50/0

V. Ramamurthy obtained his M.Sc. degree (1968) from I.I.T., Madras, and the Ph.D. degree (1974) from the University of Hawaii (Prof. R. S. H. Liu). Following postdoctoral studies at the University of Western Ontario (with P. de Mayo; 1974–75) and Columbia University (with N. J. Turro; 1975–78), he joined the Department of Organic Chemistry, Indian Institute of Science, where he is currently Associate Professor. During 1978–1985 he has spent brief periods as a Visiting Scientist at the University of British Columbia, the University of Notre Dame, Columbia University, the University of Western Ontario, and the University of Hawaii. He is a Fellow of the Indian Academy of Sciences and a Research Fellow of the Indian National Science Academy (1985–1987). His research interests lie principally in organic photochemistry.

K. Venkatesan received his degree in Physics in 1953 at Annamalai University and a Ph.D under the supervision of Prof. S. Ramaseshan at the Indian Institute of Science. He carried out postdoctoral work with Prof. J. D. Dunitz at the Swiss Federal Institute of Technology and Prof. Dorothy Crowfoot Hodgkin at Oxford University. He was on the Faculty of the Physics Department of Madras University from 1963 to 1971. In 1971 he joined the Faculty of the Department of Organic Chemistry at the Indian Institute of Science, becoming a Professor in 1981. His main research interests are solid-state chemistry and chemical crystallography.

is not included. Although these are the first known and first used negative photoresist, as the medium of reaction is not crystalline state their inclusion appeared inappropriate. This review will attempt to illustrate the main features of organic solid-state photoreactions with a range of appropriate examples. It is hoped that this treatment will demonstrate the utility of conducting reactions in crystals and stimulate further explorations in this area. A number of other reviews relevant to this topic have been published earlier.[8–14]

II. Topochemical Principles: Correlation of Structure with Reactivity in Bimolecular Reactions

Schmidt and co-workers at the Weizman Institute, studied systematically (in the early 1960s) the factors that govern the course of organic solid state, especially photoinduced, reactions.[15–17] As a result of their extensive studies on the photodimerization of cinnamic acids, they confirmed the topochemical postulate first enunciated by Kohlschutter in 1918,[18] which states that reactions in crystals proceed with a minimum of atomic and molecular movement. According to Kohlschutter, a topochemical reaction is one in which both the nature and properties of the products of the reaction are governed by the fact that it takes place under the constraining influence of the three-dimensional periodic environment. As a result of the work of Schmidt and co-workers some important principles have been established and these are discussed in this section. The important points to emerge and those that form the basis of topochemical control of both bimolecular and unimolecular transformations are the following:

(i) The intrinsic reactivity of a molecule is less important than the nature of the packing of neighboring molecules around the reactant.

(ii) The separation distance, mutual orientation, and space symmetry of reactive functional groups are crucial.

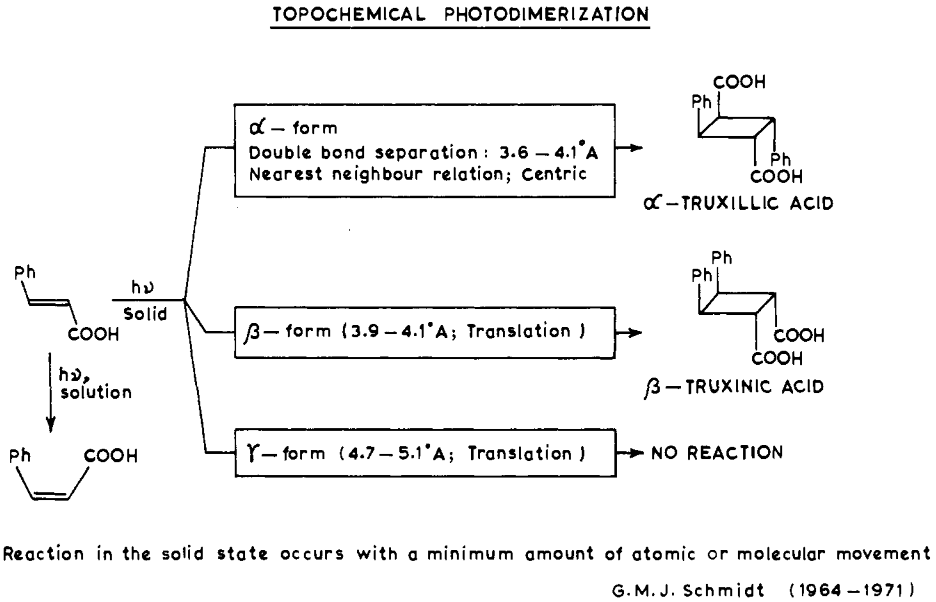
(iii) In crystalline solids there are very few (usually just one) conformations taken up by molecules which, in the dispersed state, are very flexible.

(iv) Molecular crystals (into which category the vast majority of organic solids fall) display a rich diversity of polymorphic forms, in each of which a particular conformer or particular symmetry and separation of functional groups prevails.

Following the pioneering investigations of Schmidt and his co-workers several groups have attempted to understand organic solid-state transformations on the basis of crystal structure. In this section, we highlight the role of solid-state structure in controlling solid-state reactions. Both unimolecular and bimolecular organic photoreactions are covered. Where crystal structures are available, an attempt is made to relate the structure with the reactivity.

The reactions of *trans*-cinnamic acids in the crystalline state are well known examples of [2 + 2] photodimerization and the classic studies by Schmidt and his co-workers have demonstrated that such reactions are strictly controlled by the packing arrangement of molecules in the crystals.[15–17] Since the original contributions by Schmidt and his group, several examples of photodimerization in the solid state have been reported but these have been isolated cases rather than forming a systematic investigation with the emphasis on structure reactivity correlations. In this context recent investigations on coumarins[19–24] and benzylidenecyclopentanones[25–30] are noteworthy. A large number of closely related molecules in these two series have been subjected to both photochemical and crystallo-

SCHEME 1



graphic studies. While studies on cinnamic acids resulted in very important correlations between molecular alignment in the reactant crystal and steric configuration of the product, analyses of the behavior of benzylidenecyclopentanones and coumarins in the solid state have provided an opportunity to reexamine the subtler aspects of the topochemical postulates. The following section is devoted to a brief discussion of the important factors which are crucial for topochemical dimerization in the solid state. Other known examples of dimerization of organic molecules (often unrelated) in the solid state are summarized in the form of schemes.

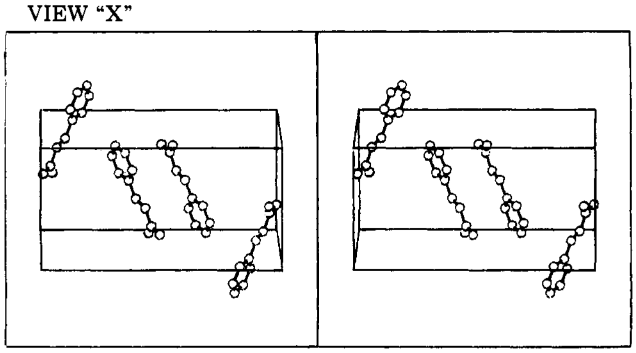


Figure 1. Stereodrawing of the α-packing of *trans*-cinnamic acid.

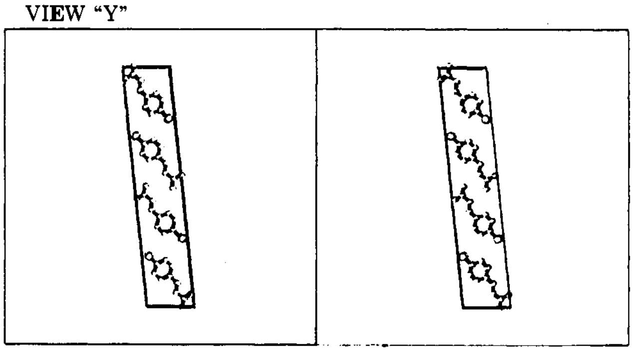


Figure 2. Stereodrawing of the β-packing of *p*-chloro-*trans*-cinnamic acid.

A. Cycloaddition Reactions

The reactions of cinnamic acids are examples of [2 + 2] photodimerization which have been investigated extensively. Some of these acids, on photolysis of the crystal, react to give dimeric products (Scheme 1) while in solution trans–cis isomerization occurs but there is no dimerization. The acids are observed to crystallize in three polymorphic forms, namely, α, β, and γ, and show photochemical behavior which is determined by this structure type. In all three modifications, cinnamic acid molecules pack in one dimensional stacks, adjacent stacks being paired by hydrogen bonding across centers of symmetry.[15-17] Within the stacks the molecules lie parallel with the normal distance between molecular planes being of the order of $\simeq$ 3.5 Å. The three structural types differ in the angle that the stack axis makes with the normals to the molecular planes. This is equivalent to a difference in the distance between equivalent points on the molecules, which is the crystallographic repeat distance, "d". In the β-type structure the molecules are separated by a short repeat distance of 3.8–4.2 Å, thus neighboring molecules up the stack are translationally equivalent and show considerable face to face overlap. All cinnamic acids which crystallize in this structure react photochemically to give products of the same stereochemistry (mirror symmetric dimers). In the γ-type structure adjacent molecules are offset so that the reactive double bonds do not overlap, and furthermore the distance between them is large (4.8–5.2 Å). Crystals of this type are photostable. In the α-type the double bond of a molecule in one stack overlaps with that of a centrosymmetrically related molecule in an adjacent stack. The distance between the equivalent double bonds is greater than 5.5 Å, but that between the overlapping double bonds is $\simeq$4.2 Å. This type of crystal upon irradiation produces centrosymmetric dimers. The examples of α, β, and γ packing are shown in Figures 1–3.

Based on extensive crystallographic and photochemical studies on cinnamic acids Schmidt deduced the following conclusions: (a) The nature of the crystal

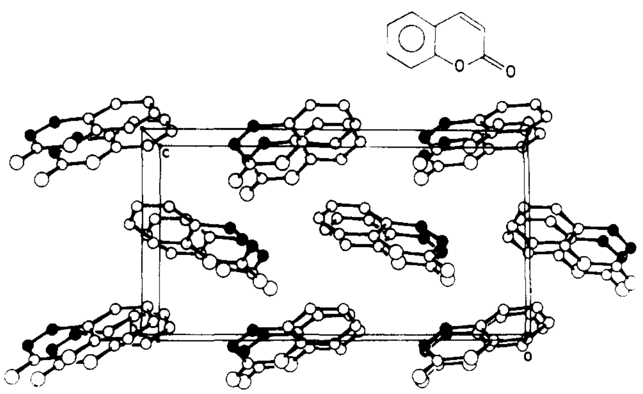
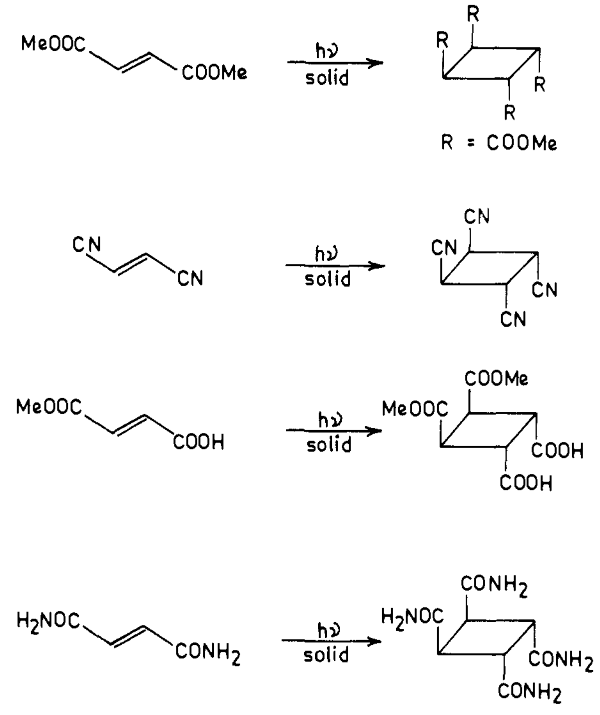


Figure 3. γ-Packing of coumarin.

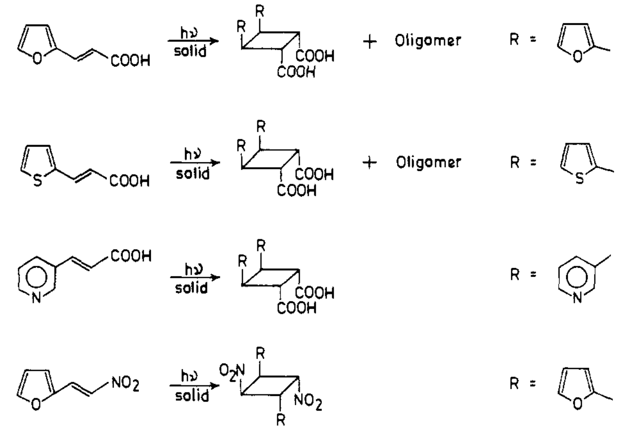
SCHEME 2



structure determines whether or not reaction occurs and the molecular structures of the products, if any. (b) The reaction involves combination between nearest neighbor molecules in a stack, and occurs with a minimum of atomic and molecular movement. Schmidt has drawn attention to the fact that not only must the double bonds of the reacting monomers of cinnamic acid be within $\simeq$ 4.2 Å, but they must also be aligned parallel for cycloaddition to occur. A reaction which behaves in this way is said to be "topochemically controlled". Schmidt has drawn the geometrical criteria for dimerization only with the view of inferring how precisely the π electron system of the reacting double bonds must be aligned in the crystal lattice for reaction to occur.

These topochemical postulates are landmarks in organic solid state photochemistry and are used as rules, as they are able to provide an understanding of a large number of [2 + 2] photodimerization reactions of widely varying structures. For example, dimerization of fumaryl derivatives[31] (Scheme 2), heterocyclic analogues of *trans*-cinnamic acid (Scheme 3),[32] butadiene derivatives (Scheme 4),[33,34] coumarins,[19-24] and benzylidenecyclopentanones[25-30] (Scheme 5 and 6) have all been

SCHEME 3



rationalized on the basis of Schmidt's criteria for dimerization.

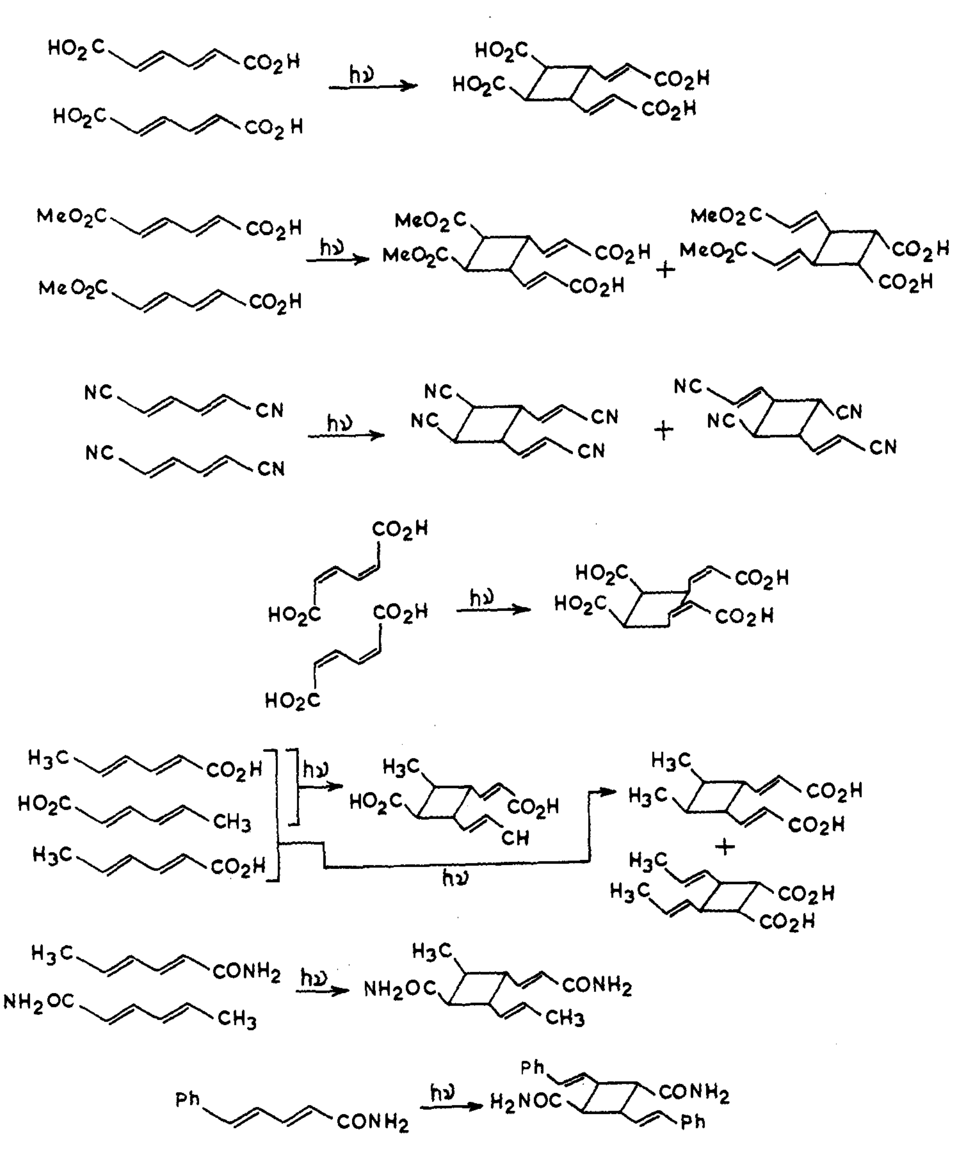
However very recent studies on the photodimerization of olefinic crystals have brought out several examples which deviate significantly from the well-accepted topochemical principles. Below we shall dwell upon such exceptional cases in the light of the original topochemical principles for dimerizations.

1. Distance Criteria

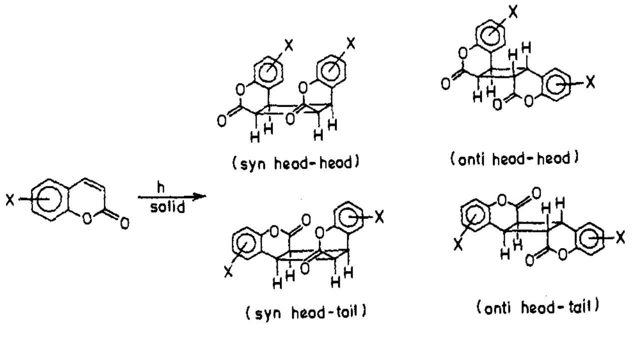
As presented above, for dimerization to occur the distance between the potentially reactive double bonds should be less than 4.2 Å. With the exception of methyl *p*-iodocinnamate, all the cinnamic acid derivatives which have adjacent double bonds separated by a distance of more than 4.2 Å in the crystalline phase are photostable.[15-17] In the case of methyl *p*-iodocinnamate, the molecules are arranged in a β-type packing with an interdouble bond distance of 4.3 Å and yet react to yield the expected photodimer.[15-17]

However, the upper limit of the critical distance for photodimerization in the solid state is not absolutely established, as the limit was set in the absence of further experimental data in the range 4.2–4.7 Å, above which photodimerization does not occur. The results with 7-chlorocoumarin are of interest in this context.[23] Irradiation of crystalline 7-chlorocoumarin yielded a single dimer (syn head–head), without induction period, in $\simeq$70% of yield (Scheme 5). The packing arrangement reveals that the two potentially reactive 7-chlorocoumarin molecules are separated by 4.45 Å, this being the repeat along the *a*-axis. Since the only dimer obtained corresponds to syn head–head, it is clear that the reaction is between the pairs translated along the a-axis. It is noteworthy that the distance of 4.45 Å lies beyond the so far accepted limit of 3.5–4.2 Å for photodimerization in the solid state. Very recently photodimerization of retinoids in the solid state has been reported.[35] Etretinate (1) dimerizes in the solid state to yield two dimers (Scheme 7). The center-to-center distance for the two sets of dimerizable bonds are 3.8 and 4.4 Å, the latter being outside the presently accepted limit. The most unusual case reported so far is *p*-formylcinnamic acid.[36] This crystal, possessing a *b*-axis of 4.825 Å, dimerizes in the solid state to yield a mirror symmetric dimer. It may however be noted that the plane to plane perpendicular distance between reactive molecules is fairly short (3.88 Å).[37] Thus the

SCHEME 4

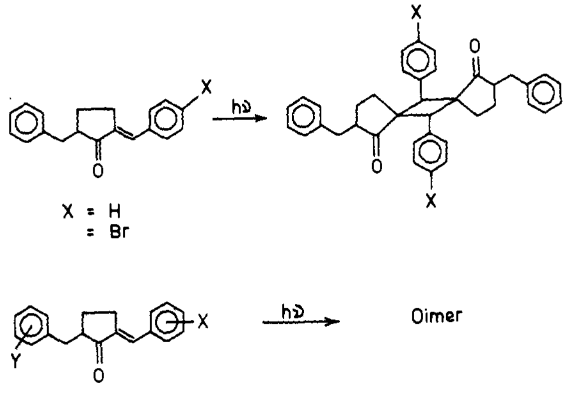


SCHEME 5



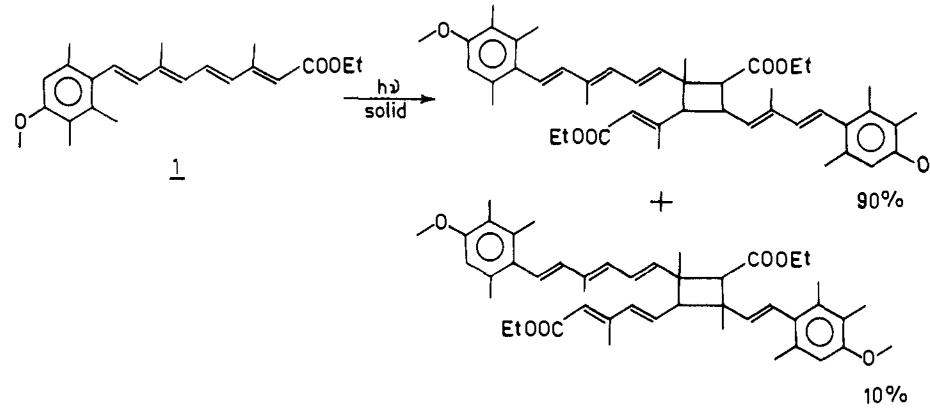
Coumarin Irradiated	Nature of Dimer
6 - Methoxy	syn HH (60%)
7 - Methoxy	syn HT (90%)
8 - Methoxy	anti HT (50%)
6 - Acetoxy	syn HH (70%)
7 - Acetoxy	syn HH (90%)
4 - Methyl 7-Acetoxy	syn HH (80%)
4 - Chloro	anti HH and syn HT (25%)
6 - Chloro	syn HH (100%)
7 - Chloro	syn HH (70%)
4 - Methyl 6 - Chloro	syn HH (50%)
4 - Methyl 7 - Chloro	syn HH (80%)
7 - Methyl	syn HH (65%)

SCHEME 6

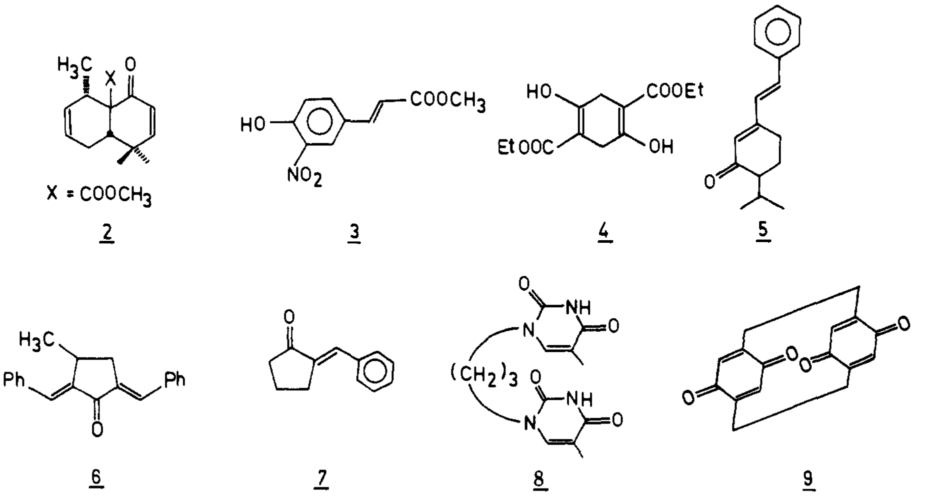


Bp-Cl BCP	Y = H, X = p-Cl	No	
Bp-Me BCP	Y = H, X = p-Me	No	
p-Cl BBCP	Y = p-Cl, X = H	Yes	Centrosymmetric dimer
p-Me BBCP	Y = p-Me, X = H	Yes	
p-Cl Bp-Br BCP	Y = p-Cl, X = p-Br	No	
p-Me Bp-Br BCP	Y = p-Me, X = p-Br	Yes	

SCHEME 7



SCHEME 8



above examples point out the need for a closer examination and modification of the distance criteria for photodimerization.

The opposite situation, namely, absence of reaction in spite of favorable distance, has also come to light and consideration of this allows us to know more about the subtler aspects of photoreactivity in crystals. One of the polymorphs of distyryl pyrazine where the potentially reactive double bonds are separated by 4.19 Å is photostable.[38] The photostability of this compound has been ascribed to the layered structure which suppresses the molecular deformation necessary for the cycloaddition reaction. Another example where the molecular packing satisfies the topochemical criteria but yet is photostable is **2**[39] (see Scheme 8 for nonreactive olefins). The potentially reactive double bonds are parallel with a center-to-center distance of 3.79 Å. Nevertheless, **2** is photochemically inert when irradiated in the solid state. The probable reason for the lack of solid-state reactivity of this enone is the steric compression experienced by the reacting molecules at the initial stages of photocycloaddition (discussed in section VI). In the crystal of methyl 4-hydroxy-3-nitrocinnamate (**3**), the neighboring molecules are related by a translation of 3.78 Å. But it has been observed that this compound is photostable in the solid state.[40,41] In the crystal structure the molecules are linked by hydrogen bonds to form a sheetlike structure close to the (102) plane. It is likely that the extensive intermolecular hydrogen bond network and C–H···O type interactions involving the ethylenic carbon atom do not permit the easy spatial movement of the atoms of the double bond in the lattice for the reaction to proceed. It has been reported that in the photodimerization of diethyl succinylsuccinate (**4**) the conversion of monomer to dimer is only 3%.[42,43] However, the crystal structure of this compound reveals that the double bonds are separated by 3.58 Å and are conducive for photodimerization. It has been observed in our laboratory that benzylidene-*dl*-pipertone (**5**) is photostable in spite of the fact that there are two pairs of centrosymmetrically related double bonds which are parallel and at a distance of 3.92 and 3.98 Å, respectively.[44] Crystalline (+)-2,5-dibenzylidene-3-methylcyclopentanone (**6**) and 2-benzylidenecyclopentanone (**7**) are photostable while closely related systems possessing similar packing arrangements undergo dimerization readily in the solid state (Scheme 9).[45,46] The distance between the centers of the olefinic bonds of the inversion related pairs in the former and in the latter are 3.87 and 4.14 Å, respectively. The photostability is attributed to the reduced overlap between potentially reactive orbitals. As we shall see in a later section the absence of photoreactivity in many of these cases can be understood by performing lattice energy calculations.

2. Parallelism of Double Bonds

According to Schmidt and co-workers, parallel alignment of double bonds is as important as the distance between them. For example, methyl *m*-bromocinnamate does not yield any photodimer even on long

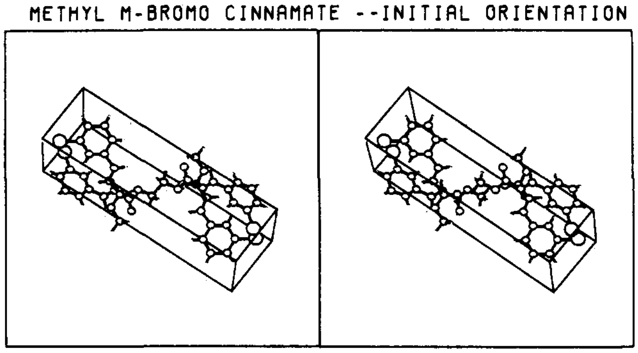
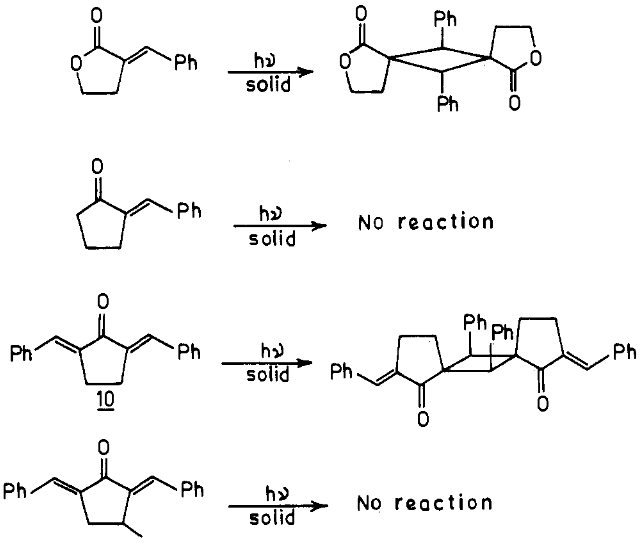
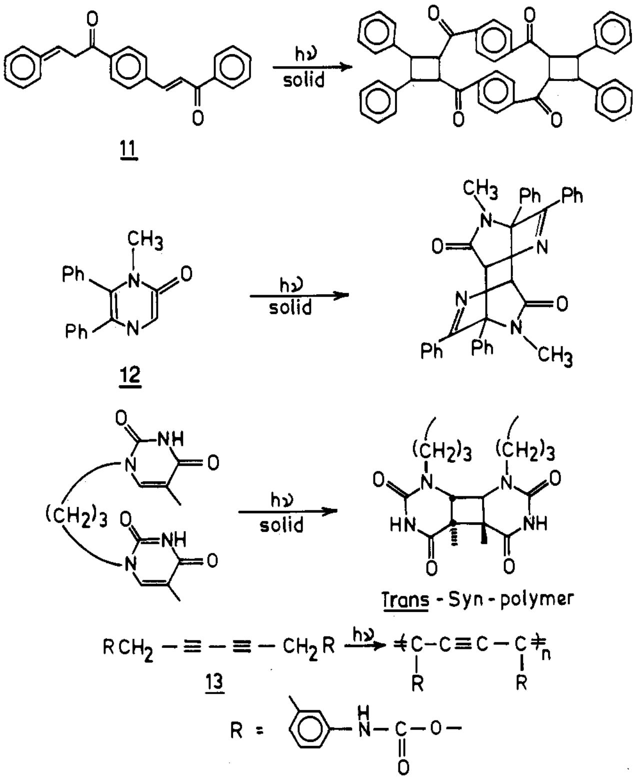


Figure 4. Stereodrawing of the packing of methyl *m*-bromocinnamate.

SCHEME 9



SCHEME 10



UV exposures. The distance between the centers of the adjacent double bonds is 3.93 Å, but the double bonds are not parallel. The double bonds make an angle of 28° when projected down the line joining the centers of the bonds (Figure 4). In the crystal of 1,1′-trimethylenebis(thymine) (**8**) the thymine rings are arranged such that both intermolecular and intramolecular photoreactions could occur.[47] Irradiation of this compound yields, however, a polymeric product which would arise from intermolecular reaction. This is because the intermolecular double bonds are nearly parallel to each other, while the intramolecular double bonds are inclined to each other at an angle of ~ 6°. Yet another convincing example is provided by [2,2]-(2,5)benzoquinophane (**9**).[48] Here both inter- and intramolecular cycloadditions are favored according to the distance criteria (~3.80 and ~3.0 Å, respectively). However, photolysis yields only intramolecular addition. This is attributed to the fact that the intermolecular adjacent double bonds are inclined to each other at an angle of 53.3°.

On the other hand, a few cases have also been reported where exact parallelism between reactant double bonds has not been adhered to and yet photodimerization occurs. For example, in the crystals of 7-methoxycoumarin, the reactive double bonds are rotated by about 65° with respect to each other, the center-to-center distance between the double bonds being 3.83 Å.[24] In spite of this "unfavorable" arrangement, photodimerization occurs giving syn head–tail dimer as the only product in quantitative yield (Scheme 5). 1,4-Dicinnamoylbenzene (*11*) crystals undergo photodimerization via a double [2 + 2] cycloaddition in a topochemical manner to the corresponding cyclic product (Scheme 10).[49] The nearest monomer units are arranged skew to each other (6°) and the distances between intermolecular double bonds are 3.97 and 4.09 Å for one cyclobutane ring and 3.90 and 3.96 Å for the other. 2,5-Dibenzylidenecyclopentanone **10** is analogous in its behavior and packing to 7-methoxycoumarin.[45] When **10** is irradiated by UV light in the crystalline state the principal product is formed by a [2 + 2] dimerization (Scheme 9). The cyclopentanone **10** molecules are arranged such that the mean distance separating the potentially reactive centers is ~3.7 Å, the angle between the two bonds being 56°. Although this is not the geometry considered conducive for a topochemical reaction, dimerization does indeed take place in the solid state.

A few examples of other closely related reactions wherein the reactive olefinic π systems are skewed with respect to each other are also reported. In the [4 + 4] photocycloaddition of 1-methyl-5,6-diphenylpyrazin-2-one (**12**), it has been reported that even though the double bonds are twisted by an angle of 24° (the angles between $C_2{=}C_3$ and $N_2{=}C_4$), dimerization does occur (Scheme 10).[50] In this case, the distances between the double bonds are 3.46 and 3.64 Å, which are well within the proposed limit. Another case in which the reaction takes place between nonparallel double bonds is the photopolymerization of the diacetylene, 2,4-hexadiyne 1,6-diylbis(*m*-tolylmethane) (**13**) where the closest distance of approach of triple bonds is 3.61 Å.[51] In this crystal although the reactive triple bonds are crossed at an angle of 72° polymerization does occur (Scheme 10). 1,1′-Trimethylenebis(thymine) undergoes photopolymerization via [2 + 2] cycloaddition in a topo-

TABLE 1. Relative Orientations of Reactive Double Bonds in Coumarins[a]

coumarin	center-to-center distance between the reactive double bonds, Å	θ_1, deg	θ_2, deg	θ_3, deg	displacement of double bonds upon projection, Å
7-chlorocoumarin					
pair I (translation)	4.45	0	131.4	85.3	0.287
pair II (centrosymm)	4.12	0	127.9	107.0	0.936
4-methyl-7-chlorocoumarin	4.08	0	121.4	88.53	0.011
7-acetoxycoumarin	3.83	0	106.4	125.45	1.329
8-methoxycoumarin					
pair I	4.07	0	122.4	63.77	1.565
pair II	3.86	0	117.4	112.88	1.333
7-methoxycoumarin	3.83	65			
ideal values	4.2	0	90	90	0.0

[a] For a definition of geometrical parameters see Figure 5.

chemical manner as described earlier.[47] Even in this case the double bonds are twisted with respect to each other by 5°.

The anomalous examples presented in this and earlier sections raise certain important questions concerning the correlation of reactivity with structure. It is important to stress that Schmidt's original criteria have explained a large number of topochemical dimerization reactions. Exceptions observed in recent studies should not be construed as serious violations of original concepts but be integrated into the original basic ideas by widening apparent limitations and scope.

3. Minimum Translational Movement in the Crystal Lattice

The topochemical principle states that *reaction in the solid state is preferred and occurs with a minimum amount of atomic or molecular movement.* This implies that a certain amount of motion of various atoms in the crystal lattice is tolerable. Based on this, one could assume that for the formation of a cyclobutane ring with C–C lengths of 1.56 Å the double bonds can undergo a total displacement of about 2.64 Å toward each other from the original maximum distance of 4.2 Å. Even under ideal conditions, movement of double bonds toward each other is essential for dimerization to take place. The criterion of less than 4.2 Å separation implicitly assumes that such a motion can be accommodated in the crystal. It would be expected that in some cases molecular motion such as (i) rotation of double bonds with respect to each other (to bring about parallelism from a nonparallel arrangement), (ii) a rotation about its own C═C axis (to achieve a maximum overlap of the π orbitals), (iii) translation of double bonds in the plane of the molecule, and (iv) movement along the C–C double bond axis may become necessary before dimerization can take place. We discuss below, based on the photodimerization of coumarins, that the types of motions mentioned above may indeed occur in the crystalline state.

Geometrical parameters that are useful in addition to center–center distance are θ_1, θ_2, θ_3, and the displacement of double bonds with respect to each other (Figure 5).[19] θ_1 corresponds to the rotational angle of one double bond with respect to the other, θ_2 corresponds to the obtuse angle of the parallelogram formed by double bond carbons C_3, C_4, C_3', and C_4', whereas θ_3 measures the angle between the least square plane through the reactive bonds C_3, C_4, C_3', and C_4' and that passing through C'_2, C_3, C_4, and C'_{10}. The basic aim in performing these rotations is to bring the π orbitals of the reacting partners to overlap, the ideal values for θ_1, θ_2, and θ_3 for the best overlap being 0, 90, and 90°, respectively. While θ_2 reflects the displacement along the double bond axis, θ_3 is a measure of its displacement in the molecular plane. Perusal of Table 1 reveals that in all the four reactive coumarins the reactive double bonds are not ideally placed. Although they are coplanar and parallel, the two double bonds are displaced with respect to each other both in the molecular plane as well as along the double bond axis. In all the four cases the configuration of the dimers obtained corresponds to the one that is expected based on molecular packing in the crystal. This suggests that motions of the molecules in the molecular plane and along the double bond axis are required and do indeed occur in the crystal lattice. Thus a certain amount of flexibility in the motions of the molecules in the crystal is to be expected. In this context a few new concepts have emerged in recent times and these will be discussed in section VI.

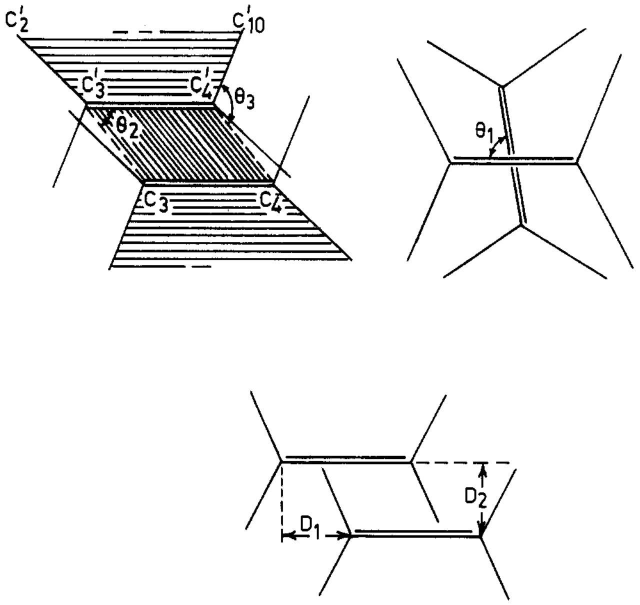


Figure 5. Geometrical parameters used in the relative representation of reactant double bonds.

TABLE 2. Crystallographic Data Associated with the Single Crystal → Single Crystal Dimerization of 2-Benzyl-5-benzylidenecyclopentanone (BBCP) and its *p*-Bromo Derivative (BpBr-BCP)

compd[a]	cell parameters	monomer	dimer	% change
BBCP	*a*, Å	31.30	31.32	0.06
	b, Å	10.78	10.81	0.28
	c, Å	8.69	8.63	−0.69
	Z	8	4	
	space group	*Pbca*	*Pbca*	
	unit cell volume, $Å^3$	2932	2922	
BpBr–BCp	*a*, Å	34.25	32.96	−3.77
	b, Å	10.88	10.27	−5.61
	c, Å	8.43	8.98	−6.52
	Z	8	4	
	space group	*Pbca*	*Pbca*	
	unit cell volume, $Å^3$	3141	3040	

[a] For structure of compounds see Scheme 6.

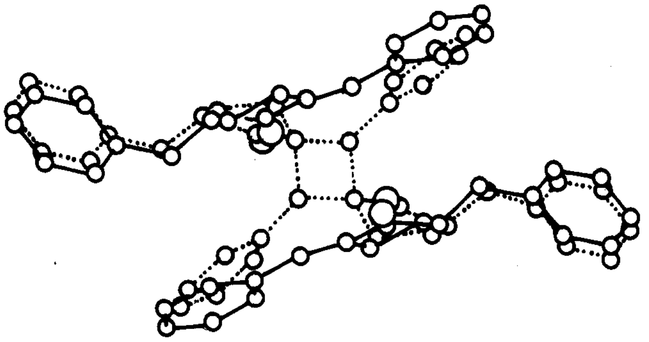


Figure 6. Composite diagram comparing the packing of the molecular units within the monomer and dimer crystal structures of BBCP.

4. *Single Crystal to Single Crystal Photodimerization*

There is cogent evidence to suggest that for certain photoinduced and thermally induced reactions the nature and stereochemistry of the product is precisely determined by the crystal packing within the perfect monomer lattice. However, the detailed mechanism by which organic reactions proceed within the solid state is not completely understood. Although in early 60s Schmidt alluded to the mechanistic details of photodimerization and suggested the possibility of occurrence of single crystal to single crystal dimerization, such examples were discovered only recently. Single crystal to single crystal polymerization of diacetylene constitutes the first example of such reactions.[52] Photodimerizations of 2-benzyl-5-benzylidenecyclopentanone (BBCP) and its *p*-bromo derivative (**14** and **15**) have also been established to be single crystal to single crystal transformations.[26,27,29] Crystallographic details provided in Table 2 illustrate the similarity in cell dimensions between monomers and dimers. Further, packing arrangements shown for BBCP and its dimer reveal that the dimerization process requires very little motion of the atoms (Figure 6). Most interestingly, the specific atoms involved in the reaction have been directly monitored during the dimerization through X-ray diffractometer measurements.

5. *Solid-State Asymmetric Synthesis*

The achievement of an asymmetric synthesis starting from an achiral reagent and in the absence of any external chiral agent has long been an intriguing challenge to chemists. The results obtained by Schmidt and coworkers on cyclodimerization in the crystalline state with well defined stereochemistry led them to the next logical step of achieving asymmetric synthesis in the solid state. Before describing their results it would be appropriate to mention a few facts relating to the symmetry of crystals. There are 230 genera of space groups which can be divided into two categories: (a) the chiral space groups, 65 in number, have only symmetry elements of the first kind, i.e., translations, rotations, and combinations of these; (b) the nonchiral space groups, of which there are 165, may contain symmetry elements such as a mirror plane or glide plane or center of inversion. Thus the unit cell of a compound belonging to an achiral space group will contain both the object and its mirror image. It is obvious that any attempt at achieving asymmetric synthesis via photochemical reactions should begin with a compound crystallizing in any one of the 65 chiral space groups. As to be discussed in section V, crystal engineering is not so advanced that any desired crystal environment can be prepared to order. In this connection the following observations are worthy of mention. In a survey of some 5000 X-ray structure determinations of homomolecular crystals reported (with data published in 1929–1975) it has been observed that organic molecules tend to crystallize in the systems of low symmetry namely, monoclinic and orthorhombic systems.[53] Of the 219 distinct space groups (11 enantiomorphous groups excluded from the total of 230) the most commonly occurring space groups (Table 3) are $P2_1/c$, $P2_12_12_1$, $P\bar{1}$, $P2_1$, $C2/c$ and $Pbca$, the chiral ones being $P2_12_12_1$ and $P2_1$. Yet another crystallographic observation of relevance for asymmetric synthesis in crystals is the phenomenon of achiral molecules crystallizing in chiral space groups. In these instances (e.g. benzophenone, γ-modification of glycine and binaphthyl) the chiral environment of the crystal forces the molecule to acquire a chiral conformation.

TABLE 3. The Most Common Space Groups of Molecular Crystals Based upon a Survey of Some 5000 Crystal Structure Determinations

space group	number	percentage
$P2_1/c$	1897	37.9
$P2_12_12_1$	839	16.8
$P\bar{1}$	449	9.0
$P2_1$	418	8.4
$C2/c$	310	6.2
$Pbca$	247	4.7

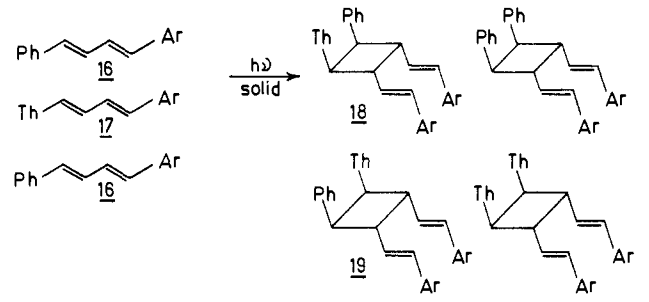


Figure 7. Asymmetric synthesis using mixed crystals of **16** and **17**.

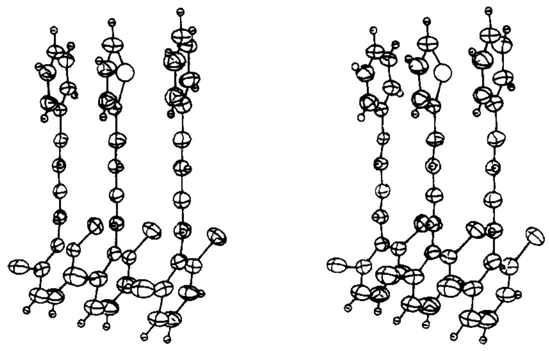
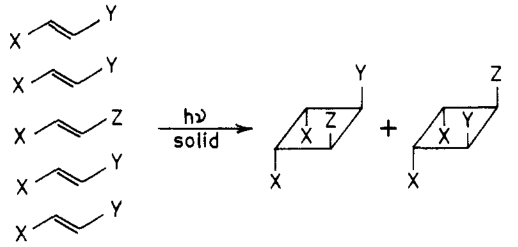


Figure 8. Stereodrawing of the intermolecular overlap in mixed crystals of **16** and **17**.

SCHEME 11



On the basis of the vast amount of knowledge gained regarding photodimerization reactions in the solid state, the Weizmann group extended their studies to design and perform solid state asymmetric syntheses.$^{54-64}$ Two approaches were mainly used in this venture. The enantiomeric yields achieved in these reactions varied from a few percent to quantitative. In the first approach the basic idea is to grow crystals containing two components (Scheme 11). It was known from their earlier studies that phenyl-substituted olefins (stilbenes and 1,4-diarylbutadienes) tend to adopt chiral structures. Further there were clear indications that dichloro derivatives bring about a 4-Å packing arrangement. As for the choice of the two components, thiophene and phenyl derivatives were favored since these molecules have been found to form mixed crystals (substitution solid solution). Thus when mixed crystals of **16** and **17** (Figure 7) are irradiated, enantiomeric heterodimers (**18** and **19**), in addition to the meso homodimers, are formed. In actual practice mixed crystals containing 85% of **16** and 15% of **17** were used yielding heterodimers in high percentage. Figure 8 represents the arrangement of host **16** and guest **17** molecules in the crystal lattice along the 4 Å axis. The absolute configuration of the mixed crystal has been established using X-ray crystallography.

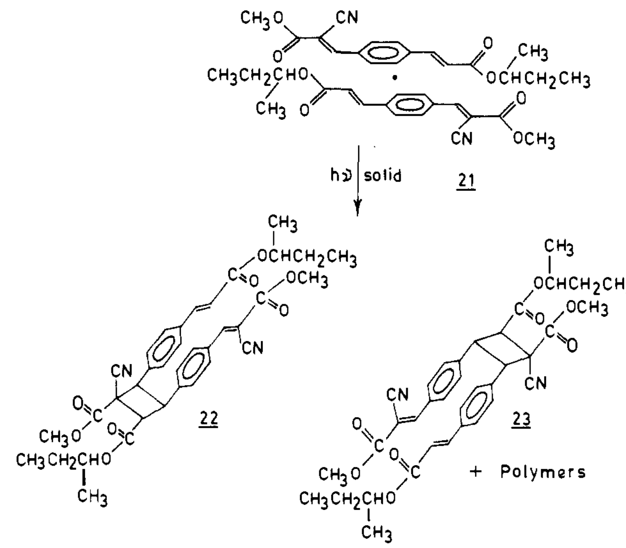
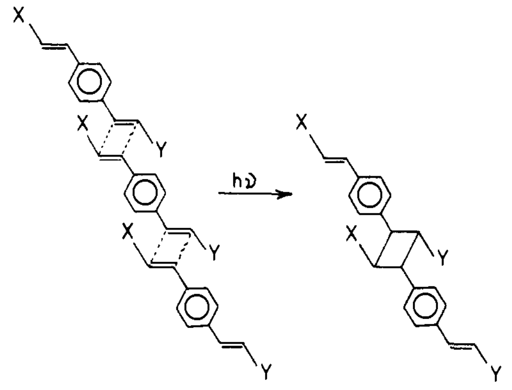


Figure 9. Schematic representation of the asymmetric dimerization of **21**.

SCHEME 12



The strategy adopted in the second approach demanded that molecules having two nonidentical reactive sites pack in a chiral crystal in such a way that the nonequivalent double bonds overlap. Such an arrangement would be expected to generate only one of the two possible enantiomers (Scheme 12). The actual system chosen for implementing this proposal was benzene-1,4-diacrylates. The chiral *sec*-butyl group was used to induce the compound to crystallize in a chiral space group. When the ethyl ester derivative (*S*)-(+)-**20** was irradiated at 5 °C, chiral dimer, trimer, and higher polycyclobutane oligomers were obtained in high yields approaching 100%. Irradiation of the enantiomeric (*R*)-(−)-**20** isomer yielded products having optical rotations of the same magnitude but of opposite sign. That the chiral induction is entirely dictated by the chirality of the crystal environment and owes not to the presence of the chiral *sec*-butyl group was also established. The enantiomeric methyl ester monomer (*S*)-(+)-*21* is dimorphic. Form one is light stable whereas form two is photoactive yielding dimers **22** and **23** (Figure 9). Although the monomer crystal is chiral, the irradiation product, after removal of the *sec*-butyl group, turns out to be racemic. This is explained in terms of the crystal packing of monomer in which the monomers are related by a pseudocenter of inversion (pseudo $P2_1/a$). There is also an interesting observation that the crystals of racemates of both ethyl ester and methyl ester of benzene-1,4-diacrylate are isomorphous with their respective enantiomers. It has been estab-

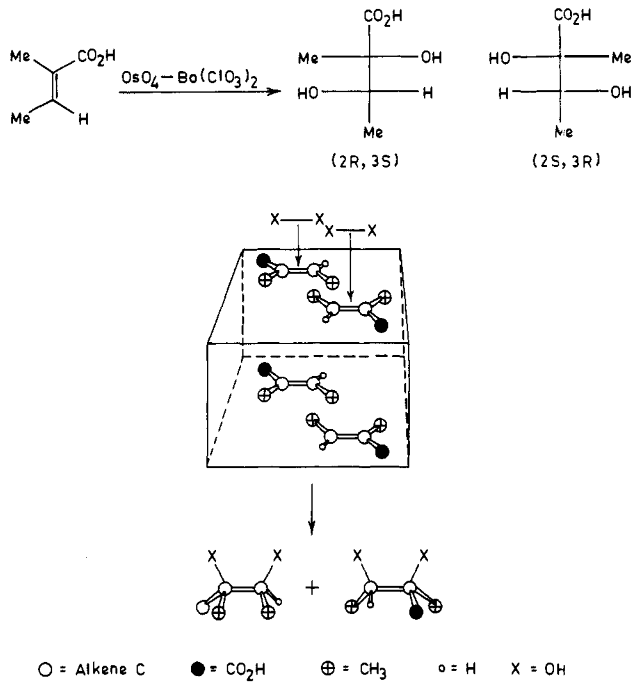


Figure 10. Hydroxylation of tigilic acid in the solid state.

lished that in the racemate of ethyl ester crystallizing in a chiral system, the (*R*)- and (*S*)-*sec*-butyl groups are disordered. The most important conclusion that may be drawn from these observations is that it is possible to synthesize optically active polymers and dimers from achiral monomer if and only if it crystallizes in a chiral space group and also with favorable intermolecular arrangements.

Although not a photoinduced reaction, the recent report of the asymmetric induction achieved by a nonchiral reactant on a nonchiral crystal deserves mention.[65,66] It was recognized that it is possible, under certain conditions, to achieve stereoselectively a chiral product from nonchiral reactants by using one surface of a single crystal as the chiral template. The conditions to be satisfied are (a) the projection of the crystal structure on the reacting surface must belong to one of the plane groups $P1$, $P2$, $P3$, $P4$, and $P6$, and (b) the molecules must be properly aligned with respect to the symmetry elements in the crystal. In their experiment, an aqueous solution of barium chlorate and osmium tetroxide was allowed to react on the $(\bar{2}10)$ and $(2\bar{1}0)$ planes (plane group $P2$) of large single crystals of tiglic acid (space group $P\bar{1}$). Enantiomeric diol (Figure 10) of high optical purity (95%) was isolated.

It may be observed that the creation of asymmetric molecules from achiral molecules in the crystalline state using the two entirely independent approaches are fascinating albeit each imposing certain stringent conditions to be taken into account. However, in light of the far reaching importance of this subject further intensive study is called for.

6. Competing Dimerization Reactions

A single molecule in the solid state can in principle undergo several different reactions to give more than one product. Although each one of these processes is expected to be governed by topochemical principles, it is important to establish the factors governing the competition between these reactions. It is well-known that in solution the competition between reactions is controlled by rate processes. Several examples of dimerization occurring in competition with topochemical polymerization and addition to different chromophores in the same molecule and addition giving several dimers have been reported. Although attempts have been made by Schmidt, the various factors controlling the competition between reactions in the solid state have not yet been firmly established. This is one area where additional input is necessary.

Irradiation of 2-furylacrylic acid in the solid state gives 40–50% dimer and an equal yield of low molecular weight polymer.[32] In the case of 2-thienylacrylic acid very small amounts of a polymer accompanies dimerization. It has been established through crystallographic investigations that packing arrangements in these two olefins control reaction types, namely, dimerization and polymerization. Schmidt attributes the small yield of oligomer in the case of 2-thienylacrylic acid, in spite of a favorable arrangement, to kinetic factors.

Photodimerization of dienes presents once again an interesting situation.[33,34] *trans,trans*-Muconic acid, its monomethyl ester, and cis,cis isomer, all of which crystallize in cells with shortest axes of 4 Å, react in the solid state upon photolysis. At room temperature all give vinyl substituted cyclobutanes of symmetry "*m*". The all trans acid and its monomethyl ester give, in addition to dimers, various amounts of oligomers. Monomethyl ester, interestingly, gives two dimers upon photolysis in the solid state (Scheme 4). Although the formation of all the products has been rationalized on the basis of the packing arrangement, no conclusions have been made regarding the factors controlling their competition. It is important to realize that Schmidt has indeed attempted to seek an answer to this problem during their studies on butadiene derivatives in the solid state.[34] Solid penta-1,3-diene-1-carboxylic acid, penta-1,3-diene-1-carboxamide, buta-1,3-diene-1,4-dicarbonitrile, styrylacrylic acid, its methyl ester, and amide all photodimerize on irradiation. The products are shown in Scheme 4. The cyclobutane derivatives obtained from these monomers are exactly accounted for by the topochemical rules (for the details the readers are referred to the original papers). The example of *trans,trans*-mucondinitrile is noteworthy from the topochemical and mechanistic points of view. The monomers are geometrically related in such a way that the distances between centers of nonequivalent and equivalent double bonds are 3.64 and 3.96 Å respectively. Reaction across the former leads to centrosymmetric products and to mirror symmetric cyclobutanes across the latter. Whether the predominent dimer always results from the shorter of the two different double bond contacts could not be confirmed.

Recent findings on etretinate (1)[35] and 7-chlorocoumarin[23] are noteworthy in this context (Schemes 5 and 7). Etretinate gives two dimers resulting from contacts between C_{13}–C_{14} and C_{11}'–C_{12}' and C_{13}–C_{14} and C_{10}–C_9' (~3.8 and ~4.4 Å, respectively). Interestingly, the yield of the products correlates with the distance of double bond separation; shorter distance favors dimerization. An observation on 7-chlorocoumarin suggests that such a correlation may not be valid under all circumstances. Irradiation of crystalline 7-chlorocoumarin yielded a single dimer (syn head–head). The

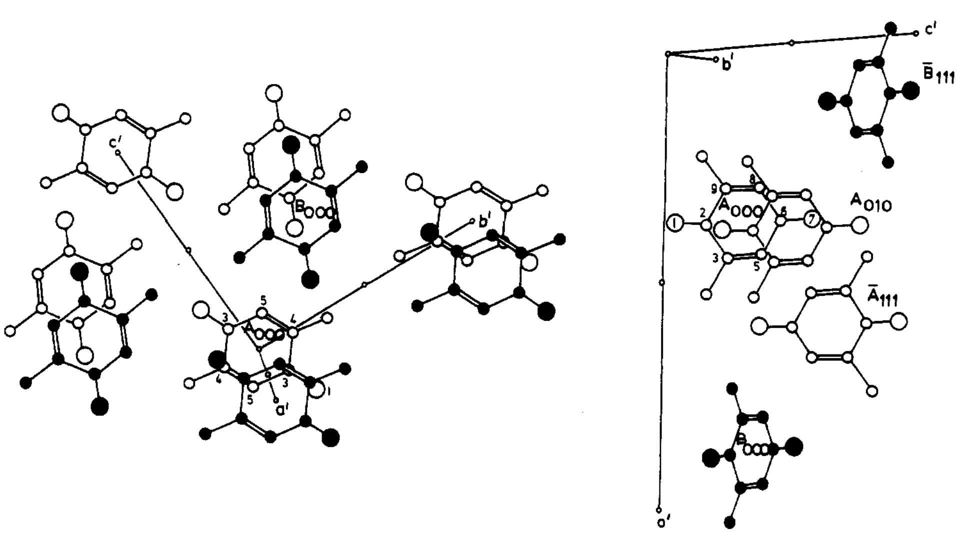


Figure 11. Packing arrangements of 2,5-dimethylbenzoquinone (a) and 2,6-dimethylbenzoquinone (b).

SCHEME 13

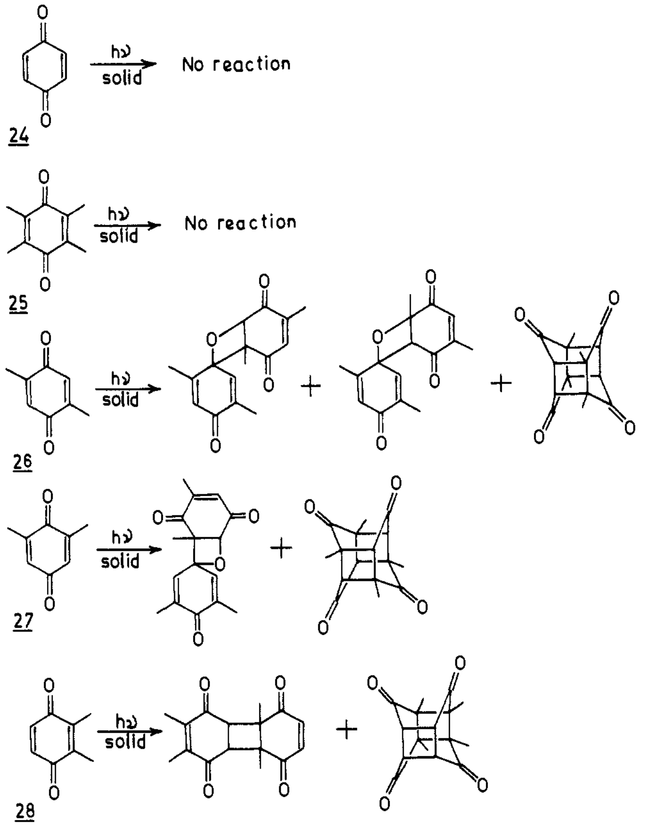


TABLE 4. Center-to-Center Contact Distance (<4.3 Å) of Double Bonds (C=C, C=O) and Corresponding Dimers

compd	double bonds	contact distance, Å
2,5-dimethyl-1,4-benzoquinone[a]	(1–3) A_{000}···(4–5) A_{100}	3.49
	(1–3) B_{000}···(4–5) B_{100}	3.62
	(1–3) B_{000}···(5′–4) B_{100}	3.75
	(2–3) A_{000}···(2–3) A_{100}	4.01
	(2–3) B_{000}···(2–3) B_{100}	4.01
	(2–3) A_{000}···(2′–3′) A_{100}	4.03
2,6-dimethyl-1,4-benzoquinone[a]	(3–5) A_{000}···(1–2) A_{010}	3.66
	(7–6) A_{000}···(8–9) A_{010}	3.70
	(9–8) A_{010}···(1–2) A_{010}	3.85
	(7–6) A_{000}···(5–3) A_{010}	3.88
	(4–8) A_{000}···(9–8) A_{010}	3.98
	(3–5) A_{000}···(3–5) A_{010}	3.98
	(7–6) A_{000}···(9–8) B_{001}	4.12
	(3–5) A_{000}···(7–6) A_{101}	4.12
	(3–5) A_{000}···(7–6) A_{111}	4.24

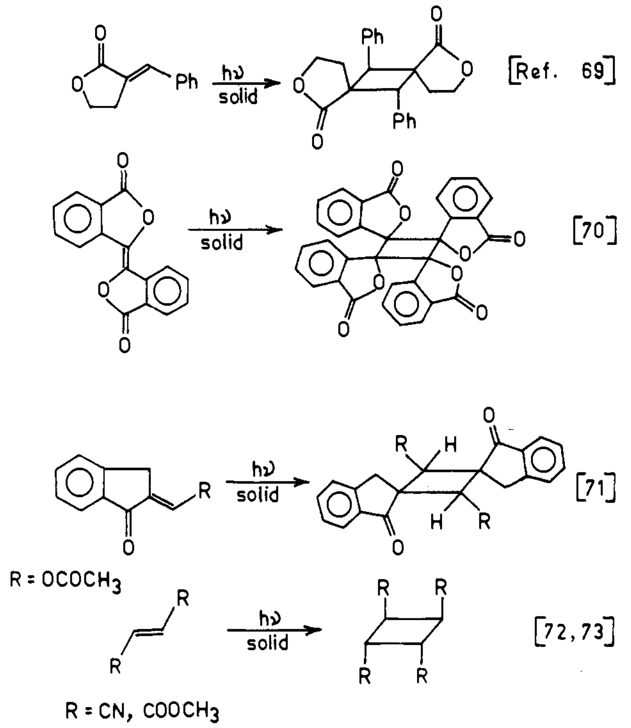
[a] See Figure 11 for atom numbering

packing arrangement reveals that the two potentially reactive 7-chlorocoumarin molecules are separated by 4.45 Å, this being the repeat along the *a*-axis. Further, the centrosymmetrically related double bonds are closer, the center-to-center distance between them being 4.12 Å. Translationally related coumarins are expected to give the syn head–head dimer and centrosymmetrically related coumarins are expected to give the anti head–tail dimer on UV excitation. The absence of reaction between centrosymmetrically related monomers in spite of the closer distance (4.12 Å) could be attributed to the influence of nearest neighbors, which is discussed at length in Section VI.

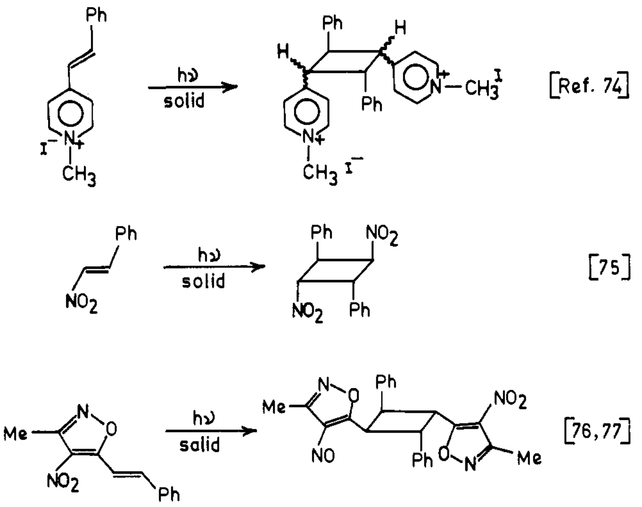
The power of topochemical principles is indeed impressive when they are applied to the solid-state photochemistry of quinones. As illustrated in Scheme 13, quinones **24** and **25** are photoinert in the solid state whereas **26**, **27**, and **28** give a large number of products resulting from dimerization.[67,68] Addition of the C=C double bond to both C=C and C=O is observed. The absence of short parallel contacts in **24** and **25** may account for the inability of these two quinones to yield dimers. The structures of the dimers (cyclobutanes and oxetanes) resulting from **26** and **27** can be related to the packing geometry in the monomer crystals, of parallel double bonds (C=C, C=O) with center-to-center distances up to 4.3 Å. The packing arrangements for 2,5-dimethylbenzoquinone and 2,6-dimethylbenzoquinone and the short contacts between reactive centers are shown in Figure 11 and Table 4, respectively. Once again no correlation could be drawn between the center-to-center distance and the yield of various products.

Thus it is clear from the examples presented above that when there is more than one possible reaction in the solid state, all can occur if they are topochemically allowed. However, at this stage, one cannot make an apriori prediction regarding the extent of feasibility based on the geometrical factors alone. Obviously the surroundings should be among the dominant factors in curtailing the reactivity and controlling competing reactions.

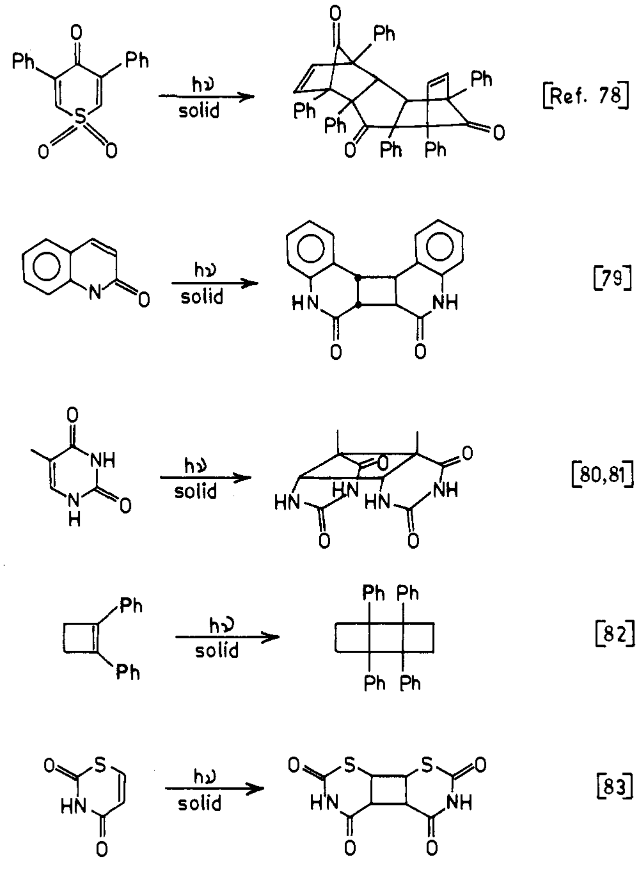
SCHEME 14



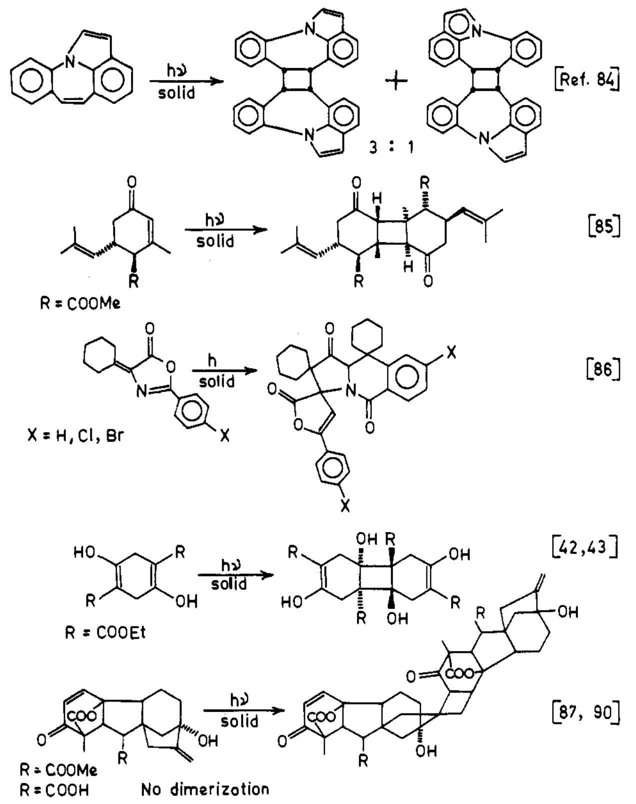
SCHEME 15



SCHEME 16



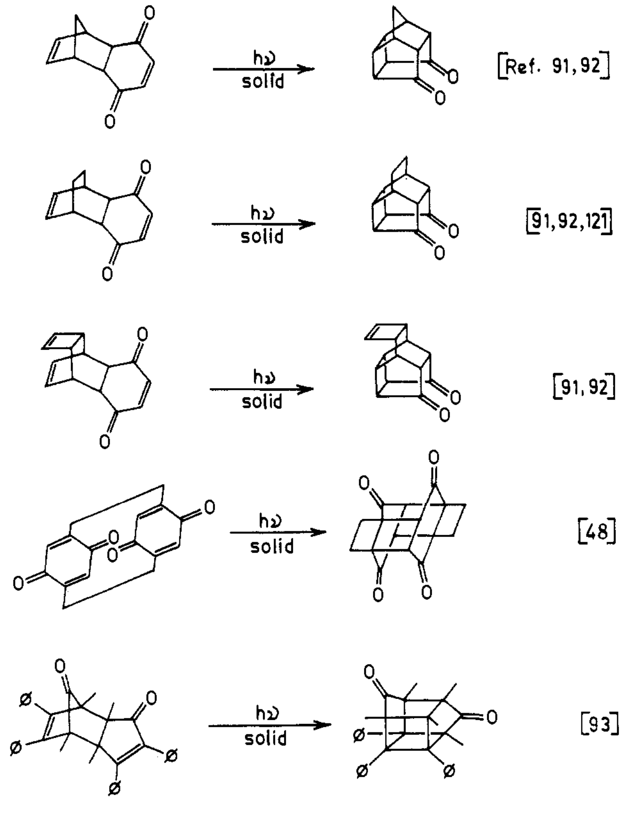
SCHEME 17



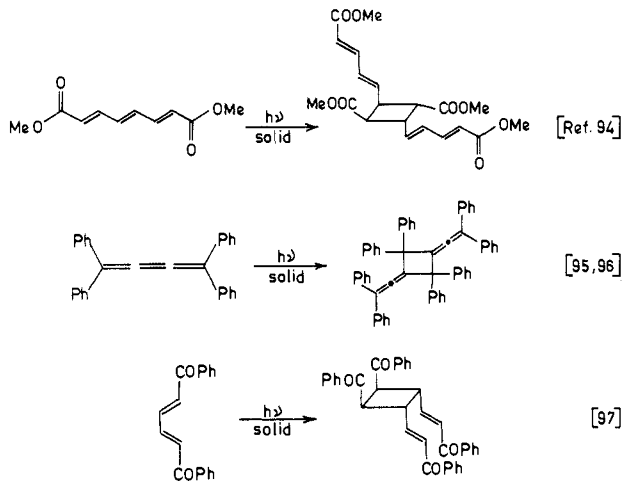
7. *Miscellaneous Dimerization Reactions*

As mentioned earlier there are a large number of examples of dimerization of molecules in the solid state. Most of them do not contain crystallographic details, often these form part of other investigations. We have summarized most of them in the form of schemes in the hope that some of these systems would attract considerable attention for in-depth studies. Dimerization of olefins which generally undergo isomerization in solution are summarized in Schemes 14 and 15. Similar dimerization of nonisomerizable olefins are summarized in Scheme 16. Several natural products and more complex olefinic systems are also reported to dimerize in the solid state (Scheme 17). Intramolecular cycloadditions are known (Scheme 18). Dimerization of dienes and other cumulenes have also been reported (Scheme 19). Some of these molecules have attracted attention in connection with photochromism. Known [4 + 4] dimerization reactions are summarized in Scheme 20. Dimerizations of imines have also been reported, and the products are dependent on the substitution (Scheme 21).[102,103] In addition to these, dimerizations of a few other molecules are also known.[104-111]

SCHEME 18

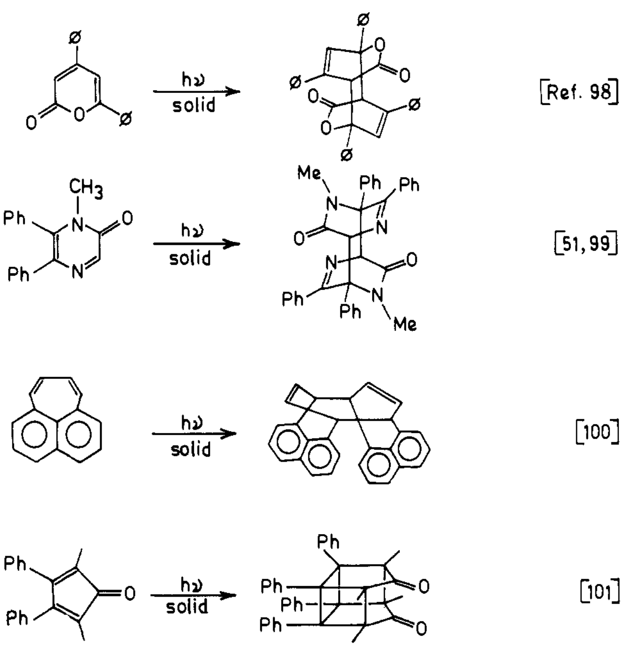


SCHEME 19

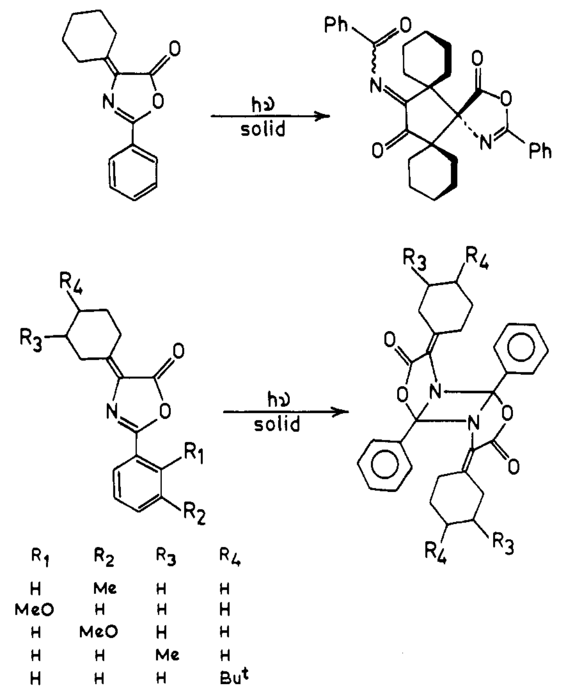


Nakanishi et al. have reported an unusual phenomenon, namely solvent incorporation during photodimerization of a few cinnamic acids.[112-114] They found that a water molecule is incorporated into the dimer when p-formylcinnamic acid was irradiated as suspensions in water or in a humid atmosphere. Similar incorporation of hydrocarbon solvents into the dimer was observed when these crystals were irradiated as suspensions in hexane etc. The mechanism of this reaction is not clear. Although the authors claim that the dimerization does not originate from the dissolved cinnamic acids, in the solvent used for suspension, it needs further attention.

SCHEME 20



SCHEME 21

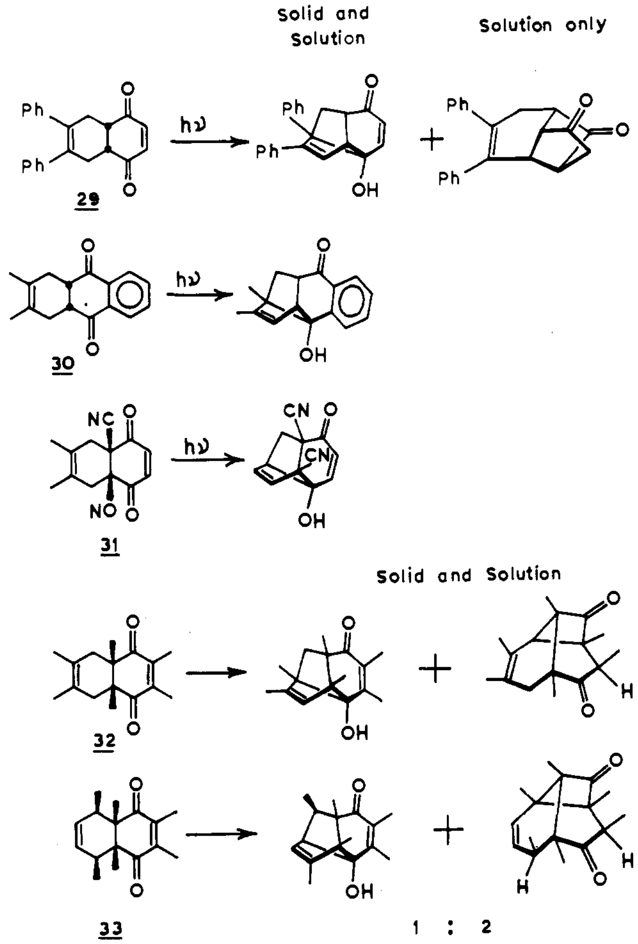


R_1	R_2	R_3	R_4
H	Me	H	H
MeO	H	H	H
H	MeO	H	H
H	H	Me	H
H	H	H	Bu^t

III. Topochemical Postulate and Unimolecular Transformations

The correlation of solid state chemical reactivity with X-ray crystal structure data has provided a valuable insight into dimerization reactions. It is now well established that the intermolecular arrangements play an important role in controlling solid-state bimolecular reactions. On the other hand, for unimolecular reactions such as intramolecular hydrogen abstraction, electrocyclization, and fragmentation reactions the intermolecular arrangement is expected to play only a secondary role. For such reactions the intramolecular geometrical considerations play a decisive role in controlling the course of the reaction. In other words, the conformation adopted by the molecule in the solid state will determine the reactivity pattern. In this section we highlight the role of packing arrangements in controlling the solid-state behavior of organic molecules with respect to unimolecular reactions.

SCHEME 22



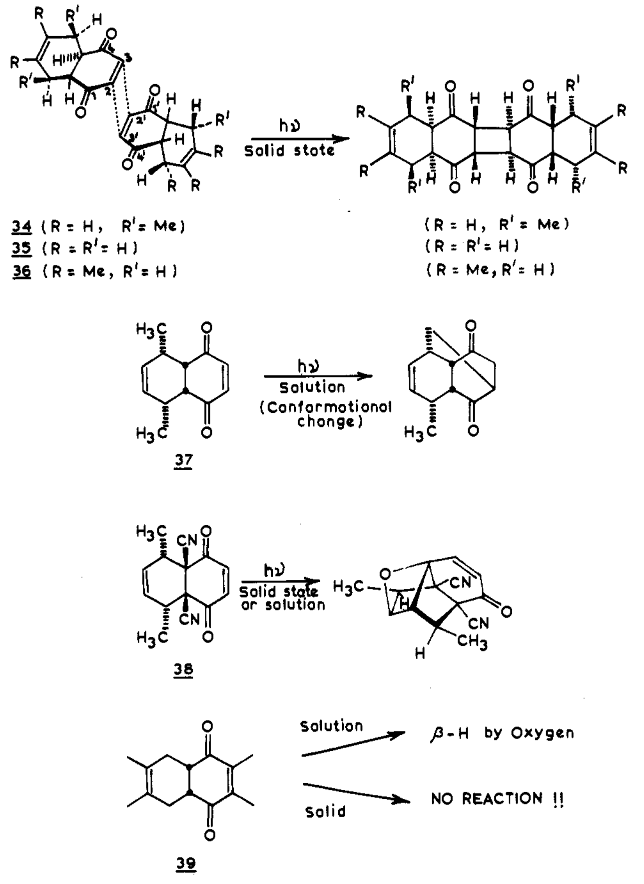
A. Intramolecular Hydrogen Abstraction Reactions

Scheffer, Trotter, and co-workers have recently elucidated how the ground-state conformations influence the excited-state behavior of tetrahydronaphthoquinones and their derivatives in the solid state.[115] These studies are concerned with the solid-state structure–reactivity relationships in a class of organic reactions not yet well examined, namely, those involving intramolecular photochemical hydrogen abstractions. Following these pioneering contributions, work related to intramolecular hydrogen abstraction in the case of arylalkyl ketones and aromatic nitro compounds have appeared in the literature. In general, all these studies are aimed at answering the following questions about the factors which influence photochemical intramolecular hydrogen abstraction: (1) Over what distances can abstraction occur? (2) What is the preferred geometry for abstraction? (3) Can abstraction be facilitated relative to the competing processes by freezing a reactant molecule in a particular conformation in the solid state? (4) Will the products of such reactions in the solid state differ in type or amount from those obtained in solution due to crystal packing? A knowledge of such information is expected to pave the way towards "crystal engineering" in unimolecular reactions.

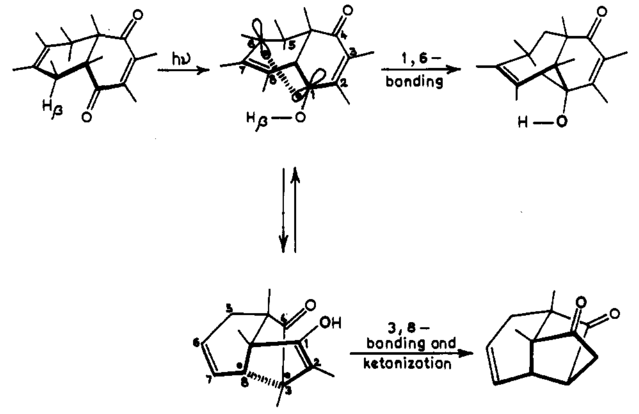
1. Tetrahydronaphthoquinones

Photolysis of *cis*-4a,5,8,8a-tetrahydro-1,4-naphthoquinone derivatives yields a plethora of products. Impressive differences in the nature and yield of the products were noticed between the solution and solid state irradiations and these are summarized in Schemes 22 and 23. The mechanism of formation of these products can be understood on the basis of three primary reactions namely, β-H abstraction by the carbonyl oxygen, γ-H abstraction by the enone double bond, and inter- and intramolecular cycloadditions.

SCHEME 23



SCHEME 24



For tetrahydronaphthoquinones **29–31** photolysis generates enone alcohols in the solid state and in solution, and for **29** an additional photoproduct is isolated from the solution irradiation.[116,117] The formation of these products can be rationalized on the basis of β-hydrogen abstraction by the carbonyl oxygen to form a biradical (Scheme 24). According to X-ray crystal structure analyses of **29–31**, H_β is in a favorable position to be abstracted by the carbonyl oxygen attached to C_1. Table 5 lists the H_β to oxygen distances for these com-

TABLE 5. Parameters Relevant to β and γ-Hydrogen Abstraction by Oxygen in the Tetrahydronaphthoquinones

(a) compd[a,c]	$H_\beta \cdots O$, Å	τ, deg	Δ_o, deg	C(1)···C(6), Å
29	2.46	3	81.3	3.51
30	2.57	5	80.7	3.46
31	2.58	8	83.6	3.38
32	2.47	0	85.1	3.35
33	2.26	1	86.4	3.33
ideal values	2.72	0	90	3.40

(b) compd[a]	$H \cdots C$, Å	τ_c, deg	Δ_c, deg	C(3)···C(5), Å
32	2.80	52	72.6	3.17
33	2.66	50	74.4	3.17
ideal values	2.90	45	90	3.40

(c) compd[b,c]	$H \cdots O$, Å	$H_\beta \cdots O$, Å	τ_0, deg	Δ_o, deg	intermolecular C_2–C_3 double-bond separation
34	2.38		15	101.4	4.04
		2.49	4	80.8	5.27
35		2.42	3	79.5	3.76

[a] See Scheme 22 for structures of compounds. [b] See Scheme 23 for structures of compounds. [c] See Figure 12 for definition of geometrical parameters.

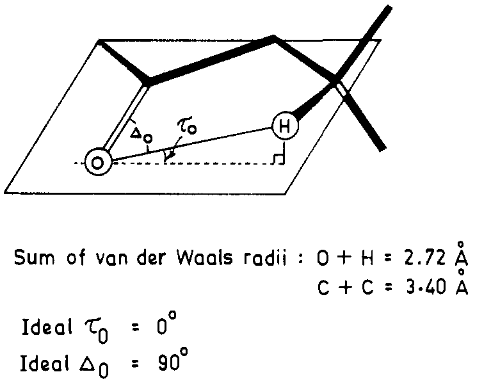
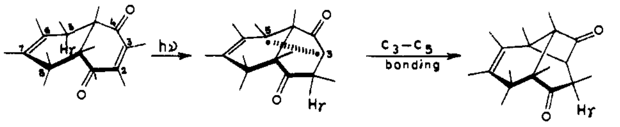


Figure 12. Definition of angles τ_0 and Δ_0 during intramolecular hydrogen abstraction by naphthoquinone.

pounds; they range from 2.26 to 2.58 Å. Also included in Table 5 are the values of τ_o and $\Delta_o \cdot \tau_o$ is the angle subtended by the oxygen to H_β vector and its projection on the plane of the C_1 carbonyl group. Δ_o is defined as the angle formed between the carbonyl carbon, the carbonyl oxygen, and the hydrogen being abstracted (Figure 12). The ideal geometry for H_β abstraction by the carbonyl oxygen ($n\pi^*$) would have a short $H_\beta \cdots O$ distance, with the C(8)–H bond in the plane of the carbonyl group, with $C_1{=}O \cdots H = 90°$. Perusal of Table 5 reveals that the $H_\beta \cdots O$ distances are shorter than the van der Waals distance of 2.72 Å, τ_o angles are 3–8° and Δ_o angles 80.7–83.6°, close to the ideal values of 0° and 90°, respectively. The biradical formed by the hydrogen abstraction process is expected to have a conformation very similar to that of the ground-state precursor, which is favorable for bonding of C_1 and C_6 to yield the final product. Therefore, X-ray structural analyses indicate that the molecular geometries are favorable for H_β abstraction by the oxygen, and subsequent C_1–C_6 bond formation to yield the enone alcohol. The formation of an additional solution product in the case of **29** is topochemically forbidden in the solid state, since the conformational changes required for its formation are prevented by the constraints of the crystal lattice (Scheme 24).

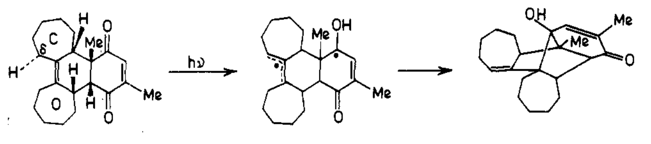
SCHEME 25



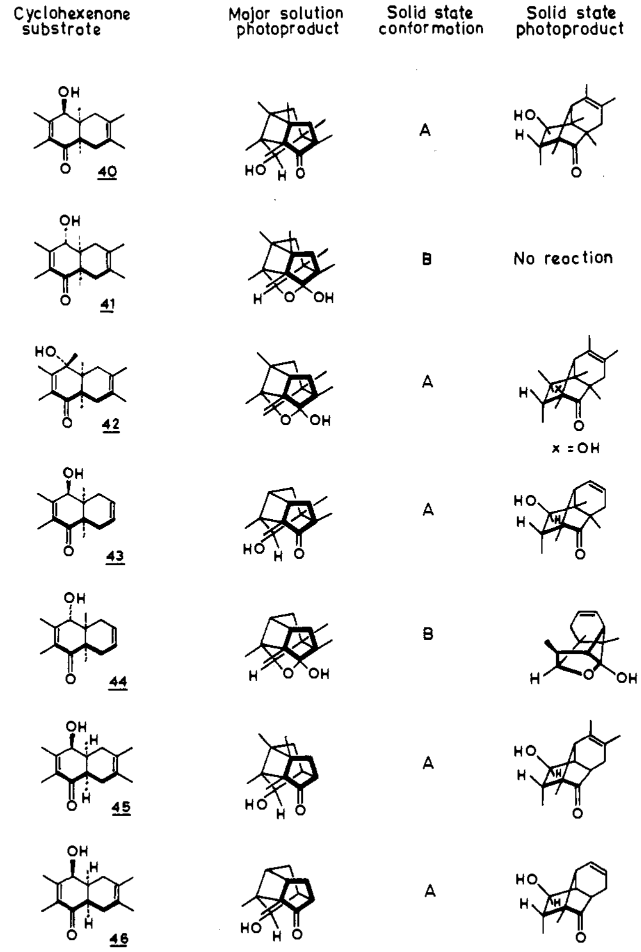
Naphthoquinones **32** and **33** give similar enone alcohols and in addition cyclobutanone products (Scheme 22). The proposed mechanism for the formation of cyclobutanone products involves γ-hydrogen abstraction by the enone carbon (Scheme 25) followed by C_3–C_5 bond formation. The geometrical parameters required for the mechanistic analyses are given in Table 5. It is evident that the $H_\gamma \cdots C_2$ and $C_3 \cdots C_5$ distances are less than the van der Waals distances of 2.90 and 3.40 Å and the τ_c and Δ_c are not far from ideal. Thus, the conformations of the molecules **32**, and **33** are well suited for the formation of the cyclobutanone products. The lack of cyclobutanone formation in the photochemistry of **29**–**31** may not be solely due to the unfavorable geometrical parameters for the hydrogen abstraction by carbon. The differences in the $H \cdots C_2$ distances are small (**29**, 2.97; **30**, 3.09; **31**, 2.86 Å; the sum of van der Waals radii is 2.90 Å). The differences in the nature of the reactive excited state between **29**–**31** and **32** and **33** may also contribute towards this unusual behavior. The above studies have thus established that the distances over which abstraction can occur range from 2.26–2.58 Å for abstraction by oxygen and 2.66–2.89 Å for abstraction by carbon.

Three of the 1,4-naphthoquinones investigated undergo *intermolecular* ene–dione double bond [2 + 2] dimerization upon photolysis in the solid state. These are **34**–**36** (Scheme 23). In solution, all of these undergo intramolecular hydrogen abstraction. The question whether the reactivity difference was due primarily to a solid-state conformation which is unfavorable for intramolecular hydrogen abstraction or to a particularly favorable intermolecular crystal packing arrangement for dimerization has once again been resolved through X-ray structural studies. Overall, the compounds **34** and **35** possessed the same "twist" conformation common to **29**–**33**. It is obvious from Table 5 that the geometrical parameters for hydrogen abstraction by oxygen in the case of **34** and **35** are well within the guidelines discussed above. However, the major crystallographic difference between the substrates **34** and **35** on one hand and **29**–**33** on the other was the presence

SCHEME 26



SCHEME 27

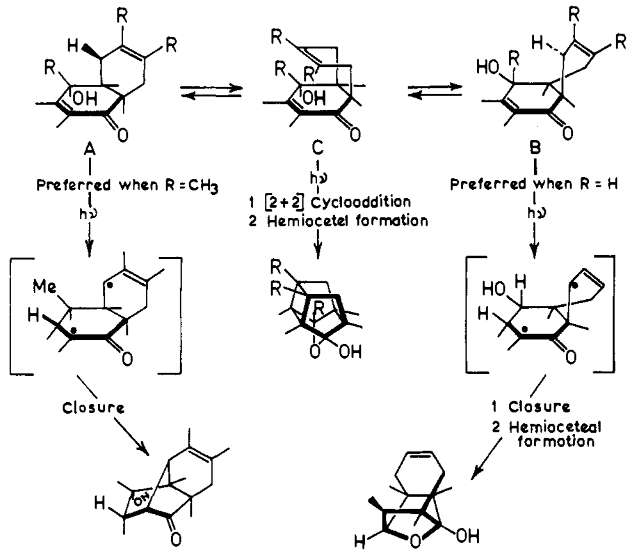


of a particularly close and parallel approach of the C_2–C_3 double bond of the neighboring molecules (**34**, 4.04 Å; **35**, 3.76 Å). Thus, it is clear that the deciding factor favoring the solid state photodimerization over the intramolecular hydrogen abstraction is the close and geometrically favorable approach of the reacting double bonds.

An example is also available where intramolecular cycloaddition occurs to yield an oxetane.[117] In this case (**38**), the crystal structure neither favors the intramolecular hydrogen abstraction nor the intermolecular dimerization. Under these conditions the geometrically feasible but least favored oxetane formation occurs. Finally, the 2,3,6,7-tetramethyl derivative **39** is unusual in that no reaction occurs upon irradiation in the solid state, while in solution the usual photoproducts due to the β-hydrogen abstraction by oxygen are obtained. The lack of reactivity in the solid state in spite of the favorable geometrical parameters is indeed intriguing. Very recently, Mandelbaum[118] et al. have reported the photorearrangement of bicyclohept-1-en-1-yl-*p*-benzoquinone in the solid state. The product of the rearrangement and the proposed mechanism are illustrated in Scheme 26.

The factors governing the hierarchy of reactions in

SCHEME 28



the solid state need further study. For example, while the naphthaquinones **29–31** have molecular structures favorable for both β-H abstraction by the carbonyl oxygens and γ-H abstraction by the enone double bonds, only the former occurs. While the naphthoquinones **34** and **35** have arrangements conducive for both intermolecular dimerization and intramolecular hydrogen abstraction, only the dimerization takes place. Furthermore, **39** is inert although intramolecular hydrogen abstraction is expected according to X-ray structural analysis. Two questions need to be answered under these circumstances: (a) whether the nature of the reactive excited state (nπ* or ππ*) is altered by the substituent and (b) whether the arrangement of molecules immediately surrounding the reactive center play a significant role in limiting the reaction.

2. *Tetrahydronaphthoquinols*[120-122]

Irradiation of naphthoquinols in solution yields products derived from the intramolecular [2 + 2] cycloaddition (Scheme 27). On the other hand, entirely different products are obtained upon photolysis in the solid state. Three different types of photoproducts are obtained (Scheme 27). These derive from hydrogen abstractions by the enone carbon and the carbonyl oxygen similar to the tetrahydroquinones discussed above. X-ray crystal structure studies have led to an understanding of the mechanism by which these products are formed and also provide an answer to the absence of formation of intramolecular [2 + 2] adducts in the solid state.

The tetrahydronaphthoquinols can exist, in two low-energy conformations as illustrated in Scheme 28. They can be interconverted by ring flipping involving a higher energy conformer. The X-ray data of **40–46** revealed that these molecules adopt either one of the low-energy conformations (A or B, Figure 13) in the solid state and the preferred conformation is determined by the nature of the substituent at C_4 and by the relative configuration at this center. The preferred conformations for **40–46** are given in Scheme 17. The X-ray crystal structure data clearly indicate that [2 + 2] photocycloaddition should be topochemically forbidden in the solid state, the double bond separation

TABLE 6. Geometrical Parameters Relevant to the Photochemical Reactons of the Tetrahydro-1-naphthoquinols

compd[a]	H(5)···C(3), Å	τ_c, deg	Δ_c, deg	$C_2 \cdots C_5$, Å
40	2.72	53.2	78.5	3.30
41	2.72	53.0	78.5	3.30
	[H(8)···C(3) = 2.92]	[τ_o = 49]	[Δ_o = 75.2]	[C(2)···C(8) = 3.23]
42	2.81	50.0	78.3	3.35
43	2.78	51.9	77.5	3.30
44	2.78	52.0	77.5	3.30
	[H(8)···C(3) = 2.85]	[τ_o = 51]	[Δ_o = 71.6]	[C(2)···C(8) = 3.17]
45	2.84	53.5	79.0	2.84
46	2.84	54.1	79.7	3.42
47	2.81	55.7		3.39
	[O(1)···H_b = 2.49]	[τ_0 = 0.6°]		[C(1)···C(6) = 3.40]
48	2.82	56.7		3.35
	[O(1)···H_b = 2.49]	[τ_o = 4.0°]		[C(1)···C(6) = 3.41]

[a] See Schemes 27 and 29 for structures of compounds. [b] See Figure 11 for definition of geometrical parameters.

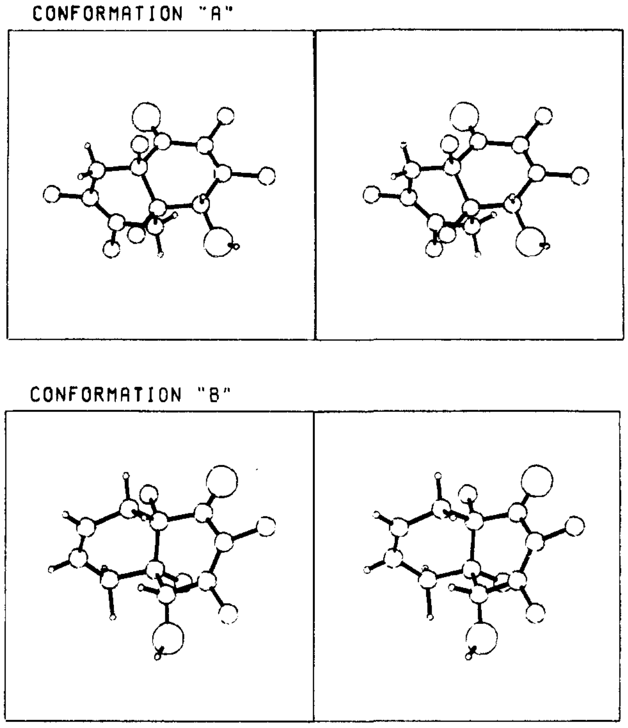


Figure 13. Stereodrawing of conformation A (a) and conformation B (b) in the case of tetrahydronaphthoquinols.

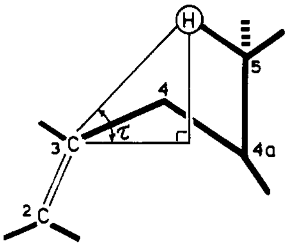


Figure 14. Definition of geometrical parameters during hydrogen abstraction by the olefinic carbon in tetrahydronaphthoquinols.

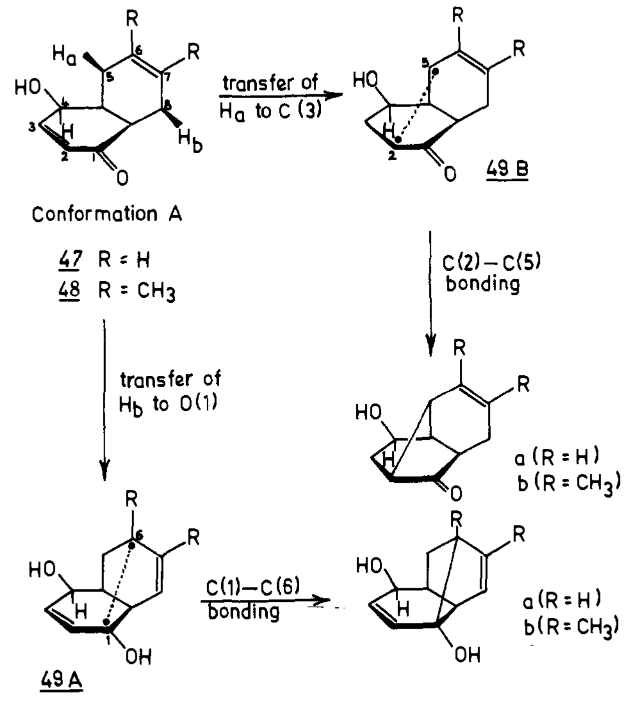
being >4.4 Å and nonparallel. Thus, it is apparent why molecules **40–46** fail to undergo intramolecular photocycloaddition in the solid state although this is preferred in solution. In solution, where the conformational equilibrium is facile, rapid [2 + 2] photocycloaddition occurs via the minor higher energy conformers.

The majority of the solid state photoreactions of tetrahydronaphthoquinols proceed via an initial hydrogen abstraction by the enone carbon C_3. The hydrogen that is abstracted is from either C_5 or C_8. The resulting biradicals then collapse by the formation of either the C_2–C_5 or the C_2–C_8 bond (Scheme 28). Interestingly, 4α-ol or anti series (4α-ol anti or trans to the 4β bridgehead substituents) which crystallize in conformation A give products derived from the C_3–H_5 abstraction while 4β-ol or syn series which crystallize in conformation B yield products via the C_3–H_8 abstraction (Scheme 27). These are indeed expected on the basis of the closeness of the reactive centers in these conformations. Molecules crystallizing in conformation A are well suited to undergo one more reaction, namely, H_8 abstraction by the carbonyl oxygen similar to the β-H abstraction by the carbonyl in the case of the naphthoquinones. The geometries for such a process are favorable for all the members of the anti series.

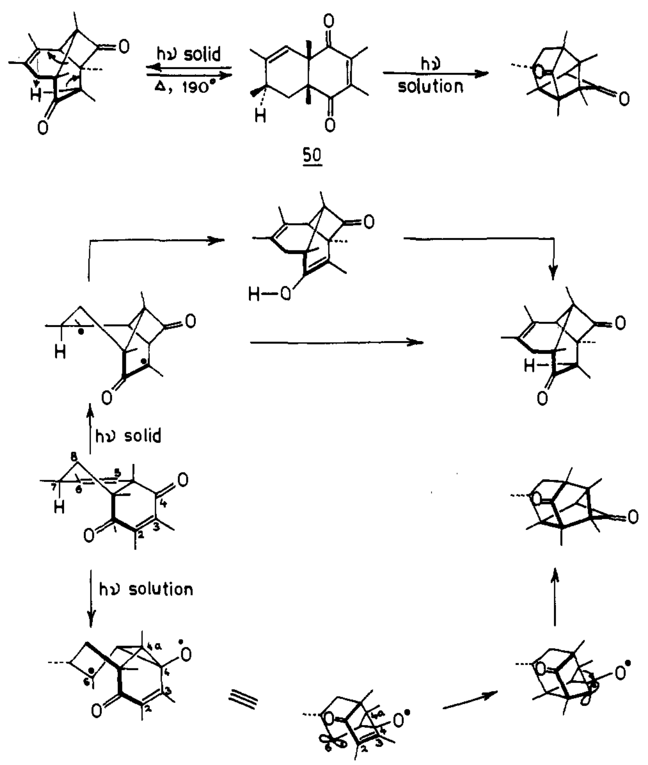
Table 6 lists the relevant geometrical parameters for hydrogen abstraction for all the nine compounds. The important parameters are similar to those discussed for the naphthoquinones: $H \cdots C_3$, τ_c, Δ_c, and $C_2 \cdots C_n$ (Figure 14). For the anti series, the $H_5 \cdots C_3$ distances are well within the van der Waals separation of 2.90 Å and are in the range 2.72–2.84 Å. τ_c and Δ_c are reasonably close to the ideal values of 90°, respectively, $\tau_c \simeq$ 52–57° and $\Delta_c \simeq$ 77.5–82.2°. Furthermore, the $C_2 \cdots C_5$ distances are close to the normal van der Waals separation. Thus, the formation of products via C_3–H_5 abstraction is topochemically expected indeed.

A striking aspect of the solid state photobehavior of the anti series is that only two members undergo carbonyl···hydrogen abstraction, although all would be expected to do so based on the geometrical factors (Scheme 29). This clearly illustrates that the examination of the crystal structure parameters alone will not provide an answer to all the reactivity problems. Based on the temperature-dependent photochemistry of **47**, the difference in behavior between **47**,**48**, and the other members of the anti series is attributed to the difference in nature of the reactive excited state.[123] It is suggested that the carbon···hydrogen abstraction occurs from a $\pi\pi^{*3}$ state and the oxygen···hydrogen abstraction from a $n\pi^{*3}$. The solid-state results are interpreted as being due to competing reactions from the $n\pi^{*3}$ and $\pi\pi^{*3}$ states, probably existing in equilibrium. Different activation energies for hydrogen abstractions from these states are suggested as the source of the product ratio changes with temperature. It is further noted that methyl substitution on the enone double bond stabilizes the $\pi\pi^{*3}$ state relative to the $n\pi^{*3}$ state. The question whether the surroundings influence the product selectivity is yet to be examined.

SCHEME 29



SCHEME 30



Two examples of the 4β-ol or syn series crystallizing in conformation B have been reported.[121] Of these one, namely, **41** does not react in the solid state. It is interesting to note that in this case, the $C_3 \cdots H_8$ distance of 2.92 Å is just outside the limit of the van der Waals sum (2.90 Å). The absence of reaction in **41** is ascribed to this long hydrogen abstraction distance and the steric compression (to be discussed in section VI) which would accompany abstraction. The molecule **44** upon photolysis in the solid state yields a product resulting from the $C_3 \cdots H_8$ abstraction (Scheme 27). The X-ray structural studies also support this observation. The appropriate geometrical parameters are favorable (2.85 Å; τ, 50°; Δ, 71.6 Å; $C_3 \cdots C_8$, 3.17 Å).

The studies of the solid-state photobehavior of tetrahydronaphthoquinones and quinols represent a very fruitful combination of the techniques of X-ray crystallography and organic photochemistry. In addition to providing information regarding the required geometries for hydrogen abstraction by the carbonyl ($n\pi^{*3}$) and olefinic bond of the enone ($\pi\pi^{*3}$), this study has clearly brought out the utility of controlling the conformation of molecules in achieving selectivity in organic reactions. The concept of "crystal engineering" in these systems means the ability to predict the conformation of a prescribed molecule in the solid state. This has become possible and a few successful examples are also reported.[122,124]

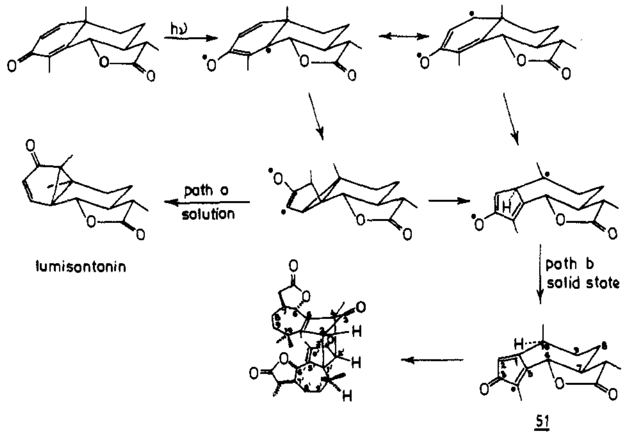
3. *β, γ-Unsaturated Ketones*[125]

Yet another elegant example of crystal lattice effects on organic reactions has been reported by Scheffer and Trotter. As shown in Scheme 30, the β,γ-unsaturated ketone **50** yields different products in solution and in the solid state upon photolysis. The X-ray structural data suggest that the formation of the solid-state product can arise either from C_7–hydrogen abstraction by oxygen or through C_5–C_3 bonding. The geometrical parameters for hydrogen abstraction (oxygen···hydrogen distance, 2.64 Å; τ, 28.5°; Δ, 84.7°) are very similar to the values discussed earlier. Furthermore, the feasibility of formation of the biradical via C_3–C_5 bonding is indicated by the fact that the p orbitals at C_3 and C_5 extend toward one another with an internuclear distance of 3.12 Å (van der Waals sum: 3.40 Å). Between the two processes, the latter is suggested to be more probable. The simplest explanation for the differences in reactivity, originating from a common $\pi\pi^{*3}$ excited state, between solution and solid state appears to be that in the solid state, the crystal lattice effects do not permit the relatively greater atomic and molecular motion necessary for the formation of the normally favored solution photoproduct, the result being an alternate unimolecular process involving much less atomic and molecular movement predominating.

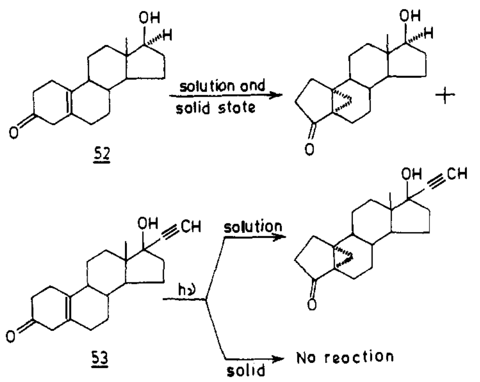
One of the earliest reported examples of rearrangement in the solid state is that due to Matsuura and co-workers on santonin.[126] Unfortunately no structural details are available to correlate the reactivity in the solid state. In benzene santonin yields lumisantonin upon irradiation whereas irradiation of crystals of santonin afforded three dimers, lumisantonin, and a new photoisomer (Scheme 31). The structure of the dimer obtained in largest amount has been determined. It has been speculated that the highly selective transformation of santonin to **51** in the solid state may be due to the larger movements associated with the formation of lumisantonin, the normal solution product.

Recently the photobehavior of two steroidal ketones in the solid state has been reported.[127] Photolysis of β,γ-unsaturated ketones usually results in a 1,3-acyl shift to form a new β,γ-unsaturated ketone or a 1,2-acyl shift to give a conjugated cyclopropyl ketone. As illustrated in Scheme 32, irradiation of the β,γ-unsaturated keto steroid **52** in solution as well as in solid state yields the same products. However, closely analogous

SCHEME 31



SCHEME 32



53 reacts only in solution and is inert in the solid state to UV radiation. Based on the reported structures of 52 and 53 the above variation in the behavior of the two closely similar molecules can be understood.[128,129] Packing arrangements and molecular conformations of 52 and 53 in the crystal are provided in Figures 15 and 16 respectively.

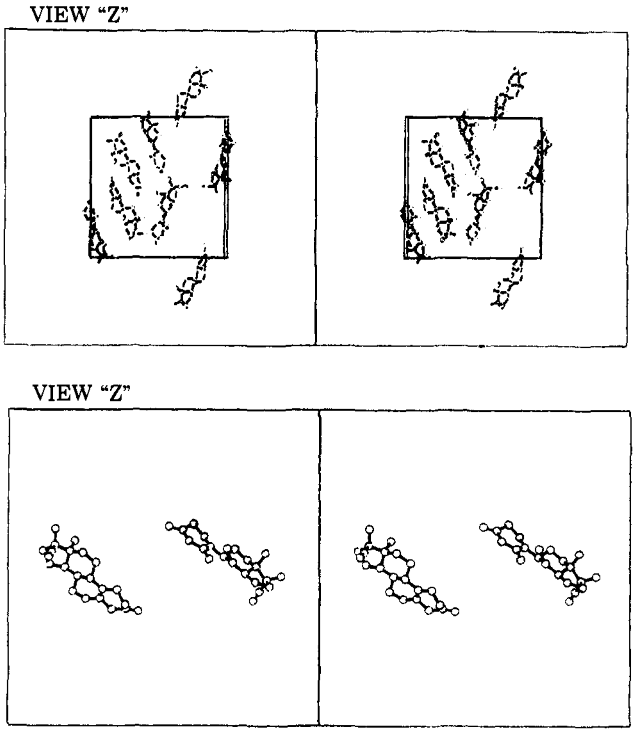


Figure 15. Stereoview of the unit cell packing in β,γ-unsaturated ketone **52**.

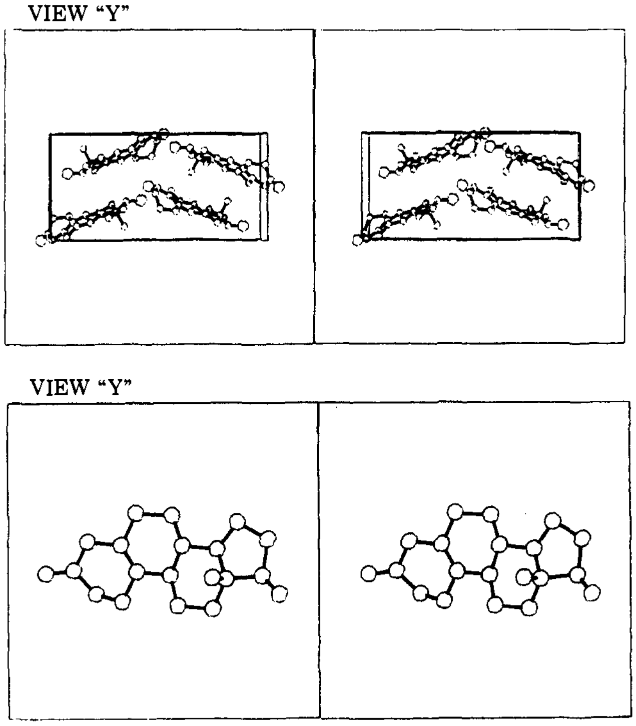


Figure 16. Stereoview of the unit cell packing in β,γ-unsaturated ketone **53**.

4. *Aryl Ketones*[130-138]

The light-induced cleavage and cyclization of organic carbonyl compounds possessing favorably oriented γ-hydrogens, termed the Norrish type II reaction, is one of the most well-studied and important photoreactions. The reaction takes place in solution, the vapor phase, and in various organized media. In spite of enormous interest in the mechanistic and synthetic aspects of this process, only a very few reports have been concerned with the γ-hydrogen abstraction reaction in the solid state. Reported examples along with solution results for comparison are summarized in Schemes 33–35. Of these only *N*,*N*-dialkyl oxo amides show remarkable selectivity in the product distribution in the solid state in comparison with that in solution.[130] In general, all other reported ketones show no significant variation in their behavior between solution and solid state. However, correlation of structure with reactivity in these cases has provided vital information regarding the geometrical parameters for hydrogen abstraction reactions.

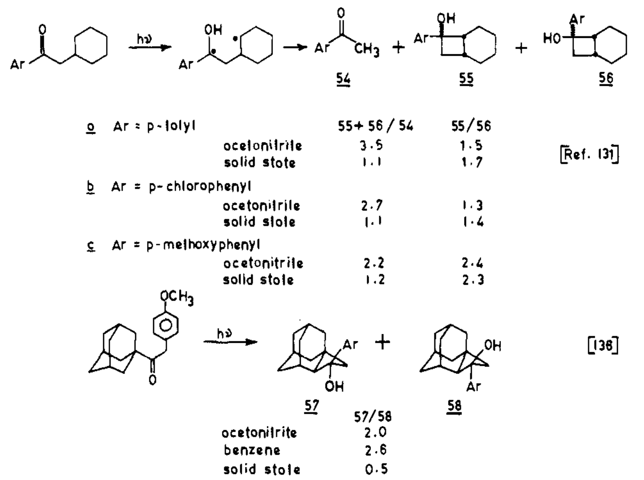
Detailed crystallographic data analysis on α-cyclohexylacetophenones[131] and *o*-*tert*-butylbenzophenone[132] have yielded useful information regarding the geometry required for γ-hydrogen abstraction by the $n\pi^*$ excited carbonyl chromophore. The geometrical parameters used in the analyses are the O···H distance and τ, which have previously been defined in the case of naphthoquinones and naphthoquinols. The data are summarized in Table 7. In the case of α-cyclohexylacetophenones, although both β- and γ-hydrogens are conveniently situated for hydrogen abstraction, products resulting from γ-hydrogen alone are obtained. In the case of *o*-*tert*-butylbenzophenone, although in principle nine hydrogens are available for abstraction, only two

TABLE 7. Geometrical Parameters[a] for the Hydrogen Abstraction in Aryl Ketones

compd	γ-Hydrogen				β-Hydrogen	
	O···H$_e$	τ_c, deg	O···H$_a$	τ_a, deg	O···H$_\beta$	τ_β, deg
α-cyclohexyl-*p*-methylacetophenone	2.60	49.6	3.83	38.4	2.57	6.8
α-cyclohexyl-*p*-chloroacetophenone	2.60	42.0	3.83	35.7	2.59	12.7
α-cyclohexyl-*p*-methoxyacetophenone	2.61	42.5	3.82	37.0	2.64	11.6

[a] See Figure 12 for definition of geometrical parameters.

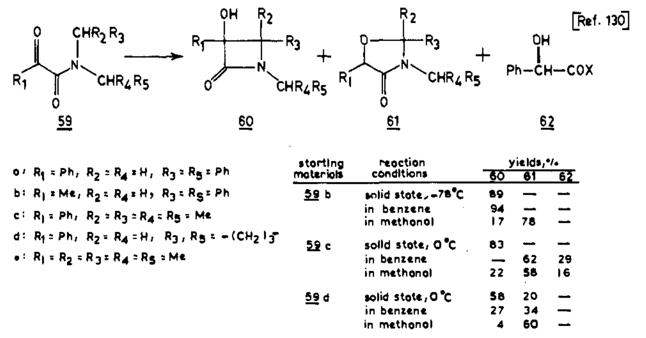
SCHEME 33



		55+56/54	55/56
a Ar = p-tolyl	acetonitrile	3.5	1.5
	solid state	1.1	1.7
b Ar = p-chlorophenyl	acetonitrile	2.7	1.3
	solid state	1.1	1.4
c Ar = p-methoxyphenyl	acetonitrile	2.2	2.4
	solid state	1.2	2.3

	57/58
acetonitrite	2.0
benzene	2.6
solid state	0.5

SCHEME 34



a: $R_1 = Ph$, $R_2 = R_4 = H$, $R_3 = R_5 = Ph$
b: $R_1 = Me$, $R_2 = R_4 = H$, $R_3 = R_5 = Ph$
c: $R_1 = Ph$, $R_2 = R_3 = R_4 = R_5 = Me$
d: $R_1 = Ph$, $R_2 = R_4 = H$, R_3, $R_5 = -(CH_2)_3-$
e: $R_1 = R_2 = R_3 = R_4 = R_5 = Me$

starting materials	reaction conditions	yields, %		
		60	61	62
59 b	solid state, −78 °C	89	—	—
	in benzene	94	—	—
	in methanol	17	78	—
59 c	solid state, 0 °C	83	—	—
	in benzene	—	62	29
	in methanol	22	58	16
59 d	solid state, 0 °C	58	20	—
	in benzene	27	34	—
	in methanol	4	60	—

are geometrically favorable for abstraction. In this case, it has not been possible to further narrow down the hydrogen being abstracted. The common features of all the above examples are that the O···H distances are well within the van der Waals sum of 2.72 Å and the abstracted hydrogens are ≃30–50° above the nodal plane of the carbonyl π system (τ). In the diketone 62 reported by Mohr,[133,134] four hydrogens are suitably located for abstraction by the two carbonyl chromophores (Figure 17). The product isolated can derive from any one of these abstractions although it has not been possible to identify which one is kinetically favored.

Thus, it is clear that a certain amount of deviation from the coplanar (τ = 0) hydrogen abstraction is tolerable in the solid state. It has been pointed out earlier[135] that coplanar hydrogen abstraction is not a strict requirement for the type II process and deviation as high as 60° (τ) would lower the rate only by a factor of four. Especially in the solid state wherein the triplet state may have a longer lifetime, abstraction reactions from nonideal geometries (probably with lower rates) can compete with the decay of the triplet. However, it is to be noted that thus generated diradicals may have a geometry different from that obtained in solution and their behavior will be dominated by the lattice effects.

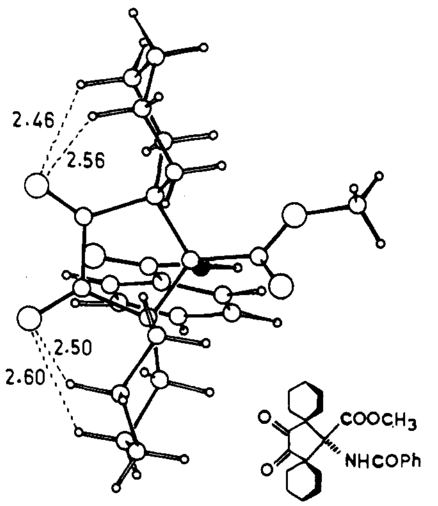
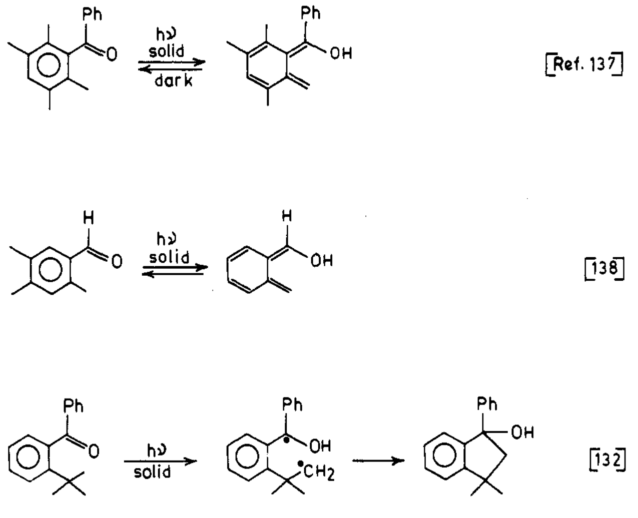


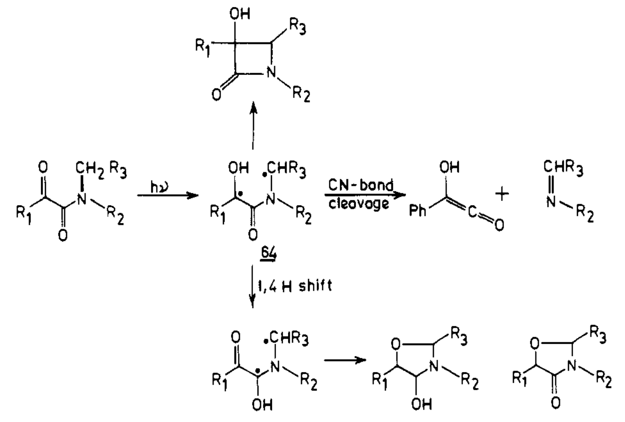
Figure 17. Molecular conformation highlighting the orientation of hydrogens for abstraction by carbonyl group in diketone 62.

SCHEME 35



As seen in Scheme 33, in the case of α-cyclohexylacetophenones, there is a small difference between the solid state and solution irradiations. The reduced amount of cyclization in the solid state has been ascribed to the crystal lattice restriction to cyclization. The motion required for the cyclization sweeps the aryl and hydroxyl groups through a large volume and would be expected to be topochemically disfavored in the solid state relative to the "least motion" pathway required for cleavage. Thus the small selectivity observed is attributable to crystal lattice control of the biradical behavior. Irradiation of α-adamantyl-*p*-methoxyacetophenone afforded the less hindered cyclobutanol (57) and the more hindered cyclobutanol 58 in a ratio of 2.6 in benzene and 2.0 in acetonitrile.[136] A dramatic reversal of stereoselectivity was observed in the solid state. In contrast to the solution results, laser irradia-

SCHEME 36



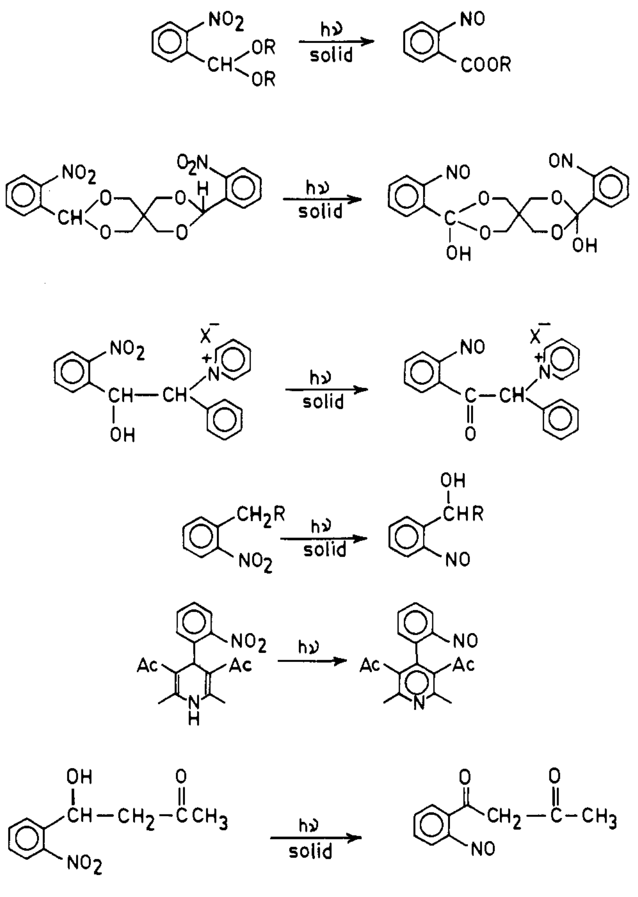
tion of α-adamantyl-*p*-methoxyacetophenone afforded the more hindered cyclobutanol isomer **58** as the major product (Scheme 33). Based on the reactant X-ray crystal structure, it is suggested that the intermediate 1,4-biradical in the solid state is born in and restricted to a conformation which is ideal for direct closure to the more hindered product.

An elegant example of such a phenomenon is provided by *N,N*-dialkyloxo amides. *N,N*-Dialkyloxo amides upon irradiation in solution undergo primary γ-hydrogen abstraction to give the type II diradical (Scheme 36). This diradical undergoes three types of reactions, namely, cyclization, elimination, and 1,4-hydrogen migration. The products of the solid state photolysis of a few oxo amides are significantly different from those of solution phase photolysis (Scheme 34). Interestingly, β-lactones are obtained in larger yields in the solid state. This has been attributed to the crystal lattice effect. The formation of oxazolidin-4-ones via 1,4-hydrogen migration involves considerably more molecular motion of the biradical intermediate than does formation of β-lactams, via cyclization. The 1,4-hydrogen migration of the biradical **64** is restricted to the planar or nearly planar cisoid transition state (Scheme 36). This would require rotation of the C(OH)–CO bond of **64** since γ-hydrogen abstraction can occur only from the transoid form of α-oxo amides. It is suggested that the crystal lattice restricts such a motion thus favoring the formation of β-lactams.

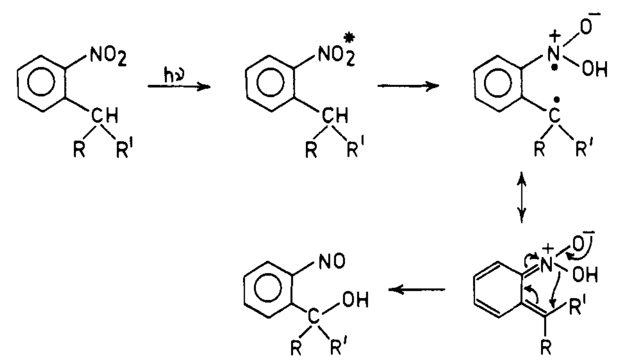
5. *Nitroaromatics*[139-158]

Photochemical hydrogen abstraction reactions of aromatic nitro compounds have long been known, and scattered reports on the solid-state photobehavior of nitro compounds have appeared since the beginning of this century.[139-149] Known examples of this process in the solid state and a common simple mechanism involving γ-hydrogen abstraction are summarized in Schemes 37 and 38. It is clear that the examples provided contain a CH group in the position ortho to the nitro group. Many such molecules have been reported to be light-sensitive in the solid state but no detailed information on the photoproducts is available. Unfortunately, X-ray data of those ortho alkyl nitro compounds, known to be light-sensitive in the solid state, are lacking. Nitromesitylene, for which X-ray structural details are available, is reported to be insensitive to light in the solid state.[150] The X-ray structure of trinitrotoluene is known but not the structure of the photoproduct.[151] Therefore, a more coordinated effort on this problem is desirable.

SCHEME 37



SCHEME 38

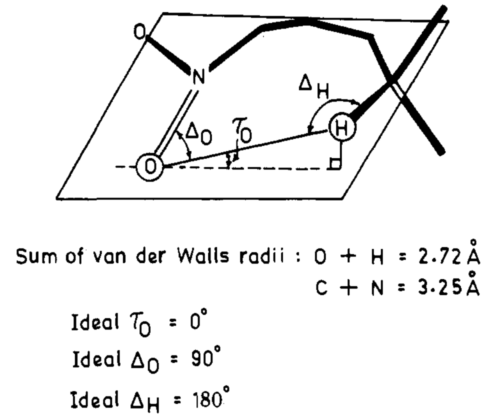


The solid state photobehavior of a few crowded aromatic nitro compounds has been investigated by Döpp.[152-156] γ-Hydrogens are not available in any of these cases and abstraction from the δ-carbon occurs. This primary reaction initiates a sequence of events leading to 3*H*-indole 1-oxides as the final products. The proposed mechanism and the molecules that undergo this unusual rearrangement in the solid state are summarized in Scheme 39. It is noteworthy that molecules **65**–**67** do not undergo intramolecular hydrogen abstraction from the benzylic methyl groups, a normal photoreaction of *o*-nitrotoluenes, to any measurable extent. Instead hydrogen abstraction from the unactivated δ-position (*tert*-butyl group) is clearly preferred. In this context, recently reported X-ray structural details on **65**–**68** are timely and immensely useful to draw conclusions on the photochemical hydrogen abstraction reactions of aromatic nitro compounds.[157,158]

TABLE 8. Intramolecular Geometrical Parameters Relevant to Hydrogen Abstraction Involving *tert*-Butyl and Nitro Groups for Compound 65[a,b]

atom pair	O···H, Å	Δ_H, deg	Δ_O, deg	τ (°)	Δ_N, deg[c]
10(13)···H(83)	2.58 (3)	135.7 (24)	100.4 (7)	−46.1 (7)	112 (112)
10(14)···H(82)	2.74 (4)	129.5 (23)	101.4 (7)	50.8 (7)	108 (109)
10(13)···H(93)	2.41 (3)	123.6 (22)	67.5 (8)	−105.3 (9)	56 (48)
20(13)···H(92)	2.90 (3)	87.1 (16)	82.9 (6)	72.0 (6)	88 (82)
20(13)···H(93)	2.45 (3)	112.7 (21)	65.9 (8)	106.5 (9)	55 (47)
10(14)···H(103)	2.42 (3)	130.4 (24)	71.5 (8)	98.1 (8)	61 (55)
20(14)···H(102)	2.57 (4)	105.9 (21)	83.1 (7)	−74.6 (7)	83 (77)
20(14)···H(103)	2.68 (3)	100.1 (21)	60.7 (7)	−105.0 (8)	59 (48)
C(8)···N(13)		3.550 (5) Å	C(8)···N(14)		3.640 (5) Å
C(9)···N(13)		2.781 (4) Å	C(10)···N(14)		2.773 (6) Å

[a] See Figure 19 for atom numbering. [b] Esd's are given in parentheses, ideal value: $\Delta_H = 180°$; $\Delta_0 90°$; $\tau = 0°$; $\Delta_N = 180°$. [c] The values outside the parentheses correspond to N–O···HYP = 90° and those inside to N–O···HYP = 120°.



Sum of van der Walls radii : O + H = 2.72 Å
C + N = 3.25 Å

Ideal τ_O = 0°
Ideal Δ_O = 90°
Ideal Δ_H = 180°

Figure 18. Definition of geometrical parameters during hydrogen abstraction by the nitro group.

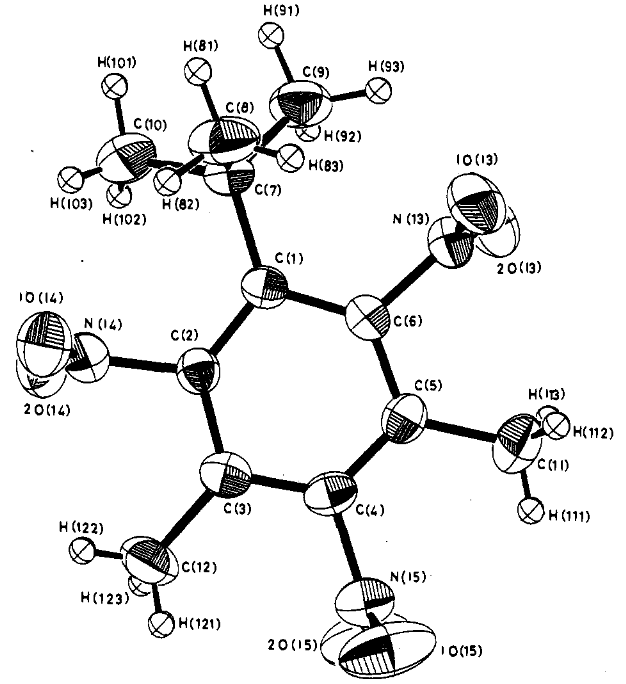
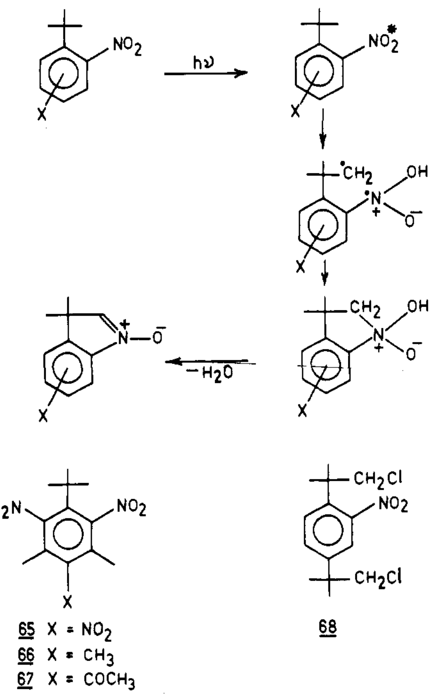


Figure 19. ORTEP projection of compound 65 with the atom numbering scheme and thermal ellipsoids at the 50% probability level. The hydrogen atoms are represented by spheres of arbitrary size.

SCHEME 39



Compounds 65–68 offer a unique opportunity to understand the solid-state reactions through structural and packing considerations. The X-ray structural data are able to answer the following questions: (1) Why is there no hydrogen abstraction from the benzylic position (i.e., from the methyl groups)? (ii) Are there any hydrogens in the *tert*-butyl group oriented in the appropriate geometry for abstraction by the nitro group? It is gratifying to note that in these cases the molecular geometry and packing considerations allow a unique identification of the hydrogen being abstracted. Since the details on all the four compounds are similar, results on one of them alone are summarized. The ideal geometry for hydrogen abstraction from the nπ* excited state of the nitro group is expected to be a short O···H distance and angles C–H···O (Δ_H), N–O···H (Δ_O), and τ close to 180, 90, and 0°, respectively. It may be recalled that similar geometrical parameters were used in the analyses of the photoreactions of enones and carbonyl–hydrogen abstraction reactions. The definitions of these angles in the case of the nitro group are illustrated in Figure 18. The general numbering scheme for the groups involved in the reaction is shown in Figure 19 and the geometrical parameters used in the analysis for 65 are summarized in Table 8. Based on the expectation that short intramolecular O···H contacts (less than the van der Waals sum) would favor hydrogen abstraction, eight possibilities for hydrogen abstraction by two adjacent nitro groups exist in the case of 65. However, from a consideration of the values of Δ_H, Δ_O,

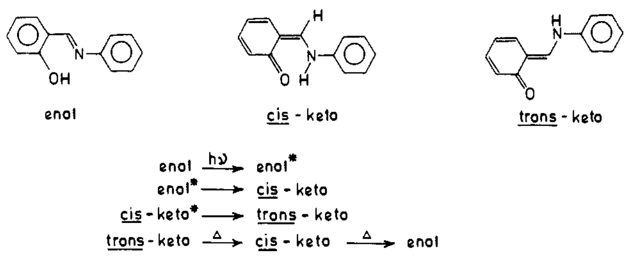
and τ in Table 8, it seems reasonable to conclude that two of the eight hydrogens of the *tert*-butyl group are better situated for abstraction by the nitro group of **65**, i.e., H(83) by 10(13) or H(82) by 10(14). This reduction in number based on structural parameters is remarkable considering the fact that there are 36 possible modes of hydrogen abstraction. The geometrical parameters for hydrogen abstraction from the benzylic methyl groups are much less favorable than for the two most probable choices obtained between the *tert*-butyl group and nitro chromophore. Thus the geometrical criteria are helpful in rationalizing the solid state behavior of **65–67**. Based on intermolecular interactions a unique identification of the hydrogen being abstracted was also possible. In order for the C and N radicals (Scheme 39) to combine, after the initial hydrogen abstraction, the *tert*-butyl group bearing the radical center has to undergo a rotation about the C(1)–C(7) bond either in the positive or negative direction. Rotation in the positive direction would bring C(9) in the proximity of N(13) and rotation in the negative direction would bring C(9) nearer to N(14). Now the question is whether such a rotation would be tolerated by the environment in the crystal lattice and if so in which direction the rotation about the C(1)–C(7) would be preferred. Based on intermolecular short contacts calculated for the rotation of the *tert*-butyl group in both directions up to ±30°, rotation in the positive direction is concluded to be less hindered. Thus abstraction of H(83) by 10(13) followed by combination of C(9) and N(13) is believed to be the most favored. The other choice, namely abstraction of H(82) by 10(14) would not lead to the isolated product as the coupling of the resulting radicals is prohibited by the packing. It is obvious that in **65** one cannot experimentally distinguish between the hydrogens being abstracted. However, the above approach gains support in its ability to uniquely identify the hydrogens being abstracted in the case of **68**. It is heartening to note that conclusions drawn based on the analysis of the crystal structure of **68** agree with the experimental observation that the nitro group abstracts hydrogen from the $-CH_2Cl$ group of the adjacent chloro-*tert*-butyl group.[158]

6. *Imines*[159-173]

Photochromism is the salient feature of this class of molecules. A large number of anils (Schiff bases with the general formula Ar—CH═N—Ar) have been reported to be photochromic in the solid state.[159-163] The most thoroughly studied photochromic solids are the benzylideneimines, especially the derivatives of salicylaldehyde.[164,165] Whether a given anil can be photochromic in the crystalline state or not is dependent on the substituent it carries on the aromatic rings, and in some cases a variation in the position of a substituent can prevent photochromism. Even for the same compound, one polymorph may be photochromic while another is not. Visible light or heat may reverse these UV-induced color changes.

Early explanations for the mechanism of photochromism in the anils involved aggregation and crystal lattice interactions. However, investigations of Cohen, Schmidt, and co-workers showed that isolated molecules in glassy solutions also exhibit photochromic activity, thus ruling out such specific solid-state interactions as prerequisite to photochromism.[166] Although the solid-state studies are important with regard to applications and understanding the mechanism in the crystals, significant evidence for the intramolecular nature of this photochromism comes from solution studies. Schmidt and co-workers first demonstrated[166,167] that the presence of an *o*-hydroxyl group is a structural requirement for the photochromism of anils. In contrast, in glassy matrix, solutions of anils from other benzaldehydes, including *p*-hydroxy and *o*-methoxy substituted aldehydes are not photochromic. It was postulated that a six-membered-ring hydrogen-transfer phototautomerism occurs to form a colored quinoid structure. Thus, in a broad sense this photochromic process involves a hydrogen-transfer process similar to the ones discussed earlier in the case of enones, ketones, and nitro compounds.

SCHEME 40



Based on extensive studies,[166-170] Schmidt has postulated that the photochromism of anils in the solid state involves two steps. The colored keto form has been suggested to be stabilized by a cis–trans isomerization immediately following the hydrogen-transfer reaction. Formation of the *trans*-keto form of *N*-salicylideneaniline upon excitation in the crystalline state has recently been confirmed through optical absorption and emission spectroscopy.[171] Thus the photochromism of anils in the solid state consists of two reactions, namely, hydrogen migration and geometric isomerization as illustrated in Scheme 40.

The most extensive crystallographic investigations on anils have been carried out by Cohen and Schmidt and more recently by Hadjoudis and co-workers.[166-170,172] Their studies indicate that the photochromism is largely topochemically dominated. They classify two major crystalline types: the α-type, which is photochromic and not thermochromic; and the β-type, which is not photochromic but is thermochromic. Thus in the crystalline anils of salicylaldehyde, photochromism and thermochromism are mutually exclusive properties. It is suggested that the α-type permits the photochemical formation of the *trans*-keto structure, whereas the β-type packing prevents this but does permit thermal formation of the *cis*-keto structure. In the thermochromic crystal structure molecules are essentially planar and are packed in stacks of parallel molecules with an interplanar distance of ≃3.4 Å. In the photochromic crystal, the aniline ring is twisted about the exocyclic N–C bond by ≃55° and the molecular packing is consequently much more open. The packing arrangements of *N*-(5-chlorosalicylidene)aniline and 2-chloro-*N*-salicylideneaniline, examples of β and α type packing, respectively, are illustrated in Figure 20. Based on the above packing consideration, it has been suggested that in the planar molecular structure the lone pair of the nitrogen does not overlap with the π

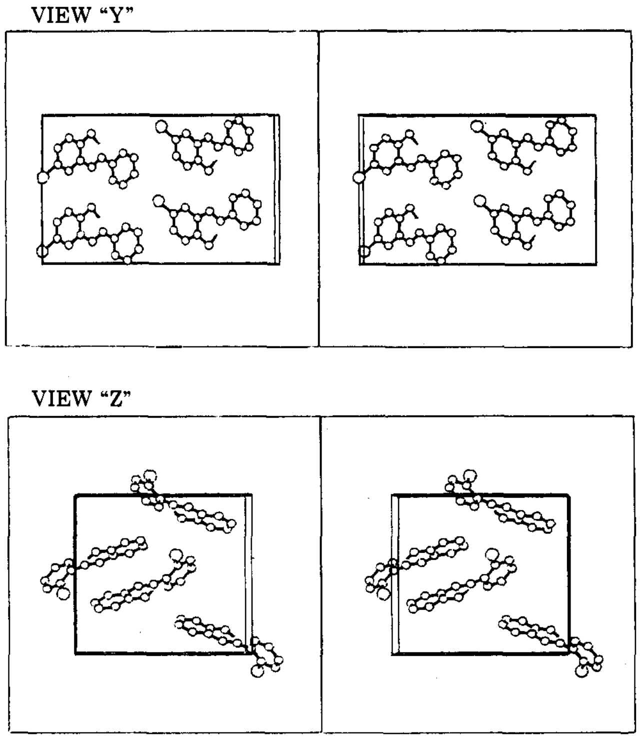
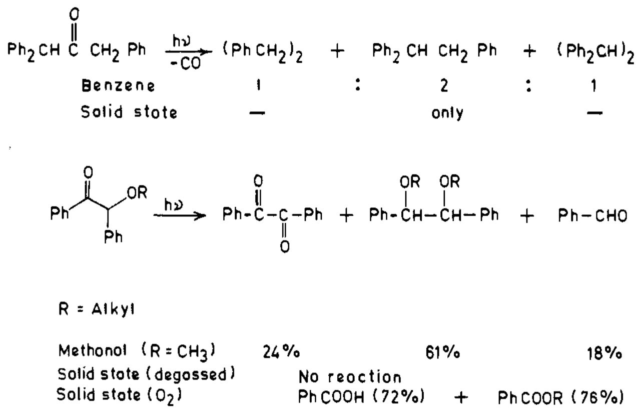


Figure 20. Stereodrawing of the packing arrangements of *N*-(5-chlorosalicylidene)aniline (a) and (α-chloro-*N*-salicylidene)-aniline (b).

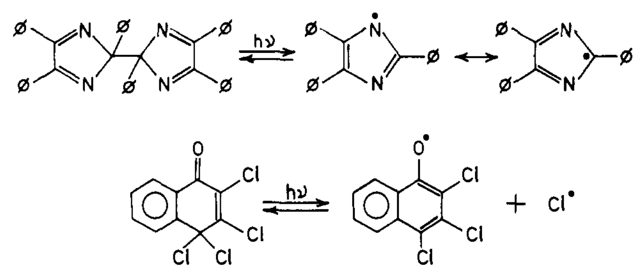
SCHEME 41



electrons of the benzene ring whereas in the twisted structure such overlap is possible. This gives rise to differences in the basicity of nitrogen, the former, i.e., planar form being more basic. The formation of the *cis*-keto form can occur readily from the planar as against the twisted conformation.

Thus, in the solid state an "open" crystal structure, associated with nonplanar molecules and allowing molecular movement, is necessary in order to allow photochromism, whereas in thermochromic crystals the molecules are planar and closely packed. Such a clear distinction in the packing arrangements between thermochromic and photochromic anils allows for "crystal engineering". Two approaches have been suggested in this connection. It has been demonstrated that the insertion of a nitrogen atom in the 2-position of the aniline ring of any anil which is normally nonplanar (photochromic) yields a planar molecule with thermochromic properties.[172] Bernstein and Schmidt have also demonstrated the use of chloro substitution in this connection.[173]

SCHEME 42



B. Fragmentation Reactions[174-184]

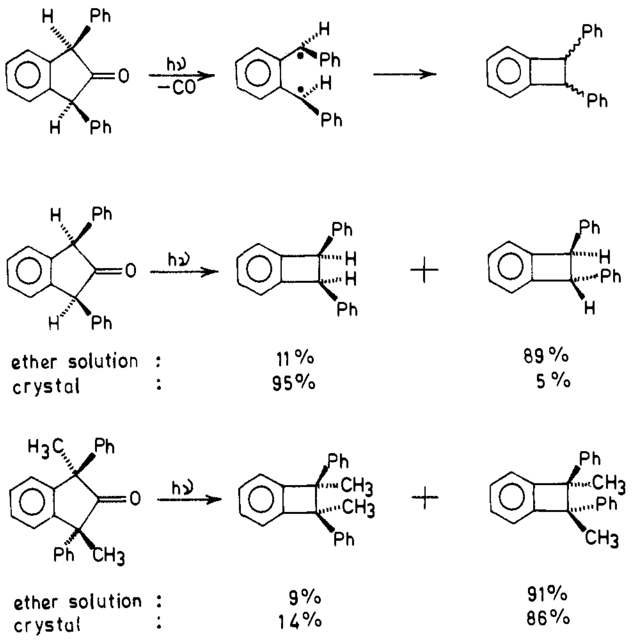
A factor of considerable topochemical and practical importance in unimolecular reactions in crystals is the fact that the crystal reaction cavity can constrain the movements of the contents of the cavity and thus give rise to the specificity of the solid-state reaction. Not only are fragments constrained to stay close together, but their rotational motions may also be restricted. Examples of such an effect are also available in the literature.

The two examples reported by Quinkert et al. illustrate the restriction brought about by the lattice on diradicals generated via decarbonylation.[174,175] Photolysis of 1,1,3-triphenylacetone in the crystal gives exclusively a single product, namely, 1,1,2-triphenylethane, while in solution a statistical mixture of products is obtained (Scheme 41). A similar observation has also been made in the case of 1,3,4-triphenylbutane-2-one.[176] Comparative results in the above systems for solid and solution phases clearly indicate the translational restriction brought on the radicals by the crystal structure. The presence of such "super cage" effects has also been reported during the photolysis of benzoin ethers (Scheme 41).[177] Benzoin ethers undergo photochemical α-cleavage to form a benzoyl–benzyl radical pair which subsequently undergoes free radical reaction in solution to give benzaldehyde, benzil, and pinacol ethers. However, when the irradiation of these crystals was conducted in the absence of oxygen, the starting material was recovered unchanged even after prolonged irradiation. Presumably the radical pair generated in the crystalline phase cannot diffuse apart and result in recombination. This was indeed demonstrated by photolyzing the above crystals in an oxygen atmosphere. Under these conditions benzoic acid and alkyl benzoates, the products resulting from the trapping of the radical pair by oxygen, were obtained in high yield.

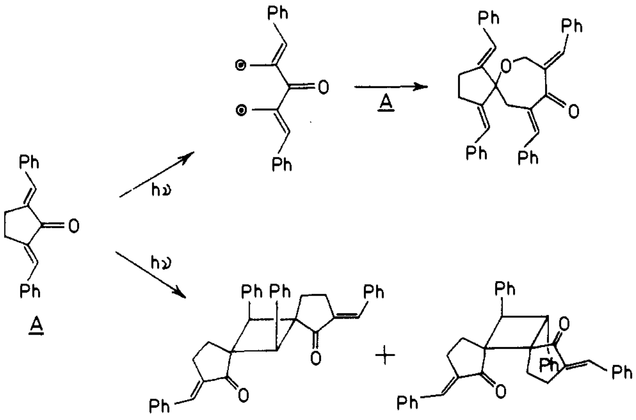
The photochromic behavior reported in the case of bis(imidazoles) and β-tetrachloroketodihydronaphthalenes in the crystalline state also result from cleavage reactions.[178-183] The proposed mechanism is illustrated in Scheme 42. These are further examples of the "super cage" offered by the crystalline medium. The radicals generated via cleavage are not free to move within the crystal structure and strong stereochemical limitations are imposed on them by the medium.

An example of rotational restriction imposed by the crystalline medium has also been provided by the investigations of Quinkert.[174] Photolysis of indanones in solution results in smooth decarbonylation to give isomeric benzocyclobutanes. The stereoselectivity observed during the photoelimination of carbon monoxide

SCHEME 43



SCHEME 44



from *cis*- and *trans*-1,3-diphenyl-substituted 2-indanones show a striking increase on going from the solution phase to the crystal as illustrated in Scheme 43.

One of the most unusual cleavage reactions has been reported during the photolysis of 2,5-dibenzylidenecyclopentanone.[184] Photolysis of the above compound in the crystalline state yielded a spiroheterocyclic compound in addition to the expected dimer (Scheme 44). The formation of the above product is suggested to result from the cleavage of the five-membered ring and subsequent cycloaddition to the C=O bond of a second molecule. An X-ray structure has recently been reported and the packing arrangement is illustrated in Figure 21.[46] It is noteworthy that the product can, in principle, be obtained from the starting crystal via the reaction of nearest neighbors. The distance between C_3–C_4 (the bond that is broken) and the carbonyl with which the diradical reacts is well within the van der Waals radii. Further, the reacting orbitals are oriented favorably towards each other.

C. Electrocyclization[185–192]

Amongst the oldest group of photochromic compounds in the crystalline state is the fulgides which were

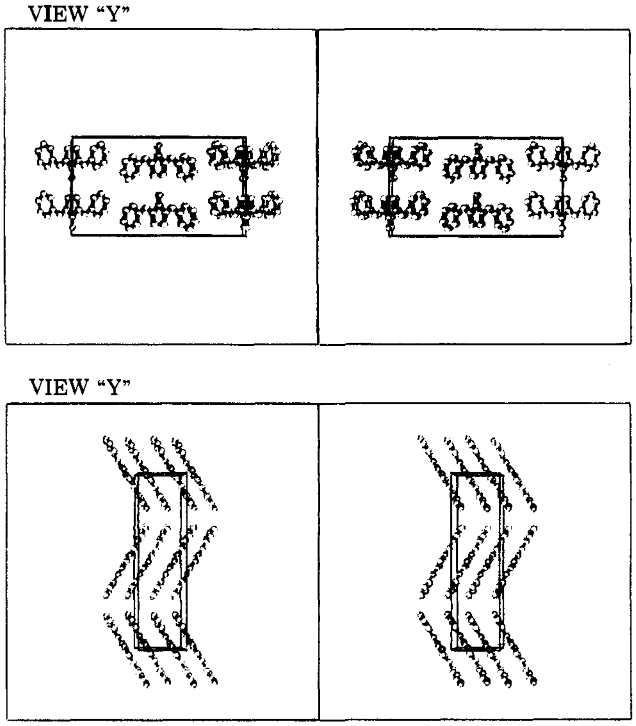
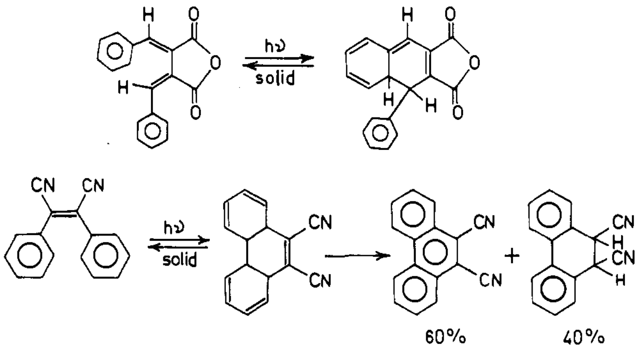


Figure 21. Stereodrawing of the packing arrangement of 2,5-dibenzylidenecyclopentanone.

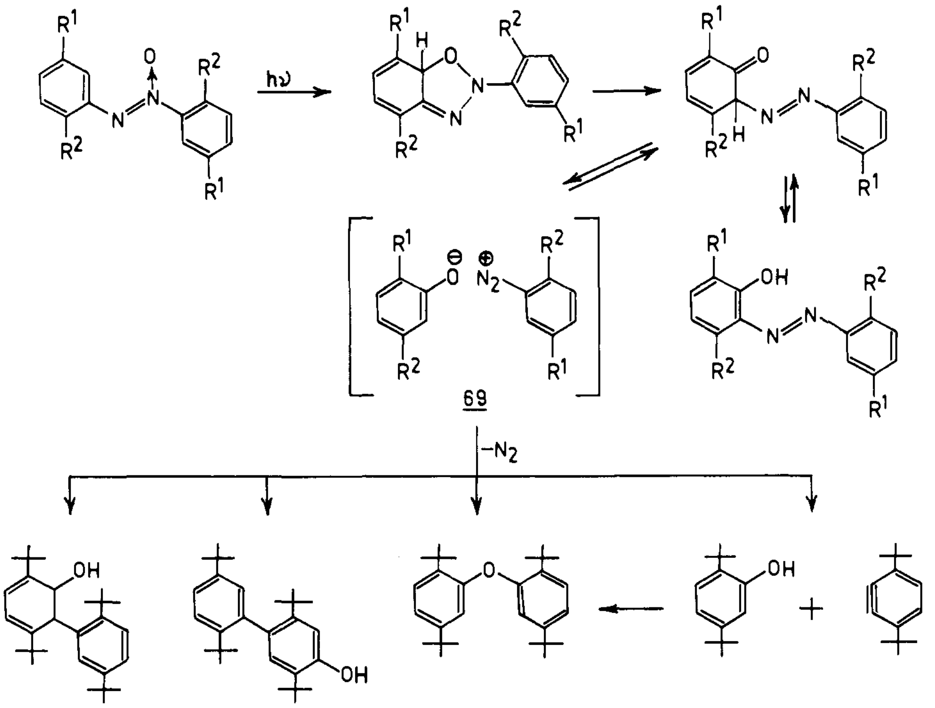
SCHEME 45



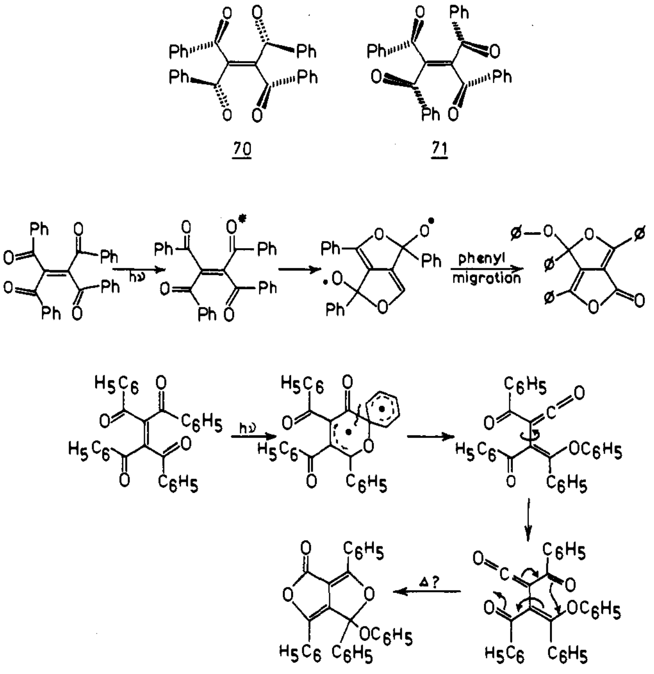
investigated extensively by Stobbe and by Hanel.[185–187] The crystals of fulgides have initially a yellow to reddish shade. The effect of light is to deepen the color. All known photochromic fulgides contain a phenyl group (Scheme 45). The mechanism of the photoprocess responsible for this photochromic behavior has been elucidated by Becker and Santiago[188] and established to be a molecular phenomenon. The primary photochemical step is a photobridging process (electrocyclization) which accounts for the formation of a cyclic colored structure (Scheme 45). No crystallographic details are available to further understand this interesting phenomenon.

An example which closely resembles the fulgides is the cyclization of diphenylmaleonitrile in the crystalline state.[189,190] A suspension of powdered diphenylmaleonitrile in water, when photolyzed, gave rise to 9,10-dicyanophenanthrene and 9,10-dihydro-9,10-dicyanophenanthrene (Scheme 45). Diphenylmaleonitrile shows polymorphism and the photobehavior of the two polymorphs (prisms and needles) are slightly different. The effect of polymorphism on the photochemical behavior cannot be fully understood unless the refined molecular structures of both crystal forms are known.

SCHEME 46



SCHEME 47



The photoreaction in the solid state occurring from both the polymorphs, although to different extents, is suggested to be electrocyclization.

A recent study on *trans*-2,5,2′,5′-tetra-*tert*-butylazoxybenzene by Döpp invokes electrocyclization as a primary step during its photolysis in the crystalline state.[191] The products and the proposed mechanism are shown in Scheme 46. The proposed pathway involves electrocyclization, fragmentation, and diazonium expulsion. The intermediate **69** has been trapped when a finely powdered mixture of β-naphthol, sodium bicarbonate, and azoxybenzene was irradiated.

One of the most interesting cyclizations reported is that of tetrabenzoylethylene.[192] Tetrabenzoylethylene crystallizes in two polymorphic forms, and X-ray structures of both are available. It is important to note that only one of these modifications gives rise to a product upon photolysis while the other is inert to UV radiation (Scheme 47). The authors have not been able to provide an explanation as to why the solid form **70** undergoes photolysis but not the form **71**. This is partly due to the fact that it has not been established whether the rearrangement is an inter or an intramolecular process. The packing arrangement for the two forms is shown in Figure 22.

D. Photochemical Oxygen-Transfer Reactions[193-210]

A number of rearrangements are known in which a transfer of an oxygen atom, originally attached to a nitrogen, takes place. This group consists of several potentially useful transformations which have not yet been fully exploited and investigated.

The transfer of an oxygen atom from the nitro group to the adjacent unsaturated center has been reported in several systems both in the solid state and in solution.[193-203] Many of these, illustrated in Scheme 48, are complex multistep solid-state reactions. Two mechanisms have been proposed for these reactions and these can be generally applied to all the transformations shown in Scheme 48. There is a fundamental difference in the first step between the two mechanisms (Scheme 49). According to the mechanism proposed by Schmidt the first step involves the attack of the excited nitro group on the ortho carbon of the unsaturated substituent whereas de Mayo[204] postulates a hydrogen abstraction by the photoactivated nitro group with the formation of a biradical (Scheme 49). The latter process is thus pictured as a particular case of γ-hydrogen abstraction by an excited hetero double bond.

Structure analyses specifically designed to ascertain the geometry of oxygen transfer have been carried out on 2-nitrobenzaldehyde and its halogen derivatives.[205,206] The packing arrangement of *o*-nitrobenzaldehyde is

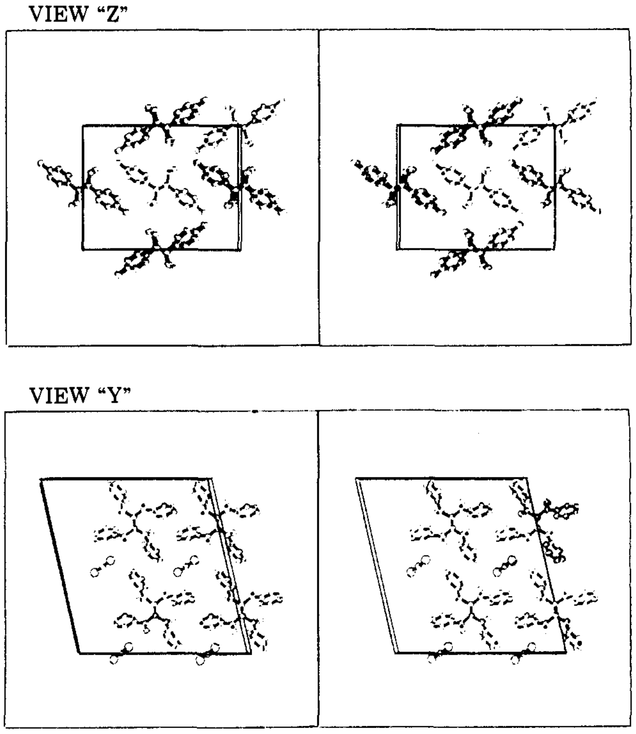
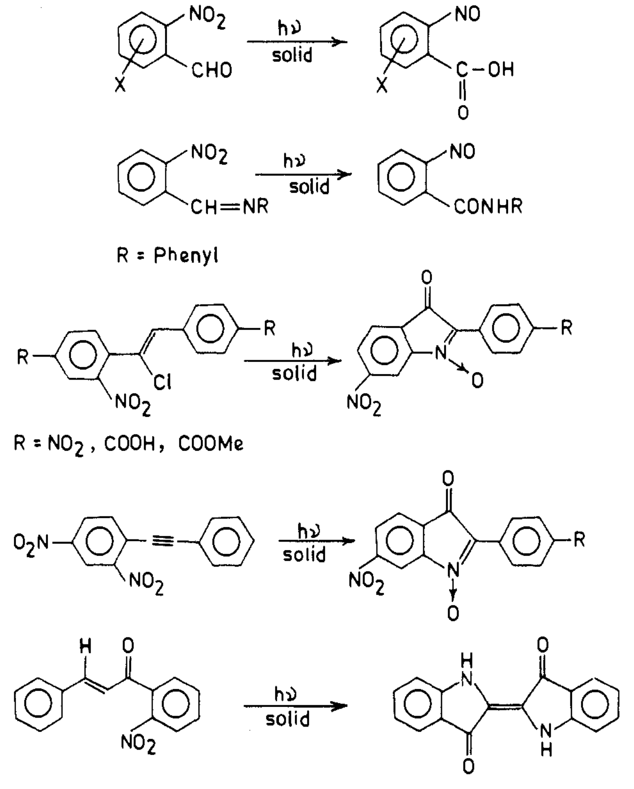


Figure 22. Stereodrawing of the packing arrangement of the two forms of tetrabenzoylethylene—reactive (a) and unreactive (b).

SCHEME 48



shown in Figure 23. On the basis of the reported X-ray crystal structures it has not been possible to provide unequivocal support for any one of the mechanisms. Additional input is required on this important problem.

The solid state photosynthesis of indigo from 2′-nitrochalcone is one of the most elegant and complicated solid state reactions (Scheme 49). Engler and Dorant reported[207] the transformation of 2′-nitrochalcone into indigo by light as early as 1895, but the reaction is still to be fully understood. While the details of the mechanism of this transformation are obscure, a conceivable mechanism involving photochemical oxygen transfer from the nitro group to the C(β) in the ethylenic bridge, a process analogous to the reaction of *o*-nitrobenzaldehyde to yield *o*-nitrosobenzoic acid, is shown in Scheme 50. The last step involves reaction of two molecules with water to give indigo and benzoic acid. It has been shown by Schmidt and his co-workers that the specific pathway of this complex photochemical reaction in the solid state is governed by two factors, namely the molecular conformation and the intermolecular packing.[208]

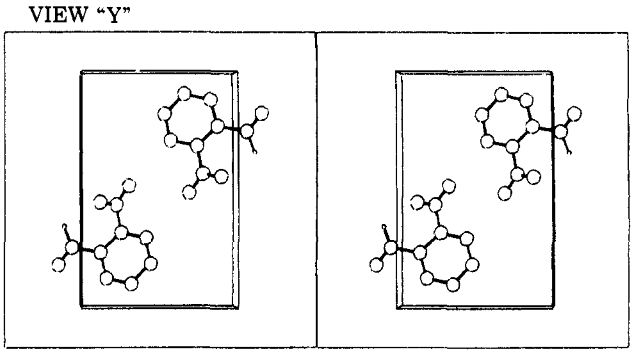


Figure 23. Stereodrawing of the packing arrangement of *o*-nitrobenzaldehyde.

2′-Nitrochalcone and those of its derivatives which are isomorphous with it display the *s-trans* conformation in the solid state and yield indigos upon irradiation.[208] This is in keeping with the assumption that this conformation is necessary for the correct contact geometry between the potentially reactive groups (NO_2 and olefinic C_β). A better understanding requires full structural analyses of a large number of 2′-nitrochalcone derivatives.

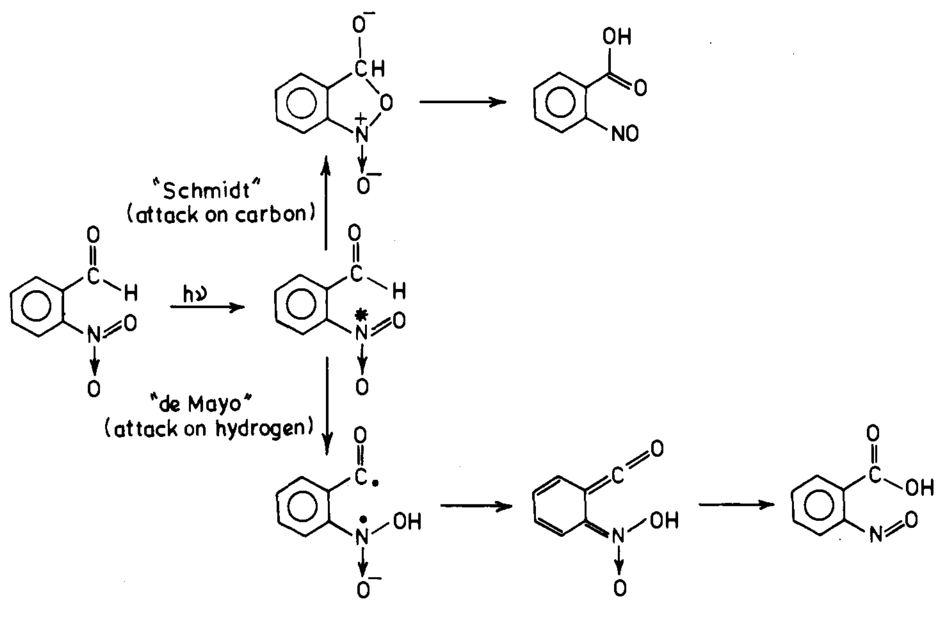
A formally analogous reaction is the photochemical rearrangement of azoxybenzenes to azophenones (Scheme 51).[209,210] No structural data are available to understand the mechanistic details of this solid-state process. There is abundant literature available on the solid-state photoreactions of nitro compounds. A careful scrutiny of them would be valuable.

E. Miscellaneous Reactions[211-221]

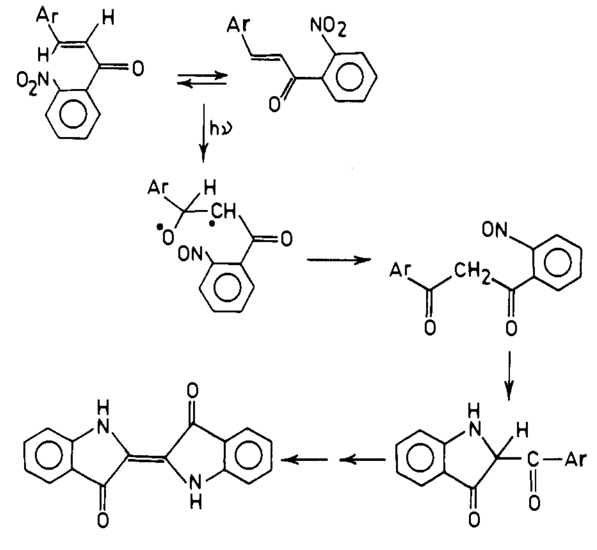
The photochemical rearrangement of acetylchloroaminobenzene to *p*-chloroacetanilide (Scheme 52) has been the subject of many early investigations.[211] Pure dry crystals of acetylchloroaminobenzene, when exposed to the radiation of a mercury vapor lamp, are converted rapidly into *p*-chloroacetanilide. A 90% conversion was achieved within 8 h. Unfortunately, no structural or mechanistic details are available for this interesting rearrangement. Even a speculation of the mechanism is not possible with the available experimental results.

Interesting transformations have also been reported to occur during X-ray bombardment of crystals. For example, crystalline esters of hirsutic acid rearranged during X-ray data collection (Scheme 52).[212] An approximately 1:1 mixture of the starting material and the rearranged product was produced by the irradiation with X-rays, without disrupting the crystal structure, and with only minor changes in lattice parameters.

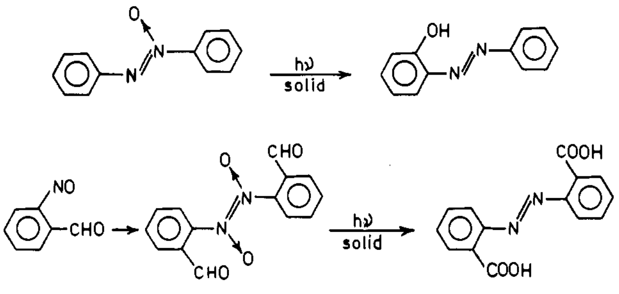
SCHEME 49



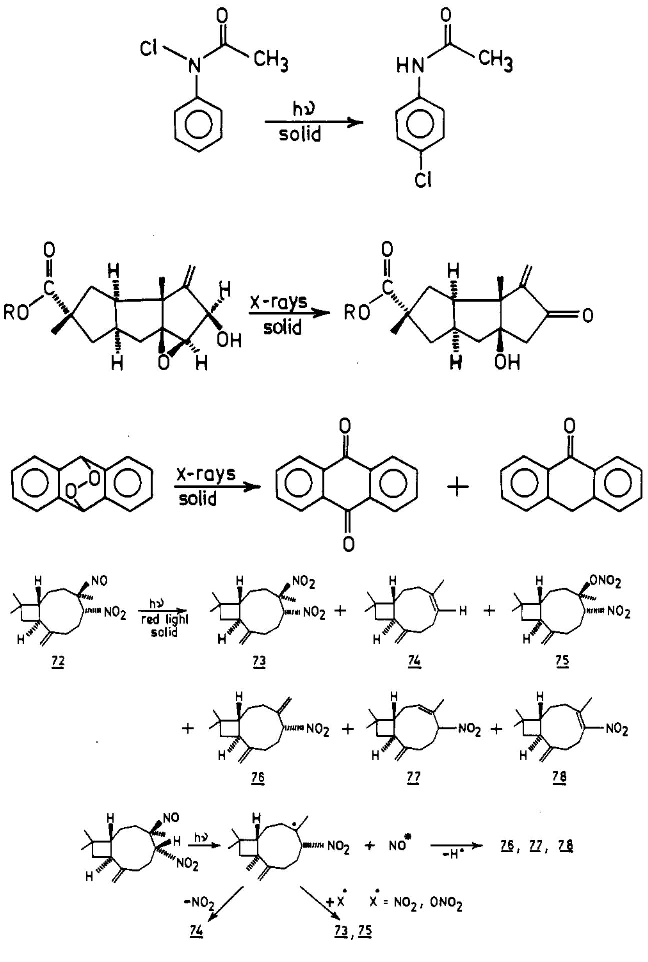
SCHEME 50



SCHEME 51

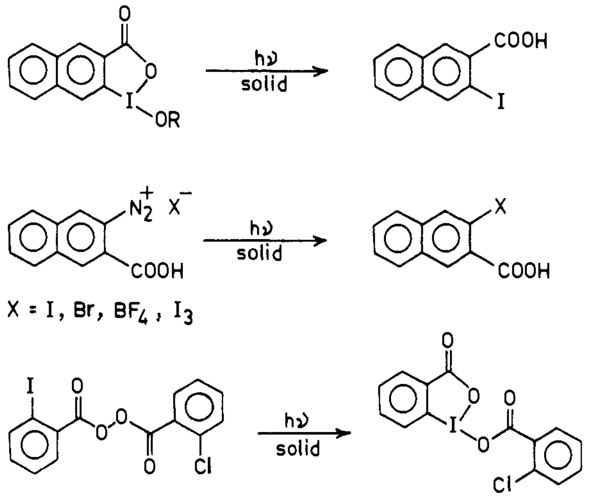


SCHEME 52

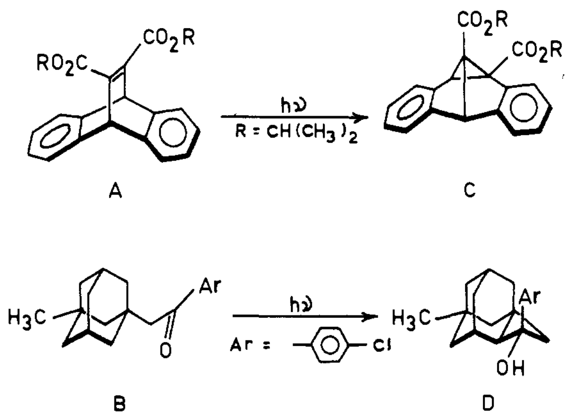


Similarly, when a single crystal of the photooxide of anthracene was subjected to X-irradiation, it changes gradually into a mixed single crystal of anthraquinone and anthrone (Scheme 52).[213] This reaction proceeds via an intermediate stage of disorder, decomposition, and recrystallization, which can be followed in detail by means of X-ray diffraction. The "single crystal" reaction generates ~5% "free space" in the original crystal, thus allowing room for the gaseous products of the reaction to remain within the structure. Caryophyllene nitrosite **72** when irradiated with red light yields several products.[214] The products formed and the proposed mechanism are given in Scheme 52. Geometric isomerizations of *cis*-cinnamic acids and dibenzoylethylenes have also been investigated.[215] Gougoutas has provided a few interesting examples of solid-state photoreactions,[219,220] and they are summarized in Scheme 53.

SCHEME 53



SCHEME 54



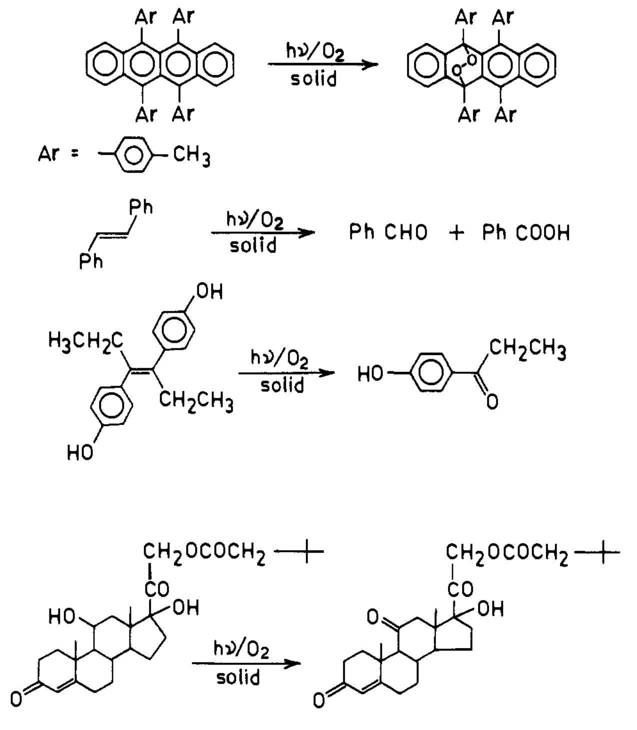
F. Asymmetric Synthesis

Recently Scheffer and his co-workers have reported[221] the first asymmetric synthesis in the solid state of two very general classes of *unimolecular* photorearrangement, namely the di-π-methane reaction and the Norrish Type II process. In both instances, very high enantiomeric yields were obtained. Crystals of diester A (Scheme 54) are dimorphic (space groups *Pbca* and $P2_12_12_1$). The ketone B (Scheme 54) crystallizes in the chiral space group $P2_12_12_1$. Irradiations of the *Pbca* crystals and solution of A gave optically inactive product C. However, irradiations of $P2_12_12_1$ crystals of A gave C exhibiting average specific rotation of 24.2 ± 2.9 (sodium D line). By optically active shift reagent H^1 NMR studies, it has been established that the products are obtained in 100% enantiomeric excess. Similarly in the case of B, the product cyclobutanol D was obtained in 80% enantiomeric excess while in solution racemic product resulted. This study clearly illustrates that the "solid state photochemistry" holds considerable interesting results to offer in the coming years.

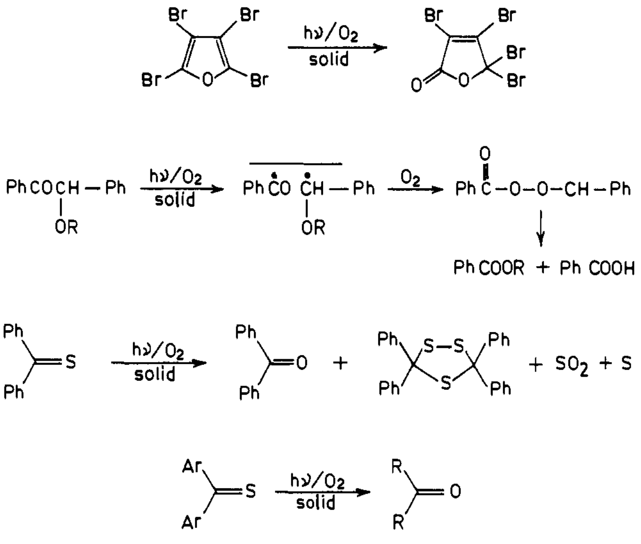
IV. Structure–Reactivity Correlations in Gas–Solid Photoreactions

In a series of papers, Paul and Curtin have provided a deep insight into the relation between the reactivity of a molecule in the solid state toward a gas and its crystal structure.[222,223] However, the examples of gas–solid reactions reported by them are thermally activated. Gas–solid reactions activated by light have also been known and all of them involve oxygen as the gaseous reactant. Most of the reported oxidation reactions in the solid state are summarized in Schemes 55 and 56.

SCHEME 55

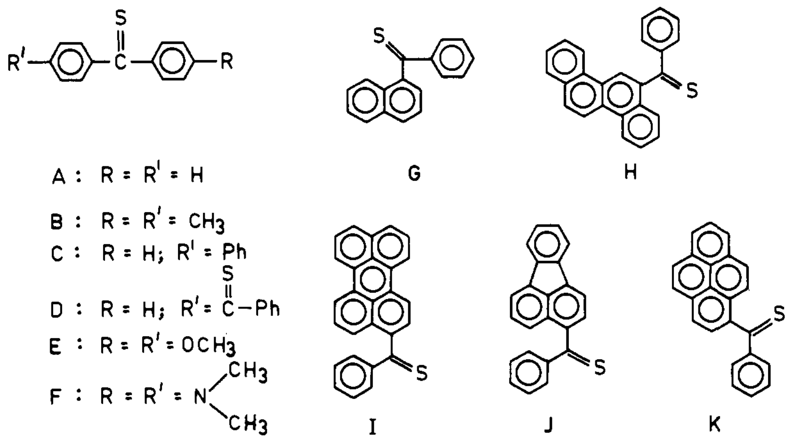


SCHEME 56



One of the earliest photooxidations to be reported in the solid state is that of tetramethylrubrene by Hochstrasser (Scheme 55).[224] Crystalline tetramethylrubrene undergoes ready oxidation to a colorless transannular peroxide when illuminated in the presence of oxygen whereas oxidation of rubrene crystals was confined to the surface. This difference in reactivity has been attributed to the possible differences in permeability of the two crystals to oxygen. Although this postulate has not yet been verified in rubrene and tetramethylrubrene through X-ray structural analyses, the combined photochemical and X-ray studies on a few other molecules discussed below support the notion that

TABLE 9. Photooxidation of Diaryl Thioketones in the Solid State and Crystal Properties of a Few Selected Thioketones



crystal studied	mp, °C	duration of irradiation, days	nature of rxn: in soln	nature of rxn: in solid state	crystal data	channel axis	cross section of the channel, Å^2
A	53	1	yes	yes	$P2_1/n$, $a = 14.042$ Å, $b = 5.863$ Å, $c = 13.402$ Å, $\beta = 106.4°$, $z = 4$	*b*	9
B	75	7	yes	yes			
C	120	15	yes	yes	$Pbca$, $a = 7.443$ Å, $b = 32.691$ Å, $c = 11.828$ Å, $z = 8$	*a*	3.7
D		12	yes	yes			
E	117	30	yes	no	$P\bar{1}$, $a = 9.810$ Å, $b = 9.635$ Å, $c = 15.015$ Å, $\alpha = 7.11$ $\beta = 102.30$, $=$ 107.76°, $z = 4$		
F	201	30	yes	no	$P2_1/c$, $a = 17.029$ A, $b = 6.706$ Å, $c = 14.629$ Å, $\beta = 113.5°$, $z = 4$	*b*	2.3
G	110	17	yes	yes	$P2_12_12_1$, $a = 5.873$ Å, $b = 13.677$ Å, $c = 15.668$ Å, $z = 4$	*a*	8.3
H	184	20	yes	yes			
I	258	30	yes	no			
J	142	30	yes	no			
K	141	30	yes	no			

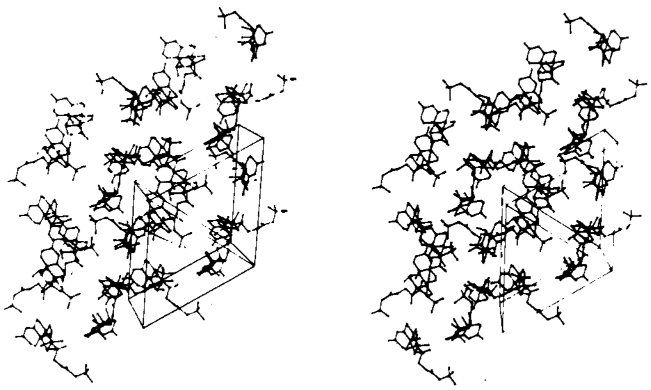


Figure 24. Stereodrawing of the crystal packing highlighting the presence of a channel in hydrocortisone *tert*-butylacetate.

permeability of the crystal toward the reacting gas is essential for efficient gas–solid reaction.

The thermal and/or photochemical oxidation of crystalline 11-hydroxy steroids to the corresponding ketones by atmospheric oxygen was reported over 15 years ago.[225,226] Most recently Byrn et al. have reinvestigated the solid-state light-induced oxidation of the polymorphs of cortisol *tert*-butylacetate and their photooxidation behavior was explained on the basis of molecular packing in the crystal lattice.[227] Cortisol *tert*-butylacetate appears to be typical of many steroids that crystallize in five polymorphs. Two of these forms are reactive toward oxygen in the presence of light. The crystal structure of one reactive form has been determined. The crystals belong to the space group $P6_1$, with the steroid molecules held together by hydrogen bonding arranged in a helix along the 6_1-helix axis. Examination of the molecular packing shows that there is a channel running through the crystal along the 6_1-helix axis with a cross sectional area of 3.5 Å^2 (Figure 24). It has been speculated that the reactivity of this form towards oxygen is due to the unique packing which allows penetration of oxygen down the helix axis of the crystal. Oxygen thus penetrating the crystal oxidizes the C_{11} carbon present in this channel.

Photochemical oxidation of 11 diaryl thioketones in the solid state has recently been reported.[228] Surprisingly, only six were oxidized to the corresponding carbonyl compound whereas the rest were photostable (Table 9). However, in solution all were readily oxidized. A comparison of the molecular packing of the above five thioketones is quite revealing in rationalizing their photoreactivity in the solid state. For the reactive thioketones there is a channel along the shortest crystallographic axis with the reactive thiocarbonyl chromophore (C=S) directed towards the channel. In the case of stable thioketones, the packing arrangement reveals no such channel in any direction in the unit cell. The cross sectional areas of the channels are recorded in Table 9. For the reactive thioketones the channel cross sectional area is fairly large. The primary step of oxidation requires an interaction between an excited thioketone and a ground-state oxygen. For the oxidation to be efficient, oxygen should be able to diffuse into successive layers of the thioketones. As discussed above the absence of a channel in **79** and **80** might then be responsible for their photostability. However, the presence of the thiocarbonyl chromophore at the crystal surface is not sufficient for oxidation to occur. It is also

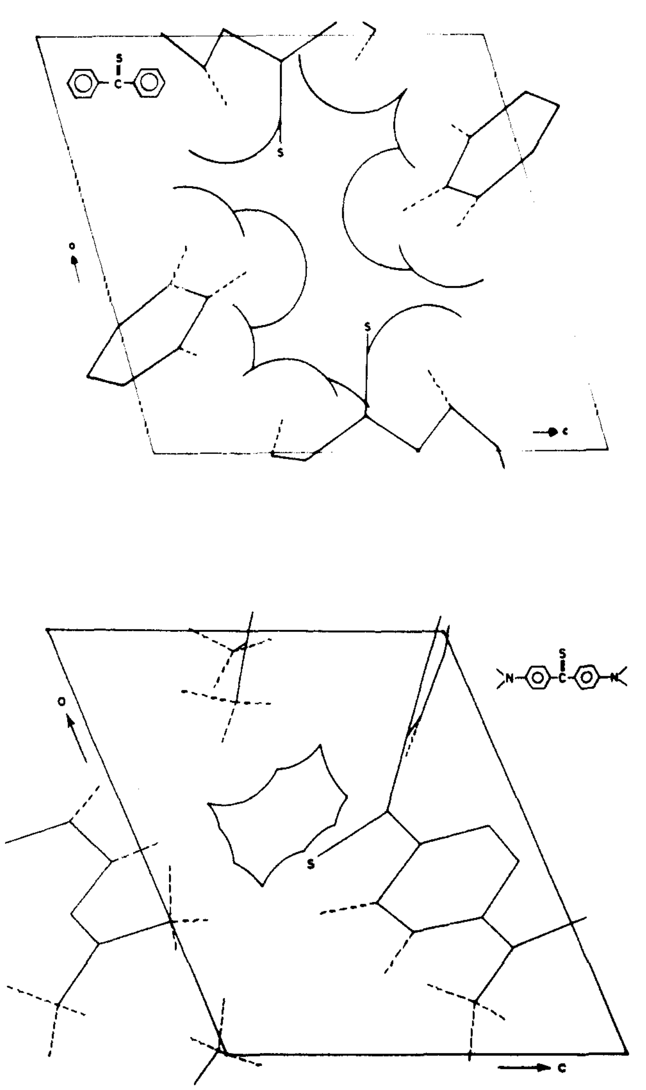


Figure 25. Packing arrangements in thiobenzophenone (a) and Michler's thione (b) illustrating the presence and size of channel. Projection of crystal packing on a plane perpendicular to the channel axis.

essential that the thiocarbonyl groups be arranged in a tight fashion so that oxidation of one molecule exposes another close neighbor to an oxygen molecule. This is evident from the differences in reactivity among the five thioketones being considered. Although in all the five cases the presence of a thiocarbonyl chromophore at the crystal surface could be identified, the above mentioned disposition of reactive chromophores is present only in the reactive thioketones. Typical packing arrangements for a reactive (thiobenzophenone) and an unreactive (Michler's thioketone) thione are shown in Figure 25.

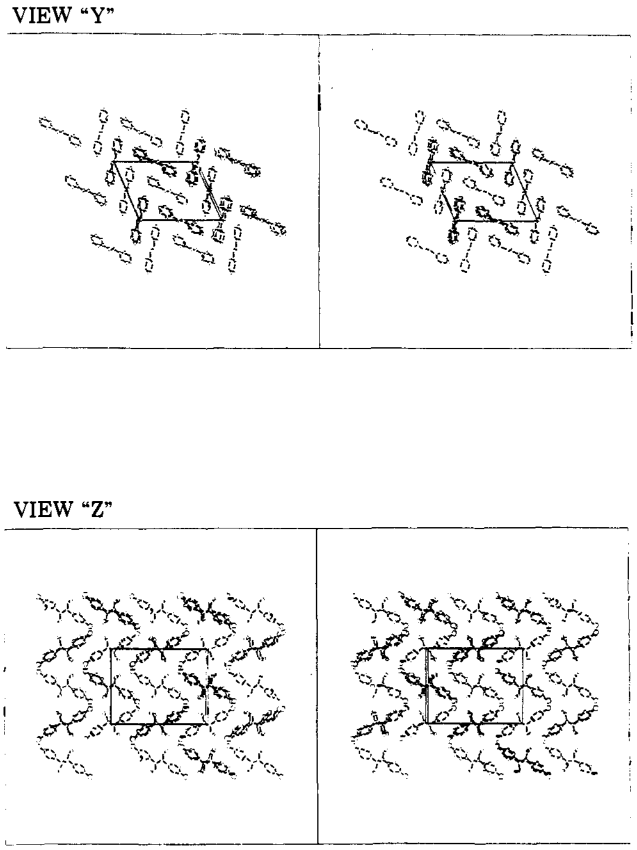


Figure 26. Stereodrawing of the packing arrangements of stilbene (a) and diethylstilbesterol (b).

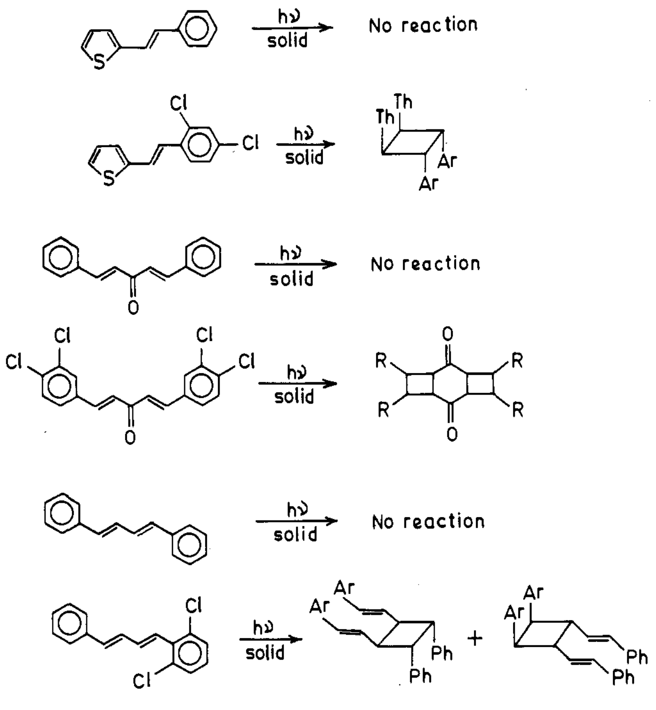
The reaction between oxygen and crystals of *trans*-stilbene and diethylstilbesterol upon UV irradiation has been investigated in order to elucidate the role played by molecular arrangement and defects in the solid state.[229,230] Crystals of *trans*-stilbene, exposed to UV radiation in an aerated atmosphere on a microscope stage, rapidly liquified to give a mixture of benzaldehyde and benzoic acid. The attack of gas is more rapid on the crystal edges. The attack on diethylstilbesterol crystals is very much slower than on *trans*-stilbene. The crystal structure of *trans*-stilbene is less tight than that of diethylstilbesterol in which hydrogen bonds provide strong intermolecular binding. This is suggested to be responsible for the formation of benzaldehyde faster than *p*-hydroxypropiophenone. Further it has been pointed out that these different rates of oxidation are due to the presence of the ethyl groups in the α,α' positions of the stilbene skeleton; these groups play the role of a shield for the reaction. Inspection of the molecular packing (Figure 26) of these two olefins reveals the presence of a channel along the c-axis with the olefinic bond adjacent to it in the case of *trans*-stilbene. Although, diethylstilbesterol has a similar packing with a channel, the size is smaller. This may also be expected to contribute toward the difference in reactivity between the two stilbenes. Thus a similarity in packing and reactivity between steroids, thiones and stilbenes is evident. The role of structural defects in the reaction rates seems to be important and this has been investigated only in the ozonolysis of stilbenes.

It has been reported recently that crystals of tetrabromofuran undergo photochemical transformation in the presence of oxygen into the γ-lactone 2,3,4,4-tetrabromobut-2-en-4-olide (Scheme 56).[231] The initial step in this transformation is presumed to be the homolysis of an α-C–Br bond.

V. Crystal Engineering

Although an understanding of the relationship between reactivity and structure enables one to explain the product formation and selectivity in many solid state reactions, these principles are not of much im-

SCHEME 57



mediate practical value unless one can engineer a particular polymorphic form possessing the necessary topochemical attributes. There are some obvious difficulties. One of the main problems is the difficulty of achieving the desired type of crystal structure in any given case, for the factors that control crystal packing are not yet well understood. If one had a complete understanding of the ways in which inter- and intramolecular forces control packing of molecules in crystals it would become feasible to design template groups of temporary attachment to functional molecules to guide photochemically reactive groups into appropriate juxtaposition in crystals. In the absence of such knowledge, it has been the usual practice to study a series of closely related compounds, so that a common structural principle can be deduced. The concept of designing molecules so as to guide their choice of crystal structure has been termed "crystal engineering" by Schmidt.

The strategy to be adopted may vary from one reaction to the other. Therefore, before embarking on "crystal engineering" activity one must have a good knowledge of the crystal packing, conformation etc. required for a particular reaction or phenomenon under consideration. Under the premise that the photodimerization of olefins in the solid state requires an exact parallel alignment of double bonds the strategies adopted are outlined in section A–F below.

A. Chloro Substitution

Monochloro substitution and especially dichloro substitution in aromatic molecules are very effective devices. Schmidt and his colloborators at the Weizman Institute have exploited this device to achieve a number of disparate objectives.[232-237] By introducing the dichlorophenyl group into unsaturated systems of the type Ar—CH=CHX where X = CHO, COOH, COOMe, CN, Ph, and Ar = 2,4-, 3,4-, and 2,6-dichlorophenyl, Schmidt et al. succeeded in controlling the packing geometry with a unit cell having the shortest axis of about 4 Å.

The first indication that dichlorophenyl substitution would steer the molecule towards β-packing came during studies on cinnamic acids.[15-17] While cinnamic acid crystallizes in both α and β forms, the dichlorocinnamic acids (2,4- and 3,4-, and 2,6-dichloro) crystallize only in the β-form. Since then, a large number of olefins which do not show any reactivity in the solid state, have been induced to react through dichloro substitution. A few examples are provided in Scheme 57. Unfortunately, details of this technique pioneered and practiced by the group at the Weizmann Institute are not available. However, following the initial observation by Schmidt, several groups[22,237] have analyzed the mode of packing of chloro substituted aromatic compounds. It has become clear through these analyses that the "chlorine" atom has a specific role to play in "crystal engineering".

Recent results on the photodimerization of coumarins in the solid state throw much light on the use of "chlorine" as a steering agent for solid-state photodimerizations.[22] It is noteworthy that, whereas coumarin itself does not undergo dimerization in the solid state, all the five chlorocoumarins investigated underwent dimerization in the solid state. Syn head–head dimers obtained in 6-chloro, 7-chloro, and 4-methyl-7-chloro coumarins are the direct consequence of their β-packing arrangements. Thomas and co-workers have also employed chloro substitution in the 2-benzyl-5-benzylidenecyclopentanone framework.[30]

Regarding "chlorine" as a steering group, the generality in the mode of packing in crystal structures containing a chloro group attached to an aromatic ring have been investigated by us.[22] The experimental information for this analysis was taken from the Cambridge Crystallographic Data Base. Metal complexes and molecules carrying charges were eliminated from the analysis. For detailed analysis only structures which contained Cl···Cl distances <4.2 Å were considered. Out of a total of 132 structures, only 22 did not contain any Cl···Cl interaction within this limit. This itself speaks for the success of chloro substitution in crystal engineering. The geometrical parameters used in the analysis are shown in Figure 27; d_0 is the distance between two chlorines and χ is the dihedral angle about $Cl_1 \cdots Cl_2$ (C_1–$Cl_1 \cdots Cl$–C_2). When $\chi = 0°$ the atoms C_1 and C_2 are in the cis configuration, whereas $\chi = 180°$ corresponds to the trans configuration. Figure 27 shows a plot of the angles θ_1 vs. θ_2 (for definition of θ see Figure 27). Sixty points lie on the line with $\theta_1 + \theta_2 = 180°$ and in these cases ($\chi = 0°$) the arrangement of the molecule is similar to β-type packing. Sixty-six points are on the line with $\theta_1 = \theta_2$, and this condition simulates the packing similar to α-type arrangement. In this arrangement C–Cl···Cl–C are related by a crystallographic center of inversion. Similarly, in the α-type of packing the reactive double bonds are related by the above symmetry. It is noteworthy from Figure 28 which portrays the plot of N (number of interactions) vs. d (Cl···Cl distance) that when $\chi = 0°$ most of the Cl···Cl distances lie within a narrow range of 3.8–4.0 Å whereas the range is broad (3.5–4.2 Å) when $\chi = 180°$. The observed smaller width for $\chi = 0°$ may be attributed to the additional interaction between the close neigh-

TABLE 10. Crystallographic Data and Photoreactivities of Members of the Benzylidenecyclopentanone Series

compd[a]	Y	X	a, Å	b, Å	c, Å	space group	dimerization
B-*p*-Cl-BCP (81)	H	*p*-Cl	30.97	8.50	11.57	*Pbca*	no
B-*p*-Me-BCP (82)	H	*p*-CH_3	31.04	8.45	11.68	*Pbca*	no
p-Cl-BBCP (83)	*p*-Cl	H	17.18	10.59	8.80	$P2_1/c$	yes
p-Me-BBCP (84)	*p*-CH_3	H	17.34	10.68	8.74	$P2_1/c$	yes
p-Cl-B-*p*-Br-BCP (85)	*p*-Cl	*p*-Br	17.53	7.91	11.89	$P2_1/c$	no
p-Me-B-*p*-Br-BCP (86)	*p*-CH_3	*p*-Br	18.88	11.21	8.29	$P2_1/c$	yes

[a] See Scheme 6 for structures of compounds.

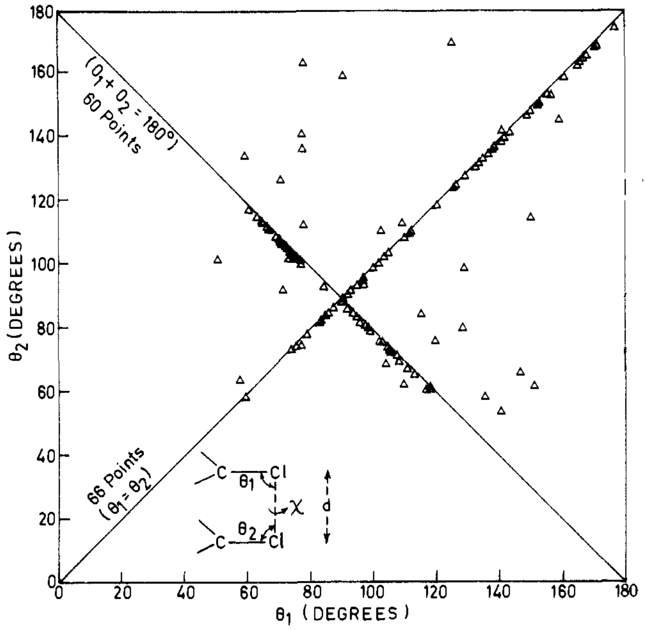


Figure 27. Mode of packing in chlorosubstituted aromatic organic crystals within < 4.2 Å.

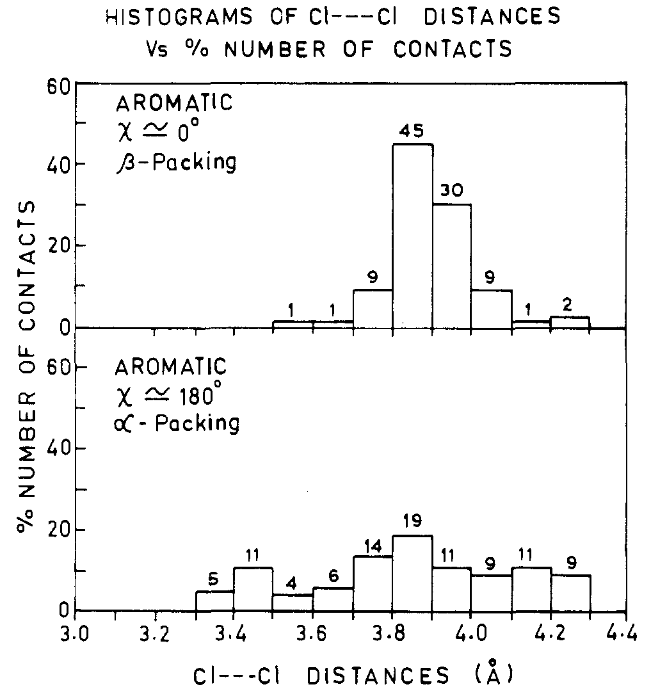


Figure 28. Histograms of Cl···Cl interactions vs. number of contacts.

bors. One may conclude from the results discussed above that when there is chlorine substitution, the chlorine atoms of the neighboring molecules in the crystal lattice tend to come closer to one another within a distance of about 4.2 Å. Additional interactions arising from the other groups may be expected to steer the molecule toward either an α or β type of packing arrangement. Maybe this is responsible for the dichloro substitution being more effective than the monochloro in driving the molecules towards β-packing.

A convenient method of gauging the magnitudes and relative importance of weak intermolecular Cl···Cl forces is to study cases where more than one type of interaction is possible. In this context, a limited survey on the packing modes of polychloroanilines, phenols, and related compounds has been made.[238,239] A graphical analysis has been made of hydrogen bonding patterns and nonbonded interactions in the crystal structures of six dichlorophenols. Of the six isomeric phenols, three crystallize with the β structure. From their analysis, the authors have concluded that hydrogen bonding is the primary factor, but the chlorine atoms are active in steering the molecule into energetically favorable packing modes, provided this is possible within the framework of the energetically stronger hydrogen-bonded geometry. In the three β structures, the chlorine atoms perform the function of bringing stacks closer via Cl···Cl interactions, whereas in the three non-β structures stabilization is achieved by means of strong Cl···Cl interactions and minimization of H···H repulsive forces. The ability for "Cl" to steer the molecules into β structure is felt more in the case of thiophenols and anilines than in phenols where strong hydrogen bonded networks are prevalent.

B. Methyl Substitution and the Question of Isomorphism with Chloro Derivatives

One of the strategies that has been explored in crystal engineering operations is the replacement of groups of equal molecular or atomic volume. In this connection, the interchangeability of chloro (19.9 Å^3) and methyl (23.5 Å^3) groups has been mentioned in the literature.[240] Methyl derivatives frequently crystalize in structures isomorphous with those of the correspondingly substituted chloro compounds. If this principle holds good, the promise of methyl substitution as a steering group is obvious in light of the above discussion on chloro substitution.

A remarkable observation with respect to chlorine-methyl interchangeability has been made in the 2-benzyl-5-benzylidenecyclopentanone series.[30] In accordance with expectation, compounds 81 and 82 are isomorphous (Table 10) and both are light stable, whereas compounds 83 and 84, which are also an isomorphous pair, are photoreactive. The crystallographic and photochemical properties of compounds 81 to 84 are therefore well behaved so far as the chlorine-methyl interchangeability is concerned. However, Schmidt has reported that crystal structures of *o*- and *p*-methyl-

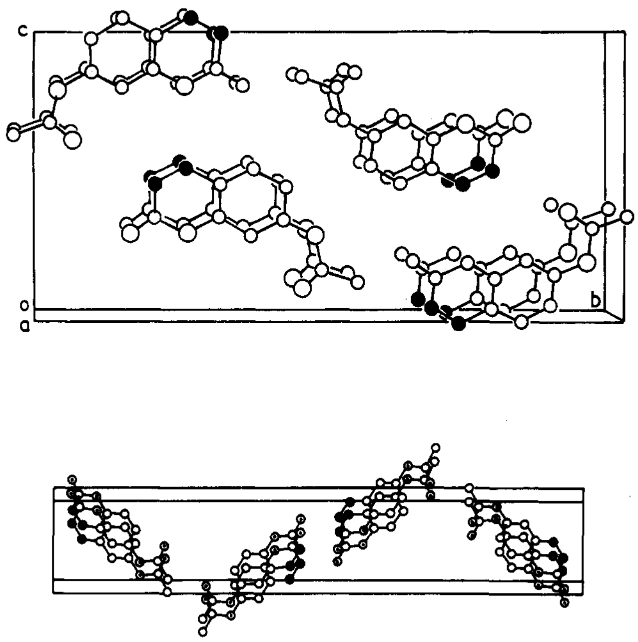


Figure 29. Unit cell packing arrangements in 7-acetoxycoumarin (a) and 6-acetoxycoumarin (b).

cinnamic acids are not related in an obvious manner to the corresponding chloro acids.[17] Further, in the cyclopentanone series itself, compounds **85** and **86** display a marked difference in reactivity with respect to one another (Table 10). Further, recent studies on coumarins[19] demonstrate clearly that the interchangeability, solely based on the closeness of the size of methyl and chlorine substituents, cannot be taken to be valid under all circumstances. The crystallographic and photochemical properties of the methylcoumarins turned out to be entirely different from those of the corresponding chlorocoumarins. While three of the five chlorocoumarins undergo topochemical dimerization and pack in a β-type arrangement, none of the corresponding methylcoumarins show topochemical behavior. The validity of the interchangeability or otherwise of chlorine by methyl may depend upon the importance of the contribution of the interaction energy of the interchangeable atoms in comparison with the contributions from the remaining atoms.

C. Acetoxy Substitution

Although the significance of the acetoxy group for bringing the molecules into a suitable geometry in the solid state for either polymerization or dimerization was recognized earlier, only recently has a systematic analysis on the mode of packing in aromatic and aliphatic compounds with acetoxy substitution been carried out.[241] The results, although encouraging, are not as clear cut as in the case of "chlorine" substitution.

Recent studies on coumarins provide some insight into the role of "acetoxy" substitution in dimerization reactions. Of the five acetoxycoumarins investigated, three underwent dimerization in fairly high yield to the corresponding syn head–head dimers. The packing diagram for 7-acetoxy and 6-acetoxycoumarins are shown in Figure 29. A similar packing arrangement is expected to be present in photodimerizable crystals of 4-methyl-7-acetoxycoumarin also. Thus, it is clear that the acetoxy group plays a strategic role in steering coumarin rings to pack themselves into a β-type stacked structure. Packing similar to the above has been reported with 4-(2-carboxyvinyl)-α-cyanocinnamic acid and its dimethyl ester.[242,243] A parallel plane to plane stack is found along the short c-axis (3.956) in which the molecules overlap completely. But, as to be described below, the analysis based on the Cambridge Data Base does not show clearly that acetoxy group substitution ensures β-type packing. From what is observed in acetoxycoumarins it may be reasonable to conclude that the nature of the ring system, e.g., coumarin in this case, has also an important role to play in achieving β-packing.

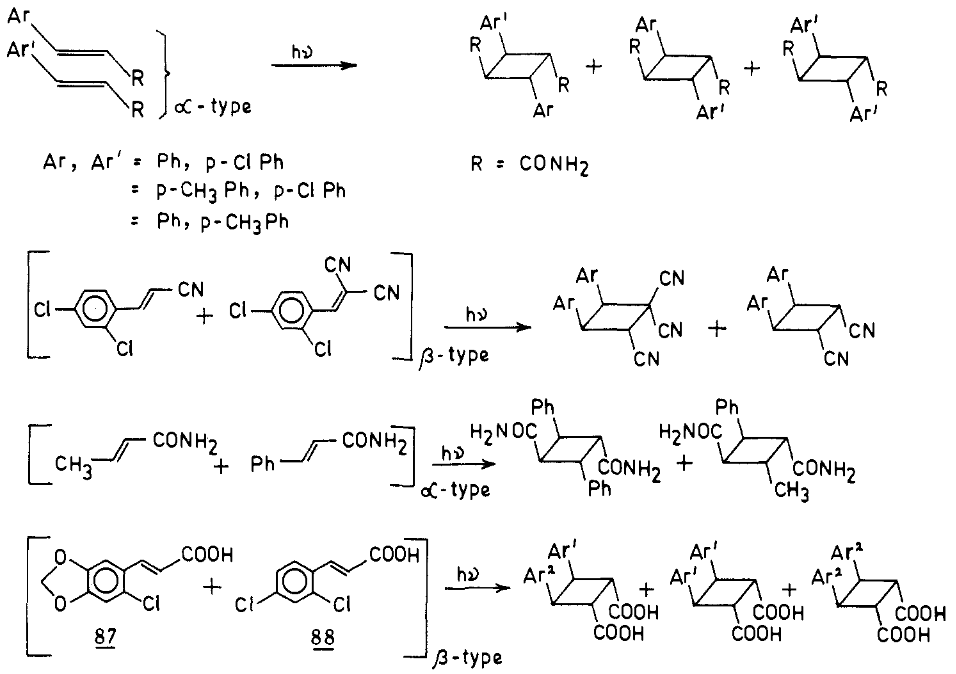
Interactions involving the overlap of an ester group of one molecule with the benzene ring of another have been utilized to steer acrylic acids into packing arrangements suitable for solid-state polymerization. Similarly, Addadi and Lahav have utilized ester functionality as steering groups during their elegant asymmetric syntheses of chiral dimers and polymers from benzene-1,4-diacrylates.[63,64] In these two cases an attractive interaction between carbonyl and phenyl groups of adjacent molecules has been proposed to be responsible for juxtaposing the double bonds at a distance of ~4 Å.

The above observations suggest that the acetoxy group is a potential steering group. In order to assess the generality of this tentative conclusion, a search in the connectivity file for the acetoxy group has been performed and some general conclusions have been arrived at based on 53 cases.[241] Out of the 53 cases examined, 39 had contacts less than 4.2 Å between the acetoxy groups. Of these, 20 structures exhibited dipolar interactions between the carbonyl groups. In six structures, the arrangement of the acetoxy group is such that the carbonyl carbon of one molecule is within 4.2 Å of the oxygen of the neighboring molecule. In four cases intermolecular contacts (~3.4 Å) are observed between a methyl group and an oxygen of the carbonyl group. In only three cases did one find the acetoxy group oriented in a syn head–head fashion with all atoms of the group at a distance of ~4.0 Å (Figure 29). From the results obtained based on the above analysis, it appears that the acetoxy group is capable of bringing potentially reactive centers within 4.2 Å, in majority of the cases through dipolar interactions; however, no generalizations can be made regarding the preferred mode of packing.

D. Methylenedioxy Substitution

Very recently, Desiraju et al. have observed that the presence of the methylenedioxy substituent in a planar aromatic molecule such as 3,4-(methylenedioxy)cinnamic acid tends to favor its crystallization in highly overlapped structures.[244] They have noticed that in a series of (methylenedioxy)cinnamic acid derivatives, there is a preference for β-structure over the α and γ. This has been attributed to the nonbonded interactions involving oxygen. However, in the case of dimethoxy derivatives, the β structure is not expected due to the

SCHEME 58



repulsive intersheet H···H interactions. Such an interaction would become prohibitively large if the sheets were to be stacked with a 4-Å repeat axis. Although the methylenedioxy group is useful in a few compounds its generality is yet to be realized. Further, the interactions responsible for the β stacking are not established.

E. Complexation with Lewis Acids

An additional technique that has been utilized in crystal engineering is to cocrystallize α,β-unsaturated ketones with mercuric chloride which itself crystallizes in a cell of dimensions $a = 5.96$, $b = 12.74$, and $c = 4.33$ Å. For example, coumarin which is photostable in the solid state, forms a 1:1 complex with mercuric chloride which upon photolysis gives the topochemically expected syn head–head dimer. Coumarin in its stable form crystallizes with a shortest axis of 5.68 Å. The crystals of the complex have a repeat distance of 4.03 Å along the c-axis. Similarly, cinnamaldehyde and benzalacetophenone give crystalline 1:1 complexes with mercuric chloride having a 4 Å axis.

Recently, Lewis and co-workers reported the photodimerization of Lewis acid complexes of alkyl cinnamate esters with $SnCl_4$ and BF_3.[245] The exclusive formation of syn head–tail dimer upon irradiation of the crystalline $SnCl_4$ complex is in accord with the postulates of topochemical control of solid-state dimerization. The molecular structure of the 2:1 complex (ethylcinnamate: $SnCl_4$) displays the expected octahedral geometry with Sn at the center of inversion. The distance between the reactive double bonds in the infinite stacks of esters is 4.023 Å for one symmetry-related pair and 4.12[illegible] Å for the second symmetry-related pair, well within the range of values observed for photodimerizable cinnamic acids. Efficient solid-state photodimerization to yield α-truxillate dimers is observed also for the 2:1 $SnCl_4$ complexes of the trans isomers of methyl and n-propyl cinnamates and methyl α-methylcinnamate.

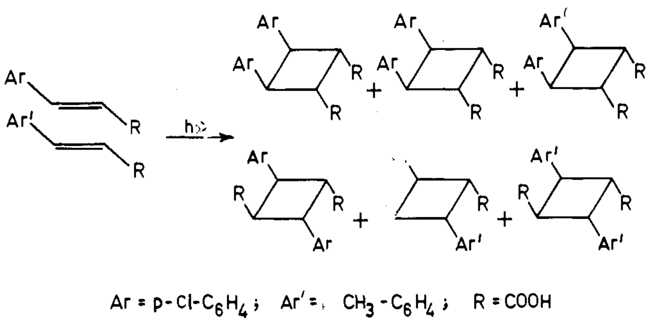
Yet another illustrative example is provided by $(UO_2)Cl_2$ complexes with *trans,trans*-dibenzylideneacetone.[246] Praetorius and Kohn reported as early as 1910 that uranyl chloride complexes of dibenzylidene acetone yields truxillic acid type dimer upon irradiation as a solid material.[247] This is to be contrasted with the photostability of dibenzylideneacetone in the absence of uranyl chloride. Light sensitive 2:1 complexes possess two pairs of ethylenic bonds adjacent to each other within a distance of 4.1 Å. The production of the "truxillic" dimer follows directly from the structure of the complex. The examples thus far reported provide optimism and certainly encourage further exploration of this technique.

F. Solid Solution or Mixed Crystal Formation

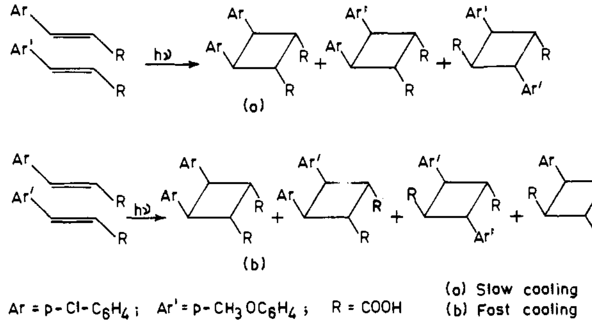
A logical extension of the technique of cocrystallization would be to use closely similar molecules to orient the unreactive olefins in a proper geometry for reaction. This technique, often termed "mixed crystal" or "solid solution" formation, has been originally investigated by Schmidt, Cohen, and their co-workers[235,236] and recently by others.[248,249]

Studies by Schmidt on cinnamic acids and cinnamides have shown that one can obtain a solid solution between either the two reactive or between a reactive and an unreactive molecule.[235,236] In all of these cases, upon irradiation, in addition to obtaining homodimers, hetero dimers were also obtained. For example, photolysis of solid solutions prepared by melting equimolar quantities of pairs of β-arylacrylamides (α-forms) produced in every one of the eight examples studied, three products, two homodimers, identical with the photodimers obtained by solid-state dimerization of the respective solid monomer amides and a hetero dimer, identified in each case as the pseudocentrosymmetric dimer (Scheme 58). Very recently mixed-crystal formation between 6-chloro-3,4-(methylenedioxy)cinnamic acid and 2,4-dichlorocinnamic acid has been reported.[247] Both individually crystallize in the β-structure and yield topochemically expected β-truxinic acids. Mixed crystals with the ratio 2:1 (87 and 88) are obtained from

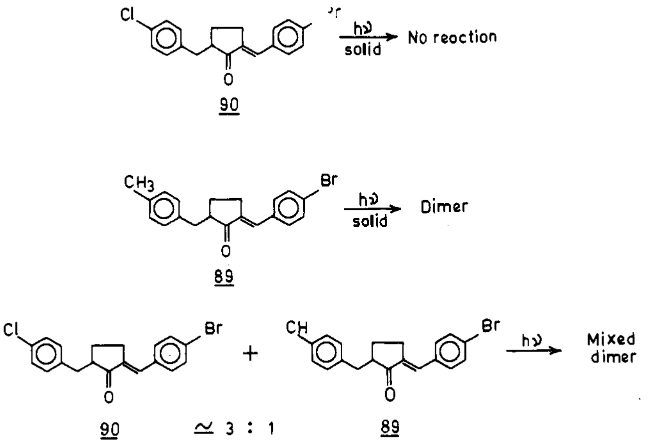
SCHEME 59



SCHEME 60



SCHEME 61



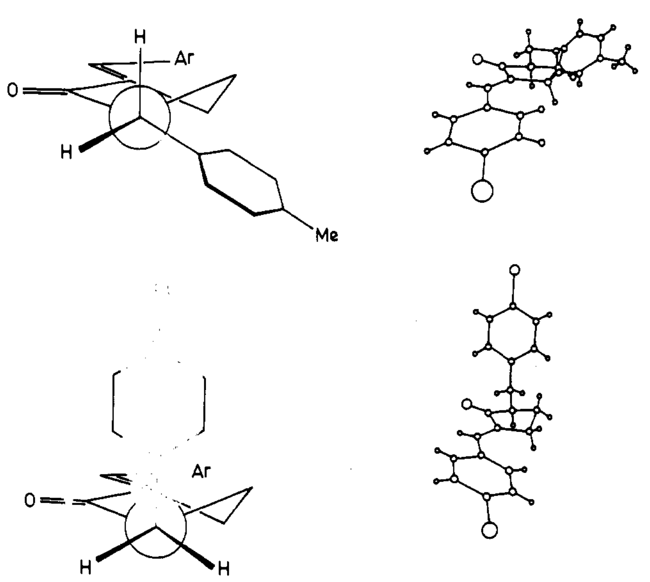


Figure 30. Molecular conformations of 89 and 90 as found in their crystals. Neuman projections (top) and computer drawings (bottom).

ethanol, and photolysis of this solid solution leads to three mirror symmetric or pseudomirror symmetric (homo and hetero) dimers. It is of particular interest to note the behavior of solid solutions from monomers which by themselves crystallize in α and β types. Two such pairs were studied.[236] Cinnamic (α) and *p*-chlorocinnamic (β) acids; and *p*-methyl (α) and *p*-chlorocinnamic (β) acids. Each pair produced six dimers, the α and β homodimers of each monomer and the two (α and β) heterodimers (Scheme 59). The results reported above may be most simply interpreted by assuming a degree of mutual miscibility of each of the two constituents in the phase of its partner, without any drastic change in each others crystal structure.

The most useful and interesting situation would be to induce reactivity of the photostable form through the formation of mixed crystals of a photostable compound with a reactive one. This has indeed been achieved. For example, an equimolar solution of an α-type monomer, *p*-methylcinnamic acid, and a γ-monomer, *p*-methoxycinnamic acid, yields three α-dimers, i.e., dimers from both *p*-methyl and *p*-methoxycinnamic acids.[235,236] Further, an equimolar solid solution prepared from *p*-chlorocinnamic acid which crystallizes in a β-type structure, and *p*-methoxycinnamic acid which gives a light stable γ-type, gave two different kinds of mixed crystals affording, on irradiation, different product distributions (Scheme 60). It therefore appears that small quantities of guest molecules can stabilize polymorphic forms which are normally metastable or unavailable.

The above type of study has recently been extended to crystals composed of solid solutions of various benzylidenecyclopentanones which differ only by a chloro and methyl interchange.[248,249] The most noteworthy result was obtained in the cocrystals of **89** and **90**. Ketone **89** crystallizes in a photoactive modification while compound **90** crystallizes in a photostable form (Scheme 61). The main difference between the forms lies in the molecular conformation (Figure 30). Yet, these two compounds form mixed crystals, isostructural to ketone **89** with the reactive centers in the mixed structure separated by 3.866 Å. Photolysis of these mixed crystals yielded an unsymmetrical cyclobutane, the structure of which is yet to be established.

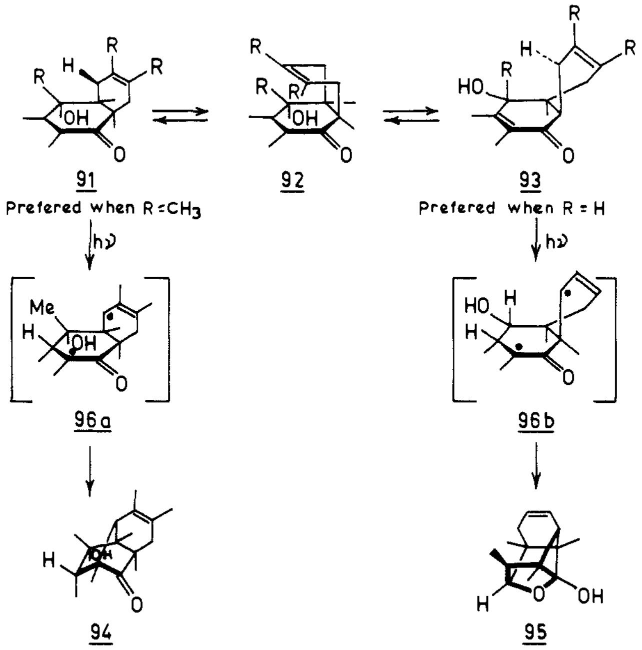
It appears from these results that the strategy of mixed crystal formation may be successfully used to incorporate molecules into new and photoactive modifications. Further, it is clear that two compounds having completely different crystal structures form mixed crystals primarily as a result of forced changes imposed upon the molecular packing of one component by the second component.

Very recently Thomas et al.[250] have proposed a general method of predicting the packing of the molecules in crystals. Based on extensive analysis of the crystal structures of BBCP derivatives, the influence of substituents on solid-state reactivities and modes of molecular packing have been rationalized. They claim that this approach could lead to engineering of solids to desired reactivity.

G. Unimolecular Reactions

In principle, the reactivity predictions should be easier to make for unimolecular processes since con-

SCHEME 62



formation rather than intermolecular orientation is often the controlling factor. As opposed to dimerization reactions, systematic studies on unimolecular transformations in the solid state have been limited. This is also reflected in "crystal engineering" investigations. Such an attempt has been made only in one unimolecular reaction.

It has been established that altering the configuration at C(4) in analogues of 91 changes the solid-state photoproduct (Schemes 28 and 62).[122] Based on systematic studies it became clear that the bulkier of the two groups at C(4) adopts the pseudoequatorial position which in turn determines the preferred conformation of the molecule in the solid state and hence the photochemistry. This logic led to correct predictions of products in 92. The solid-state conformation of 92 is predicted to be A. Product 93 is expected and indeed obtained in >75% yield in solid state.[122]

VI. Subtler Aspects of Photoreactivity in Solids

A. Role of Neighbors in Solid-State Reactions: Concept of Reaction Cavity

The topochemical postulate states that "reactions in the solid state occur with minimum atomic or molecular movement". This implies that the reactive centers must initially be properly juxtaposed in the crystal for the reaction to occur. Further, it is believed that the photochemical processes in molecular crystals are constrained by lattice forces which are assumed to maintain electronically excited molecules in structures close to the positions and orientations they had in their ground states. This concept of preformation is obviously deficient in at least two respects. Firstly, it does not take into consideration the importance of nearest neighbors. The role of the nearest neighbors is reduced to that of passive spectators during the progress of the reaction. Secondly, it does not give due consideration to the changes that may be caused by molecular excitation. In essence the topochemical principle is an expression of the mechanical stiffness of the lattice surrounding the reaction site, allowing only small displacement as the excited reactants progress towards the products. In this context, Cohen has advanced the concept of the "reaction cavity" which gives due importance to the presence of nearest neighbors.[251,252] More recently Craig and his co-workers have emphasized the possible effect of electronic excitation in a molecular crystal.[253-256] They have introduced a new concept termed "dynamic preformation". These concepts which are refinements of original "topochemical principles" enable one to understand many photoreactions which are apparent violations of original topochemical rules.

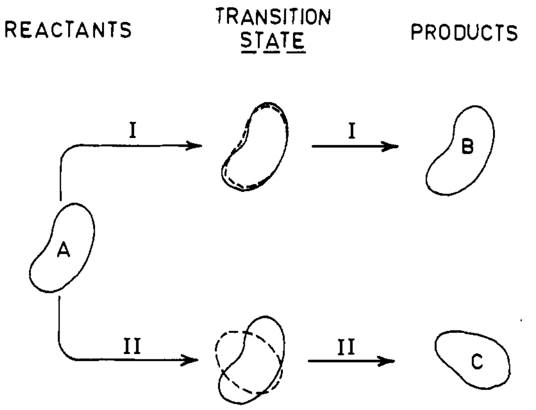
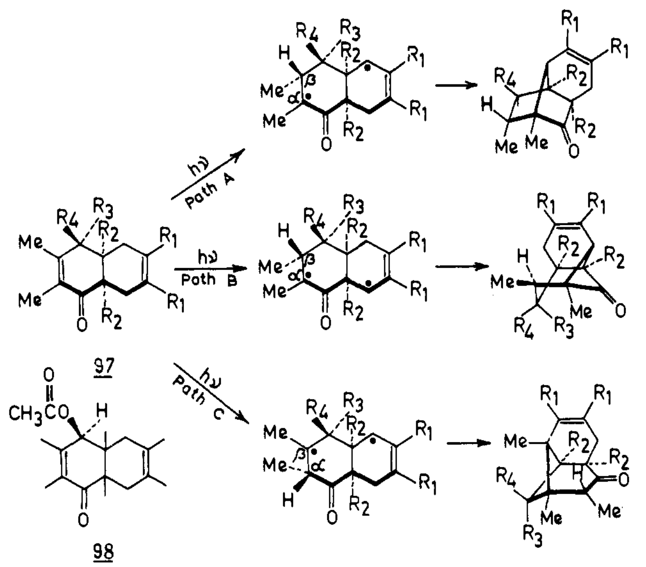


Figure 31. Pictorial representation of "reaction cavity" concept.

Cohen introduced the concept of the "reaction cavity" in the crystal as an aid to interpret the course of a variety of solid-state reactions. This concept has been extensively utilized by him to understand the geometries of the excimers of polyaromatics in the crystal.[257-263] The molecules taking part in a reaction occupy a certain size and shape in the crystal. This space occupied by the molecules is the reaction cavity and is surrounded by other molecules. The atomic movements constituting the reaction would cause "pressure" on the cavity wall which may tend to become distorted. This distortion, then, involves a large decrease in the number of attractive forces and/or a large increase in the number of repulsive forces. However, any such distortion in shape would be restricted by the close-packed environment; as a result only those reactions which involve minimal change in the external contacts of the reacting molecules would be energetically feasible. Therefore, the topochemical postulate can be redefined as "reactions proceeding under lattice control do so with minimal change or distortion of the surface of the reaction cavity". This concept is valuable in predicting the course of a reaction when more than one reaction is topochemically permitted. If more than one product is topochemically permitted, the preferred one will be that for which the transition state involves the least change in shape of the reaction cavity. Consider two hypothetical reactions giving products B and C from A (Figure 31). 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. While for reaction I the shape of the cavity remains practically unchanged during reaction, for II the transition state is energetically very unfavorable because of the bulges and voids formed. Thus the nearest neighbors constrain the system to act by path I (to give B) rather than by path II (Figure 31).

SCHEME 63



Two elegant examples have become available recently which illustrate the use of the "reaction cavity" concept in predicting the course of solid-state reactions. Enones of general structure **97**, when irradiated in the solid state undergo one of the two possible photorearrangements (Scheme 63) as discussed in detail in section III. Scheffer and his co-workers have reported recently that in one instance, however, that of enone **98**, irradiation in the solid state lead exclusively to the product resulting from initial hydrogen atom abstraction by the α-carbon atom of the enone chromophore (path C, Scheme 63).[39,264] Hydrogen abstraction by both C_α and C_β carbons are favorable in the case of **98** ($H\cdots C_\alpha$: 2.74 and $H\cdots C_\beta$: 2.70 Å). Thus the preference for C_β abstraction is not evident from the geometrical criteria. This suggests that nearest neighbors control the hydrogen being abstracted. A change in hybridization at C_α and C_β from sp^2 to sp^3 is expected to accompany the hydrogen transfer process and this would force the methyl groups at these centers into close contact with certain hydrogen atoms on neighboring molecules and thus sterically impede the reaction. Computer simulation of the pyramidalization process at C_α and C_β in **98** (with stationary lattice neighbors) showed no short contacts (termed "steric compression") during pyramidalization at C_α and significant steric compression during the pyramidalization at C_β. Figure 32 shows stereodiagrams of enone **98** before and after pyramidalization at C_β. The steric compression accompanying full 55° pyramidalization is indicated by the dotted lines and consists of short hydrogen$\cdots$hydrogen contacts. An estimate of the steric compression energies accompanying pyramidalization was made using semiempirical calculations (Allinger's MM2 force field program and Lennard-Jones' 6-12 potential function). The steric compression energy for fully pyramidalized **98** at C_β corresponds to ~12 kcal/mol. This, when compared with zero steric compression during pyramidalization at C_α, accounts for the preference in hydrogen abstraction by C_α. Thus, it is clear that consideration of the unfavorable interaction between the reacting molecules and their stationary neighbors could provide an insight into the mechanism of solid-state reaction.

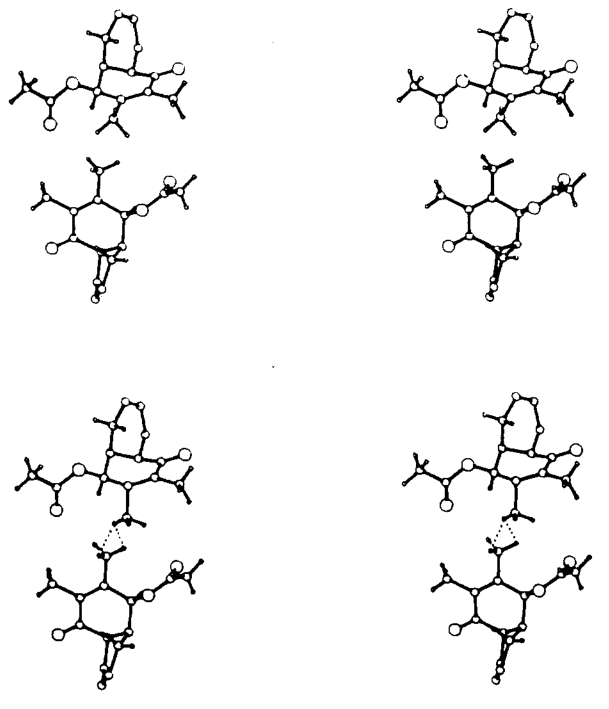


Figure 32. Stereodrawings of enone **98** before (a) and after pyramidalisation at the β-carbon. The steric compression contacts are shown by dotted lines.

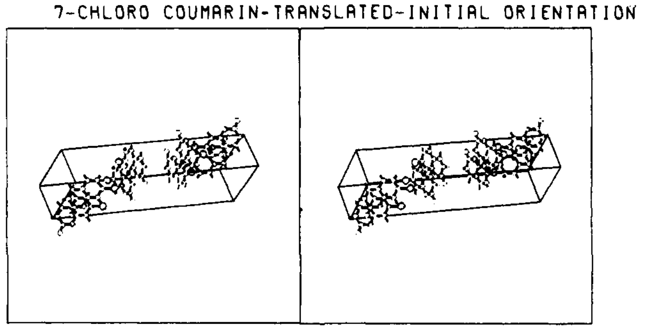


Figure 33. Stereodrawing of the packing arrangement of 7-chlorocoumarin.

A similar observation was made in the case of 7-chlorocoumarin.[23] Irradiation of crystalline 7-chlorocoumarin yielded a single dimer (70% yield) assigned the syn head-head configuration. The packing arrangement shown in Figure 33 reveals that there are two potentially reactive pairs of 7-chlorocoumarin. One pair being translationally related has a center-to-center distance of 4.54 Å. Further, the centrosymmetrically related double bonds are closer, the center-to-center distance between them being 4.12 Å. Translationally related coumarins are expected to yield syn head–head dimer whereas the centrosymmetrically related coumarins would give anti head–tail dimer upon excitation. However, the only dimer obtained on excitation corresponds to the syn head–head dimer. The reason for the absence of reaction between centrosymmetrically related monomers in spite of a closer distance (4.12 Å) is not immediately obvious. We have estimated[265] the energies involved in bringing these two pairs of molecules to a geometry ideally suited for dimerization in the crystal lattice. It is believed that the best π overlap between the reacting double bonds can be achieved when θ_1, θ_2, θ_3, and θ_4 (Figure 5 for definition) are 0, 90, 90, and 0°, respectively. One of the assumptions in this

TABLE 11. **Results of Lattice Energy Calculations for Reactive and Nonreactive Olefins**[a,b]

compd	d, Å	initial arrangement				initial energy, kcal mol^{-1}	final energy, kcal mol^{-1}	rise in energy, kcal mol^{-1}
		θ_1, deg	θ_2, deg	θ_3, deg	θ_4, deg			
methyl *m*-bromocinnamate	3.93	38.2	65.2	104.8	31.5	−20.4	6705.6	6726.0
4,4,8α-trimethyl-8αβ-carbomethoxy-4aβ,5,8,8a-tetrahydro-1(4*H*)-naphthalen-1-one	3.79	0.0	81.65	63.5	0.0	−21.5	1482.9	1514.4
7-methoxycoumarin	3.83	67.5	109.9	66.5	0.5	−37.3	162.8	200.1
7-chlorocoumarin								
pair I (translational)	4.454	0.0	131.8	85.3	0.0	−17.9	159.1	177.0
pair II (centrosymmetric)	4.12	0.0	127.9	73.0	0.0	−17.9	18064.9	18082.8
8-methoxycoumarin								
pair I	4.07	0.0	122.4	63.8	0.0	−37.2	7.8	45.0
pair II	3.87	0.0	117.4	67.7	0.0	−37.2	−9.1	28.1
methyl 6-isobutyl-2-methyl-4-oxocyclohex-2-enecarboxylate	3.86	0.0	102.2	108.1	0.0	−19.7	10.0	29.7
7-acetoxycoumarin	3.83	0.0	106.4	110.3	0	−20.1	147.6	167.6
6-acetoxycoumarin	3.90	0.0	94.1	118.3	0	−21.2	−12.9	8.3
benzylidenebutyrolactone	3.66	0.0	109.3	77.0	0	−18.5	−13.6	4.9

[a] For a definition of geometrical parameters see Figure 5. [b] For structures of compounds see Scheme 8.

approach is that the first step in dimerization involves an attempt by both the molecules to reach a full π orbital overlap. But in these two pairs θ_2 and θ_3 deviate significantly from the ideal value of 90° (translated pair, $\theta_2 = 131.8°$, $\theta_3 = 85.3°$, $d = 4.454$ Å; centrosymmetric pair, $\theta_2 = 127.9°$s, $\theta_3 = 73°$, $d = 4.12$ Å). Lattice energy calculations were carried out using a computer program (WMIN) developed by Busing.[266] Molecules were treated as rigid bodies, rotated and/or translated by choosing orthogonal coordinate system appropriately. All the symmetry related molecules were subjected to the motional operation simultaneously. The program does not allow for rotation of an individual molecule in the crystal lattice. It is not possible in the program due to Busing[266] to keep the molecules surrounding the reacting partners stationary while giving necessary rotations and translations to the reactants. The rise in energy to achieve the ideal geometry in the crystal lattice for the translated pair was 177 kcal/mol whereas for the centrosymmetric pair the energy increase was much larger (18082.8 kcal/mol). Although the absolute values based on the above calculations are not meaningful, the relative values are generally useful to explain the excited-state reactions. It is evident then why the dimerization is preferred between the translated pair although the distance criteria alone would lead us to predict the reaction between the centrosymmetric pair. The two examples provided, one each from unimolecular and bimolecular photoreactions, illustrate the importance of considering the role of nearest neighbors in controlling the course of solid-state reactions.

The reaction cavity approach is also helpful in understanding the nonreactivity of a few molecules in spite of a favorable topochemical arrangement in the solid state. Compound 2 (Scheme 8), although crystallizing in a lattice arrangement which is ideal for intermolecular [2 + 2] photodimerization, surprisingly exhibits complete lack of photoreactivity when irradiated in the solid state. The potentially reactive double bonds are oriented in a head–tail fashion and are parallel, directly one above the other and only slightly offset along the double bond axis. The geometrical parameters for 2, useful to identify the orientation of the double bonds, are $\theta_1 = 0°$, $\theta_2 = 81.65°$, $\theta_3 = 63.5°$, $\theta_4 = 0°$, and center–center distance 3.79 Å. Scheffer and his co-workers have attributed,[39,264] the lack of reactivity to the steric compression (short contacts) developed between the reactive molecules and the nearest neighbors when reactive molecules X and $\bar{X}$ start to move towards one another. The packing diagram in Figure 34 reveals the situation. The molecules Y and $\bar{Y}$ act as stationary impediments to photodimerization. Using semiempirical calculations they have shown that both the single-motion (one molecule moves and the other is stationary) and the dual-motion pathways (both the reactive molecules move toward each other) involve significant activation energy. We have come to the same conclusion using lattice energy calculations.[265] As elaborated above we have estimated the lattice energy using the WMIN program for various geometries of the potentially reactive pairs of molecules in the crystal. Table 11 summarizes the results for a few reactive and nonreactive olefins. It is clear that for the reactive olefins the rise in lattice energy to bring the two molecules to the total π orbital overlap is small whereas for the nonreactive olefin 2 the rise in energy is enormous (1514 kcal/mol^{-1}). As mentioned earlier the absolute values are not meaningful although the relative values could be of some help. Therefore, it is clear that the nearest neighbors or the surroundings could inhibit the progress of the reaction even though the reactive molecules could be suitably geometrically arranged in the crystal.

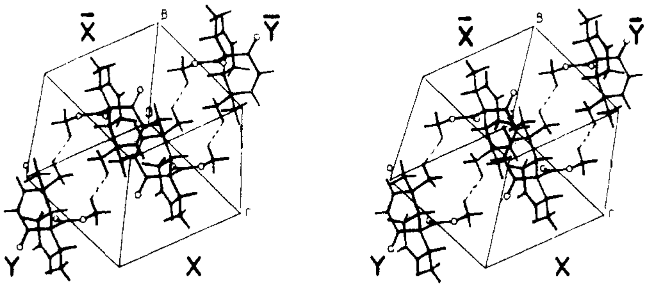
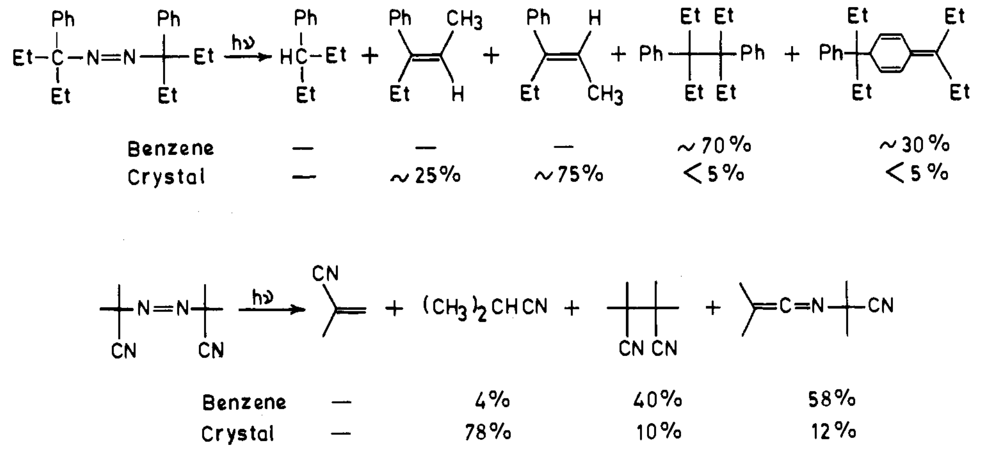


Figure 34. Stereopacking diagram of enone 2 (see Scheme 8).

Recently, Gavezzotti has explored the role of molecular environment in the crystal towards reactivity and has generalized that a prerequisite for crystal reactivity is the availability of free space around the reaction site.[267] He has developed a computer program which can be used to perform volume analysis of various kinds of molecular systems and structured media.[267-269] Using this he has successfully identified the presence of a void in the crystal structure of azobis(isobutyronitrile)

SCHEME 64



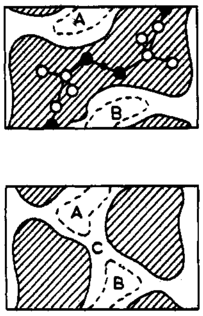


Figure 35. D_i (the fraction of the occupied space) map of azobis(isobutyronitrile) before (a) and after (b) elimination of nitrogen.

(AIBN). The solid state photoproducts of AIBN are mainly isobutyronitrile and methacrylonitrile (Scheme 64). The D_i (the fraction of occupied space in the i-th elementary volume) map for AIBN shown in Figure 35 is indicative of the packing mode of this compound, which consists basically of a parallel arrangement of molecules with large pockets of intermolecular free space. Gavezzotti proposes that the reactivity of AIBN crystals is greatly favored by the voids in proximity with the azo chromophore. These voids provide space for the incipient N_2 molecule and help relax the otherwise prohibitive internal stress that results from its formation.

B. Photoinduced Lattice Instability: Concept of Dynamical Preformation

The static concept of preformation or a topochemical postulate based on ground-state lattice equilibria is deficient in not taking into account changes caused by molecular excitation. Craig and his co-workers, based on extensive theoretical calculations, have drawn attention to another type of preformation, "dynamic preformation" which may influence product formation.[253-256] According to them "dynamic topochemical rules" may control in many cases the product formed and may even determine whether a reaction proceeds at all. In such a model there is transient preformation of the reactant pair not evident in the equilibrium local structure. Thus, Craig suggests that a reaction that may not be expected based on the ground-state structure may indeed occur if the dynamic preformation can be tolerated in the crystal lattice by the nearest neighbors.

We present below a qualitative picture of the model due to Craig which can be of considerable use in understanding solid-state reactions. This model is expected to play a significant role in coming years and attract considerable attention of experimentalists.

Localized electronic excitation of a molecular crystal is expected to produce a particular type of instability of the lattice configuration leading to large molecular displacements. Localized excitation means the existence of an excited molecule which on account of its altered properties is seen by its neighbors as an impurity. The creation of this "impurity" molecule introduces a local instability in the lattice configuration and leads to relaxation. This relaxation process could involve large displacements from the original lattice structure and in that sense far from the equilibrium configuration of the unexcited crystal. This logic has indeed been found to be valid by Craig and Collins[253] for a simple one-dimensional lattice. Based on a simple monoatomic lattice model they conclude that photoexcitation does produce a local instability in the lattice structure which is relieved by large amplitude displacements in more than one possible way.

In three recent papers, Craig and his co-workers[254-256] have cited examples where excimers or exciplexes form on excitation in the solid state but are not preformed in the ground state. They have shown through extensive theoretical calculations that in these polyaromatics, a short term lattice instability created via excitation has the effect of driving one molecule close to a neighbor thus promoting excimer or exciplex formation. Lattice energy calculations on excited molecules in crystals of anthracene, 9-cyanoanthracene, and 9-methylanthracene were carried out by Craig and Mallet[254] using a simple center-of-mass attractive excitation potential. Interestingly, excitation of the crystal of 9-cyanoanthracene led to the result that for a short period after excitation, an excited molecule can be displaced away from its equilibrium position into a asymmetrical local structure, with the excited molecule closer to one neighbor in the stack of molecules than to the other. In such a model there is a transient preformation of an excimer not evident in the equilibrium local structure. This is illustrated in Figure 36. It is clear that the excited molecule moves increasingly off-center towards its nearest neighbors in the stack with increasing excitation potential parameter. For 9-methylanthracene there is also a significant movement on excitation

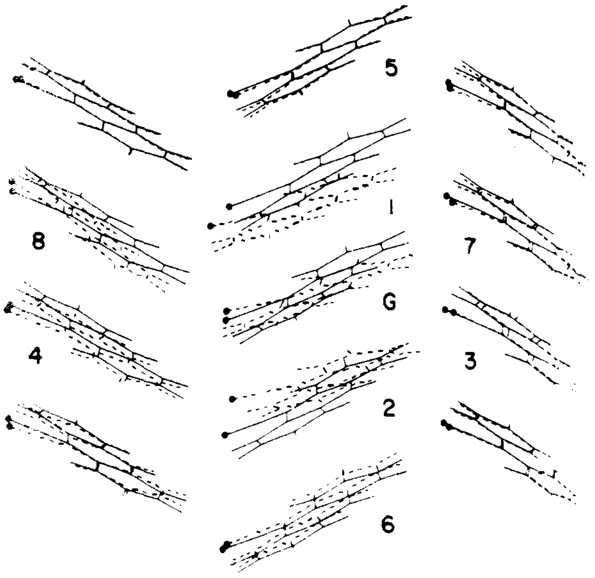


Figure 36. The structure of 9-cyanoanthracene containing an excited molecule and allowing the near neighbors to relax their positions and orientation.

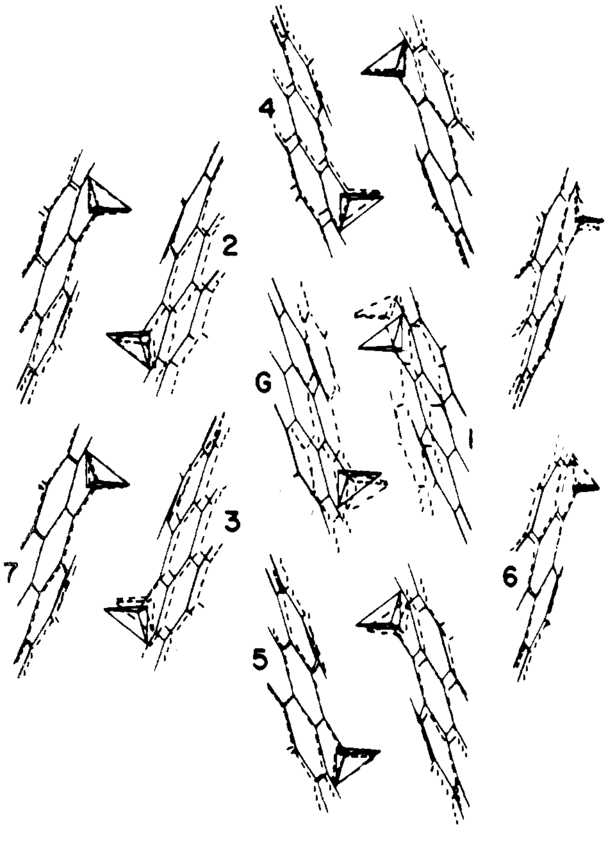


Figure 37. An excited molecule of 9-methylanthracene in a relaxed environment of nearest neighbors.

(Figure 37). There are similar indications for the mixed crystal 9-methoxyanthracene in 9-cyanoanthracene as well as 9-cyano- and 9,10-dimethylanthracene mixed crystals. Such findings draw attention to the need in experiments to look for evidence of dynamical factors in solid-state reactivity.

On the basis of the above presentation, dynamical preformation can be summarized as follows: short-term lattice instability caused by photoexcitation can have the effect of driving one molecule close to a neighbor so as to cause a photochemical reaction. If a reaction proceeds in the short time available before general lattice relaxation to the equilibrium ground-state structure it can be said to be dynamically promoted or preformed. We discuss two cases from the literature which may indeed be ideal examples of the dynamic topochemical postulate.

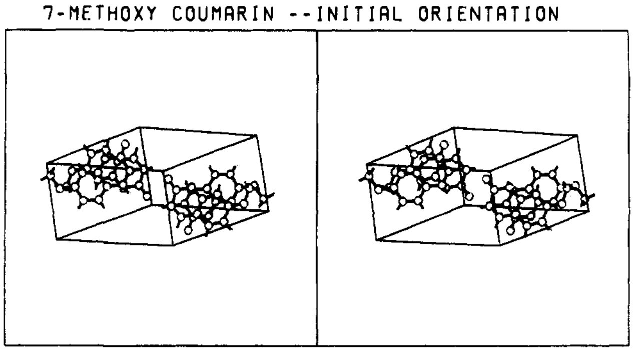


Figure 38. Stereodrawing of the packing arrangement of 7-methoxycoumarin.

X-ray crystal structure analysis of 7-methoxycoumarin reveals that the reactive double bonds are rotated by 65° with respect to each other, the center-to-center distance between the double bonds being 3.83 Å.[24] In spite of this unfavorable arrangement, photodimerization occurs in the crystalline state yielding syn head–tail dimer as the only product. As seen in Figure 38, the two double bonds, although within the reactive distance, are not suitably juxtaposed for dimerization. Having ruled out defects as the possible loci for the reaction, we have investigated the possible presence of a certain degree of inherent orientational flexibility of the molecules in the crystal lattice.[21,265] We believe that radiation energy absorbed by the reacting molecules is sufficient to allow the molecules to undergo the required rotation, provided the motion is cooperative and extends through the crystal. In order to investigate the inherent flexibility that may be available for such a cooperative motion, lattice energy calculations for the monomer crystal were carried out. This approach, although different from that of Craig's and lacking its rigor, yields results that are revealing. Lattice energy calculations performed using the WMIN program show that the energy increase to bring the two reactant molecules to proper orientation is only 200 kcal/mol, roughly similar to the value obtained in many ideally oriented pairs (Table 11), discussed earlier. In most crystals, electronic excitation increases the attractive forces, so that the excited molecule is bound more tightly to its nearest neighbor. With an increase in attractive forces between the reactive molecules upon excitation, one may expect that the motion of the molecules towards the maximum overlap geometry would involve less energy than that for the ground-state molecules. We believe that this is indeed the case with 7-methoxycoumarin. This example when compared with the photoinertness of methyl *m*-bromocinnamate is definitely interesting. In this case, similar to 7-methoxycoumarin, the double bonds are not topochemically oriented for dimerization (Figure 4). The distance between the centers of adjacent double bonds is 3.93 Å, but the double bonds are not parallel. They make an angle of 28° when projected down the line joining the centers of the bonds. Based on the behavior of 7-methoxycoumarin one would expect this molecule to undergo dimerization in the solid state. But it is photostable. The reason becomes obvious when one carries out lattice energy calculations. The energy increase to align the molecules parallel to each other in a geometry suitable for dimerization is enormous (~ 6726 kcal/mol) when compared to 7-methoxycoumarin. Such an increase will not favor dimerization. Thus "dynamic preformation" although it could favor dimerization, is resisted by the nearest neighbors.

The original topochemical postulate states that the reactions in the solid state involve minimal atomic movement. Recently, a few examples, most of which were mentioned in section II, have been reported which are exceptions to the traditionally accepted criteria regarding the alignment of reactive double bonds. Many photochemical dimerizations, polymerization, and excimer formations occur between double bonds or aromatics having poor initial orbital overlap. It is unnecessary to emphasize that many of these cases could be rationalized in the light of the "dynamic preformation" concept.

C. Consequences of "Local Stress" on Solid-State Reactions

The topochemical postulate discussed above has no doubt been outstandingly successful, but it has its limitations. For example, *cis*-cinnamic acid derivatives photoisomerize in the solid state before dimerization. More interesting exceptions which lead to an entirely different kind of rationalization are photostimulated reactions of azoalkanes and diacyl peroxides.[270–279] There are several examples of radical pairs which yield coupling products in solutions but give predominantly disproportionation products in the solid state. Photolysis of azobis(3-phenyl-3-pentane) in solution gives 3,4-diethyl-3,4-diphenylhexane and a photostable product (Scheme 64). However, in the crystalline state at −78 °C disproportionation products 3-phenylpentane and 3-phenyl-2-pentene as a 3:1 mixture of the *E* and *Z* isomers are obtained. From topochemical considerations, however, a predominance of the *Z*-isomer would be expected. It follows that more than token motion of the photolytic fragments must precede their reaction. It was observed that azobisisobutyronitrile upon photolysis accounts for only 5% radical–radical reactions in the solution phase but for 95% in the crystalline phase. From EPR studies and dynamic computer simulations it was concluded that one of the radicals formed in a first dissociation step has to rotate about the C—C≡N axis before abstracting a hydrogen atom from another radical (Figure 39). The difference observed in the solid-state behavior of acetyl benzoyl peroxide from that in solution is marked. While in solution or the melt more than a dozen products have been identified, photolysis of crystals gave only the simple cage products, methyl benzoate from loss of one CO_2 and toluene from loss of both (Scheme 65). X-ray studies showed that the incipient methyl radical in acetyl benzoyl peroxide is closer to the peroxy oxygen of the benzoyloxyl group than to its carbonyl oxygen (3.62 and 4.07 Å), but that the incipient CO_2 molecules should shield the peroxy oxygen from the methyl much more effectively than it shields the carboxyl group.

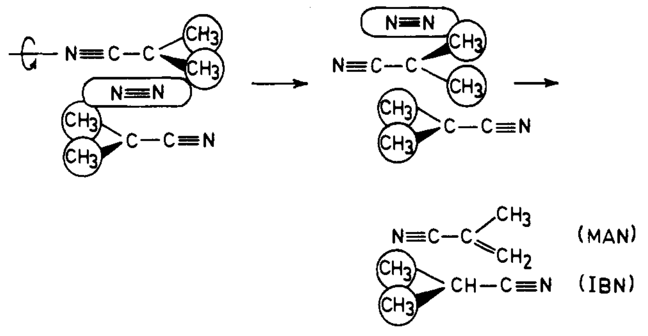


Figure 39. Schematic representation illustrating the rotational requirement during the disproportionation of AIBN.

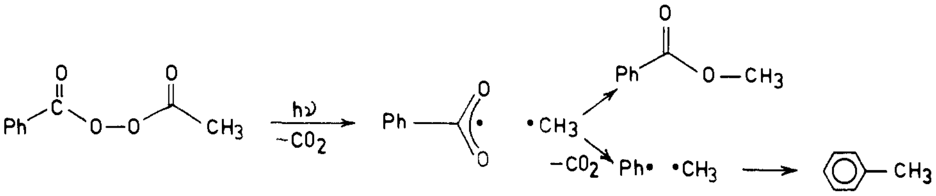
From an incisive study of the EPR spectra, the kinetic anomalies of methyl phenyl and methyl benzoyloxyl pairs were attributed to the environment's mechanical properties. When a molecule undergoes homolysis, the molecule must undergo expansion to allow for the cleavage of the bond and this in turn would produce stress or pressure in the lattice. The effect of the stress would be to influence the behavior of the radicals and also the reactions of the surrounding molecules. The confirmation of the stress hypothesis was obtained by investigating the photolytic behavior of dibenzoyl peroxide which gives a 5 K a phenyl–benzoyloxyl radical pair. Detailed investigations of different phenomena such as hindered rotation of neophyl radicals in 3-methyl-3-phenylbutanoyl peroxide, nontopochemical neophyl rearrangement in 3,3,3-triphenylpropanyl peroxide and rotational translation of decyl radicals in undecanoyl peroxide provide convincing proof in support of the hypothesis that local stress rather than topochemical factors control these reactions.[279]

D. Role of Defects

In a vast number of solid-state photodimerization reactions the crystal structure of the monomer predicts directly the stereochemistry of the dimer. But even before topochemical control in solid-state reactions were fully exploited in useful molecular transformations, examples of the breakdown of such control were reported. Some of the first well-studied examples of nontopochemically controlled reactions are the photodimerization of substituted anthracenes. In a classic communication, Craig and Sarti-Fantoni reported[280] that 9-cyanoanthracene and 9-anthraldehyde yield head–tail photodimers whereas from the crystal structure head–head dimers would be expected. These authors suggested that in these examples reaction occurs at defects or surfaces or in zones already disordered. It has now become established due to the pioneering contributions of Thomas and his co-workers that defects play a significant role in controlling the nature of the solid state dimerization of anthracenes.[281–291]

The crystal structure obtained by X-ray crystallography is an averaged structure and describes the environment of the vast majority of molecules in the solid. This has provided the basis for topochemical arguments. However, it is known that the real crystal has surfaces, dislocations and other defects which are not readily detectable by X-ray diffraction methods. It is not obvious a priori what role these minor features of a crystal plays in controlling the nature of a photo-

SCHEME 65



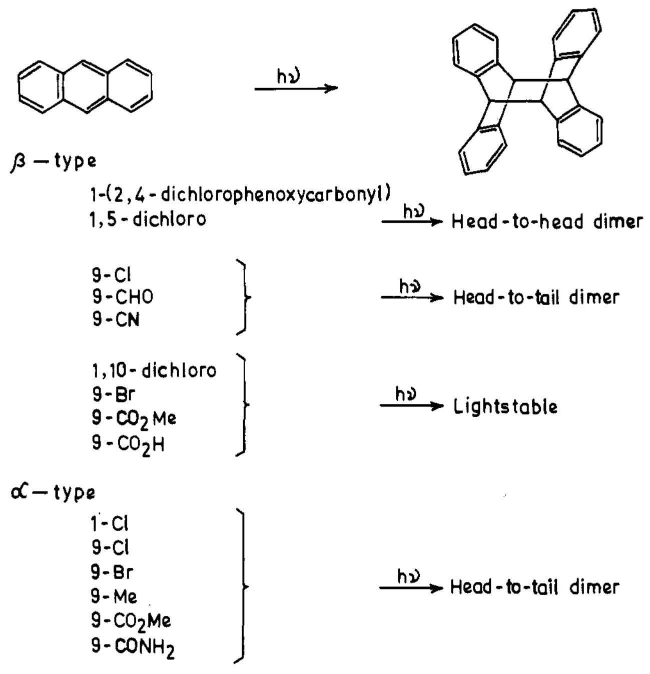
reaction. Craig and Sarti-Fantoni have proposed conditions under which the influence of defects are likely to be of importance.[280] When a crystal with defects is irradiated, radiation will initiate three events, namely, deactivation, dimerization, and transfer of excitation to another site. If it is assumed that the deactivation process is independent of the nature of the site, then, when the dimerization is slow, the process of transfer of excitation to a neighboring site would occur with a higher probability. Since the normal symmetry of the sites is disrupted at the dislocation, molecules at these sites are likely to act as trapping centers for excitation. This means that dislocations can function as favored areas of reaction. In other words, if the light energy can be transferred rapidly within the crystal after absorption then the photochemistry of the ideal lattice need not be important. Instead photoreaction would become more probable in regions where excitation energy can preferentially migrate. Since the number of molecules at defect sites will be small, the reaction must be accompanied by defect multiplication to give an appreciable yield of product. Because of the importance of transfer of energy in these systems, the reaction is very sensitive to impurities and is readily inhibited by suitable dopants.

The need to determine the nature of local or abnormal structure in the vicinity of structural imperfections is, therefore, paramount. What we require is an insight into the situation that prevails at the disrupted regions that have been locked into the crystal either during its genesis or as a result of subsequent deformation and maltreatment. Further, it is necessary to establish a correlation between sites of enhanced photoreactivity and sites of emergence of linear defects. The extensive tools available for attacking the problem of characterization of dislocations in metals and alloys is not suitable for the study of organic crystals. For example, in transmission electron microscopy, by far the most powerful technique for this purpose, it is desirable that the specimens to be studied be chemically stable under high-energy electron beams and relatively nonvolatile. These requirements are not usually satisfied by organic crystals, though the difficulties have, to some extent, been circumvented. Topographical studies (using optical and replica electron microscopy) of cleavage and habit faces have yielded valuable information about the sites of emergent dislocations. Chemical etching has, to date, proven to be the most convincing method of locating and characterizing dislocations in organic solids. The potential of X-ray diffraction topography[292] in characterizing the nature of defects and their correlation with reactivity in the field of organic solid state photochemistry has not been explored fully. An attractive feature of this method appears to be that it would allow us to follow up the changes taking place on the crystalline sample bathed in the X-ray beam when it is irradiated by UV radiation. When coupled with synchrotron sources the technique offers a promising area of activity. The value of atom–atom potential calculations in the elucidation of photoreactions in crystals originating in defects or in a metastable phase already present in the parent crystalline matrix has been recognized.[289]

A systematic chemical and crystallographic study in the laboratory of Schmidt has shown that the substituted anthracenes fall into at least three packing types corresponding to α,β, and γ classification.[293,294] In the γ-types, the molecular planes are not parallel and the distances between the meso atoms of neighboring molecules are greater than 5 Å. As expected these compounds are light stable in the crystalline state though they photodimerize in solution. In the α-type, anthracene molecules are packed pairwise across centers of symmetry such that the C(9)···C(10′) distances are short (<3.6 Å). β-type packing is analogous to γ except that the meso atoms are closer (<4 Å) and the molecules pack parallel and with appreciable overlap. A few examples of anthracenes belonging to each class and their photobehavior are summarized in Scheme 66. It is clear from the scheme that dimerization reactions of anthracenes generally do not conform to the topochemical principles. The photodimerization reactions of anthracenes which do not conform to topochemical postulates can be classified into two major categories: (i) the monomer matrix is topochemically favorable for dimerization, but the product is controlled by defects or lattice imperfections, and (ii) the monomer matrix is not suitable for topochemical dimerization, but irradiation results in dimer. In the first category lattice imperfections could lead to products that would be obtained either from the bulk matrix or to nontopochemical dimers (Scheme 66). In the following paragraphs a few of the systems which have been subjected to detailed investigations are summarized.

The crystal structure of anthracene shows no molecules that are separated by <4 Å, hence not appearing to permit any reactivity. Yet photolysis of anthracene in the crystalline state yields dimer.[295–299] Experimentally there is strong evidence to indicate that appreciable distortion of the anthracene lattice is required to permit photodimerization. Chandross and Ferguson[297] had originally suggested that the free surface rather than the bulk, of the crystalline anthracene functions as the seat of the reaction. Thomas and Williams,[281] supported by etch-pit studies, proposed that crystal defects may function as the preferred centers for reaction, it being possible that anthracene molecules have their excitation energies slightly reduced when they are displaced from regular lattice sites. When one half of a cleaved, melt grown crystal of anthracene is etched to reveal the emergent dislocations and the other separated half is exposed to radiation and ultimately examined by interference contrast microscopy, the degree of correspondence between etch pits and dimerization

SCHEME 66



centers is very high. It is of considerable importance to note that the recent electron microscopic study by Thomas and co-workers[290] has revealed that dislocations are probably not quite as important as was originally thought during the photodimerization of anthracene. Electron microscopic observations have indicated the coexistence inside "normal" anthracene, of thin regions of a metastable phase and that moderate stress produces crystallites of a new phase in coherent contact with the parent crystal matrix in one specific direction. It is interesting to note that in the new phase (space group $P1$) the $C_9 \cdots C_9'$ distance is 4.2 Å whereas in the original crystal ($P2_1/a$) this value is 4.5 Å. Further, electron microscopic observations, following UV irradiations, revealed that these crystallites of metaphase act as nuclei for photodimerization, which, in due course, spreads throughout the specimen. Thus, this particular example emphasizes that the existence of some kind of defect in organic crystals could be of little consequence photochemically. Also it illustrates the continued interest in seeking newer understandings for the nontopochemical phenomenon.

9-Cyanoanthracene molecules pack in an orthorhombic structure in which the molecules are arranged in columns with an interplanar distance of 3.5 Å. The marked overlap between molecules in the stack makes this structure ideal for head–head dimer formation. However, irradiation of 9-cyanoanthracene crystals results in a photodimer with head–tail geometry. This so called violation of the topochemical principle has been interpreted as being due to a photoreaction at defect sites.[280] Interference contrast and fluorescence microscopy have been employed by Cohen, Thomas, and their co-workers for the examination of cleaved and partially dimerized faces of the monomer.[283,284] As in the case of anthracene, discussed previously, a good 1:1 correspondence between regions of etch pits and regions of reaction was also observed in 9-cyanoanthracene crystals. Further, it was suggested that along the (221) slip plane preformation of monomer molecules having the antiregistry is feasible and that the photodimerization reaction occurs at such specific sites in crystals. Luminescence studies by Ludmer[300,301] and recently by Ebeid and Bridge[302] convincingly demonstrate the importance of defects in the photodimerization of 9-cyanoanthracene. Crystals of 9-cyanoanthracene show an excimer emission (9-head–head configuration). Most interestingly, such emission can be quenched in the presence of suitable dopants such as 9-chloro-10-anthraldehyde, anthraquinone, etc. More importantly, dopant molecules which influence the excimer decay of 9-cyanoanthracene also quench the photodimerization reaction. The most important observation is the total quenching of the photoreaction by means of the doping with 9-chloro-10-anthraldehyde. This together with the quenching of excimer fluorescence decay proves unequivocally that the photoreaction does not occur at the site of absorption.

The crystal structure of 1,8-dichloro-10-methylanthracene, like that of 9-cyanoanthracene, would lead us to expect the production of head–head dimer. Yet it is the head–tail dimer which is produced (Scheme 66).[303] This anomalous situation has once again been attributed to the defects in the crystal and support for this postulate comes from optical microscopic studies.[286–288] It has been shown with the help of optical microscopic investigation that dimer nuclei appear at emergent dislocations and tend to be aligned along the [001] and to a less extent, the [100] directions. It has been proposed that the slip system (210) [I20] brings about an incipient trans configuration accounting for the head–tail dimer formation. Crystals of 1,8-dichloro-9-methylanthracene belong to the space group *Pnma*. Examination of the structure shows that the molecules are too far apart (~7 Å) and unfavorably oriented to form a photodimer in the ordered crystal. Nevertheless, irradiation gives exclusively the head–tail dimer (Scheme 66). Efforts of Thomas and co-workers[286–288] have resulted in the identification of structural imperfections, chiefly dislocations, in the crystals of 1,8-dichloro-9-methylanthracene. It has been suggested that slip along [010] is conducive for the photoproduction of the *trans*-dimer.

Other examples in which defects have been proposed as the loci for photodimerization include 1,8-dichloro-, 1,4-dichloro-, and 1,5-dichloroanthracenes and -acenaphthylenes.[303] For detailed descriptions of defects in organic solids and for their importance in phototransformations readers are referred to excellent available reviews.[305–309]

VII. Conclusion

Interest in solid-state reactivity is not as widespread as solution-phase studies and remains in the cradle of a limited number of investigators. Although the main factors required for the dimerization reaction to occur in the solid state have been very well understood and the subtleties of the topochemical factors have come to light from recently reported results, the strategies for aligning the reactive bonds still remain to be achieved. The future strength of the field will be clearly determined by increased progress in our understanding of the factors controlling molecular packing. On the experimental side, apart from looking for chemical groups which may be of potential value in steering molecules in the crystal lattice, other avenues for achieving the topochemical requirements need to be explored. In this connection the strategies which are being employed for achieving segregated stacks of molecules in organic metals may be worth trying. Further, the possibility of using special topological features of molecules such as organic and inorganic systems as hosts exists and may prove fruitful.

It is also clear from the present review that although some successful attempts with regard to asymmetric synthesis in the solid state have been reported, further development in this very important area has not progressed and demands attention. There is a clear lack of understanding the mechanism of solid-state reactions. Present knowledge exists only on the initial and final stages of the organic solid-state reactions. Progress in this direction is expected in the coming years. Finally, many new solid-state reactions need to be discovered and many remarkable reactions reported in the beginning of the century should be investigated thoroughly. It seems likely that properly understanding reactions in organic crystals and fully realizing their synthetic potential will require better insight into the chemical and physical properties of solids at the molecular level. It is hoped that the knowledge gained through the studies of organic reactions in crystals, in turn, may be relevant to the solution of a number of pending problems such as the development of organic materials possessing unusual electrical and optical properties.

Acknowledgments. Our thanks are due to Drs. P. Arjunan and G. Usha and G. S. Murthy, K. Padmanabhan, and D. Kanagapuspam for their help in the preparation of the manuscript. We greatly appreciate Prof. J. R. Scheffer for constructive suggestions and for continued encouragement. The University Grants Commission, Government of India is thanked for financially supporting our solid-state program.

References

(1) Stobbe, H.; Steinberger, F. K. *Chem. Ber.* **1922**, *55*, 2225.
(2) Ribber, *Chem. Ber.* **1902**, *35*, 2411.
(3) Ciamician, G.; Silber, P. *Chem. Ber.* **1902**, *35*, 4128.
(4) Ramamurthy, V. *Tetrahedron* **1986**, *42*, 5753.
(5) Hasegawa, M. *Chem. Rev.* **1983**, *83*, 507.
(6) Dilling, W. L. *Chem. Rev.* **1983**, *83*, 1.
(7) Hasegawa, M. *Adv. Poly. Sci.* **1982**, *42*, 1.
(8) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.
(9) Cohen, M. D.; Green, B. S. *Chem. Br.* **1973**, *9*, 490.
(10) Thomas, J. M. *Philos. Trans. R. Soc. London* **1974**, *277*, 251.
(11) Thomas, J. M.; Morsi, S. E.; Desvergne, J. P. *Adv. Phy. Org. Chem.* **1977**, *15*, 63.
(12) Thomas, J. M. *Pure Appl. Chem.* **1979**, *51*, 1065.
(13) Addadi, L.; Ariel, S.; Lahav, M.; Leiserowitz, L.; Popovitz-Biro, R.; Tang, C. P. *Chemical Physics of Solids and their Surfaces*; Specialist Periodical Reports; Royal Society: London, 1979; Vol. 8, p 202.
(14) Schmidt, G. M. J. et. al. *Solid State Photochemistry* Ginsburg, D., Ed.; Verlag Chemie: New York, 1976.
(15) Cohen, M. D.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 1996.
(16) Cohen, M. D.; Schmidt, G. M. J.; Sonntag, F. I. *J. Chem. Soc.* **1964**, 2000.
(17) Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 2014.
(18) Kohlshutter, H. W. *Z. Anorg. Allg. Chem.* **1918**, *105*, 121.
(19) Gnanaguru, K.; Ramasubbu, N.; Venkatesan, K.; Ramamurthy, V. *J. Org. Chem.* **1985**, *50*, 2337.
(20) Ramasubbu, N.; Gnanaguru, K.; Venkatesan, K.; Ramamurthy, V. *Can. J. Chem.* **1982**, *60*, 2159.
(21) Bhadbhade, M. M.; Murthy, G. S.; Venkatesan, K.; Ramamurthy, V. *Chem. Phys. Lett.* **1984**, *109*, 259.
(22) Gnanaguru, K.; Murthy, G. S.; Venkatesan, K.; Ramamurthy, V. *Chem. Phys. Lett.* **1984**, *109*, 255.
(23) Gnanaguru, K.; Ramasubbu, N.; Venkatesan, K.; Ramamurthy, V. *J. Photochem.* **1984**, *27*, 355.
(24) Ramasubbu, N.; Guru Row, T. N.; Venkatesan, K.; Ramamurthy, V. Rao, C. N. R. *J. Chem. Soc., Chem. Commun.* **1982**, 178.
(25) Nakanishi, H.; Jones, W.; Thomas, J. M. *Chem. Phys. Lett.* **1980**, *71*, 44.
(26) Nakanishi, H.; Jones, W.; Thomas, J. M.; Hursthouse, M. B.; Motevalli, M. *J. Chem. Soc., Chem. Commun.* **1980**, 611.
(27) Jones, W.; Nakanishi, H.; Theocharis, C. R.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1980**, 610.
(28) Thomas, J. M. *Nature (London)* **1981**, *289*, 633.
(29) Nakanishi, H.; Jones, W.; Thomas, J. M.; Hursthouse, M. B.; Motevalli, M. *J. Phys. Chem.* **1981**, *85*, 3636.
(30) Jones, W.; Ramdas, S.; Theocharis, C. R.; Thomas, J. M.; Thomas, N. W. *J. Phys. Chem.* **1981**, *85*, 2594.
(31) Sadeh, T.; Schmidt, G. M. J. *J. Am. Chem. Soc.* **1962**, *84*, 3970.
(32) Lahav, M.; Schmidt, G. M. J. *J. Chem. Soc. B* **1967**, 239.
(33) Lahav, M.; Schmidt, G. M. J. *J. Chem. Soc. B* **1967**, 312.
(34) Green, B. S.; Lahav, M.; Schmidt, G. M. J. *J. Chem. Soc. B* **1971**, 1552.
(35) Pfoertner, K. H.; Englert, G.; Schoenholzer, P. *Abstracts of Papers*, 12th International Conference on Photochemistry, Tokyo, Japan, 1985; p 487. Pfoertner, K. H.; Englert, G.; Schoenholzer, P. *Tetrahedron*, in press.
(36) Nakanishi, F.; Nakanishi, H.; Tsuchiya, M.; Hasegawa, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 3096.
(37) Nakanishi, H.; Hasegawa, M.; Mori, T. *Acta Crystallogr, Sect. C: Cryst. Struct. Commun.* **1985**, *C41*, 70.
(38) Nakanishi, H.; Parkinson, G. M.; Jones, W.; Thomas, J. M.; Hasegawa, M. *Isr. J. Chem.* **1979**, *18*, 261.
(39) Ariel, S.; Askari, S.; Scheffer, J. R.; Trotter, J.; Walsh, L. *J. Am. Chem. Soc.* **1984**, *106*, 5726.
(40) Hanson, A. W. *Acta Crystallogr. Sect. B* Struct. *Crystallogr. Cryst. Chem.* **1975**, *B31*, 1963.
(41) Sen, N.; Venkatesan, K., unpublished results.
(42) Mez, H.; Rihs, G. *Helv. Chim. Acta* **1973**, *56*, 2766.
(43) Sinnreich, J.; Batzer, H. *Helv. Chim. Acta* **1973**, *56*, 2760.
(44) Kanagapushpam, D.; Venkatesan, K.; Ramamurthy, V. *Acta Crystallogr.*, in press.
(45) Theocharis, C. R.; Jones, W.; Thomas, J. M.; Motevalli, M.; Hursthouse, M. B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 71.
(46) Kearsley, S. K.; Desiraju, G. R. *Proc. R. Soc. London, Ser. A* **1985**, *397*, 157.
(47) (a) Frank, J. K.; Paul, I. C. *J. Am. Chem. Soc.* **1973**, *95*, 2324. (b) Leonard, N. J.; McCredie, R. S.; Logue, M. W.; Cundall, R. L. *Ibid.* **1973**, *95*, 2320.
(48) Irngartinger, H.; Aeker, R. D.; Rebafka, W.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 674.
(49) Hasegawa, M.; Nohara, M.; Saigo, K.; Mori, T.; Nakanishi, H. *Tetrahedron Lett.* **1984**, *25*, 561. Hasegawa, M.; Saigo, K.; Mori, T.; Uno, H.; Nohara, M.; Nakanishi, H. *J. Am. Chem. Soc.* **1985**, *107*, 2788.
(50) Kaftory, M. *J. Chem. Soc., Perkin Trans. 2* **1984**, 757.
(51) Patel, G. N.; Duesler, E. N.; Curtin, D. Y.; Paul, I. C. *J. Am. Chem. Soc.* **1980**, *102*, 461.
(52) Wegner, G. *Pure Appl. Chem.* **1977**, *49*, 443. Misin, V.; Cherkashin. *Russ. Chem. Rev.* **1985**, *54*, 562.
(53) Blasky, V. K.; Zorkii, P. M. *Acta Crystallogr. Sect. A Cryst. Phys., Diff., Theor. Gen. Crystallogr.* **1977**, *33A*, 1004.
(54) Addadi, L.; Cohen, M. D.; Lahav, M. *J. Chem. Soc., Chem. Commun.* **1975**, 471.
(55) Addadi, L.; Cohen, M. D.; Lahav, M. *Mol. Cryst. Liq. Cryst.* **1976**, *32*, 137.
(56) Addadi, L.; Lahav, M. *J. Am. Chem. Soc.* **1978**, *100*, 2838.
(57) Addadi, L.; Gati, E.; Lahav, M.; Leiserowitz, L. *Isr. J. Chem.* **1976–77**, *15*, 116.
(58) Addadi, L.; Lahav, M. *J. Am. Chem. Soc.* **1979**, *101*, 2152.
(59) Addadi, L.; van Mil, J.; Lahav, M. *J. Am. Chem. Soc.* **1982**, *104*, 3422.
(60) van Mil, J.; Addadi, L.; Lahav, M.; Leiserovitz, L. *J. Chem. Soc., Chem. Commun.* **1982**, 584.
(61) Elgavi, A.; Green, B. S.; Schmidt, G. M. J. *J. Am. Chem. Soc.* **1973**, *95*, 2058.
(62) Green, B. S.; Lahav, M.; Schmidt, G. M. J. *Mol. Cryst. Liq. Cryst.* **1975**, *29*, 187.
(63) Green, B. S.; Lahav, M.; Rabinovich, D. *Acc. Chem. Res.* **1979**, *12*, 191.
(64) Addadi, L.; Lahav, M. *Pure Appl. Chem.* **1979**, *51*, 1269.
(65) Holland, H. L.; Richardson, M. F. *Mol. Cryst. Liq. Cryst.* **1980**, *58*, 311.
(66) Chenchaiah, P. C.; Holland, H. L.; Richardson, M. F. *J. Chem. Soc., Chem. Commun.* **1982**, 436.
(67) Rabinovich, D.; Schmidt, G. M. J. *J. Chem. Soc. B* **1967**, 144.
(68) Cookson, R. C.; Cox, D. A.; Hudec, J. *J. Chem. Soc.* **1961**, 4499.
(69) Kaupp, G.; Jostkleigrewe, E.; Hermann, H. J. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 435.
(70) Chase, D. B.; Amey, R. L.; Holtje, W. G. *Appl. Spectrosc.* **1982**, *36*, 155.
(71) Waschen, E.; Matusch, R.; Krampity, D.; Hartke, K. *Liebigs Ann. Chem.* **1978**, 2137.

(72) Griffin, G. W.; Basinski, J. E.; Vellturo, A. F. *Tetrahedron Lett.* **1960**, 13.
(73) Griffin, G. W.; Vellturto, A. F.; Furukawa, K. *J. Am. Chem. Soc.* **1961**, *83*, 2725.
(74) Williams, J. L. R. *J. Org. Chem.* **1960**, *25*, 1839.
(75) Miller, D. B.; Flanagan, P. W.; Scechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 3912.
(76) Donati, D.; Fiorenza, M.; Sarti-Fantoni, P. J. *J. Heterocycl. Chem.* **1979**, *16*, 253.
(77) Donati, D.; Fiorenza, M.; Moschi, E.; Sarti-Fantoni, P. J. *J. Heterocycl. Chem.* **1977**, *14*, 951.
(78) Ried, W.; Bopp, H. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 653.
(79) Taylor, E. C.; Paudler, W. W. *Tetrahedron Lett.* **1960**, *25*, 1.
(80) Wang, S. Y. *Nature (London)* **1963**, *200*, 879.
(81) Powell, B. M.; Martel, P. *Photochem. Photobiol.* **1977**, *26*, 305.
(82) DeBoer, C. D.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1968**, *90*, 803.
(83) Bremner, J. B.; Warrener, R. N.; Adman, E.; Jensen, L. H. *J. Am. Chem. Soc.* **1971**, *93*, 4574.
(84) Bates, R. B.; Christensen, K. A.; Hallberg, A.; Klenck, R. E.; Martin, A. R. *J. Org. Chem.* **1984**, *49*, 2978.
(85) Begley, M. J.; Crombie, L.; Knapp, T. F. W. B. *J. Chem. Soc., Perkin Trans. 1* **1979**, 976.
(86) Mohr, S. *Tetrahedron Lett.* **1979**, 3139.
(87) Adam, G. *Tetrahedron* **1973**, *29*, 3177.
(88) Kutschabsky, L.; Reck, G.; Adam, G. *Tetrahedron* **1975**, *31*, 3065.
(89) Adam, G. *Tetrahedron Lett.* **1971**, 1357.
(90) Adam, G.; Voigt, B. *Tetrahedron Lett.* **1971**, 4601.
(91) Cookson, R. C.; Crundwell, E.; Hill, R. R.; Hudic, J. *J. Chem. Soc.* **1964**, 3062.
(92) Cookson, R. C.; Hill, R. R.; Hudec, J. *J. Chem. Soc.* **1964**, 3043.
(93) Houk, K. N.; Northington, D. J. *Tetrahedron Lett.* **1972**, 303.
(94) Lahav, M.; Schmidt, G. M. J. *Tetrahedron Lett.* **1966**, 2957.
(95) Uhler, R. O.; Tiers, G. V. D. *J. Am. Chem. Soc.* **1962**, *84*, 3397.
(96) Berkovitch-Yellin, Z.; Lahav, M.; Leiserovitz, L. *J. Am. Chem. Soc.* **1974**, *96*, 918.
(97) Perlmutter, H. D.; Trattner, R. B. *J. Org. Chem.* **1978**, *43*, 2056.
(98) Riecke, R. D.; Copenhafer, R. A. *Tetrahedron Lett.* **1971**, 879.
(99) Nishio, T.; Nakajima, N.; Omote, Y. *Tetrahedron Lett.* **1980**, *21*, 2529.
(100) Hazell, A. C.; Pagni, R. M.; Persy, G.; Rommel, E.; Wirz, J. *Helv. Chim. Acta* **1981**, *64*, 2830.
(101) Fuchs, E.; Pasternak, M. *J. Chem. Soc., Chem. Commun.* **1977**, 537.
(102) Mohr, S. *Tetrahedron Lett.* **1979**, 2461.
(103) Lawrenz, D.; Mohr, S.; Wendlander, B. *J. Chem. Soc., Chem. Commun.* **1984**, 863.
(104) Bradshaw, C. K.; Bearers, L. E.; Jones, J. H. *J. Org. Chem.* **1957**, *22*, 1740.
(105) Vansant, J.; Toppet, S.; Smets, G.; Declercq, J. P.; Germain, G.; van Meerssehe, M. *J. Org. Chem.* **1980**, *45*, 1565.
(106) Marciani, S.; Dallacqua, F.; Rodighiero, P.; Caporalle, G.; Rodighiero, G. *Gazz. Chim. Ital.* **1970**, *100*, 435.
(107) Rodighiero, G.; Cappellina, V. *Gazz. Chim. Ital.* **1961**, *91*, 103.
(108) Quina, F. H.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 1602.
(109) Guru Row, T. N.; Ramachandra Swamy, H.; Ravi Acharya, K.; Ramamurthy, V.; Venkatesan, K.; Rao, C. N. R. *Tetrahedron Lett.* **1983**, *24*, 3263. Ramachandra Swamy, H.; Guru Row, T. N.; Ramamurthy, V.; Venkatesan, K.; Rao, C. N. R. *Curr. Sci.* **1982**, *51*, 381. Ramachandra Swamy, H.; Ramamurthy, V.; Venkatesan, K. *Indian J. Chem.* **1982**, *21B*, 79.
(110) Werbin, H.; Strom, E. T. *J. Am. Chem. Soc.* **1968**, *90*, 7296.
(111) Nalini, V.; Desiraju, G. R. *Tetrahedron*, in press. Kato, S.; Nakatani, M.; Harashina, H.; Saigo, K.; Hasegawa, M.; Sato, S. *Chem. Lett.* **1986**, 847. Hasegawa, M.; Arioka, H.; Harashina, H.; Nohara, M.; Kubo, M.; Nishikubo, T. *Isr. J. Chem.* **1985**, *25*, 302.
(112) Nakanishi, F.; Nakanishi, H.; Suzuki, Y.; Hasegawa, M. *Chem. Lett.* **1974**, 525.
(113) Nakanishi, F.; Yamada, S.; Nakanishi, H. *J. Chem. Soc., Chem. Commun.* **1977**, 247.
(114) Nakanishi, F.; Hirakawa, H.; Nakanishi, H. *Isr. J. Chem.* **1979**, *18*, 295.
(115) Scheffer, J. R. *Acc. Chem. Res.* **1980**, *13*, 283. Shklover, V. E.; Timofeeva, T. V. *Russ. Chem. Rev.* **1985**, *54*, 619.
(116) Dzakpasu, A. A.; Phillips, S. E. V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1976**, *98*, 6049.
(117) Scheffer, J. R.; Dzakpasu, A. A. *J. Am. Chem. Soc.* **1979**, *100*, 2163.
(118) Weisz, A.; Kaftory, M.; Vidavsky, I.; Mandelbaum, A. *J. Chem. Soc., Chem. Commun.* **1984**, 18.
(119) Appel, W. K.; Greenhough, T. J.; Scheffer, J. R.; Trotter, J.; Walsh, L. *J. Am. Chem. Soc.* **1980**, *102*, 1158.
(120) Appel, W. K.; Greenhough, T. J.; Scheffer, J. R.; Trotter, J.; Walsh, L. *J. Am. Chem. Soc.* **1980**, *102*, 1160.
(121) Appel, W. K.; Jiang, Z. Q.; Scheffer, J. R.; Walsh, L. *J. Am. Chem. Soc.* **1983**, *105*, 5354.
(122) Jiang, Z. Q.; Scheffer, J. R.; Secco, A. S.; Trotter, J. *Tetrahedron Lett.* **1981**, *22*, 891.
(123) Greenhough, T. J.; Scheffer, J. R.; Secco, A. S.; Trotter, J.; Walsh, L. *Isr. J. Chem.*, in press.
(124) Ariel, S.; Evans, S.; Hwang, C.; Jay, J.; Scheffer, J. R.; Trotter, J.; Wong, Y. F. *Tetrahedron Lett.* **1985**, *26*, 965.
(125) Appel, W. K.; Greenhough, T. J.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1979**, *101*, 213.
(126) Matsuura, T.; Sata, Y.; Ogura, K. *Tetrahedron Lett.* **1968**, 4627.
(127) Williams, J. R.; Abdel-Magid, A. *Tetrahedron* **1981**, *37*, 1675.
(128) Sobti, R. R.; Levine, S. G.; Bordner, J. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2292.
(129) Mc Phail, A. T.; Luhan, P. A.; Ts-Chang, P. S. W.; Onan, K. D. *J. Chem. Soc., Perkin Trans. 2* **1977**, 379.
(130) Aoyama, H.; Hasegawa, T.; Omote, Y. *J. Am. Chem. Soc.* **1979**, *101*, 5343.
(131) Ariel, S.; Ramamurthy, V.; Scheffer, J. R.; Trotter, J. *J. Am. Chem. Soc.* **1983**, *105*, 6959.
(132) Wagner, P. J.; Giri, B. P.; Scaiano, J. C.; Ward, D. L.; Gabe, E.; Lee, F. L. *J. Am. Chem. Soc.* **1985**, *107*, 5483.
(133) Mohr, S. *Tetrahedron Lett.* **1980**, *21*, 593.
(134) Mohr, S. *Tetrahedron Lett.* **1979**, 3139.
(135) Wagner, P. J. *Top. Curr. Chem.* **1976**, *66*, 1.
(136) Evans, S.; Omkaram, N.; Scheffer, J. R.; Trotter, J. *Tetrahedron Lett.* **1985**, *26*, 5903.
(137) Gore, P. H.; Hoskins, J. A.; Lott, K. A. K.; Waters, D. N. *Photochem. Photobiol.* **1970**, *11*, 551. Migirdicyan, E.; Despres, A.; Lejeune, V.; Leach, S. *J. Photochem.* **1974–75**, *3*, 383.
(138) Ito, Y.; Matsuura, T. *Tetrahedron*, in press.
(139) Bamberger, E.; Elger, F. *Ann. Chem.* **1909**, *371*, 319.
(140) Tanasescu, I.; Tanasescu, H. *Chem. Abstr.* **1926**, *20*, 749.
(141) Steiger, R. *Helv. Chim. Acta* **1933**, *16*, 793.
(142) Schultz, G.; Ganguly, K. L. *Ber. Dtsch. Chem. Ges.* **1925**, *58*, 702.
(143) Berson, J. A.; Brown, E. *J. Am. Chem. Soc.* **1955**, *77*, 447.
(144) Tanasescu, I. *Chem. Abstr.* **1925**, *19*, 2932.
(145) Tanasescu, I.; Macovsky, E. *Chem. Abstr.* **1930**, *24*, 2429.
(146) Ried, W.; Wilk, M. *Ann. Chem.* **1954**, *590*, 91.
(147) Sachs, F.; Hilpert, S. *Ber. Dtsch. Chem. Ges.* **1905**, *37*, 3425.
(148) Sachs, F.; Hilpert, S. *Ber. Dtsch. Chem. Ges.* **1906**, *39*, 899.
(149) Kröhnke, F.; Kröhnke, G.; Vogt, I. *Chem. Ber.* **1953**, *86*, 1500.
(150) Trotter, J. *Acta Crystallogr.* **1959**, *12*, 605.
(151) Carper, W. R.; Davis, L. P.; Extine, M. W. *J. Phy. Chem.* **1982**, *86*, 459.
(152) Döpp, D. *Org. Photochem. Synth.* **1976**, *2*, 43.
(153) Döpp, D.; Sailer, K.-H. *Chem. Ber.* **1975**, *108*, 3483.
(154) Döpp, D. *Tetrahedron Lett.* **1971**, 2757.
(155) Döpp, D.; Sailer, K.-H. *Tetrahedron Lett.* **1971**, 2761.
(156) Döpp, D.; Sailer, K.-H. *Chem. Ber.* **1975**, *108*, 301.
(157) Padmanabhan, K.; Döpp, D.; Venkatesan, K.; Ramamurthy, V. *J. Chem. Soc., Perkin Trans. 2* **1986**, 897. Padmanabhan, K.; Ramamurthy, V.; Venkatesan, K.; Ponnuswamy, M. N.; Trotter, J. *Acta Cryst. Sect. C. Cryst. Struct. Commun.* **1986**, *42*, 610.
(158) Padmanabhan, K.; Schmidt, R.; Döpp, D.; Venkatesan, K.; Ramamurthy, V. *J. Chem. Soc., Perkin Trans. 2*, in press.
(159) Senier, A.; Shepheard, F. G. *J. Chem. Soc.* **1909**, *95*, 1943.
(160) Senier, A.; Shepheard, F. G.; Clarke, R. *J. Chem. Soc.* **1912**, *101*, 1950.
(161) Senier, A.; Shepheard, F. G. *J. Chem. Soc.* **1909**, *95*, 441.
(162) Senier, A.; Forster, R. B. *J. Chem. Soc.* **1914**, *105*, 2462.
(163) de Gaouck, V.; le Fevre, R. J. W. *J. Chem. Soc.* **1939**, 1457.
(164) Schmidt, G. M. J. *Reactivity of the Photoexcited Organic Molecules*; Interscience: New York, 1967; pp 227–288.
(165) Cohen, M. D.; Schmidt, G. M. J. In *Reactivity of Solids*; de Boer., Ed.; Elsevier: Amsterdam, 1961; pp 556.
(166) Cohen, M. D.; Schmidt, G. M. J.; Flavian, S. *J. Chem. Soc.* **1964**, 2041.
(167) Cohen, M. D.; Hirshberg, Y.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 2051.
(168) Cohen, M. D.; Hirshberg, Y.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 2060.
(169) Bregman, J.; Leiserowitz, L.; Schmidt, G. M. J. *J. Chem. Soc.* **1964**, 2068.
(170) Bregman, J.; Leiserowitz, L.; Osaki, K. *J. Chem. Soc.* **1964**, 2086.
(171) Higelin, D.; Sixi, H. *Chem. Phys.* **1983**, *77*, 391.
(172) Hadjoudis, E.; Moustakali-Mavridis, I.; Xexakis, J. *Isr. J. Chem.* **1979**, *18*, 202.
(173) Bernstein, J.; Schmidt, G. M. J. *J. Chem. Soc., Perkin Trans. 2* **1972**, 951.
(174) Quinkert, G.; Tabata, T.; Hickmann, E. A. J.; Dobrat, W. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 199.
(175) Quinkert, Q.; Opitz, K.; Wiersdorff, W. W.; Weinlich, J.

Tetrahedron Lett. **1963**, 1863.
(176) Baretz, B. H.; Turro, N. J. *J. Am. Chem. Soc.* **1983**, *105*, 1309.
(177) Tomioka, H.; Izawa, Y. *J. Chem. Soc., Chem. Commun.* **1980**, 445.
(178) Hoppe, W.; Rauch, R. *Z. Kristallogr.* **1960**, *115*, 141.
(179) Weigert, F. *Z. Elektrochem.* **1918**, *24*, 222.
(180) Marckwald, W. *Z. Phys. Chem.* **1899**, *30*, 140.
(181) Scheibe, G.; Feichtmayr, F. *J. Phys. Chem.* **1962**, *66*, 2442.
(182) Gutowsky, H. S.; Rutledge, R. L.; Hunsberger, J. H. *J. Chem. Phys.* **1958**, *29*, 1183.
(183) Hub, W.; Shneider, S.; Dörr, F. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 323.
(184) Kaupp, G.; Zimmerman, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 1018.
(185) Stobbe, H. *Justus Liebigs Ann. Chem.* **1911**, *380*, 1.
(186) Hanel, H. *Naturwissenchaften* **1950**, *37*, 91.
(187) Stobbe, H. *Justus Liebigs Ann. Chem.* **1908**, *359*, 1.
(188) Santiago, A.; Becker, R. S. *J. Am. Chem. Soc.* **1968**, *90*, 3654.
(189) Ichimura, K.; Watanabe, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2220.
(190) Ichimura, K.; Watanabe, S. *Tetrahedron Lett.* **1972**, 821.
(191) Döpp, D.; Müller, D. *Tetrahedron Lett.* **1978**, 3863.
(192) Canon, J. R.; Patrick, V. A.; Raston, C. L.; White, A. H. *Aust. J. Chem.* **1978**, *31*, 1265.
(193) Ciamician, G.; Silber, P. *Ber. Dtsch. Chem. Ges.* **1901**, *34*, 2040.
(194) Cohn, P.; Friedländer, P. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 1265.
(195) Pleiffer, P. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 1819.
(196) Pleiffer, P.; Kramer, E. *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 3655.
(197) Leighton, P. A.; Lucy, F. A. *J. Chem. Phys.* **1934**, *2*, 756.
(198) Lucy, F. A.; Leighton, P. A. *J. Chem. Phys.* **1934**, *2*, 760.
(199) Brown, E. J.; Hartley, H.; Scott, W. D.; Watts, H. G. *J. Chem. Soc.* **1924**, *125*, 1218.
(200) Ruggli, P. *Justus Liebigs Ann. Chem.* **1912**, *392*, 92
(201) Sachs, F.; Hilpert, S. *Ber. Dtsch. Chem. Ges.* **1904**, *37*, 3425.
(202) Senier, A.; Clarke, R. *J. Chem. Soc.* **1914**, *105*, 1917.
(203) Pleiffer, P. *Justus Liebigs Ann. Chem.* **1954**, *590*, 91, 111.
(204) de Mayo, P.; Reid, S. T. *Q. Rev.* **1961**, *15*, 393.
(205) Coppens, P. *Acta Crystallogr.* **1964**, *17*, 573.
(206) Coppens, P.; Schmidt, G. M. J. *Acta Crystallogr.* **1964**, *17*, 222.
(207) Engler, C.; Dorant, K. *Chem. Ber.* **1895**, *28*, 2497.
(208) Jungk, A. E.; Luwish, M.; Pinchas, S.; Schmidt, G. M. J. *Isr. J. Chem.* **1977**, *16*, 308.
(209) Ellam, R. M.; East, P. B.; Kelly, A.; Khan, R. M.; Lee, J. B.; Linsey, D. C. *Chem. Ind.* **1974**, 74.
(210) Badger, G. M.; Buttery, R. G. *J. Chem. Soc.* **1954**, 2243.
(211) Porter, C. W.; Wilbur, P. *J. Am. Chem. Soc.* **1927**, *49*, 2145.
(212) Comer, F. W.; Trotter, J. *J. Chem. Soc. B* **1966**, 11.
(213) Lonsdale, D. K.; Nare, E.; Stephens, J. F. *Proc. R. Soc. London, A* **1966**, *261*, 1.
(214) Freer, A. A.; Mac Alpine, D. K.; Peacock, J. A.; Porte, A. L. *J. Chem. Soc., Perkin Trans. 2* **1985**, 971.
(215) Bregman, J.; Osaki, K.; Schmidt, G. M. J.; Sonntag, F. I. *J. Chem. Soc.* **1964**, 2021.
(216) Bryan, R. F.; Hartley, P. *J. Chem. Soc., Perkin Trans. 2* **1982**, 591.
(217) Griffin, G. W.; O'Connel, E. J.; Kelliher, J. M. *Proc. Chem. Soc.* **1964**, 337.
(218) Bart, J. C. J.; Schmidt, G. M. J. *Rec. Trav. Chim. Pays-Bas* **1978**, *97*, 231.
(219) Gougoutas, J. Z.; Naae, D. G. *J. Phys. Chem.* **1978**, *82*, 393.
(220) Gougoutas, J. Z. *J. Am. Chem. Soc.* **1979**, *101*, 5672. Gougoutas, J. Z.; Toeplitz, B. K. *Cryst. Struct. Commun.* **1977**, *6*, 331.
(221) Evans, S. V.; Garcia-Garibay, M.; Omkaram, N.; Scheffer, J. R.; Trotter, J.; Wireko, F. *J. Am. Chem. Soc.* **1986**, *108*, 5648.
(222) Paul, I. C.; Curtin, D. Y. *Acc. Chem. Res.* **1973**, *6*, 217.
(223) Paul, I. C.; Curtin, D. Y. *Science, (Washington, D.C., 1883–)* **1975**, *187*, 19.
(224) Hochstrasser, R. M. *Can. J. Chem.* **1959**, *37*, 1123.
(225) Brenner, G.; Roberts, F. E.; Hoinowski, A.; Budavari, J.; Powell, B.; Hinkley, D.; Schoenewaldt, E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 975.
(226) Lewbart, M. L. *Nature (London)* **1969**, *222*, 663.
(227) Lin, C. T.; Perrier, P.; Clay, G. G.; Sutton, P. A.; Byrn, S. R. *J. Org. Chem.* **1982**, *47*, 2978.
(228) Arjunan, P.; Ramamurthy, V.; Venkatesan, K. *J. Org. Chem.* **1984**, *49*, 1765.
(229) Desvergne, J. P.; Bouas-Laurent, H.; Blackburn, E. V.; Lapouyade, R. *Tetrahedron Lett.* **1974**, 947.
(230) Desvergne, J. P.; Thomas, J. M. *J. Chem. Soc., Perkin Trans. 2* **1975**, 584.
(231) Shoppee, C. W. *J. Chem. Soc., Perkin Trans. 1* **1985**, 45.
(232) Cohen, M. D.; Green, B. S.; Ludmer, Z.; Schmidt, G. M. J. *Chem. Phys. Lett.* **1970**, *7*, 486.
(233) Greer, B. S.; Schmidt, G. M. J. *Tetrahedron Lett.* **1970**, 4249.
(234) Cohen, M. D.; Elgavi, A.; Green, B. S.; Ludmer, Z.; Schmidt, G. M. J. *J. Am. Chem. Soc.* **1972**, *94*, 6776.
(235) Hung, J. D.; Lahav, M.; Luwisch, M.; Schmidt, G. M. *J. Isr. J. Chem.* **1972**, *10*, 585.
(236) Cohen, M. D.; Cohen, R.; Lahav, M.; Nie, P. L. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1095. Green, B. S.; Heller, L. *J. Org. Chem.* **1974**, *39*, 196.
(237) Desiraju, G. R.; Sarma, J. A. R. P. *Acc. Chem. Res.* **1986**, *19*, 222. Ramasubbu, N.; Parthasarathy, R.; Murray-Rust, P. *J. Am. Chem. Soc.* **1986**, *108*, 4308.
(238) Thomas, N. W.; Desiraju, G. R. *Chem. Phys. Lett.* **1984**, *110*, 99.
(239) Sarma, J. A. R. P.; Desiraju, G. R. *Chem. Phys. Lett.* **1985**, *117*, 160.
(240) Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: New York, 1973.
(241) Murthy, G. S.; Venkatesan, K.; Ramamurthy, V., unpublished results.
(242) Nakanishi, H.; Sasada, Y. *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 332.
(243) Ueno, K.; Nakanishi, H.; Hasegawa, M.; Sasada, Y. *Acta Crystallogr. Sect. B Struct. Crystallogr. Cryst. Chem.* **1978**, *B34*, 2034.
(244) Desiraju, G. R.; Kamala, R.; Hanuma Kumari, B.; Sarma, J. A. R. P. *J. Chem. Soc., Perkin Trans. 2* **1984**, 181.
(245) Lewis, F. D.; Oxman, J. D.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 466.
(246) Alcock, N. W.; de Meester, P.; Kemp, T. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 921.
(247) Praetorius, P.; Kohn, F. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 2744.
(248) Theocharis, C. R.; Desiraju, G. R.; Jones, W. *J. Am. Chem. Soc.* **1984**, *106*, 3606. Jones, W.; Theocharis, C. R.; Thomas, J. M.; Desiraju, C. R. *J. Chem. Soc., Chem. Commun.* **1983**, 1443.
(249) Sarma, J. A. R. P.; Desiraju, G. R. *J. Am. Chem. Soc.* **1986**, *108*, 2791. Sarma, J. A. R. P.; Desiraju, G. R. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1905.
(250) Thomas, N. W.; Ramdas, S.; Thomas, J. M. *Proc. R. Soc. London, A* **1985**, *400*, 219.
(251) Cohen, M. D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 386.
(252) Cohen, M. D. *Mol. Cryst. Liq. Cryst.* **1979**, *50*, 1.
(253) Collins, M. A.; Craig, D. P. *Chem. Phys.* **1981**, *54*, 305.
(254) Craig, D. P.; Mallet, C. P. *Chem. Phys.* **1982**, *65*, 129.
(255) Craig, D. P.; Lindsay, R. N.; Mallet, C. P. *Chem. Phys.* **1984**, *89*, 187.
(256) Norris, K.; Gray, P.; Craig, D. P.; Mallet, C. P.; Markey, B. R. *Chem. Phys.* **1983**, *79*, 9.
(257) Yakhot, Y.; Cohen, M. D.; Ludmer, Z. *Adv. Photochem.* **1979**, *11*, 489.
(258) Warschel, A.; Huller, E. *Chem. Phys.* **1974**, *6*, 463.
(259) Cohen, M. D.; Haberlcorn, R.; Huller, E.; Ludmer, Z.; Michel-Beyerle, M. E.; Rabinovich, D.; Sharon, R.; Warshel, A.; Yakhot, V. *Chem. Phys.* **1978**, *27*, 211.
(260) Warshel, A.; Shakked, Z. *J. Am. Chem. Soc.* **1975**, *97*, 5679.
(261) Cohen, M. D.; Klein, E.; Ludmer, Z. Yakhot, V. *Chem. Phys.* **1974**, *5*, 15.
(262) Cohen, M. D.; Yakhot, V. *Chem. Phys.* **1974**, *5*, 27.
(263) Cohen, M. D.; Yakhot, V. *Chem. Phys.* **1974**, *5*, 478.
(264) Ariel, S.; Askari, S.; Scheffer, J. R.; Trotter, J.; Walsh, L. In *Organic Phototransformations in Nonhomogeneous Media*; Fox, M. A., Ed.; ACS Symposium Series 278; American Chemical Society: Washington, DC, 1985; pp 243–256.
(265) Arjunan, P.; Murthy, G. S.; Venkatesan, K.; Ramamurthy, V. *Tetrahedron*, in press.
(266) Busing, W. R. WIMIN, a Computing program to Model Molecules and Crystals in Terms of Potential Energy Function, Oak Ridge National Laboratory: Oak Ridge, 1981.
(267) Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220. Gavezzotti, A.; Simonetta, M. *Chem. Rev.* **1982**, *82*, 1.
(268) Gavezzotti, A. *J. Am. Chem. Soc.* **1985**, *107*, 962.
(269) Gavezzotti, A. *Nouv. J. Chim.* **1982**, *6*, 443.
(270) McBridge, J. M. *J. Am. Chem. Soc.* **1971**, *93*, 6302.
(271) Skinner, K. J.; Blaskiewicz, R. J.; McBridge, J. M. *Isr. J. Chem.* **1972**, *10*, 457.
(272) Jaffe, A. B.; Skinner, K. J.; McBride, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 8510.
(273) Karch, N. J.; Koh, E. T.; Whitsel, B. L.; McBride, J. M. *J. Am. Chem. Soc.* **1975**, *97*, 6729.
(274) McBride, J. M.; Gisler, M. R. *Mol. Cryst. Liq. Cryst.* **1979**, *52*, 121.
(275) Vary, M. W.; McBride, J. M. *Mol. Cryst. Liq. Cryst.* **1979**, *52*, 133.
(276) Walter, D. W.; McBride, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 7069.
(277) Walter, D. W.; McBride, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 7064.
(278) McBride, J. M.; Vary, M. W. *Tetrahedron* **1982**, *38*, 765.
(279) McBride, J. M. *Acc. Chem. Res.* **1983**, *16*, 304.
(280) Craig, D. P.; Sarti-Fantoni, P. *Chem. Commun.* **1966**, 742.
(281) Thomas, J. M.; Williams, J. O. *Chem. Commun.* **1967**, 432.
(282) Williams, J. O.; Thomas, J. M. *Trans. Faraday Soc.* **1967**, *63*, 1720.

(283) Cohen, M. D.; Ludmer, Z.; Thomas, J. M.; Williams, J. O. *Chem. Commun.* **1969**, 1172.

(284) Cohen, M. D.; Ludmer, Z.; Thomas, J. M.; Williams, J. O. *Proc. R. Soc. London, A* **1971**, *324*, 459.

(285) Thomas, J. M. *Isr. J. Chem.* **1972**, *10*, 573.

(286) Desvergne, J. P.; Thomas, J. M.; Williams, J. O.; Bouas-Laurent, H. *J. Chem. Soc., Perkin Trans. 2* **1974**, 362.

(287) Desvergne, J. P.; Bouas-Laurent, H.; Lapouyade, R.; Gaultier, J.; Hauw, C.; Dupuy, F. *Mol. Cryst. Liq. Cryst.* **1972**, *19*, 63.

(288) Thomas, J. M.; Williams, J. O.; Desvergne, J. P.; Guarini, G.; Bouas-Laurent, H. *J. Chem. Soc., Perkin Trans. 2* **1975**, 84.

(289) Ramdas, S.; Thomas, J. M.; Goringe, M. J. *J. Chem. Soc. Faraday Trans. 2* **1977**, *73*, 551.

(290) Parkinson, G. M.; Goringe, M. J.; Ramdas, S.; Williams, J. O.; Thomas, J. M. *J. Chem. Soc., Chem. Commun.* **1978**, 134.

(291) Ramdas, S.; Jones, W.; Thomas, J. M.; Desvergne, J. P. *Chem. Phys. Lett.* **1978**, *57*, 468.

(292) Tanner, B. K. *X-ray Diffraction Topography*; Pergamon Press: Oxford, 1976.

(293) Bart, J. C. J.; Schmidt, G. M. J. *Isr. J. Chem.* **1971**, *9*, 429.

(294) Heller, E.; Schmidt, G. M. J. *Isr. J. Chem.* **1971**, *9*, 449.

(295) Luther, R.; Weigert, F. *Z. Phys. Chem.* **1905**, *51*, 297.

(296) Stevens, B.; Dickinson, T.; Sharpe, R. R. *Nature (London)* **1964**, *204*, 876.

(297) Chandross, E. A.; Ferguson, J. *J. Chem. Phys.* **1966**, *45*, 3564.

(298) O'Donnel, M. *Nature (London)* **1968**, *218*, 460.

(299) Bouas-Laurent, H.; Lapouyade, R.; Faugere, J. G. C. R. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1967**, *265*, 506.

(300) Ludmer, Z. *Chem. Phys.* **1977**, *26*, 113.

(301) Ludmer, Z. *J. Lumin.* **1978**, *17*, 1.

(302) Ebeid, E. Z. M.; Bridge, N. J. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1131.

(303) Cohen, M. D.; Ron, I.; Schmidt, G. M. J.; Thomas, J. M. *Nature (London)* **1969**, *224*, 167.

(304) Desvergne, J. P.; Chekpo, F.; Bouas-Laurent, H. *J. Chem. Soc., Perkin Trans. 2* **1978**, 84.

(305) Jones, W.; Thomas, J. M. *Prog. Solid State Chem.* **1979**, *12*, 101.

(306) Williams, J. O. *Sci. Prog. Oxford*, **1977**, *64*, 247.

(307) Williams, J. O.; Thomas, J. M. *Surface and Defects Properties of Solids*, Specialist Periodical Reports; Chemical Society: London, 1973; Vol. 2, p 229.

(308) Thomas, J. M.; Williams, J. O. *Surface and Defects Properties of Solids*; Specialist Periodical Reports; Chemical Society: London, 1972; Vol. 1, p 129.

(309) Thomas, J. M.; Williams, J. O. *Prog. Solid State Chem.* **1971**, *6*, 119.