STRUCTURE-REACTIVITY CORRELATIONS IN SOLID STATE PHOTOCHEMISTRY: STUDIES ON SOME NOVEL CARBONYLS, THIOCARBONYLS AND INCLUSION COMPOUNDS

by

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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY in THE FACULTY OF GRADUATE STUDIES (DEPARTMENT OF CHEMISTRY)

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

AUGUST 1994

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ABSTRACT

Four N-alkylsuccinimides were synthesized for solid state photochemical studies and all were found to undergo γ-hydrogen abstraction in the solid state. The crystal structures of N-(t-butyl)succinimide as well as its photoproduct were determined, and the structure-reactivity correlations were derived. The phase changes during the solid state photolysis of N-(t-butyl)succinimide were also studied by X-ray powder diffraction and were interpreted using a simplified phase diagram.

Chiral crystals of salts of 4-[2,4,6-tris(1-methylethyl)benzoyl]benzoic acid (21) and different optically active amines were prepared for solid state asymmetric induction studies. The solid state photolyses of these complexes afford photoproducts in enantioenriched form. The crystal structure of one complex (21 • S-proline) was determined. The low ee obtained in its solid state photolysis was correlated with its crystal structure.

Crystals of 2,4,6-triisopropylthiobenzophenone (14) and its 4'-methoxy derivative (15) were synthesized for solid state photochemical studies of their γ-hydrogen abstraction reactions. The X-ray crystal structures of these two
compounds reveal information about the hydrogen abstraction geometry for
thiones. These results are discussed and compared with the well-established
preferred hydrogen abstraction geometry for n,\pi^* excited carbonyl compounds.

N-Phenyln-(phenylthioxomethyl)benzenepropanamide and some of its
derivatives were prepared. The original intention was to study their hydrogen
abstraction reactions in the crystalline state. However, both solid state structure-
reactivity correlation studies and deuterium labeling experiments indicate that the
photocleavage of these compounds does not involve initial \gamma-hydrogen
abstraction as originally suggested in the literature. Alternative mechanistic
possibilities are presented and discussed.

Several inclusion complexes of 9,10-dihydro-9,10-ethenoanthracene-
11,12-bis(diphenylmethanol) (22) were prepared and their photochemistry
studied in both solution and the solid state. The X-ray crystal structures of three
different complexes of 22 were determined and correlated with their
photochemical reactivities. The structures of three solvent inclusion complexes of
9,10-dihydro-9,10-ethenoanthracene-11,12-bis(diphenylphospine) oxide were
also determined by X-ray crystallography. Their photochemistry and structures
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ACKNOWLEDGEMENT

I would like to thank my supervisors Professor John R. Scheffer and Professor James Trotter for their valuable guidance and encouragement on my research and study throughout the years. I would also like to express my gratitude to several people who have given me a lot of assistance and suggestions during these years: Dr Steve Rettig, Dr Ray Jones and Dr Bozena Borecka. Over the course of my doctoral research, Mr Zhaoqing Liu has become a good friend and an excellent collaborator. Special thanks are given to him.

I acknowledge Professor Helen Burt and her student Mr Charles Winterintz for their assistance with the powder diffraction experiments. Thanks are also given to Ms Janet Gamlin and Mr Mardy Leibovitch for proof-reading this thesis. I would like to thank Professor Yoshikatsu Ito for his suggestions in some parts of my thesis. Financial support by the University of British Columbia in the form of H. R. MacMillan Family Fellowship (UGF) is also gratefully acknowledged.

I appreciate the support of my parents and family throughout my education. I am grateful to Rebecca for constant encouragement and support.
DEDICATION

To my parents
Chapter 1  INTRODUCTION

1.1. Photochemistry in the Solid State and the Topochemical Postulate

Despite the fact that solid state photoreactions have been known since the 19th century, early solid state photochemical study was very limited. The major reason was the lack of knowledge about molecular and crystal structures. With the development of single crystal X-ray diffraction techniques, more attention has been placed on solid state photochemistry. Structures of crystalline solids can be determined very precisely with the help of X-ray crystallography and thus solid state photochemistry has been growing rapidly over the last thirty years.

Why do chemists study photochemistry in the crystalline state? The major advantage offered by the crystal environment is its "rigidity". Molecules in the solid state are confined to a constrained lattice that is governed mainly by molecular packing. Under these conditions, molecular motions are restricted and intermolecular interactions are severe and anisotropic in nature. As a different type of medium, the crystalline state can quite often lead to different reactivity from that in solutions. But the most important point is that it allows chemists to correlate reactivity in the solid state with structural information. This is the so-called "structure-reactivity correlation method". In this method, the chemical reactivity of a series of closely related compounds is determined in the crystalline state and correlated with structural data for the same compounds as measured by X-ray crystallography. The structure-reactivity correlation method has become the most important approach to solid state photochemistry and is the basis of this thesis. More importantly, with the geometric criteria obtained from this method, it is now possible to predict the course of various reactions (e.g. Norrish
Type II reaction, di-\(\pi\)-methane rearrangement) with geometric data from force field calculations.\(^3\)

In fact, the idea that solid state reactivity is controlled by the molecular and crystal structure of the reactant already existed at the beginning of this century. The first theory for solid state chemical reactions was proposed by Kohlschutter in 1918 and was termed the "topochemical postulate".\(^4\) It was suggested that reactions in crystals proceed with a minimum atomic and molecular movement. Such a reaction is said to be "topochemically controlled". It takes place under the constraining three dimensional environment in which the molecules exist. It is suggested that only reactions that can satisfy the "minimum motion" criteria will be allowed in the solid state. This fundamental topochemical postulate was further modified, most notably by the pioneering work of Schmidt and coworkers in the 1960s. They studied the solid state \([2 + 2]\) photocycloaddition reactions of \textit{trans}-cinnamic acid derivatives.\(^5\) Schmidt’s systematic investigations revealed some important principles about solid state photodimerization reactions. It was proposed that the course of the \([2 + 2]\) photocycloaddition reaction in the crystalline state is governed by the molecular packing in the crystal lattice, which determines the orientation and distance between the two reacting double bonds. Photodimerization of \textit{trans}-cinnamic acid (1) is a classical example (Figure 1.01).

There are three packing modes for unsubstituted and/or substituted cinnamic acids (\(\alpha\), \(\beta\) and \(\gamma\)). Photolysis of \textit{trans}-cinnamic acid in solution results in \textit{cis/trans} isomerization; in contrast, photolysis of crystals of the \(\alpha\)-form gives the \([2 + 2]\) cycloaddition product 3. The \(\beta\)-form photolyses to give adduct 4. Some derivatives crystallize in a \(\gamma\)-form but it is unreactive. Schmidt and coworkers proposed that the center-to-center distance between two neighboring
double bonds should be less than a critical distance of 4.2 Å; above this, no photocycloaddition reaction can occur in the solid state.

![Chemical structures with reactions and forms]

**Figure 1.01.** Photochemistry of *trans*-cinnamic acid in solution and crystalline states.

A parallel alignment of the two reacting double bonds is also important for the [2 + 2] photocycloaddition reaction to take place in the solid state. There are examples where the distance between the centers of adjacent double bonds is within the proposed reaction limit, but the double bonds are not parallel to each other. In these cases, no photodimerization reaction was observed in the solid state.⁶

Another concept, called the "reaction cavity", was introduced by Cohen as an aid in interpreting the course of solid state reactions.⁷ He suggested that as a molecule reacts in a crystal, the physical geometry of the species changes while
proceeding from the reactant through the transition state(s) to product. The proposed reaction cavity is the space occupied by the reacting molecule and surrounded by the neighboring molecules. The shape of the cavity is determined by the crystal packing. Those reactions with minimal changes in geometry will proceed without much interference from the reaction cavity walls. On the other hand, reactions with transition state geometries incompatible with the cavity will be disfavored. Recently, Ramamurthy *et al.* expanded this concept of reaction cavity to include other organized and constraining media.

McBride *et al.* introduced the concept of "local stress" to explain the mechanism by which diacyl peroxides decompose in the solid state (Figure 1.02). An anisotropic "local stress" is suggested to have developed inside the crystal lattice by the liberated CO$_2$ molecule upon solid state irradiation. Such a stress was postulated to be the controlling factor in the migration of the phenyl group. It was suggested that the stress was transmitted to one side of the migration terminus thereby inclining the radical carbon in the opposite direction, more towards the migrating phenyl group. By studying a variety of diacyl peroxides, it was shown that "local stress" is so important in these reactions that it overrides the topochemical postulate.

![Figure 1.02. Photochemistry of a diacyl peroxide.](image)

---

**Figure 1.02.** Photochemistry of a diacyl peroxide.
Gavezzotti developed a method to calculate the volumes of the empty and filled spaces in the lattice.\textsuperscript{10} Packing density diagrams, calculated from a computer program, allowed him to locate void space in the crystal structure. With the help of these maps, a variety of solid state reactions was analysed. It was concluded that the prerequisite for crystal reactivity is the availability of free space around the reaction site.

Another approach to the effect of the crystalline environment, termed steric compression control, was suggested by Scheffer and Trotter.\textsuperscript{11} As an example, compound 5 (Figure 1.03) was found to be unreactive towards [2 + 2] photocycloaddition in the solid state even though the double bonds are arranged in a topochemically favorable orientation. It was suggested that the lack of reactivity is related to the arrangement of the neighbouring molecules in the crystal lattice. If the [2 + 2] reaction were to proceed, the steric compression of the two methyl groups of the reacting molecules with those of the surrounding molecules would increase, and thereby prevent the photocycloaddition.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Steric compression control in solid state photochemistry of compound 5.}
\end{figure}
1.2. Intramolecular Photochemical Hydrogen Abstraction Reactions by Carbonyl and Thiocarbonyl Containing Compounds

Most of the reactions studied in this thesis concern the intramolecular photochemical hydrogen abstraction reaction by a C=X moiety, where X is either oxygen or sulphur. A brief summary of this type of reaction follows.

The most well-known and well-studied example of an intramolecular photochemical hydrogen abstraction reactions by a carbonyl compound is the Norrish Type II reaction.\textsuperscript{12} It involves the abstraction of a γ-hydrogen atom by the excited carbonyl oxygen atom through a cyclic six membered transition state to produce a 1,4-biradical intermediate. These biradical intermediates can cyclize to give cyclobutanol derivatives (Yang photocyclization),\textsuperscript{12} undergo β-cleavage to an alkene and an enol, and regenerate the parent ketone through reverse hydrogen atom transfer (Figure 1.04).

![Figure 1.04. γ-Hydrogen atom abstraction by excited carbonyl oxygen.](image)

Photochemical γ-hydrogen abstraction reactions in aliphatic carbonyl compounds are known to involve both singlet and triplet n,π* excited states, where the non-bonding half-filled n-orbital of the electron deficient oxygen atom
is believed to take part in the abstraction process. Although several hydrogen abstraction reactions of aromatic carbonyl compounds are thought to occur from excited states other than the $n,\pi^*$ state, it is generally believed that the $\pi,\pi^*$ excited state is some $10^4$ times less reactive than the $n,\pi^*$ state.

Carbonyl compounds other than ketones (e.g. imides) are also known to undergo similar photochemical reactions. Imides will be discussed in more detail in the next chapter.

Thiocarbonyl compounds have also been reported to undergo photochemical hydrogen abstraction reactions. Thioketones and thioimides are the two most studied systems. There are two major differences between the hydrogen abstraction reactivities of the excited carbonyl and thiocarbonyl groups:

1. The $\pi,\pi^*$ excited state ($S_2$) of the thiocarbonyl compound is usually the photoreactive state.
2. The abstraction of hydrogen atoms by excited $\text{C=S}$ is more likely to occur at the $\delta$-position. If a $\delta$-hydrogen atom is not available, abstraction may also occur at the $\beta$, $\gamma$, and $\epsilon$ positions.

The photochemistry of thioketones and thioimides will be further discussed in chapters 4 and 5, respectively.
1.3. Geometry for Intramolecular Photochemical Hydrogen Abstraction

Wagner has suggested that the geometry for the $\gamma$-hydrogen abstraction reaction involves a strain-free, chair-like, six-membered transition state.$^{15}$ Later work by Scheffer and Trotter$^{16}$ on the solid state photochemistry of $\alpha$-cycloalkylacetophenones indicated that this chair-like transition state is not essential. Houk et al., from their force-field and \textit{ab initio} calculations, showed that the preference for $\gamma$-hydrogen abstraction over $\delta$-abstraction is the result of a favorable entropy of activation, rather than an unstrained chair-like transition state geometry.$^{17}$

The geometry for $\gamma$-hydrogen abstraction can be described by four parameters: $d$, the C=O→H$_\gamma$ abstraction distance; $\omega$, the degree to which the abstracted hydrogen atom lies outside the mean plane of the carbonyl group; $\Delta$, the C=O→H$_\gamma$ angle and $\theta$, the C-H⋯O angle, as shown in Figure 1.05.

![Figure 1.05. Definition of geometric parameters d, o, $\Delta$ and $\theta$ for intramolecular hydrogen atom abstraction.](image)

The "ideal" values for these four parameters in the case of hydrogen abstraction by the C=O π,π$^*$ excited state have been suggested by Scheffer.$^{16}$ The ideal value for $d$ of $\leq 2.72$ Å comes from the sum of the Van der Waals radii.
for hydrogen and oxygen\textsuperscript{18}, and the ideal value of 0° for \( \omega \) is based on the well established principle that oxygen utilizes its in-plane \( n,\pi^* \) n-orbital for abstraction\textsuperscript{19}. This orbital makes an angle of between 90° and 120° with the C=O axis depending on the model selected\textsuperscript{16}, hence the same range of values for \( \Delta \); the ideal value of 180° for \( \theta \) is also theoretically based.\textsuperscript{20} Ab initio calculations by Houk \textit{et al.} indicate that the enthalpy barrier for hydrogen abstraction increases dramatically with large deviations from \( \theta = 180^\circ \) or \( \omega = 0^\circ \).\textsuperscript{17b}

As mentioned earlier, the singlet \( \pi,\pi^* \) state is believed to be the reactive species for the hydrogen atom abstraction reactions of most thiocarbonyl compounds. The geometric criteria for efficient photochemical hydrogen abstraction by C=S is therefore expected to be quite different from those of the \( n,\pi^* \) excited C=O. These differences stem not only from the larger size of the sulphur atom, but also from the spatial alignment of the half-filled \( \pi \) orbital of the excited C=S group. Details will be discussed in Chapter 4.

1.4. Phase Changes in Solid State Photochemistry

Another important aspect of solid state photochemistry is the possibility that phase changes occur during the course of a solid state reaction. If a reactant crystal transforms to a product crystal without any phase separation during the reaction, it is called a topotactic (single-crystal-to-single-crystal) solid state reaction.\textsuperscript{21} These reactions are homogeneous, i.e. the product molecules form a continuous solid solution with the reactant molecules in all proportions. The reactants and the products in topotactic reactions have similar structures and polarities. Topotactic reactions have received a lot of attention because of their potential to transform reactant crystals to product crystals with similar dimensions and structural perfection.\textsuperscript{22} One example is the photodimerization of
2-benzyl-5-benzylidenecyclopentanone.\textsuperscript{21} Crystallographic studies on this reaction indicated that the cell parameters change continuously with conversion and that no phase separation occurs.

![Chemical structure](image)

**Figure 1.06.** Topotactic photodimerization reaction of 2-benzyl-5-benzylidenecyclopentanone.

In some other reactions where there are larger differences in structures and polarities between reactant and product molecules, phase separations are likely to occur. This happens when the solubility limit of the product in the reactant lattice is reached, and the product begins to "precipitate out". In the next chapter, we will see an example of this type of solid state reaction.

### 1.5. Asymmetric Induction in the Solid State

Asymmetric synthesis is defined as a process which converts a prochiral (or racemic) unit in a substrate molecule into a chiral unit in such a way that the product enantiomers are produced in unequal amounts.\textsuperscript{23} There has been enormous interest in asymmetric synthesis lately, including asymmetric synthesis via photochemical reactions.\textsuperscript{24} Asymmetric synthesis can be achieved by conducting a reaction in an optically active environment. Such an asymmetric influence on a prochiral or racemic reactant will lead to diastereomeric transition states of different energy. As a result, enantiomerically (or diastereomerically)
enriched products will be generated. Methods of introducing an asymmetric influence into a photochemical reaction include the use of resolved chiral reactants, solvents, sensitizers, auxiliaries and circularly polarized light. However, asymmetric syntheses via photochemical reactions in solution usually give photoproducts with low optical purities because molecules are often too loosely coordinated in solution for one to exert a definitive asymmetric influence on the reactivity of the other.24

The use of crystal chirality to generate molecular chirality was first demonstrated by Schmidt et al in 1969.25 They showed that 4,4'-dimethylchalcone although itself achiral, crystallizes spontaneously in the chiral space group P2_12_12_1 and when single crystals of this material are treated with gaseous bromine in a gas-solid reaction, the chiral dibromide is produced in 6% ee. Schmidt termed this process, which proceeds from a prochiral starting material to a chiral product without using any chiral reagent, an "absolute asymmetric synthesis". The first photochemical absolute asymmetric synthesis was also reported by Schmidt and co-workers in 1973.26 However, the drawback of the "absolute asymmetric synthesis" approach is the fact that the spontaneous crystallization of achiral reactant molecules in a chiral space group is rare and cannot be predicted.

A more practical approach to obtain enantioenriched product in solid state reactions involves the use of an external resolved chiral handle. The idea is to cocrystallize a prochiral photoreactive molecule with a photostable but optically active counterpart. Since an optically active component is included, a chiral space group is guaranteed. Also, due to the fact that these two components are in close contact in the crystalline state, the effect of asymmetric induction may be expected to be greater than for the corresponding reaction in the solution phase. In order to form a stable complex, these two components should be held by
strong intermolecular forces, e.g. ionic bonding or hydrogen bonds (see chapter 3 for details).

A recent example of using chiral handles in asymmetric induction involves the use of a diphosphine oxide molecule with P-chirality (Figure 1.07).27 Four optically active diphosphine oxides with different "Ar" groups were prepared and all were found to form 1:2 crystalline complexes with dibenzobarrelene 7. Solid state photolyses of these crystals give compounds 8 and 9 with low to moderate enantioselectivities.27

\[ \text{Figure 1.07. Asymmetric induction using P-chirality.} \]

1.6. Inclusion Complex Photochemistry

The use of host-guest complexes (inclusion complexes) in photochemistry has not been fully explored. In particular, very little attention has been given to the study of photoreactive host molecules that have the ability to cocrystallize with different solvents, despite the fact that such systems are ideal models for structure-reactivity correlation studies. The major advantage is the relative ease of preparing a large number of different crystals with the same chromophore molecule. The effects of different crystalline environments on photochemistry in
the solid state can be studied without the need to worry about the difference in intrinsic reactivities among different compounds.

Weber and Czugler have summarized some of the features that lead to good host molecules. It was suggested that good hosts should be bulky and pack inefficiently with voids, and they should contain appended sensor groups that will coordinate to the guests. Such compounds have been termed "coordinatoclathrates". In chapter 6, the inclusion phenomena and photochemistry of two coordinatoclathrate systems will be discussed in detail.

1.7. Research Objectives

The major objective of the present research is concentrated on developing structure-reactivity correlations in solid state photochemistry. This is achieved by conducting photochemical reactions in the solid state and determining structures of the reactant crystals by single crystal X-ray crystallography.

One of the goals of my research was to determine the hydrogen abstraction geometry for "non-ketone" carbonyl compounds as a continuation of the previous work from our laboratory. The cyclic imides (10 - 13) that were chosen for solid state photochemical studies are shown in Figure 1.08. The phase changes in the solid state photoreaction of imide 10 were also studied by powder diffraction techniques.

\[
\begin{align*}
10 & : \text{R} = \text{t Bu} \\
11 & : \text{R} = \text{cyclohexyl} \\
12 & : \text{R} = \text{cyclopentyl} \\
13 & : \text{R} = \text{i Pr}
\end{align*}
\]

Figure 1.08. Cyclic imides that have been investigated in this thesis.
A second goal of the present research was to determine the geometric criteria for hydrogen abstraction by excited thiocarbonyl compounds. Different thiocarbonyl compounds which are known to undergo hydrogen abstraction in solution were studied by the solid state structure-reactivity correlation method. These include 2,4,6-triisopropylthiobenzophenone (14) and its 4'-methoxy derivative (15) (Figure 1.09).

![Figure 1.09. 2,4,6-Triisopropylthiobenzophenone (14).](image)

The photochemistry of some monothioimides (16 - 20) has also been studied in the solid state (Figure 1.10). However, as readers will see in chapter 5, these compounds were found not to undergo γ-hydrogen abstraction reactions, and the objective of this part of the research became one of determining the mechanism for the photocleavage reaction. The use of the structure-reactivity correlation method in reaction mechanism determination will be demonstrated.

![Figure 1.10. Some monothioimides that have been investigated in this thesis.](image)

16 : Ar1 = Ar2 = Ph  
17 : Ar1 = 4-MeOPh, Ar2 = Ph  
18 : Ar1 = Ph, Ar2 = 4-Br-2,6-diMePh  
19 : Ar1 = Ph, Ar2 = 4-BrPh  
20 : Ar1 = Ph, Ar2 = 4-MeOPh
The third goal was to produce asymmetric induction by using ionic chiral handles. The aim was to extend and explore further the recently reported method of asymmetric induction in the solid state. A prochiral acid 21 (Figure 1.11) is designed to form salts with different optically active amines. The resulting chiral crystals are used for asymmetric synthesis through solid state photolyses. The asymmetric induction ability is correlated with the X-ray crystal structure of the salt.

![Compounds 21 and 22](image)

Figure 1.11. Compounds 21 and 22.

Finally, the present research also covers the design and structural and photochemical studies of some inclusion host molecules. The compounds that were investigated include diol 22 (Figure 1.11) and its phosphine oxide analogue.
Chapter 2  SOLID STATE PHOTOCHEMISTRY OF N-ALKYL SUCCINIMIDES

2.1. Hydrogen Abstraction Reactions of Carbonyl Compounds in the Solid State

By using the structure-reactivity correlation method, the geometric requirements for photochemical hydrogen abstraction reactions for a wide range of ketones in the crystalline state have been studied extensively in our laboratory.\textsuperscript{16} Those studies unveiled three main points about ketone hydrogen abstractions in the solid state. First, it was found that the chairlike conformation originally proposed by Wagner\textsuperscript{15} is not essential. The X-ray crystal structures of $\alpha$-cycloalkylacetophenones revealed three different types of $\gamma$-hydrogen abstraction geometries - chairlike, boatlike and half-chairlike.\textsuperscript{16} Secondly, the Yang cyclization reaction in the solid state was shown to be largely stereospecific. The photolyses of the two dimorphs of diketone 23 having different conformations in their crystalline states led to very different product ratios of cis/trans-cyclobutanol (Figure 2.01).

\[
\begin{align*}
\text{23} & \xrightarrow{\text{h.v.}} \text{(CH}_2\text{)}_{10}\text{(CH}_2\text{)}_8 \text{HO} + \text{(CH}_2\text{)}_{10}\text{(CH}_2\text{)}_8 \text{HO} + \text{HO} \text{(CH}_2\text{)}_{11}\text{(CH}_2\text{)}_8 \\
\text{Solution} & \quad 15\% \quad 35\% \quad 50\% \\
\text{Plates} & \quad >95\% \quad <5\% \quad 0\% \\
\text{Needles} & \quad <10\% \quad >90\% \quad 0\%
\end{align*}
\]

\textbf{Figure 2.01.} Photochemistry of macrocyclic diketone 23.
Finally, hydrogen abstraction in the crystalline state was found to be strongly dependent on the distance between the hydrogen atom and the carbonyl oxygen involved. When the C=O···H contacts exceed the sum of the van der Waals radii by 0.3-0.4 Å, hydrogen atom abstraction by oxygen fails. Dependencies on various angular parameters (see Chapter 1) were also suggested but the correlations were less obvious.

2.2. Photochemistry of Imides in Solution Phases

The photochemistry of imides has received considerable attention. One of the main reasons is the possibility of making a wide range of fused heterocyclic systems by intramolecular hydrogen transfer accompanied by cyclization. Photolyses of simple N-alkylphthalimides can afford benzazepinediones that are difficult to prepare otherwise (Figure 2.02).

![Figure 2.02. Photolysis of N-propylphthalimide.](image)

Hydrogen abstractions at positions other than γ were also reported. These reactions are potentially useful in organic synthesis. An example is the synthesis of a 38-membered macrocyclic ring by remote photocyclization of a long-chain imide (Figure 2.03).
It was suggested that the reason for the success of reaction\(^3\) lies in the establishment of a charge transfer interaction in the excited state that leads to a preferential conformation in which the sulphur (\(\delta^+\)) and imide (\(\delta^-\)) are in close proximity.

2.3. Solid State Photochemistry of N-Alkylsuccinimides

Kanaoka and co-workers have carried out extensive studies on the photoreactions of cyclic imides\(^3\). One of the examples involves the ring-expansion photoreaction of alicyclic imides illustrated in Figure 2.04.\(^{35-37}\)
Irradiations of a series of N-substituted succinimides \((n = 2)\) and glutarimides \((n = 3)\) leads in moderate yields to the corresponding ketolactams with a ring enlargement by the two-carbon unit derived from the N-alkyl side chain. By activation due to introduction of heteroatoms into the side chain, \(\delta\) (or other) hydrogen abstraction is also possible. The quantum yield (254 nm) for formation of compound 25a \((R_1 = R_2 = R_3 = R_4 = H, n = 2)\) is 0.64, indicating practical efficiency of the photolysis of the alicyclic imide system. Piperylene is found to quench the formation of 25a indicative of a triplet intermediate. The mechanism is thought to be a typical Yang cyclization though the formation of a biradical intermediate.

In order to delineate the stereoelectronic requirements for intramolecular hydrogen atom abstractions by imides, some of the N-alkylsuccinimides \((10 \text{ to } 13)\) were prepared and photolysed at 254 nm in the solid state (Figure 2.05).

![Figure 2.05. Photolyses of N-alkylsuccinimides in the solid states.](image)

All four \(N\)-alkylsuccinimides were found to be reactive in the solid state. The photoproducts were found to be the same as those reported by Kanaoka from solution phase photolyses. The \(cis\) stereochemistry of ketolactam 28 was
confirmed by NOE experiments. The same isomer was reported by Kanaoka. Photolysis of N-cyclohexylsuccinimide (11) in the solid state gave a 70:30 mixture of cis and trans isomers. The assignment of cis to the major isomer was based on $^1$H NMR: the mixture had two low field proton signals at $\delta$ 3.3 and $\delta$ 4.1 with integral ratios of 70:30. The two signals can be assigned as the -NHCH- protons in the two stereoisomers. By comparison with the -NHCH- signal in compound 28 ($\delta$ 4.3), which was known to have a cis configuration, it is tentatively concluded that the major product is the cis isomer. The cis:trans product ratio of compound 27 from solution photolysis was not reported by Kanaoka. Attempts to separate the two isomers by column chromatography were not successful.

Photolysis of a single crystal of 10 was also performed. The extent of conversion to photoproduct 26 (as indicated by gas chromatography) leveled off at approximately 60%, and continued irradiation led to little additional product. The crystals did not change in appearance except for the development of an overall light yellow tinge and an opaque center; no melting was detectable. It seemed likely that the limiting conversion was due to a surface reaction that screens the interior of the crystal. By grinding the starting crystals to powder before photolysis, complete conversions of 10 to 26 could be achieved, and photoproduct 26 could be isolated in 79% yield following column chromatography to remove traces of the unknown yellow material. The solid state chemical yield is considerably higher than the reported solution phase yield of 49%.

Concomitant with the chemical studies, single crystal X-ray diffraction studies of N-(t-butyl)succinimide 10 were undertaken. Compound 10 crystallizes in space group $P2_1/n$ with two independent molecules in the asymmetric unit. They are shown in Figure 2.06. It can be seen that they possess very similar (but not identical) conformations.
Figure 2.06. ORTEP stereodiagrams of the two independent molecules in compound 10.

With the photochemical and crystallographic results, we are now ready to correlate the two in terms of the hydrogen abstraction geometry. As shown in Figure 1.05 (chapter 1), intramolecular hydrogen atom abstraction may be
characterized geometrically by four parameters: \( d \), the \( \text{C}=\text{O} \cdots \text{H}_7 \) abstraction distance; \( \omega \), the degree to which the abstracted hydrogen atom lies outside the mean plane of the carbonyl group; \( \Delta \), the \( \text{C}=\text{O} \cdots \text{H}_7 \) angle and \( \theta \), the \( \text{C}-\text{H} \cdots \text{O} \) angle. The crystallographically-determined values of these four parameters for \( \text{N-}(t\text{-butyl})\text{succinimide} \ 10 \) are compiled in Table 2.1. There are six separate values for each parameter because there are three "abstractable" hydrogen atoms for each of the two independent molecules in the crystallographic asymmetric unit. The term "abstractable" refers to hydrogens for which the abstraction distance \( d \) is less than 3.1 Å. This stems from previous studies in our laboratory\(^{16} \) and others\(^{38} \) which showed that hydrogen atoms exceeding this distance are unreactive towards intramolecular abstractions. The hypothetical "ideal" values for \( d \), \( \omega \), \( \Delta \) and \( \theta \) are also listed and their origins have been discussed in Chapter 1.

Four of the six values of \( d \) recorded in Table 2.1 are remarkably short, ranging from 2.17-2.24 Å. These represent the shortest hydrogen abstraction distances yet measured by the crystal structure-reactivity correlation method. The four \( \gamma \)-hydrogen atoms that are favored for abstraction in \( \text{N-}(t\text{-butyl})\text{succinimide} \) by low values of \( d \) are also associated with much more favorable values of \( \omega \), \( \Delta \) and \( \theta \) (Table 2.1). In overall terms, these four hydrogen atoms are better situated for abstraction than any that have been reported heretofore. However, there is no way of determining experimentally which of the six hydrogen atoms is abstracted, since abstraction of any of them leads to the same product.
Table 2.1. Hydrogen Abstraction Geometry for \( N\)-(t-butyl)succinimide 10. \( \text{O}(1) \) and \( \text{O}(2) \) refer to one independent molecule in the asymmetric unit and \( \text{O}(3) \) and \( \text{O}(4) \) refer to the other.

<table>
<thead>
<tr>
<th>C=O⋯H</th>
<th>( d (\text{Å}) )</th>
<th>( \omega (^\circ) )</th>
<th>( \Delta (^\circ) )</th>
<th>( \theta (^\circ) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Ideal&quot;</td>
<td>( \leq 2.72 )</td>
<td>0</td>
<td>90-120</td>
<td>180</td>
</tr>
<tr>
<td>( \text{O}(1)\cdots\text{H}(9)^a )</td>
<td>2.24</td>
<td>6.5</td>
<td>101.6</td>
<td>115.9</td>
</tr>
<tr>
<td>( \text{O}(1)\cdots\text{H}(8) )</td>
<td>2.88</td>
<td>33.5</td>
<td>83.7</td>
<td>74.8</td>
</tr>
<tr>
<td>( \text{O}(2)\cdots\text{H}(13) )</td>
<td>2.19</td>
<td>21.7</td>
<td>100.0</td>
<td>123.4</td>
</tr>
<tr>
<td>( \text{O}(3)\cdots\text{H}(19) )</td>
<td>2.17</td>
<td>17.5</td>
<td>100.7</td>
<td>121.4</td>
</tr>
<tr>
<td>( \text{O}(3)\cdots\text{H}(20) )</td>
<td>2.98</td>
<td>39.1</td>
<td>79.7</td>
<td>68.8</td>
</tr>
<tr>
<td>( \text{O}(4)\cdots\text{H}(25) )</td>
<td>2.24</td>
<td>19.1</td>
<td>100.3</td>
<td>120.2</td>
</tr>
</tbody>
</table>

It is necessary to point out that the geometric data reported in Table 2.1 are ground state data. Recent theoretical calculations by Houk et al. indicate that excitation of amides and imides results in pyramidalization of both the carbonyl and amine groups. This means that the present crystallographic data may serve only as a rough guideline to hydrogen abstractability in similar compounds.

2.4. Phase Changes in the Solid State Photochemistry of \( N\)-(t-Butyl)succinimide

In an attempt to detect the cyclobutanol intermediate 30 (Figure 2.07) in the photolysis of imide 10, the course of the photoreaction was followed by solid state Fourier transform infrared spectroscopy and X-ray powder diffractometry. The infrared studies were carried out by recording the FTIR spectra of KBr discs of compound 10 as a function of irradiation time. This showed a regular and
progressive transformation of \( N\)-(t-butyl)succinimide into keto-lactam 26 with no obvious absorptions for cyclobutanol 30; the final infrared spectrum was identical to that of pure 26. These results indicate that cyclobutanol 30 undergoes ring opening to 26 nearly as rapidly as it is formed and is present, if at all, only in small steady-state amounts.

![Figure 2.07. The mechanism in the photolysis of imide 10.](image)

A similar conclusion was reached from the X-ray powder diffraction studies. Figure 2.08 shows the powder diffraction patterns as a function of the extent of conversion as determined by gas chromatography. Figure 2.09 shows an expansion of Figure 2.08 in the region \( 8^\circ \leq \theta \leq 12^\circ \). The powder patterns can be interpreted in terms of a two component phase diagram in which the starting material 10 and the photoproduct 26 have a limited mutual solubility in the solid state.\(^{40}\) The solid state photolysis can be understood as a system going across such a heterogeneous phase diagram, as shown qualitatively in Figure 2.10 (line MNPQ).
Figure 2.08. X-ray powder diffraction pattern at different stages of photolysis of compound 10  
($5^\circ \leq 2\theta \leq 50^\circ$).
Figure 2.09. X-ray powder diffraction pattern at different stages of photolysis of compound 10
($8^\circ \leq 2\theta \leq 12^\circ$).
Figure 2.10. A heterogeneous two-component phase diagram. $\alpha = A$ enriched solid solution, $\beta = B$ enriched solid solution, $L$ = liquid.

The horizontal line (MNPQ) passes through single-phase and two-phase regions alternatively. In region MN, the additions of B to A go into solid solution ($\alpha$) in the A lattice, which may expand or contract as a result, depending on the relative sizes and shapes of molecules A and B. Ultimately, the solubility limit of B in A is reached at point N, and further additions of B cause the precipitation of a second phase $\beta$. This second phase is a B-rich solid solution with a structure similar to that of B. Across NP, there is a two-phase region where a change in composition produces a change in the relative amounts of the two phases but no change in their individual compositions. These compositions are fixed at point N and P at the boundaries. The powder pattern in a single-phase region will show a shift in the positions of the diffraction lines of that phase due to changes in the lattice parameters. In the two-phase region, the powder pattern will contain the same diffraction lines at the same positions but the intensity of the lines of the $\alpha$
phase relative to those of the β phase will decrease in a regular manner as the concentration of B increases.

Thus, initial photolysis induces small shifts in the diffraction peaks that correspond to changes in the cell dimensions of the primary solid solution formed between compound 10 and a small amount of photoproduct 26. Figure 2.09 shows an expansion of the powder patterns in the region $8^\circ \leq \theta \leq 12^\circ$. New diffraction peaks corresponding to a second phase rich in compound 26 (the terminal solid solution) begin to grow between 6% and 14% conversion as the solubility limit of compound 26 in the primary solid solution is reached. At the same time, the diffraction peaks due to the primary solid solution stop shifting at this two phase stage, and gradually decrease in intensity as reaction proceeds. At complete conversion, the powder pattern indicates that the reaction mixture retains the crystal structure of the terminal solid solution (point P in Figure 2.11), which is slightly different from (but very similar to) the crystal structure of the recrystallized photoproduct 26 (figure 2.08g). Analysis of other regions of the powder diffraction data lead to identical conclusions.

For those solid state photoreactions which behave similarly to that of 10, the solubility limit of the product in the reactant lattice is reached at a relatively early stage of the reaction, and the product begins to "precipitate out" in its own crystal structure. Despite the fact that such reactions are common, no special attention has been paid to them. On the other hand, topotactic (single-crystal-to-single-crystal) solid state reactions have received a great deal of attention. The major reason is the potential for such reactions to transform reactant crystals to product crystals with similar dimensions and structural perfection. Topotactic reactions are homogeneous, i.e. the product molecules form a continuous solid solution with the reactant molecules in all proportions. This kind of behavior has been reported in photodimerizations, polymerization
reactions and racemization of cobaloxime complexes. These reactions share a common feature that the reactants and the products have similar structures and polarities. These properties are crucial in preventing phase separation. Topotactic solid state reactions can be understood as traversing a homogeneous two-component phase diagram from M to Q (Figure 2.11).

![Homogeneous two-component phase diagram](image)

**Figure 2.11.** A homogeneous two-component phase diagram. $\alpha =$ solid solution, $L =$ liquid.

It should be pointed out that in the photolysis of imide 10, the reaction mixture retains the crystal structure of the terminal solid solution at complete conversion. Although the powder pattern indicates that this structure is similar to that of the recrystallized keto-imide 26, the above experiment may serve as an example of obtaining a metastable structure by a heterogeneous solid state photolysis. A preparation of a metastable structure by a topotactic (homogeneous) photoreaction was reported recently.

2.5. X-ray Crystal Structures of $N$-(t-Butyl)succinimide (10) and Tetrahydro-7,7-dimethyl-1H-azepine-2,5-dione (26)
A brief discussion of the crystal and molecular structures of compound 10 and 26 is presented here.

Imide 10 crystallizes in the monoclinic space group P2_1/n with two independent molecules in the asymmetric unit (Z = 8) while its ketolactam photoprodct 26 crystallizes in the P2_1/c space group (Z = 4). Their packing diagrams are shown in Figures 2.12 and 2.13 respectively.

Figure 2.12. Packing diagram for compound 10.
Careful examination of the crystal structure of 10 reveals the approximate planarity of the imide moieties: O1-C1-N1-C4 = 172.8(7)°, O2-C4-N1-C1 = 168.1(6)°, O3-C9-N2-C12 = -167.4(6)°, O4-C12-N2-C9 = 166.3(6)°. The imide C-N bond lengths are found to be around 1.4 Å and are longer than a normal amide C-N bond distance (1.32 Å). The introduction of an additional carbonyl group results in a competition for the nitrogen lone pair delocalization to the two carbonyls. As a result, the C-N bond has less double bond character than that of amide. The carbonyl oxygen atoms are also more electron deficient than those in amides and such an effect has been suggested to be important in the photoreactivity of imides in hydrogen abstraction reactions.\textsuperscript{50}

An ORTEP stereodiagram for compound 26 is shown in Figure 2.14. The crystal structure of photoprodct 26 shows that the amide hydrogen and the ketone carbonyl are involved in intermolecular H-bonding: O1···H13 = 2.14 Å; O1···N1 = 2.95 Å; O1···H13-N1 = 159°. As this intermolecular hydrogen bonding is absent in compound 10, compound 26 has a much higher melting point than
10 (175° for 26 and 44° for 10) despite the fact that they possess the same molecular weight.

Figure 2.14. ORTEP stereodiagram for compound 26.
Chapter 3  SOLID STATE ASYMMETRIC INDUCTION IN 2,4,6-TRISOPROPYLBENZOPHENONE PHOTOCHEMISTRY

3.1. Crystal to Molecular Chirality Transfer in Solid State Photochemistry

Asymmetric induction reactions in the solid state can be divided into two categories. The first type is called absolute asymmetric synthesis, and occurs when an achiral molecule happens, rarely and unpredictably, to crystallize in one of the 65 chiral space groups (spontaneous resolution). If the reaction of such a molecule gives rise to a chiral product in the solid state, it is likely that the chiral lattice environment may favour the formation of one enantiomer over the other. Enantioenriched products can then be obtained. Problems with this strategy include, (1) an inability to predict spontaneous resolution at the present time, and (2) there are equal probabilities of obtaining both enantiomorphous crystals upon recrystallization, as has been demonstrated by Pincock et al. However, by careful seeding of the recrystallization solution with one enantiomorphous crystal, or by stirring, optically pure enantiomers can be prepared. Absolute asymmetric inductions in solid state photochemistry have been observed in photocycloadditions, di-π-methane rearrangements, Yang photocyclizations, and hydrogen abstractions by photo-generated radicals.

The second type of asymmetric induction is characterized by the presence of an external resolved chiral source. The use of an optically active ion to induce asymmetry is particularly interesting. It involves chemical reactions of crystalline salts formed between photoreactive, achiral carboxylic acids and
optically active amines (or vice versa). Advantages of using crystalline salts in solid state photochemistry include:

(1) It is usually easier to grow crystalline salts from the corresponding acid and amine than to bond a chiral group to an organic molecule. In addition, removal of the chiral auxiliary after asymmetric induction is simpler for salts. It usually involves only aqueous extraction.

(2) Salts formed between carboxylic acids and amines usually provide high-melting crystalline materials. Therefore, the danger of melting the sample as photolysis proceeds is minimized. Such a property is important in allowing a solid state reaction to be carried out to higher conversion without loss of topochemical selectivity.

(3) There is a wide variety of naturally occurring and synthetic optically active acids and amines commercially available at low prices. These provide many options for asymmetric reactions in the solid state.

The first use of salts in asymmetric induction was reported from our laboratory in 1990. Some dibenzobarrelene salts (31) were prepared (Figure 3.01). These chiral salts were photolysed to give di-π-methane rearrangement products with enantiomeric excesses ranging from 0% to 80% depending on the ammonium counterions used.
The same idea of using ionic chiral auxiliaries in the Norrish type II reaction was also reported from our laboratory.\textsuperscript{29} The chiral salt 34 was found to crystallize in two different polymorphic forms: needles and plates, which gave the major product 35, after photolysis and subsequent workup with diazomethane, in (+)-97\% and (-)-12\% ee respectively (Figure 3.02). The difference in ee was interpreted by their X-ray crystal structures: the carboxylate anions in the needle crystals adopt a single, homochiral conformation, whereas in the plate form, there are two independent carboxylate anions in the asymmetric unit that have opposite absolute configurations, even though each is associated with an (S)-(−)-prolinol-derived cation.

Figure 3.02. Photolysis of chiral salt 34.
In constrast to the solid state results, the products from solution phase photolyses of the salts were found to be racemic. The asymmetric induction observed was thus attributed to the overall supramolecular environment of the chiral crystal lattice, and the role of the chiral auxillary was suggested to be primarily one of guaranteeing a chiral space group rather than exerting a direct asymmetric influence on the reaction. This leads to the concept of "crystal to molecular chirality transfer".

3.2. Photochemistry of 2,4,6-Triisopropylbenzophenone and Derivatives

The photochemistry of ortho-alkyl-substituted benzophenones has received much attention, the major reason being the interesting hydrogen abstraction reactions that are observed. The photochemistry of 2,4,6-triisopropylbenzophenone is particularly interesting because of its potential use as an energy storage system. The first photochemical study of 2,4,6-triisopropylbenzophenone was published by Hammond and co-workers in 1966. The effect of steric hindrance to energy transfer from various benzophenones to stilbenes was studied. However, no cyclobutenol products were reported. In the 1980s, Ito et al. performed extensive studies on the photochemistry of 2,4,6-triisopropylbenzophenone and related compounds. The results can be summarized as follows:

(1) 2,4,6-Triisopropylbenzophenones undergo efficient Yang photocyclization reactions upon photolysis to give the corresponding cyclobutenols (Figure 3.03).
Steric crowding is important in promoting cyclization. This is indicated by the quantum yields of cyclobutenol formation for trimethyl, triethyl, and triisopropyl ketones: 0.008, 0.14 and 0.60 respectively.

2,4,6-Triisopropylbenzophenone possesses an unusual para-substituent effect on the triplet rate constant for \( \gamma \)-hydrogen abstraction: electron-donating groups increase triplet rate constants while electron-withdrawing groups decrease them. These inductive effects are exactly opposite to those found for simple hydrogen abstractions by substituted benzophenones.\(^7\) There is a 30-fold difference in abstraction rate constant between the \( p \)-OMe and the \( p \)-CN derivatives.

The rate constants are two orders of magnitude lower than those reported for \( o \)-methylketones\(^7\) and a primary isotope effect of 1.5 exists when the \( \gamma \) -hydrogens are replaced by deuterium.\(^6\)

Based on these results, Ito \textit{et al.} suggested that the rate determining step for triplet decay is not hydrogen abstraction but coupled rotation around the two aryl carbonyl bonds.\(^6\) It was pointed out that the ground state of 2,4,6-triisopropylbenzophenone has the triisopropylphenyl ring out of conjugation with the carbonyl group, thus making the \( \gamma \)-hydrogens poorly oriented for hydrogen abstraction. Therefore, Ito \textit{et al.} proposed that the reaction takes place only from a conformation in which the triisopropylphenyl ring is more nearly coplanar with the carbonyl group (Figure 3.03). It was suggested that the more a para substituent stabilizes the \( n,\pi^* \) excited state (electron withdrawing group), the greater the barrier there must be to the rotation that deconjugates the moiety. As a result, the overall rate of hydrogen atom abstraction is reduced by an electron withdrawing group because the abstraction geometry is more difficult to achieve.
Figure 3.03. Ito's mechanism for the solution phase photochemistry of 2,4,6-triisopropylbenzophenones
This mechanism was criticized by Wagner, who argued that since the two aryl-carbonyl bond rotations had been shown to be slow \( (k_{\text{rot}} = 14 \text{ s}^{-1}) \) by dynamic NMR studies, it does not seem very likely that the rates of rotation could be much faster in the excited state than in the ground state as would be required for Ito's mechanism.

Hamanoue et al. refined Ito's mechanism based on their work on the picosecond laser spectroscopy of some meta- and para- substituted derivatives of 2,4,6-triisopropylbenzophenone with the general structure shown below.

They observed that the triplet-triplet absorption spectra due to the lowest triplets of these compounds in solution shifted progressively to the blue region with time on the subnanosecond time scale. These results were interpreted in terms of the conformational change in the lowest triplet states. Based on their results, they proposed that 2,4,6-triisopropylbenzophenones have at least two conformational structures which give the corresponding triplet states, i.e., the \( T_a \) and \( T_b \) states; the \( T_a \) state may be similar to the less crowded \( T_1 \) state proposed by Ito et al. (Figure 3.03) and the \( T_b \) state may have a structure intermediate between that of the \( T_a \) state and the more crowded \( T_1 \) state. Since the time constant for rotational relaxation (from \( T_a \) to \( T_b \)) is much shorter than the lifetime of \( T_b \), hydrogen abstraction via the \( T_a \) state is negligible. Thus, the rate of the intramolecular hydrogen abstraction may be determined by the restricted rotation in the \( T_b \) state. They believed that once the coplanar structure
(more crowded T₁ in Figure 3.03) is achieved, the hydrogen abstraction will occur very easily. It was suggested that similar conformational changes in the triplet excited state are also expected to occur for monocarbonyl 2,4,6-triisopropylbenzophenones. However, the blue shift was not observed in these compounds due to the difficulty in observing any spectral shift at ~700 nm on account of the broad band absorption.

3.3. Solid State Photochemistry of Chiral Complexes of 4-[2,4,6-Tris(1-methylethyl)benzoyl]benzoic Acid

Despite the fact that the mechanistic detail in 2,4,6-triisopropylbenzophenone photochemistry is still a subject of debate, this system offers excellent prospects for ionic chiral handle-induced asymmetric synthesis. This is because:

(1) 2,4,6-triisopropylbenzophenone is achiral so that salt formation does not lead to diastereomers.

(2) It is known to give a cyclobutenol product that contains a new stereogenic centre upon photolysis in both solution and the solid state.$^{66,75}$

Salts of 4-[2,4,6-tris(1-methylethyl)benzoyl]benzoic acid (21) were easily prepared by mixing individual equimolar ethanol solutions of acid and amine. The resulting crystalline salts were collected by suction filtration. Details are summerized in the experimental section (chapter 7). Two different chiral salts/complexes were prepared as depicted in Figure 3.04. Attempts were also made to cocrystallize acid 21 with other amines (e.g. [1R, 2S]-(-)-ephedrine, [1S, 2S]-(+)-pseudoephedrine, (S)-(−)-alanine) but were not successful.

40
Crystals of the salts obtained were ground to a fine powder and were photolysed at $\lambda \geq 290$ nm. The reaction mixture was then dissolved in ethanol, acidified with dilute HCl and treated with diazomethane. The methyl ester of the cyclobutenol (38) obtained was purified by column chromatography and was tested for optical purity by chiral HPLC (Chiralcel OD column). The sign of optical rotation of 38 (in chloroform) at the sodium D-line was determined by using a JASCO J-710 spectrophotometer. The results are summarized in Table 3.1. The corresponding photolyses of the complexes in methanol solution did not give any ee.

![Figure 3.04. Photolyses of chiral salts 36 and 37.](image)

Table 3.1. Solid state photolysis results with compounds 36 and 37. The signs of optical rotations are shown in parentheses.

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Photolysis Temperature</th>
<th>Conversion</th>
<th>ee of product 38</th>
</tr>
</thead>
<tbody>
<tr>
<td>36</td>
<td>-40°C</td>
<td>2%</td>
<td>(+)-66%</td>
</tr>
<tr>
<td>36</td>
<td>20°C</td>
<td>10%</td>
<td>(+)-17%</td>
</tr>
<tr>
<td>37</td>
<td>-40°C</td>
<td>6%</td>
<td>(-)-26%</td>
</tr>
<tr>
<td>37</td>
<td>20°C</td>
<td>16%</td>
<td>0</td>
</tr>
</tbody>
</table>
The enantiomeric excesses obtained can be related to preferential photochemical reaction at either the Re or the Si face of the carbonyl group. This is illustrated in Figure 3.05. The reason for an asymmetric "preference" may be related to one or a combination of the following structural features:

1. different hydrogen abstraction geometry for the two γ-hydrogen atoms;
2. different cyclization geometry for the two possible biradicals;
3. presence of any intermolecular steric effects\(^\text{11}\) which may favour the formation of one of the enantiomers.

The effect of the first factor can be understood easily: a better abstraction geometry for the hydrogen atom on one side will lead to a greater abstraction rate on that side and thus favor the formation of one enantiomer over the other (Figure 3.05). Since the abstraction step can be reversible, faster abstraction may not guarantee a greater overall rate of product formation. So, the cyclization geometry may also be crucial. There is, however, no way to tell which factor controls the enantioselectivity. Therefore, the following discussion in this chapter aims only to explain the experimental results from these different viewpoints.

How the crystal structure affects the reactivity remains a difficult question, one of the reasons being our inability to determine the absolute configuration of the product. An attempt was made to determine the X-ray crystal structure of cyclobutanol 38 in order to determine its absolute configuration by anomalous dispersion. However, the crystals of 38 were too small to make data collection possible.

From Table 3.1, it can be seen that the highest \(ee\) of 66\% is obtained from the photolysis of salt 36 at -40\(^\circ\)C. The crystal quality of salt 36 was unfortunately not good enough for single crystal structure analysis, but the structure of compound 37 was determined. Compound 37 was found to
Figure 3.05. Enantioselectivity in the photochemistry of 2,4,6-trisopropylbenzophenone derivatives ($Y^+$ = conjugate acid of optically active amine).
crystallize in the monoclinic space group P2₁ with Z = 4. There are two independent formula units in the asymmetric unit. Because proline is not sufficiently basic to form a salt with carboxylic acid 21, crystals of complex 37 consist of neutral acid molecules hydrogen bonded to zwitterions of proline rather than the corresponding carboxylate anions and ammonium cations.

The two independent molecules of the benzophenone moiety adopt chiral conformations in the solid state due to their non-planarity. These two conformations have a near mirror image relationship which is illustrated in Figure 3.06. Some of the geometric parameters which may be important in the asymmetric induction are summarized in Table 3.2.

The definitions and the "ideal values" for four geometric hydrogen abstraction parameters d, θ, ω and Δ were discussed in Chapter 1. Three more parameters are introduced here: α, d₁₄ and β. The parameter α is defined as the dihedral angle between the triisopropylphenyl group and the carbonyl group. The d₁₄ value is the distance between the carbonyl carbon and the γ-carbon atom and β is the angle between the carbonyl plane and the plane formed by the β-carbon, the γ-carbon and the γ-hydrogen atom. The last two parameters are related to the cyclization geometry of the biradical intermediate.
Figure 3.06. Two independent benzophenone moieties in complex 37.
Table 3.2. Crystallographic parameters in complex 37 ($\alpha =$ dihedral angle between the triisopropylphenyl group and C=O group; $\beta =$ angle between the carbonyl plane and the plane formed by the $\beta$-carbon, the $\gamma$-carbon and the $\gamma$-hydrogen atom; $d_{14} =$ distance between carbonyl carbon and $\gamma$-carbon). aThe first molecule refers to the one that contains the O1 atom and the second refers to the other.

<table>
<thead>
<tr>
<th></th>
<th>First molecule(^a)</th>
<th>Second molecule</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Re face</td>
<td>Si face</td>
</tr>
<tr>
<td>$d$ (Å)</td>
<td>3.14</td>
<td>2.58</td>
</tr>
<tr>
<td>$\Delta$ (°)</td>
<td>47</td>
<td>69</td>
</tr>
<tr>
<td>$\omega$ (°)</td>
<td>47</td>
<td>63</td>
</tr>
<tr>
<td>$\theta$ (°)</td>
<td>117</td>
<td>126</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
<td>-77.7</td>
<td></td>
</tr>
<tr>
<td>$d_{14}$ (Å)</td>
<td>2.96</td>
<td>2.92</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>98.3</td>
<td>73.2</td>
</tr>
</tbody>
</table>

From Table 3.2, it can be seen that the C=O$\cdots$H$\gamma$ distance, $d$, is smaller at the $Si$ face for one independent molecule but is greater at the $Si$ face for the second molecule. Making the assumption that the closest $\gamma$-hydrogen atom is the one to be abstracted, the two independent molecules in the crystal thus lead to different (enantiomeric) biradical intermediates. Racemization of the biradical intermediate is not very likely since it involves bond rotation about the triisopropylaryl-carbonyl bond in the solid state which is topochemically unfavored. Assuming ring closure is fast, these two biradicals will tend to give products of opposite absolute configuration.

This may explain why the $ee$ obtained for complex 37 is low. A similar conclusion can be drawn from the angle $\alpha$. This angle is a convenient measure
of the absolute configuration of the benzophenone units. It can be noticed from Table 3.2 that these angles are of opposite sign but of similar magnitude. This indicates the near mirror image relationship in their conformations.

Another point about the abstraction geometry comes from the low values of the \( \Delta \) angles observed. The \( \Delta \) values for the \( \gamma \)-hydrogen atoms are between 45° and 69°, which are very different from the ideal value of 90°-120°. This may provide an insight into the excited state nature of the reactions. Ito et al. had suggested that the \( \pi,\pi^* \) excited state is responsible for the hydrogen abstraction in 2,4,6-triisopropylbenzophenones in the solid state in contrast to the same reaction in the solution phase. They observed the same cyclobutenol formation when various 2,4,6-triisopropylbenzophenone derivatives were photolysed in the solid state. They also observed a higher quantum efficiency of cyclobutenol formation for 2,4,6-triisopropylbenzophenones with electron donating groups at the \( \text{para} \) position. Based on that, they suggested that the \( \pi,\pi^* \) state is the reactive state in solids. They also pointed out that the mechanism for the solution phase (Figure 3.03), which requires significant conformational changes, is topochemically unfavorable in the solid state. The \( \Delta \) values for some 2,4,6-triisopropylbenzophenone derivatives as determined by X-ray crystal structure analysis were found by Ito and Matsuura to be between 52° and 59°. Wagner disagreed with this mechanism on the basis that the \( \pi,\pi^* \) excited states normally are \( 10^4 \) times less reactive than the \( \pi,\pi^* \) states of aralkyl ketones. However, since the measurement of hydrogen abstraction rate constants in the solid state has never been achieved, we feel that the \( \pi,\pi^* \) excited state cannot be completely excluded as the reactive state.

If the reactive excited state is \( \pi,\pi^* \) in the solid state, the ideal value of \( \omega \) for hydrogen abstraction would be 90° and \( \Delta \) would have an ideal value of <90° due to the spatial arrangement of the half-filled \( \pi \) orbital in the \( \pi,\pi^* \) excited state.
In fact, previous work from our laboratory indicated that the \( \Delta \) values so far reported for \( \pi,\pi^* \) hydrogen abstraction by carbon atoms in enones are never higher than 82°, while the corresponding values for oxygen atoms \( (n,\pi^*) \) are usually around 80° to 110°.\(^1\) In rigid matrices, several hydrogen abstraction reactions by aromatic carbonyl compounds are thought to occur from excited states other than the \( n,\pi^* \) state.\(^1\) Hence, Ito's suggestion proposing the \( \pi,\pi^* \) as the reactive excited state is still possible.

There are two parameters introduced in Table 3.2 to describe the cyclization geometry of the biradical intermediate. The first parameter, \( d_{14} \), gives a rough idea of the distance between the two radicals in the 1,4-biradical intermediate. All four \( d_{14} \) values listed in Table 3.2 are well below the sum of the van der Waals radii of two carbon atoms (3.40 Å).\(^1\) There is not much difference between the \( d_{14} \) values on the \( Re \) and \( Si \) faces for both independent molecules. Recent results from our laboratory suggest that \( d_{14} \) may have a critical value of around 3.1 Å, above which cyclization is very slow.\(^5\) It thus does not seem to be a limiting factor in the cyclobutenol formation.

The other parameter, \( \beta \), concerns the angular arrangement of the two radicals (Figure 3.07). The angle \( \beta \) is defined as the angle between the carbonyl plane and the plane formed by the \( \beta \)-carbon, the \( \gamma \)-carbon and the \( \gamma \)-hydrogen atom. Assuming the ground state geometry applies to the biradical intermediate (least nuclear motion), one would expect that the two radicals would have the best overlap when \( \beta \) is roughly 90°. At the other extreme, a \( \beta \) value of zero will lead to a perpendicular alignment of the radicals. Such a geometry will give a net overlap of zero. The \( \beta \) values listed in Table 3.2 are close to 90° but slightly favour the formation of the \( (R) \)-enantiomer for the first independent molecule and the \( (S) \)-enantiomer for the other in constrast to what was predicted from the \( d \) values.
3.4. Crystal and Molecular Structure of the Complex of S-proline and 4-[2,4,6-tris(1-methylethyl)benzoyl]benzoic acid (37)

A brief discussion of the crystal and molecular structures of compound 37 is presented here.

Complex 37 crystallizes in the monoclinic space group $\text{P}2_1$ with two independent molecules in the asymmetric unit ($Z = 4$). Figure 3.08 illustrates the packing arrangement. The two independent proline zwitterionic molecules are held together by intermolecular hydrogen bonding between the amino and the carboxylate groups and these form a "chain" along the a-axis. The two 4-[2,4,6-tris(1-methylethyl)benzoyl]benzoic acid molecules are attached to this chain by forming hydrogen bonds with their carboxylic acid groups. These form two ten-membered hydrogen bonded structures which are depicted in Figure 3.09. Also present in the crystal structure are intramolecular hydrogen bonds between the amino and the carboxylate groups of the two proline zwitterions.
Figure 3.08. Packing diagram for complex 37.

Figure 3.09. Hydrogen bonding in complex 37.
Chapter 4  Structure-Reactivity Correlations in Photochemical Hydrogen Abstraction of Thiones

4.1. Excited States in Thiones

Thiones are known to have very different photophysical and photochemical properties compared to their oxygen analogs. One of the important differences is the much lower energy of the \( n,\pi^* \) transition bands in thioketones. The \( n,\pi^* \) transitions in ketones usually lie in the near UV region whereas for thioketones these bands lie in the visible region and thus give rise to their colors. Mulliken attributed this effect to the lower ionization potential of the non-bonding p-electrons of sulphur as compared with those of oxygen. As an example, Table 4.1 summarizes the spectral characteristics (in ethanol) of benzophenone and thiobenzophenone.

Table 4.1. Spectral characteristics (in ethanol) of benzophenone and thiobenzophenone.

<table>
<thead>
<tr>
<th></th>
<th>( \pi,\pi^* )</th>
<th>( n,\pi^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_{\text{max}} ) (nm)</td>
<td>( \varepsilon_{\text{max}} )</td>
</tr>
<tr>
<td>benzophenone</td>
<td>250</td>
<td>18200</td>
</tr>
<tr>
<td>thiobenzophenone</td>
<td>315</td>
<td>15100</td>
</tr>
</tbody>
</table>

Another point that can be noted from Table 4.1 is the large energy gap between the two excited states in thioketones in contrast to their oxygen analogs. It is these differences in the spacing of the two lowest excited states that lead to dramatic differences in the photochemistry and photophysics of the
two classes of compounds. As a result, there is a strong Franck-Condon inhibition of the rates of radiationless decay from the \( ^1(\pi,\pi^*) \) states to the \( ^1(n,\pi^*) \) states of thioketones. The \( ^1(\pi,\pi^*) \) states (or \( S_2 \)) can therefore be relatively long-lived, and this enables them to react chemically with other species or to fluoresce\(^85\) in violation of Kasha's rule.\(^89\)

Thiocarbonyl compounds are known to undergo many different photochemical reactions: for example, photooxidation, photocycloaddition, intermolecular and intramolecular hydrogen abstraction, \( \alpha \)-cleavage in strained systems and bimolecular self-quenching.\(^84\) The intramolecular hydrogen abstraction reactions are particularly interesting due to the reactivities of both \( \pi,\pi^* \) and \( n,\pi^* \) states as well as the ability of thiocarbonyls to abstract hydrogen atoms at various positions. It is now known that \( n,\pi^* \) excitation almost always gives \( T_1 \) rapidly in high yield and is normally assumed to be the photochemically reactive species.\(^85\) However, since \( S_2 \) [or \( ^1(\pi,\pi^*) \)] states decay efficiently to \( T_1 \) in most thiones, any differences in photochemical reactivity of \( S_2 \) and \( T_1 \) can only be determined by comparing the nature and the quantum yields of the products formed from irradiation with different frequencies.

This is well demonstrated by the work of de Mayo et al. on the photochemistry of thione 39 (Figure 4.01).\(^90\) \(^91\) Photolysis of thione 39 (\( \pi,\pi^* \)) results in both \( \gamma \) and \( \epsilon \) hydrogen abstraction products, whereas irradiation into \( n,\pi^* \) gives only \( \gamma \) abstraction products with much lower quantum efficiencies.
4.2. Intramolecular Hydrogen Abstraction Reactions in Thiones

The photochemistry of aryl alkyl thiones has been studied systematically by de Mayo and coworkers. Such studies have revealed important information about the intramolecular hydrogen abstraction reactions by thiones. From the above example, it can be noticed that thione hydrogen abstraction reactions by the $\pi, \pi^*$ states mimic the reactivities of their oxygen analogs. Upon excitation to the $\pi, \pi^*$ states, thiones undergo $\gamma$-hydrogen abstraction (via $T_1$) to give the 1,4-biradicals which may give rise to cyclization or cleavage products. Such behaviour is very similar to that of the corresponding ketone with one difference: abstraction by the $T_1$ states of thiones generally requires the C-H bonds be weakened by substitution, whether by an adjacent oxygen atom or the introduction of unsaturation.

Intramolecular hydrogen abstraction also competes successfully with radiationless relaxation in the $S_2$ excited thione molecule. The $S_2$ excited state has a short lifetime ($< 0.5$ ns) and the abstraction reactions are barrier free. On excitation to $S_2$, intramolecular hydrogen abstraction occurs preferentially from the $\delta$ position. When $\delta$ hydrogen atoms are not available, abstraction may also occur from the $\gamma$, $\epsilon$ or $\beta$ positions.
Intermolecular hydrogen abstraction reactions for diaryl thiones are also known. Among them, photoreduction of thiobenzophenone is one of the most studied reactions. This reaction is also found to be wavelength dependent. A similar but not identical mixture is obtained upon \( n,\pi^* \) and \( \pi,\pi^* \) irradiations in ethanol. It should be noted that the \( n,\pi^* \) excited state of thiobenzophenone does not have enough energy to abstract a hydrogen atom from hydrocarbon solvents. However, upon excitation to the \( S_2 \) state, it can be reduced by cyclohexane.

An interesting example of an intramolecular hydrogen abstraction of an aromatic thiobenzaldehyde was also reported (Figure 4.02). This reaction involves a hydrogen transfer to the carbon atom of the thiocarbonyl group and is believed to involve a radical intermediate. Exitations into both the \( n,\pi^* \) and \( \pi,\pi^* \) states give the same product.

![Figure 4.02. Photolysis of 2,4,6-tri-t-butylthiobenzaldehyde.](image)

The only reported hydrogen abstraction reaction by the sulphur atom of a diaryl thione is from the work by Ohno et al. on the photoenethiolization of \( \alpha \)-benzylthiobenzophenone (40) (Figure 4.03). Thione 40 was found to undergo hydrogen abstraction upon excitation to the \( n,\pi^* \) state to give enethiol 41 which is stable for days at -78°C and can be trapped by diazomethane but reverts to thione 40 at room temperature (Figure 4.03).
Figure 4.03. Photolysis of o-benzylthiobenzophenone (40).

The o-methyl derivative 42 however, does not undergo such a reaction. Ramamurthy\textsuperscript{84} suggested that this is because a more highly activated hydrogen is required for photothioenolization.

4.3. Determination of Hydrogen Abstraction Geometry by the Crystal Structure-Reactivity Correlation Method

Despite the relatively large number of thione hydrogen abstraction reactions known in solution phases, the corresponding reaction in the solid state has never been reported. The major reason for this may be the fact that thiones exhibit exceptionally efficient self-quenching in both their $S_2$ and $T_1$ excited states with rate constants characteristic of diffusion-controlled processes.\textsuperscript{85} Owing to this, very low concentrations of thiones must usually be employed in studies of their intramolecular processes in solutions so that self-quenching does not dominate. Due to the long $T_1$ lifetimes ($10^{-5}-10^{-6}$s), $T_1$ self-quenching
cannot be totally eliminated in solutions even at a concentration of $10^{-6}$ M.\textsuperscript{99} Considering the fact that the molecular concentration of simple organic molecules in molecular crystals is of the order of 1 to 10 M, it can be easily seen how serious self-quenching can be in the solid state. Therefore the investigation of the photochemical reactions of thiones by the structure-reactivity correlation method, which relies on solid state reactions, faces a very difficult technical problem.

In order to achieve the reaction, the molecules in the crystalline state should have a relatively slow energy transfer (quenching) rate. One way to decrease the rate of energy transfer is to employ a sterically hindered molecule. Turro\textsuperscript{100} has demonstrated that steric hindrance to exothermic triplet energy transfer is significant, with azo-$n$-butane a better energy acceptor from various sensitizers than azo-$t$-butane by a factor of 3.6-10.7. The work by Hammond\textsuperscript{65} on energy transfer from 2,4,6-triisopropylbenzophenone leads to a similar conclusion.

Thus, to make self-quenching less dominant in the solid state, a thione with steric bulkiness around the thiocarbonyl group would be helpful. In this regard, 2,4,6-triisopropylthiobenzophenone (14) offers a good opportunity. The thiocarbonyl group in 14 is surrounded by two isopropyl groups as well as two phenyl groups. In fact, it has been shown by dynamic NMR studies that the two $o$-isopropyl groups in 2,4,6-triisopropylbenzophenone and its analogues cause severe steric hindrance around the carbonyl moiety.\textsuperscript{79,101} This was first noted by lto\textsuperscript{79} who found that the methyl groups of the two $o$-isopropyl groups in 2,4,6-triisopropylbenzophenone are not equivalent.\textsuperscript{102}

Similar results were obtained by Bonini \textit{et al.} from their work on 2,4,6-triisopropylthiobenzophenone and other derivatives.\textsuperscript{101} The free energies of activation for the rotation of triisopropylphenyl ring and the other phenyl were
measured by dynamic NMR techniques. These results, which are summarized in Table 4.2, indicate that the free energy for the triisopropylphenyl ring rotation increases with the size of the C=X moiety. The trend for the phenyl group rotations is more complicated. Bonini\textsuperscript{101} suggested that it is due to the simultaneous conjugative and steric effects.

![Chemical structure](image)

**Table 4.2.** Free energies of activation for the triisopropylphenyl and the phenyl ring rotation in various derivatives of 2,4,6-triisopropylbenzophenone.\textsuperscript{101}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Free energy of activation ((\Delta G^\circ) in kcal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>enantiotopomerization</td>
</tr>
<tr>
<td>(X = O)</td>
<td>16.3</td>
</tr>
<tr>
<td>(X = NH)</td>
<td>19.1</td>
</tr>
<tr>
<td>(X = S)</td>
<td>22.6</td>
</tr>
<tr>
<td>(X = CPh_2)</td>
<td>&gt;27</td>
</tr>
</tbody>
</table>

These results indicate that 2,4,6-triisopropylthiobenzophenone is even more sterically hindered than its ketone analog and almost certainly possesses a geometry in which the triisopropylphenyl ring is perpendicular to the thiocarbonyl group, even in solution at room temperature. This could be an advantage for solid state studies, since the steric bulkiness might help to decrease the self-
quenching rate so that appreciable amounts of product may be isolated within a reasonable period of time.

2,4,6-Triisopropylthiobenzophenones can be prepared conveniently by reaction of the corresponding ketones with Lawesson's reagent. To this end, two different 2,4,6-triisopropylthiobenzophenones have been prepared. They are triisopropylthiobenzophenone (14) and its p-methoxy derivative (15). These two compounds, like thiobenzophenone, show absorption peaks in both the visible and UV regions at around 600 nm and 320 nm respectively. These can be assigned to the n,π* and the π,π* transitions. Irradiations of 14 or 15 in benzene solutions in the visible region by a 200 W tungsten lamp for two weeks do not lead to any reaction. However, UV irradiations of benzene solutions of 14 and 15 give cyclobutenethiol 43 and 44 respectively in high yields (Figure 4.04).

![Figure 4.04. Photolyses of 2,4,6-triisopropylthiobenzophenones.](image)

Both products 43 and 44 are stable compounds in inert atmosphere at room temperature. Just like their oxygen analogues, these two cyclobutenethiols display similar NMR spectra, which are characterized by a large difference in chemical shift between the two methyl groups on the cyclobutene ring (see experimental section). Such a difference in chemical shift can be attributed to the interaction between the phenyl group and the cis-methyl group on the four membered ring. The exact nature of the interaction is not
known for certain but is very likely a result of the anisotropic effect from the phenyl group.

The mechanism of these photoreactions is most simply viewed as an initial photochemical $\gamma$-hydrogen abstraction followed by cyclization of the biradical intermediate (Figure 4.04). The same reactions were also found to occur in the solid state upon UV irradiation. Again, the visible light photolyses do not lead to any reactions. The reactions are thus thought to originate from the $S_2$ excited state. The crystal structures of both 14 and 15 were determined by single crystal X-ray diffraction. Stereodiagrams of thiones 14 and 15 are shown in Figures 4.05 and 4.06 respectively. Some of the geometric parameters related to the hydrogen atom abstractions are summarized in Table 4.3.

![Figure 4.05. ORTEP stereodiagrams of compound 14.](image-url)
Table 4.3. Hydrogen Abstraction Geometry for sulphur in thiones 14 and 15.

<table>
<thead>
<tr>
<th>Thiones</th>
<th>d (Å)</th>
<th>ω (°)</th>
<th>Δ (°)</th>
<th>θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;ideal&quot; values for n,π* (T₁)</td>
<td>3.00</td>
<td>0</td>
<td>90-120</td>
<td>180</td>
</tr>
<tr>
<td>&quot;ideal&quot; values for π,π* (S₂)</td>
<td>3.00</td>
<td>90</td>
<td>≤ 90</td>
<td>180</td>
</tr>
<tr>
<td>14</td>
<td>S(1)···H(8)</td>
<td>3.06</td>
<td>51</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>S(1)···H(15)</td>
<td>3.28</td>
<td>46</td>
<td>47</td>
</tr>
<tr>
<td>15</td>
<td>S(1)···H(7)</td>
<td>3.27</td>
<td>49</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>S(1)···H(9)</td>
<td>3.07</td>
<td>50</td>
<td>52</td>
</tr>
</tbody>
</table>

Also included in Table 4.3 are the "ideal" values for hydrogen abstraction reactions by the n,π* and the π,π* excited states of thiones. The origins of some of these parameters have been discussed in Chapters 1 and 2. However, it should be mentioned here that the "ideal" d value is based on the sum of van der
Waals radii of the hydrogen and the sulphur atoms. The ω value of 90° for the π,π* state is based on the fact that the π orbital of the thiocarbonyl group is perpendicular to the plane of C=S group. The ideal Δ angle for π,π* abstraction is expected to be less than or equal to 90° due to the fact that the half-filled π orbital in the excited state lies between the sulphur and the carbon atoms of the thiocarbonyl group (Figure 4.07).

![Figure 4.07. Thiocarbonyl hydrogen abstraction geometry.](image)

From Table 4.3, it can be seen that the shortest C=S···Hγ distances for both compounds are around 3.1Å. The other γ-hydrogen atoms are about 3.3Å away from the sulphur atoms. The value of 3.1Å, which is roughly the sum of the van der Waals radii of sulphur and hydrogen, is considerably larger than the corresponding carbonyl hydrogen abstraction distance of 2.72Å. The θ angles are approximately 120° for all cases.

It should also be noted that the Δ values are about 50°. These values are more suitable for hydrogen abstraction from the π,π* state than from the lower energy n,π* state (Figure 4.07). The ω values are, however, less informative, as they have values that are roughly the average of the "ideal" ω values of n,π* and π,π* states (Table 4.3).
The γ-hydrogen atoms are also reasonably close to the thiocarbonyl carbon atoms. Table 4.4 summarizes the S=C–H distances for thione 14 and 15. These distances are all well below the sum of van der Waals radii for carbon and hydrogen (2.90 Å). As has been discussed in the previous section (Figure 4.02), aromatic thiocarbonyl compounds have been reported to undergo hydrogen abstraction reactions by carbon. Considering this as well as the short S=C–H contacts, an alternate mechanism which involves initial hydrogen abstraction by the carbon atom followed by a 1,2-hydrogen shift to the sulphur atom cannot be completely excluded.

Table 4.4. Hydrogen Abstraction Geometry for carbon in thiones 14 and 15.

<table>
<thead>
<tr>
<th>Thiones</th>
<th>d (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;ideal&quot; values for π,π* (S2)</td>
<td>2.90</td>
</tr>
<tr>
<td>14</td>
<td></td>
</tr>
<tr>
<td>C(1)–H(8)</td>
<td>2.43</td>
</tr>
<tr>
<td>C(1)–H(15)</td>
<td>2.47</td>
</tr>
<tr>
<td>15</td>
<td></td>
</tr>
<tr>
<td>C(1)–H(7)</td>
<td>2.56</td>
</tr>
<tr>
<td>C(1)–H(9)</td>
<td>2.43</td>
</tr>
</tbody>
</table>

As in the case of carbonyl compounds, it should be mentioned that the geometries discussed above are all ground state geometries. Spectroscopic and theoretical studies of several tetraatomic thiocarbonyls have provided some information about their excited state structure. Spectroscopic studies have shown that tetraatomic thiocarbonyls (Cl₂CS, FCICS, F₂CS, H₂CS) are non-planar and have considerable C=S bond elongation in their T₁, S₁ and S₂ states. Thiomethanal (H₂CS), for example, has been found to have C=S bond lengths of 1.81 Å, 1.80 Å and 2.23 Å in the T₁, S₁ and S₂ states respectively.
compared to 1.61Å in the ground state. In the solid state, however, large changes in geometry upon excitation are topochemically disfavored and highly unlikely. Therefore the above crystallographic data (ground state) can still serve as a rough guide for the excited state geometries in the solid state.

4.4. Crystal and Molecular Structures of Phenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione (14) and 4-Methoxyphenyl-[2,4,6-tris(1-methylethyl)phenyl]methanethione (15)

A brief discussion of the crystal and molecular structures of compounds 14 and 15 is presented here.

Both thiones 14 and 15 crystallize in the monoclinic space group P21/n with Z = 4. Their packing diagrams are shown in Figures 4.08 and 4.09 respectively.

![Figure 4.08. Packing diagram of compound 14.](image)
The C=S bond distances for 14 and 15 are 1.628(3)Å and 1.638(3)Å respectively. These distances are very close to the C=S bond distance of thiobenzophenone (1.636(9)Å) reported by Rindorf and Carlsen but are shorter than the normal C=S bond length of 1.71Å. The p-methoxy group in thione 15 is almost in the plane of the phenyl ring: C12-C11-O1-C23 = 5.2° (Figure 4.06).

In each of the thiones, the thiocarbonyl group is almost perpendicular to the triisopropylphenyl ring but is coplanar with the other phenyl ring. For thione 14, the torsional angle between the thiocarbonyl and the triisopropylphenyl ring is 95.3° (S1-C1-C8-C13) and the angle between the thiocarbonyl and the other phenyl ring is 3.5° (S1-C1-C2-C3). The corresponding angles for compound 15 are 91.0° and -0.8° respectively. This conformation is clearly the result of the steric effect from the two bulky o-isopropyl groups. In the absence of the two o-
isopropyl groups, the corresponding angles for thiobenzophenone has been determined to be 42.7° and 31.9°.105
Chapter 5  PHOTOCLEAVAGE OF MONOTHIOIMIDES

5.1. Hydrogen Abstractions in Monothioimides, Dithioimides and Similar Systems - A Brief History

Nitrogen-containing thiocarbonyl compounds with the general structure -(C=S)N(C=X)-, where X=O or S, are known to undergo intramolecular photochemical hydrogen abstraction reactions.\textsuperscript{107-121} β, γ, δ and ε abstractions have all been found to occur. In most cases, the evidence for an abstraction mechanism comes from isolation of the cyclization products.\textsuperscript{109-120} In a few cases, however, no cyclization products were found, but abstraction mechanisms were proven by observing racemization of the chiral centre from which the hydrogen atom was abstracted.\textsuperscript{107, 108} One example concerns the photochemistry of N-substituted dithiosuccinimides 45 and 46 carried out by Kanaoka and co-workers (Figure 5.01).\textsuperscript{108}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure501.png}
\caption{Photolysis of N-substituted dithiosuccinimides 45 and 46.}
\end{figure}
Photolysis of optically active thioimide 45 gave rise to racemization of the starting material. This suggested that δ-hydrogen abstraction had occurred to afford biradical 47. Since reverse hydrogen transfer to the Si and Re faces of the δ-radical are equally possible (assuming biradical 47 has a sufficiently long lifetime), this would lead to racemization. Kanaoka also demonstrated the lower intrinsic reactivity of the γ-H towards abstraction from the observation that the chiral centre of compound 46 remained unaltered after photolysis (Figure 5.01).

As far as the author is aware, in all cases where cyclization products have been isolated, there exists one common feature: that is, the C-H positions being attacked by the excited thiocarbonyls are adjacent to either phenyl, alkoxy or dialkyl groups.108-121 There are two different explanations for this phenomenon. Sakamoto explained this in terms of enhancement of cyclization by either (1) hydrogen bonding between the alkoxy group and the mercapto group in the biradical intermediate (Figure 5.02) or (2) steric bulkiness of the substituents (in cases of phenyl and dialkyl groups).113,114 The presence of the bulky groups is believed to force the two radicals into close contact by limiting the conformation of the biradical intermediate (Figure 5.02).

![Figure 5.02. Sakamoto's model of enhancement of cyclization by an alkoxy group or bulky groups.](image-url)
Another explanation involves the hydrogen abstraction step. It is well known that the reactive excited states of thiocarbonyl compounds usually have lower energy than their C=O analogs.\textsuperscript{87, 88} The effect of this lower energy on the photoreactivity of the C=S excited state can be seen from its general inertness to $\alpha$-cleavage except in strained systems.\textsuperscript{122} It is thus not surprising that "activation" of the C-H bond may be necessary for the hydrogen abstraction reaction to occur in thioimides. The presence of adjacent phenyl, alkoxy or dialkyl groups provides the required activation.\textsuperscript{118} This implies that hydrogen abstraction reactions in thioimides probably will not occur without activated groups regardless of the consequent reactions. The effect is expected to be even more pronounced in the case of a $\gamma$-hydrogen abstraction due to its lower intrinsic reactivity.\textsuperscript{108}

5.2. Photocleavage in Monothioimides - A New Mechanism

$\beta$-Photocleavage reactions in thioimides and similar compounds have also been reported. In most cases, the reactions are thought to be preceded by a $\gamma$-hydrogen abstraction followed by a Type II-like $\beta$-cleavage.\textsuperscript{107, 110, 113, 114, 116, 117, 119, 123, 124} In some cases, however, a direct C-N bond cleavage was also included as a possible mechanism.\textsuperscript{114, 116, 123, 124} In only one case was the suggested mechanism supported by further experiments. White \textit{et al.} have reported a photolysis of an optically active $N$-acyl-thionothiazolidine 48 (Figure 5.03). Compound 48 is not actually a thioimide but its photochemistry is similar.\textsuperscript{107}
The ethyl ester formed in the photolysis was found to be racemic. This suggests that a \( \gamma \)-hydrogen abstraction had occurred. A mechanism involving a ketene intermediate was proposed. Presumably, trapping of the ketene by ethanol at both the \( Re \) and \( Si \) faces is equally possible leading to the racemic ethyl ester product. It should also be noted that \( N \)-acyl-thionothiazolidine 48 contains a C-H bond that is activated by a phenyl and a methyl group.

Other examples of photocleavage reactions, however, did not provide evidence for their proposed mechanisms. As can be seen from the previous section, the need for an activated group in photocyclization reactions and the lower intrinsic reactivity of \( \gamma \)-hydrogen atoms are the two important characteristics of thioimide photochemical abstraction reactions. Although Type II cleavage is a well-known photoreaction for ketones\(^{12} \) and imides\(^{30} \), the occurrence of a hydrogen abstraction in a thioimide system without any activating groups at the \( \gamma \)-position is doubtful. A similar problem arises when some thioimides without \( \gamma \)-hydrogens were found to undergo photocleavage reactions. These findings suggest that some other cleavage mechanism must be operating. Compound 49 is a typical example of a monothioimide that undergoes a photocleavage reaction but possesses no \( \gamma \)-hydrogen. This compound has been studied by two different
research groups, who reported basically identical results. They both isolated monothioimide 50 as the major photoproduct upon irradiation.

![Diagram of monothioimide 49](image)

**Figure 5.04.** The proposed direct photohomolysis of monothioimide 49.

Both Sakamoto\textsuperscript{114} and Oda\textsuperscript{123} attributed the formation of thiobenzanilide 50 to direct homolysis of the C-N bond (Figure 5.04). Oda referred to this as an "\(\alpha\)-cleavage" since the C-N bond is \(\alpha\) to the benzoyl group. It is unfortunate, however, that the fate of the acyl radical was not reported in either paper.

In order to understand the reaction fully, the above photolysis has now been repeated. In anhydrous benzene, photolysis of 49 leads to no reaction, even after prolonged irradiation. A solid state photolysis under anhydrous conditions also gave no reaction. In benzene that had been allowed to equilibrate with the moisture in the atmosphere, however, photolysis afforded benzoic acid and thiobenzanilide 50 (10\% yield). A solid state photolysis without special attempts to exclude moisture afforded the same two products. In 10\% methanol in benzene (v/v), photolysis gave methyl benzoate and thiobenzanilide (76\% yield). These findings indicate that the reaction is probably a photosolvolysis. In the absence of solvolytic agents (e.g. water, alcohol), the photoreaction simply does not proceed. An incomplete mechanism is shown in Figure 5.05.
Figure 5.05. A new proposed mechanism for photolysis of 49.

An X-ray crystal structure of 49 was determined. Details are summarized in the experimental section. An ORTEP stereodiagram is shown in Figure 5.06.

Figure 5.06. ORTEP stereodiagram of monothioimide 49.

*N-Phenyl-N-(phenylthioxomethyl)benzenepropanamide* (16) and its derivatives represent another series of monothioimides that has been reported to undergo photocleavage reactions. Sakamoto *et al.* reported that, upon irradiation in benzene using a 1000 W high pressure mercury lamp, monothioimide 16 gave
thiobenzanilide 50 along with substantial amounts of a δ-hydrogen abstraction cyclization product.\textsuperscript{110} Once again, however, the fate of the oxygen-containing products in those photolyses was not mentioned. The formation of thiobenzanilide was attributed to an initial γ-hydrogen abstraction followed by a β-cleavage. Figure 5.07 illustrates the proposed mechanism.

![Diagram](image)

**Figure 5.07.** Type II mechanism as proposed by Sakamoto.

With the assumption that the presence of activating groups is necessary in the hydrogen abstraction reactions of thioimides, the problem with the proposed mechanism is obvious: the γ-position is poorly activated. It would not be surprising, therefore, if this photocleavage reaction were to proceed through some other mechanism.

Experiments were carried out to clarify this point. Photolyses in the solid state were also performed to determine the geometric requirements for an intramolecular hydrogen atom abstraction by sulphur (if there is one) through the structure-reactivity correlation method. Without any access to a 1000 W high pressure mercury lamp, photolyses were carried out with a 450 W Havnovia lamp and Pyrex immersion well setup (Ace Glass). The results are similar to those with monothioimide 49 (Figure 5.5). Photolyses of 16 under anhydrous...
conditions in both benzene solution and the solid state did not lead to any reactions. Without special attempts to exclude moisture, photolyses afforded thiobenzanilide (50) and 3-phenylpropanoic acid (51) in 20% yield respectively. In the presence of methanol, thiobenzanilide and methyl 3-phenylpropanoate (52) were obtained upon irradiation (82% yield). Similar results were obtained for four other derivatives of \(N\text{-Phenyl-}N\text{-}(\text{phenylthioxomethyl})\text{benzenepropanamide (17 to 20).}

\[\begin{align*}
17 & : \text{Ar1} = 4\text{-MeOPh, Ar2 = Ph} \\
18 & : \text{Ar1} = \text{Ph, Ar2 = 4-Br-2,6-diMePh} \\
19 & : \text{Ar1} = \text{Ph, Ar2 = 4-BrPh} \\
20 & : \text{Ar1} = \text{Ph, Ar2 = 4-MeOPh}
\end{align*}\]

In order to provide evidence for a possible ketene intermediate, the photolysis of monothioimide 16 was performed with 10% \(\text{CH}_3\text{OD}\) in benzene (v/v). GC/MS analysis of the ester 52 formed in the photolysis indicated that it was non-deuterated. The results are clearly inconsistent with the Type II mechanism, by which mono-deuterated ester 52 would be expected (Figure 5.07). Exactly the same conclusion was obtained from the photolysis of monothioimide 16-\(\gamma\text{-d}_2\) in undried benzene or in the solid state. In those cases, no deuterium loss was found in 51.

Concomitant with the photochemical studies, the crystal and molecular structures of four monothioimides (16 to 19) were determined by direct method single crystal X-ray diffraction. The results of these investigations showed that
compounds 16 to 19 adopt conformations in the solid state for which neither the 
\(\gamma\) or \(\delta\)-hydrogen abstraction is likely to occur. Their ORTEP stereodiagrams are 
shown in Figure 5.08-5.11.

Figure 5.08. ORTEP stereodiagram of monothioimide 16.

Figure 5.09. ORTEP stereodiagram of monothioimide 17.
All four monothioimides have essentially identical solid state conformations. The shortest C=S···H$\gamma$ and C=S···H$\delta$ contacts in these compounds are summarized in Table 5.1.
Table 5.1. Intramolecular contacts in monothioimides.

<table>
<thead>
<tr>
<th>Monothioimide</th>
<th>C=S⋯H₇ (Å)</th>
<th>C=S⋯Hδ (Å)</th>
<th>O⋯C=S (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>5.06</td>
<td>6.33</td>
<td>2.86</td>
</tr>
<tr>
<td>17</td>
<td>5.07</td>
<td>6.44</td>
<td>2.81</td>
</tr>
<tr>
<td>18</td>
<td>5.06</td>
<td>6.55</td>
<td>2.82</td>
</tr>
<tr>
<td>19</td>
<td>5.14</td>
<td>6.22</td>
<td>2.77</td>
</tr>
<tr>
<td>49</td>
<td>-</td>
<td>-</td>
<td>2.82</td>
</tr>
</tbody>
</table>

All of the C=S⋯H contacts are at least 5 Å, which is considerably greater than the sum of the van der Waals radii for sulphur and hydrogen (3.00 Å). Based on Scheffer's and Trotter's previous work, which indicates that hydrogen atom abstraction by oxygen fails when the C=O⋯H contacts exceed the sum of the van der Waals radii by 0.3-0.4 Å, it can be concluded that the distances listed in Table 5.1 are too great to allow abstraction of either γ or δ hydrogen atoms.

Having established that photocleavage of monothioimide 16 (and presumably 17 to 20 as well) does not involve an initial γ-hydrogen abstraction, it was of interest to see whether fully oxygenated imides behave similarly. N-Acetylpropanamide was synthesized and photolyzed in CH₃OD. The major cleavage product, methyl propanoate, was analysed by GC/MS and the results showed that one deuterium atom was incorporated. The Type II cleavage mechanism originally proposed by Mazzocchi, et al, is therefore verified in this case (Figure 5.12).
Figure 5.12. Type II cleavage mechanism of N-acetylpropanamide.

The difference in mechanistic photochemistry between imides and monothioimides is clear. A new mechanism is needed for at least some monothioimide photocleavage reactions as depicted in Figure 5.05. The unknown intermediate must satisfy the following criteria:

1. It should have a reasonably long lifetime in order to react with other molecules.
2. It should react in the presence of alcohol or water to give the corresponding ester or acid respectively.
3. In the absence of alcohol and water, it should revert to starting material.

To this end, two different mechanisms were proposed. The first one involves direct heterolysis of the N-CO bond as illustrated in Figure 5.13.
This mechanism is simple and involves relatively stable anionic and cationic intermediates. Heterolytic cleavage of monothioimides has been proposed before. Coyle and co-workers reported the photolyses of some \( N \)-(dialkylaminomethyl)thiophthalimides.\(^{126}\) They suggested that direct heterolysis (at the N-R bond) was the first step in one of the plausible mechanisms for the formation of \( N \)-thioformylamines (Figure 5.14). However, heterolytic cleavage at the N-CO bond may be less energetically favored, not only because the N-CO bond is a stronger bond but also because the ionic intermediates formed (Figure 5.13) are less stable.
The clue to the second mechanistic possibility was found in the close contact that is evident in Figures 5.06 and 5.8-5.11 between the oxygen atom of the C=O group and the carbon atom of the C=S group. These contacts, which are given in Table 5.1, are well below the sum of the van der Waals radii for oxygen and carbon (3.22 Å). Thus, in the solid state, the oxygen atom is ideally positioned for excited state nucleophilic attack on the C=S double bond, and this process may be the first step of the mechanism by which thiobenzanilides are formed in this medium as well as in solution. Figure 5.15 illustrates this idea. Such an attack would lead to the 1,3-oxazetidinium ion (53), which would react with the water present in the medium and then break down, via species 54, to the enol of thiobenzanilide and 3-phenylpropanoic acid. Attempt to trap intermediate 53 by photolysing monothioimide 16 in a solution containing 10% methyl iodide in benzene (v/v) was unsuccessful.

Figure 5.15. A new proposed mechanism involving a 1,3-oxazetidinium ion.

The intermediate 54 has a close literature analogy. Barton et al. reported the photolysis of some o-phenethyl thiobenzoate derivatives (55). A Type II
elimination, which involves an oxetan intermediate (56), was found to occur (Figure 5.16).

Figure 5.16. Photolysis of o-phenethyl thiobenzoate derivatives.

The analogy between the two mechanisms lies not only in the structures of the intermediates, but also in the way they react. The conversion of species 56 into 58 and benzaldehyde (when R = Ph) corresponds to the suggested cleavage of intermediate 54 (Figure 5.14). Moreover, the ring opening of species 56 to give 57 (when R = alkyl) is similar to the reverse backward reaction from intermediate 53 to monothioimide (16).

In principle, intermediate 54 could also cleave to form thiobenzoic acid and the enol of N-phenyl-3-phenylpropanamide. However, gas chromatographic analysis of the reaction mixture did not reveal any signals corresponding to these two compounds. The preference for breakdown of 54 into 3-phenylpropanoic
acid and the enol of thiobezanilide may be related to the resonance stability of the latter product.

Summarizing all the experimental findings, it is clear that some monothioimidines require a new mechanism for photocleavage reactions. These include monothioimidines which (1) do not possess a γ-hydrogen (e.g. 49) or (2) possess γ-hydrogens which cannot be abstracted (e.g. 16). In the latter case, the lack of photoabstraction is thought to be a consequence of the absence of activation at the γ-position. Two new mechanisms are proposed and discussed. The use of the solid state structure-reactivity correlation method in determining reaction mechanisms is also shown. Those reactions (or mechanisms) which involve too much "motion" would not be favored in the solid state.

One last point worth mentioning is the absence of any δ-hydrogen abstraction products in our photolyses of thioimidines 16 and 17. These findings contradict what was reported by Sakamoto,\textsuperscript{110} who claimed that photolysis of 16 and 17 with a 1000 W high pressure mercury lamp gave, in addition to cleavage products, the δ-photocyclization products 59 and 60, respectively (Figure 5.17). The reason for these experimental differences is not clear, but may be related to the local heat generated by the irradiation with the high power lamp. Such heat may result in molecular conformations favorable for δ-hydrogen abstraction reactions. In our experiments, however, the use of a lower power lamp (450 W medium pressure mercury arc) as well as our maintaining the reaction mixture at room temperature may prevent such a high energy conformation from forming in any significant extent. However, photolysis of a refluxing solution of monothioimide 16 in anhydrous benzene with a 450 W medium pressure mercury lamp did not afford any traces of the cyclization product 59.
5.3. Crystal and Molecular Structures of Monothioimides

A brief discussion of the crystal and molecular structures of the five monothioimides mentioned in the previous section is presented here.

Compounds 16 and 49 crystallize in the orthorhombic space group P2_12_12_1 (Z = 4). Monothioimide 17 and 18 crystallize in the orthorhombic space groups Pbca (Z = 8) and Pca2_1 (Z = 4) respectively while monothioimide 19 crystallizes in the monoclinic space group P2_1/a (Z = 4).

Some important crystallographic contacts have been summarized in Table 5.1 and discussed in the previous section. In summary, compound 16 to 19 all possess γ and δ hydrogen atoms > 5Å away from the sulphur atom. Such distances are much greater than the sum of the van der Waals radii of sulphur and hydrogen and have a profound influence on the photoreactivities of these compounds in their solid states (see previous section).

All five monothioimides have their functional groups [-\(\text{C=S}\text{N}-(\text{C=O})\]- aligned in the so-called \((E_S, Z_0)\)-conformation (Figure 5.06 and 5.08-5.11).\(^{128}\) In this conformation, the thioimide moiety adopts an E conformation while the imide moiety adopts a Z conformation (Figure 5.18). This leads to a close contact between the carbon atom of the C=S group and the oxygen atom of C=O group. These contacts are tabulated in Table 5.1 in the previous section. MMX
calculations on compound 49 by PCModel\textsuperscript{129} indicate that this $(E_s, Z_o)$-conformation is the most stable conformation. The relative energies of the four different conformations are listed in table 5.2.

![Figure 5.18. Conformational equilibrium in acyclic monothioimides.](image)

<table>
<thead>
<tr>
<th>Conformation</th>
<th>Relative energy (kJmol\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Z, Z$</td>
<td>1.12</td>
</tr>
<tr>
<td>$E_s, Z_o$</td>
<td>0</td>
</tr>
<tr>
<td>$E_o, Z_s$</td>
<td>1.46</td>
</tr>
<tr>
<td>$E, E$</td>
<td>1.18</td>
</tr>
</tbody>
</table>

Table 5.2. Relative stabilities of different conformations of 49 from MMX calculations.

Two factors, electrostatic interactions and steric effects, seem to be of primary importance in determining the conformational preferences of acyclic monothioimides. The 1,3-steric interactions are illustrated in Figure 5.19. In this regard, $(E_s, Z_o)$ and $(Z, Z)$-conformations suffer from smaller 1,3-steric repulsion and should be more preferred. The electronic factor concerns the arrangement of the two dipoles for the carbonyl and thiocarbonyl groups. The parallel alignment of dipoles like the one in the $(Z, Z)$-conformation is disfavored. A stabilizing contribution from the dipole interaction like the one shown in Figure
5.20 may also favour the two \((E, Z)\) conformations. A combination of the all these factors is believed to make the \((E_s, Z_o)\)-conformation the most stable.

\[
\begin{align*}
(Z, Z) & \\
(E_o, Z_s) & \\
(E_s, Z_o) & \\
(E, E) & 
\end{align*}
\]

**Figure 5.19.** 1,3-Interactions in acyclic monothioimides.

\[
\begin{align*}
\text{S} & \delta^+ \\
\text{N} & \delta^- \\
\text{R}_2 & \\
\text{R}_3 & \\
\text{R}_1 & 
\end{align*}
\]

**Figure 5.20.** Dipole interaction in acyclic monothioimides.

Detailed examinations of the crystal structures of the five monothioimides reveal the approximate planarities of the thioimide moieties. The \(S=\text{C}-\text{N}-(\text{CO})\) and \((\text{CS})-\text{N}-(\text{C}=\text{O})\) torsional angles are summarized in Table 5.3. The observed planarities can be explained by the delocalization of the nitrogen lone-pair into both carbonyl and thiocarbonyl \(\pi\) systems.
Table 5.3. Some torsional angles in the monothioimides studied.

<table>
<thead>
<tr>
<th>Monothioimide</th>
<th>torsional angle $\text{S=\text{C-N-(CO)}}$</th>
<th>torsional angle $(\text{CS})\text{-N-C=O}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>-158</td>
<td>30</td>
</tr>
<tr>
<td>17</td>
<td>-148</td>
<td>0</td>
</tr>
<tr>
<td>18</td>
<td>-147</td>
<td>14</td>
</tr>
<tr>
<td>19</td>
<td>-146</td>
<td>24</td>
</tr>
<tr>
<td>49</td>
<td>-154</td>
<td>31</td>
</tr>
</tbody>
</table>

Packing diagrams of compounds 49 and 16 to 19 are shown in Figures 5.21 to 5.25.

Figure 5.21. Packing diagram of compound 49.
Figure 5.22. Packing diagram of compound 16.

Figure 5.23. Packing diagram of compound 17.
Figure 5.24. Packing diagram of compound 18.

Figure 5.25. Packing diagram of compound 19.
Chapter 6  Inclusion Phenomena and the Photochemistry of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol) derivatives

6.1. Coordinatoclathrates

The design and applications of new host molecules in molecular recognition and materials science is a topic of much current interest. These studies have provided important information about the properties of inclusion compounds. It is now generally accepted that good host molecules should be bulky and pack inefficiently with voids, and they should contain appended sensor groups that will coordinate to the guests. These compounds are called "coordinatoclathrates".

11,12-Dihydrodibenzobarrelene derivatives have been shown to be good basic skeletons for host compounds. The roof-shaped molecular structure of these compounds is important in developing molecular bulkiness. By introducing polar substituents which are capable of forming hydrogen bonds, many different coordinatoclathrate inclusion compounds have been prepared and studied. A typical example is compound 61, which was reported to form crystal inclusion compounds with nearly thirty different guest molecules including alcohols, acids and rather non-polar species.

\[
\begin{align*}
\text{HOOC} & \quad \text{COOH} \\
\end{align*}
\]

61
The so-called "wheel-and-axle-shaped" compounds represent another basic skeletal class of inclusion host molecules. This involves molecules with a long molecular axis ("axle") and with large and relatively rigid groups at each end ("wheels"). These "wheels" act as spacers and prevent the hosts from packing efficiently in the solid. 1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol (62), for example, is reported to form inclusion compounds with many different guest molecules.

Diols are often used as the appended sensor groups in coordinatoclathrates. In fact, diols have been known for many years to form solid complexes with guest molecules such as dicyclohexylamine in simple stoichiometric ratios. In those cases, the alcohol is believed to form hydrogen bonds with the guest molecule. An alternate approach involves using a hydrogen bond acceptor such as a phosphine oxide in the host molecule. Etter et al. have carried out important studies in this area, including the demonstration that triphenylphosphine oxide forms crystalline complexes with a wide variety of hydrogen-bond donors.

6.2. Photochemistry of Coordinatoclathrates

Photochemical interest in inclusion complexes stems from the two advantages offered by such systems: (1) chemists can provide a well-defined
small "reaction cavity" for reactant molecules as in their pure crystalline states; (2) it is possible for chemists to control molecular packing and hence the selectivity of photo-transformations by using different hosts with different properties.

Despite the relatively large number of known host molecules, the potential of inclusion complexes in photochemistry is yet to be fully explored. Most of the known examples in this area concern the photochemistry of complexes between photostable hosts and photoreactive guest molecules. Cyclodextrins and "wheel-and-axle" type compounds are the two most commonly used host systems, mainly because of their ability to include relatively large guest molecules. One example is 1,6-bis(o-chlorophenyl)-1,6-diphenyl-2,4-diyn-1,6-diol (63). Many asymmetric transformations of guest molecules using host compound 63 have been reported by Toda and Kaftory and co-workers.

\[
\text{S,S-(\text{-})-63}
\]

For example, when several 1:1 complexes of \(\alpha\)-oxoamides with S,S-(\text{-})-63 were irradiated, optically active type II photoproducts were obtained. In the case of \(N,N\)-dimethyl \(\alpha\)-oxobenzenacetamide, 100% \(ee\) in the cyclization product was reported (Figure 6.01).
Figure 6.01. Photolysis of the complex formed between α-oxobenzenacetamide and the optically active diol 63.

6.3. Molecular and Crystal Structures of Inclusion Compounds of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylphosphine oxide)

An alternate approach to utilizing inclusion compounds in photochemistry involves photoreactive host molecules. This is an excellent model for studying photochemistry in the crystalline state because one can generate a large number of different crystals with the same chromophore molecule simply by introducing different photostable guest molecules. The effect of the crystalline environment on the photochemistry in the solid state can then be studied and compared without the need to worry about the difference in intrinsic reactivity among different compounds.

In fact, this has been achieved in our laboratory. The photoreactive host molecule 64 (Figure 6.02) was prepared by Liu and Scheffer and found to form complexes with a wide variety of solvent molecules including acetone, 2-butanone, 2-pentanone, methyl vinyl ketone, THF, dimethoxyethane, ethyl acetate, ethanol, 1-propanol and 2-propanol.
Compound 64 possesses the features that are believed to be necessary for a good host: (1) its roof-shaped molecular structure as well as the four phenyl groups make the crystal packing inefficient and help to create voids in the parent lattice; (2) the two phosphine oxide groups act as hydrogen bond acceptor groups that will coordinate to the guests.

The author has performed the X-ray single crystal structure analyses of the ethanol, ethyl acetate and 2-propanol complexes of the diphosphine oxide 64. The ethyl acetate complex (64-EtOAc) crystallizes in the monoclinic space group P2\textsubscript{1}/c with Z = 4, while the ethanol complex 64-EtOH and the 2-propanol complex 64-iPrOH are isomorphous and crystallize in the chiral space group P2\textsubscript{1}2\textsubscript{1}2\textsubscript{1} (Z = 4). Liu and Scheffer found that all the crystalline complexes of 62 undergo the di-\(\pi\)-methane rearrangement\textsuperscript{138} upon solid state irradiation to give
compound 65 as the only product (Figure 6.02). This dibenzosemibullvalene derivative 65 was characterized spectroscopically as well as by reduction to the corresponding bis(phosphine) 66, whose structure was also established by X-ray crystallography.

Since photoproduct 65 is a chiral compound, an absolute asymmetric di-π-methane rearrangement may be carried out in the solid state. In accordance with this, it was found that single crystal photolysis of 64-EtOH at room temperature gives photoproduct 65 in 89% ee even at 84% conversion. Photolysis of a single crystal of 64-iPrOH leads to similar results (96% ee at 43% conversion). In contrast, solution phase photolysis of 64-EtOH or solid state photolysis of 64-EtOAc gives racemic 65.

The absolute configurations of compounds 66, 64-EtOH and 64-iPrOH were all determined. Assuming that the absolute configuration of photoproduct 65 does not change upon reduction to 66, the absolute configurations of, for example, pro-(+)-64-EtOH (the 64-EtOH crystal that photolyses to give (+)-65) and (+)-65 can be correlated (Figure 6.03).

Based on Zimmerman's mechanism for the di-π-methane rearrangement, it was proposed that the initial benzo-vinyl bridging which will give (+)-65 product, is favoured by a positive P(1)-C(11)=C(12)-P(2) dihedral angle (+23.9° for 64-EtOH). The geometry with this positive dihedral angle will lead to a better orbital overlap between the interacting orbitals in the transition state for the (+)-65 product as well as to a diminution of the steric interaction between the bulky diphenylphosphine oxide groups (Figure 6.03). In the alternative pathways leading to the unobserved enantiomer, the diphenylphosphine oxide groups would be driven toward each other during the benzo-vinyl bridging.

For 64-iPrOH, the corresponding P(1)-C(11)=C(12)-P(2) dihedral angle is -20.6° and photolysis of single crystals gives (-)-65 product. A similar explanation
has successfully accounted for the absolute steric course of three other solid-state di-π-methane photorearrangements\textsuperscript{140} and can provisionally be taken as being general.

![Reaction Diagram]

*Figure 6.03. Absolute configuration correlations for the solid state photolysis of 64\textsuperscript{EtOH}.*

Careful examination of the crystal structures of the three complexes of 64 reveal an intramolecular dipole-dipole interaction between the two phosphine oxide moieties (Figures 6.04 - 6.06). The P=O…P=O contacts are summarized in Table 6.1. In the cases of complexes 64\textsuperscript{iPrOH} and 64\textsuperscript{EtOH}, the other oxygen atom is associated with the alcohol molecule by intermolecular hydrogen bonding. These are also summarized in Table 6.1.
Figure 6.04. ORTEP stereodiagram of complex 64-EtOH (solvent not shown).

Figure 6.05. ORTEP stereodiagram of complex 64-iPrOH (solvent not shown).
Figure 6.06. ORTEP stereodiagram of complex 64-EtOAc (solvent not shown).

<table>
<thead>
<tr>
<th></th>
<th>64·EtOH</th>
<th>64·iPrOH</th>
<th>64·EtOAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>P=O⋯P=O contact (Å)</td>
<td>3.34</td>
<td>3.33</td>
<td>3.41</td>
</tr>
<tr>
<td>P=O⋯O-R distance (Å)</td>
<td>2.75</td>
<td>2.88</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 6.1. Some intermolecular contacts in the three crystalline complexes of compound 64.

The packing diagrams of the three complexes of diphosphine oxide 64 are shown in Figures 6.07 - 6.09. It can be noticed that the two alcohol complexes are isomorphorous. The alcohol molecules in each crystal are situated in a channel-like structure along the c-axis. These channels provide space, not only for the alcohol molecules, but also for the polar auxiliaries (P=O groups) for intermolecular hydrogen bonding. A similar channel structure is also present in complex 64·EtOAc along the b-axis.
Figure 6.07. Packing diagram of complex 64-EtOH.

Figure 6.08. Packing diagram of complex 64-IPrOH.
6.4. Photochemistry and X-ray Crystal Structures of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol) Complexes

Another inclusion host was designed (22) using the same molecular skeleton as in compound 64. This is different from 64 in that the sensor groups are hydrogen bond donors. The synthesis of compound 22 involves a Diels Alder reaction followed by a phenyllithium reaction and is depicted in Figure 6.10.
The diol 22 was found to include different solvent molecules upon recrystallization. Three different complexes were prepared. They are 22-EtOH, 22-acetone and 22-toluene. These three complexes are very stable compounds at room temperature in the solid state. Upon heating in an inert atmosphere, however, these complexes decompose and the solvent molecules escape from the crystal lattice at elevated temperature. The DSC analyses of these complexes are summarized in Table 6.2. The loss of solvent was also detected by a complementary TGA experiment. It is interesting to note that the final melting point of complex 22-acetone is different from that of 22-toluene and 22-EtOH. Perhaps, the solvent-free 22 formed from heating the acetone complex has a different polymorphic form from that of the other two complexes.
Table 6.2. Summary of DSC results of the complexes of diol 22.

<table>
<thead>
<tr>
<th>Complex</th>
<th>solvent evolution temperature</th>
<th>final melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>22-acetone</td>
<td>104.7-119.9</td>
<td>220.1</td>
</tr>
<tr>
<td>22-EtOH</td>
<td>102.6-151.7</td>
<td>238.7</td>
</tr>
<tr>
<td>22-toluene</td>
<td>109.4-128.9</td>
<td>238.7</td>
</tr>
</tbody>
</table>

Figure 6.11. Photochemistry of diol 22.

All three complexes possess essentially the same photochemistry in the solid state. For example, the powder form of compound 22-acetone (200 mg) was photolysed at $\lambda \geq 290$ nm for 24 h. The photoproduct 67 was isolated after chromatography in 15% yield. Photolysis of either the ethanol or the toluene complex gave similar results (Figure 6.11). However, it was found that upon irradiation in benzene, acetone or ethanol solution, diol 22 undergoes the di-$\pi$-methane rearrangement and gives 68 as the only product. The mechanism of its formation is shown in Figure 6.12.
Figure 6.12. Di-π-methane rearrangement of diol 22.

The mechanism for the photocyclization of diol 22 to give ether 67 is most easily viewed as one involving a carbonium ion as shown in Figure 6.13.

This mechanism is very reasonable based on the fact that photosolvolyses of benzyl derivatives with a variety of leaving groups including halides, nitriles, acetates, carbamates, ethers, trialkylammonium salts and dialkylsulfonium salts are well known.\textsuperscript{141, 142} The involvement of carbonium ions in these reactions is widely accepted. Despite the poor leaving ability of the hydroxyl group, Ullman \textit{et al.} demonstrated that alcohol 69 also undergoes photosolvolysis with carbonium ion 70 as the intermediate (Figure 6.14).\textsuperscript{143}
Figure 6.13. Photosolvolysis mechanism for photocyclization of diol 22.

Ar = p-C₆H₄N(CH₃)₂

Figure 6.14. Photosolvolysis of alcohol 69.
The difference between the photochemical reactivity in crystals and solution phases for diol 22 can be explained by the topochemical principle. Although the di-\(\pi\)-methane rearrangement of diol 22 proceeds in solutions, it involves substantial atomic and molecular movement of bulky groups (Figure 6.12). Such a reaction is topochemically disfavored in the solid state. The photocyclization reaction, on the other hand, requires a relatively small degree of molecular rearrangement around the diol moieties and thus predominates in the solid state.

The X-ray crystal structures of the three complexes: 22-EtOH, 22-acetone and 22-toluene were determined. Details are summarized in chapter 8. The molecular structures of diol 22 in these three complexes are very similar and are shown in Figures 6.15 - 6.17. They are all characterized by intramolecular hydrogen bonding between the two alcohol moieties.
Figure 6.15. ORTEP stereodiagram of complex 22-acetone (solvent not shown).

Figure 6.16. ORTEP stereodiagram of complex 22-toluene (solvent not shown).
The crystal packing in these complexes is very different. The packing diagrams are shown in Figures 6.18 - 6.20. In the case of 22-acetone, there is an intermolecular hydrogen bond formed between the disordered acetone molecule and the diol molecule. It can also be seen from Figure 6.18 that there is still a lot of void space present in the crystal lattice, which a third party molecule may be able to occupy. In accordance with this, yellow prismatic crystals of a three component complex of diol 22/benzoquinone/acetone (2:1:2) have been prepared by recrystallizing diol 22 in the presence of excess benzoquinone from acetone solution. The complex was characterized by proton NMR. It is unfortunate, however, that this complex decomposes within hours in air after isolated from the recrystallizing solution and hence no further work on this complex was performed.
Complex 22-toluene has a completely different packing arrangement from that of the acetone complex. The disordered toluene molecule is surrounded by aromatic rings of the diol 22 and is located under the "roof" of the dibenzobarrelene group (Figure 6.19). There is, however, no interaction between the toluene molecule and the diol moiety.

Complex 22-EtOH possesses an interesting intermolecular interaction. Two diol and two ethanol molecules form a twelve membered hydrogen bonding network which is depicted in Figure 6.21.
Figure 6.19. Packing diagram of complex 22-toluene.

Figure 6.20. Packing diagram of complex 22-EtOH.
Figure 6.21. Hydrogen bonding in complex 22-EtOH.
Chapter 7 EXPERIMENTAL (ORGANIC)

7.1. General Considerations

Infrared (IR) Spectra

Infrared spectra were recorded on a Perkin-Elmer 1700 Fourier transform infrared spectrometer, with the absorption maxima of the spectral bands reported in reciprocal centimeters (cm⁻¹). All samples were prepared as KBr pellets by grinding 100-150 mg of KBr and 1-5 mg of sample together and compressing the mixture in a Perkin-Elmer evacuated die (186-0002) with a Carver Laboratory Press (Model B, 17,000 psi).

Nuclear Magnetic Resonance (NMR) Spectra

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on Bruker AC-200 (200 MHz), Varian XL-300 (300 MHz) or Bruker WH-400 (400 MHz) spectrometers at ambient temperature in CDCl₃ unless otherwise noted. Signal positions are reported as chemical shift (δ) in parts per million (ppm) with tetramethylsilane (TMS) as an internal standard. The multiplicity of the signals, number of protons, coupling constants (J) in Hz and assignments are given in parentheses following the chemical shifts. The multiplicity of the signals are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and AB = AB quartet.

Carbon nuclear magnetic resonance spectra (¹³C NMR) were recorded on Bruker AC-200 (50.3 MHz), Varian XL-300 (75.4 MHz) and Bruker AM-400 (100.6 MHz) spectrometers. All spectra were run under broad band proton decoupling ¹³C-¹H. Chemical shifts (δ) are reported in ppm. Assignments,
where given, were supported by APT (attached proton test) and/or HETCOR (Heteronuclear Chemical Shift Correlation Spectroscopy, \(^{13}\text{C}^{1}\text{H}\)) experiments. HETCOR experiments were performed on a Bruker AMX-500 (500 MHz) spectrometer. NOE (Nuclear Overhauser Effect) experiments were performed on a Bruker WH-400 (400 MHz) spectrometer.

**Mass Spectra (MS)**

Low and high resolution mass spectra were recorded on a Kratos MS 50 instrument operating at 70 eV. Coupled gas chromatography-mass spectral analysis (GC-MS) were performed on a Kratos MS 80RFA spectrometer connected to a Carlo-Erba 4160 gas chromatograph. Ionization for the above was achieved by electron bombardment at 70 electron volts (EI). Desorption chemical ionization (DCI) spectra were done on a Delsi Nermag R10-10C spectrometer using ammonia as the CI gas. Fast atom bombardment (FAB) spectra were recorded on an AEI MS-9 mass spectrometer with xenon bombardment of a 3-nitrobenzyl alcohol matrix of the sample. Mass to charge ratios \((m/e)\) are reported with relative intensities in parentheses. Molecular ions are designated as \(M^+\).

**Ultraviolet (UV) Spectra**

Ultraviolet spectra were recorded on a Perkin Elmer Lambda-4B UV/Vis spectrophotometer. Spectral grade solvents (BDH) were used without further purification. Wavelengths \((\lambda)\) in nanometers (nm) are reported and the extinction coefficients \((\varepsilon)\) are given in brackets.

**Melting Point Measurements (MP)**
Melting points were determined on a Fisher-Johns hot stage apparatus and are uncorrected.

Microanalyses

Elemental analyses were performed by the departmental microanalyst, Mr. P. Borda.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

DSC and TGA were performed on a TA Instruments Thermal Analyst 2000 thermal analyser equipped with a DSC 910S differential scanning calorimeter and a TGA 51 thermogravimetric analyser. Data analyses were done on a IBM PS/1 personal computer connected to the above instrument running DSC Calibration Data Analysis Program Version 5.0.

X-ray Powder Diffractometry

Powder diffraction experiments were performed on a Rigaku Geigerflex PMG-VH diffractometer using Ni-filter Cu-Kα radiation (λ = 1.54184 Å) with scan range: 5° ≤ 2θ ≤ 50°.

Optical Rotations [α]

Optical rotations [α] were measured on a JASCO J-710 spectrophotometer in spectral grade chloroform (BDH). Values are reported as specific rotation [α]D, at room temperature 22 °C. Sample concentrations were approximately 2 mg/ml. Optical rotations were detected at λ = 589 nm, corresponding to the sodium D-line.
Gas Liquid Chromatography

Gas liquid chromatography (GC) analyses were performed on a Hewlett Packard 5890 A gas chromatograph fitted with a flame ionization detector and a Hewlett Packard 3392 A integrator. The following fused silica capillary columns were used: DB-1 (15 m x 0.25 mm, J & W Scientific Inc.), DB-17 (15 m x 0.25 mm, J & W Scientific Inc.) and Carbowax 20 M (20 m x 0.21 mm, Hewlett Packard).

Chromatography

Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel plates (E. Merck, type 5554). Preparative column chromatography was carried out using 230-400 mesh silica gel (E. Merck). The eluting solvents are specified in each case.

High Performance Liquid Chromatography (HPLC)

High performance liquid chromatographic analyses were conducted on a Waters 600 E system controller fitted with a tunable UV detector (Waters 486). A chiral column (Chiracel OD, 250 mm x 4.6 mm, Chiral Technologies Inc.) was used to determine enantiomeric excesses (ee).

Solvents and Reagents

Spectral grade solvents were used for spectroscopic and photochemical studies. All solvents and reagents were used directly without further purification unless otherwise stated. In those cases, literature procedures were followed to further purify the reagent or solvent.
7.2. Syntheses of Photochemical Substrates

Synthesis of 1-(1,1-Dimethylethyl)-2,5-pyrrolidinedione (N-t-Butylsuccinimide) (10). The procedure of Schreiber et al. was followed. In a round bottomed flask fitted with a reflux condenser, 3.23g (32.3 mmol) of succinic anhydride was refluxed with 10 ml of t-butylamine under a nitrogen atmosphere for 24 h. The reaction was monitored by TLC with 40% diethyl ether in petroleum ether (v/v) as eluent. Compound 10 was found to have an R_f value of 0.3. The resulting mixture was dissolved in 50 ml of diethyl ether and was washed with 2x100 ml of 0.01 M NaOH solution and then 100 ml of water. The ethereal layer was dried with anhydrous MgSO_4 and filtered. Solvent was then removed by rotary evaporation. The resulting solid mass was recrystallized from hexanes as colorless prisms (2.40 g, 48% yield).

MP 44°C, lit. 49°C
IR (KBr disc) 2980 (C-H), 1775, 1697 (C=O) cm\(^{-1}\).
\(^1\)H NMR (CDCl_3, 300 MHz) \(\delta\) 1.58 (s, 9 H, t-butyl), 2.58 (s, 4 H, \(\alpha\)-CH_2).
\(^{13}\)C NMR (CDCl_3, 50 MHz) \(\delta\), 28.34 (\(\alpha\)-CH_2), 28.61 (CH_3), 30.88 (quaternary C), 178.30 (C=O).
LRMS (EI), \(m/e\) (relative intensity) 155 (M+, 11.6), 140 (40.5), 112 (14.8), 100 (100.0), 82 (16.4), 72 (30.7), 58 (67.8), 57 (25.4), 56 (42.7), 55 (53.5), 44 (20.9), 42 (19.5), 41 (39.7). HRMS exact mass calcd for C_8H_13NO_2 155.0946, found 155.0947.
UV (CH_3CN) 242 nm (shoulder, \(\varepsilon\) 112).
Synthesis of 1-Cyclohexyl-2,5-pyrrolidinedione (N-Cyclohexylsuccinimide) (11). The procedure of Schreiber et al. was followed. In a round bottomed flask fitted with a reflux condenser, 2.70 g (27.0 mmol) of succinic anhydride was refluxed with 10 ml of cyclohexylamine under a nitrogen atmosphere for 24 h. The reaction was monitored by TLC with 40% diethyl ether in petroleum ether (v/v) as eluent. Compound 11 was found to have an Rf value of 0.28. The resulting mixture was dissolved in 50 ml of diethyl ether and was washed with 2x100 ml of 0.01 M NaOH solution and then 100 ml of water. The ethereal layer was dried with anhydrous MgSO4 and filtered. Solvent was then removed by rotary evaporation. The resulting solid mass was recrystallized from hexanes as colorless needles (2.05 g, 41% yield).

MP 40.0-41.0°C, lit. 41-42°C
IR (KBr disc): 1768, 1680 (C=O) cm⁻¹.
¹H NMR (CDCl₃, 200 MHz) δ 1.30 (m, 3 H), 1.58 (m, 2 H), 1.65(m, 1 H), 1.82(m, 2 H), 2.15(m, 2 H), 2.67(s, 4 H, α-CH₂), 3.95(triplet of triplet, 1 H, CH, J = 4 Hz and 12 Hz).
¹³C NMR (CDCl₃, 50 MHz) δ, 25.01, 25.86, 28.06, 28.74 (CH₂), 51.74 (CH), 177.37 (C=O).
LRMS (EI), m/e (relative intensity) 181 (M⁺, 1.7), 138 (6.3), 110 (9.0), 101 (20.3), 100 (100.0), 82 (40.9), 81 (10.3), 72 (38.6), 69 (15.4), 67 (38.8), 56 (42.8), 55 (63.3), 54 (39.4). HRMS exact mass calcd for C₁₀H₁₅NO₂ 181.1103, found 181.1094.
UV (CH₃CN) 243 nm (shoulder, ε 109).
Synthesis of 1-Cyclopentyl-2,5-pyrrolidinedione (N-Cyclopentylsuccinimide) (12). The procedure of Mitsunobu et al. was followed.\textsuperscript{147} A solution of succinimide (0.78 g, 7.9 mmol), diethylazadicarboxylate (1.37 g, 7.9 mmol), triphenylphosphine (2.06 g, 7.9 mmol) and cyclopentanol (1.02 g, 11.8 mmol) in THF (15 ml) was stirred at room temperature under anhydrous conditions for two days. The solution was then concentrated under reduced pressure and diluted with a small quantity of ether. The mixture was then chromatographed on silica gel using 20% ether in hexanes (v/v) as eluent. The product obtained was further purified by recrystallization from hexanes to afford needles (0.50 g, 38% yield).

MP 64.0-65.0°C
IR (KBr disc) 1776, 1693 (C=O) cm\textsuperscript{-1}.
\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) $\delta$ 1.60 (m, 2 H), 1.90 (m, 6 H), 2.62 (s, 4 H, α-CH\textsubscript{2}), 4.50 (m, 1 H, CH).
\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 50 Mz) $\delta$ 25.11, 28.05, 28.50 (CH\textsubscript{2}), 51.63 (CH), 177.33 (C=O).
LRMS (El) m/e (relative intensity) 167 (M$^+$, 0.2), 138 (1.5), 110 (2.6), 101 (6.6), 100 (100.0), 97 (1.4), 82 (10.4), 72 (11.5), 69 (11.5), 68 (11.5), 67 (11.8), 56 (16.4), 55 (24.1). HRMS exact mass calcd for C\textsubscript{9}H\textsubscript{13}NO\textsubscript{2} 167.0946, found 167.0949.

Synthesis of 1-(1-Methylethyl)-2,5-pyrrolidinedione (N-Isopropylsuccinimide) (13). The procedure of Mitsunobu et al. was followed.\textsuperscript{147} A solution of succinimide (0.78 g; 7.9 mmol), diethylazadicarboxylate (1.37 g, 7.9 mmol), triphenylphosphine (2.06 g, 7.87 mmol) and isopropanol (0.71 g, 11.81 mmol) in THF (15 ml) was stirred at room temperature under anhydrous conditions for two
days. The solution was then concentrated under reduced pressure and diluted with a small quantity of ether. The mixture was then chromatographed on silica gel using 20% ether in hexanes (v/v) as eluent. The product obtained was further purified by recrystallization from hexanes to afford prisms (0.30 g, 27% yield).

MP 64.0-64.5°C, lit.\textsuperscript{145} 64-65°C

IR (KBr disc) 1756, 1698 (C=O) cm\textsuperscript{-1}.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 Mz) \(\delta\) 1.39 (d, \(J = 8\) Hz, 6 H, CH\textsubscript{3}), 2.62 (s, 4 H, \(\alpha\)-CH\textsubscript{2}), 4.40 (septet, \(J = 8\) Hz, 1 H, CH).

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 50 Mz) \(\delta\), 19.16 (CH\textsubscript{3}), 28.08 (CH\textsubscript{2}), 43.73 (CH), 177.33 (C=O).

LRMS (EI) \textit{m/e} (relative intensity) 141 (M\textsuperscript{+}, 62.5), 126 (54.8), 113 (19.4), 101 (4.7), 100 (100.0), 99 (6.9), 98 (51.6), 84 (3.9), 82 (16.0), 72 (16.5), 70 (24.2), 58 (9.4), 57 (13.6), 56 (27.3), 55 (40.8). HRMS exact mass calcd for C\textsubscript{7}H\textsubscript{11}NO\textsubscript{2} 141.0790, found 141.0790.

UV (CH\textsubscript{3}CN) 242 nm (shoulder, \(\epsilon\) 108).

\textbf{Synthesis of \(N\)-Phenylbenzenecarbothioamide (Thiobenzanilide) (50).} The procedure of Lawesson et al. was followed.\textsuperscript{148} Benzanilide (3.00 g, 15.2 mmol), 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphate-2,4-disulphide (Lawesson's reagent) (4.30 g, 10.7 mmol) and toluene (15 ml) were refluxed for 24 h under nitrogen. The solution was then concentrated under reduced pressure and purified by silica gel column chromatography using 10% ether in hexanes (v/v) as eluent. The yellow solid obtained was recrystallized from ethanol to afford yellow prisms (2.30 g, 72% yield).
MP 102.0-103.0°C, lit.\(^{149}\) 101-103°C

IR (KBr disc) 3158, 3104 (N-H stretch), 1207 (C=S stretch) cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.00-8.20 (m, 10H, arom), 9.20 (s, broad, 1 H, NH).

\(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 123.75, 126.63, 126.74, 128.26, 128.69, 131.05 (arom CH), 138.70, 142.46 (arom C), 198.20 (C=S).

LRMS (El) \(m/e\) (relative intensity) 213 (M\(^+\), 47.9), 212 (61.5), 180 (14.9), 121 (100), 110 (23.9), 77 (39.2), 51 (13.3). HRMS exact mass calcd for C\(_{13}\)H\(_{11}\)NS 213.0612, found 213.0605.

Synthesis of 4-Methoxy-\(\alpha\)-Phenylbenzenecarbothioamide (71). 4-Methoxy-\(\alpha\)-Phenylbenzamide (3.50 g, 15.4 mmol), Lawesson's reagent\(^{148}\) (3.74 g, 9.3 mmol) and toluene (50 ml) were refluxed for 24 h under nitrogen. The solution was then concentrated under reduced pressure and the resulting mixture was purified by silica gel column chromatography using 15% ether in hexanes (v/v) as eluent. The yellow solid obtained was recrystallized from ethanol to afford yellow prisms (2.0 g, 53% yield).

MP 159.0-160.0°C, lit.\(^{150}\) 159-161°C, lit.\(^{149}\) 153°C.

IR (KBr disc) 3155, 3105 (N-H stretch), 1178 (C=S stretch) cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 3.89 (s, 3 H, OMe), 6.80-8.20 (m, 9 H, arom), 8.98 (s, broad, 1 H, NH).

\(^13\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 55.53 (OMe), 113.71, 123.88, 126.75, 128.71, 129.01 (arom CH), 134.05, 139.19, 162.31 (arom C), 190.05 (C=S).

LRMS (El) \(m/e\) (relative intensity) 243 (M\(^+\), 40.2), 242 (27.5), 210 (20.9), 151 (100), 134 (11.7), 108 (32.3), 77 (29.6), 65 (30.2). HRMS exact mass calcd for C\(_{14}\)H\(_{13}\)NOS 243.0718, found 243.0716.
Synthesis of $N$-(4-Bromo-2,6-dimethylphenyl)benzenecarbothioamide (72).

$N$-(4-Bromo-2,6-dimethylphenyl)benzamide (2.00 g, 6.6 mmol), Lawesson's reagent\textsuperscript{148} (1.86 g, 4.6 mmol) and toluene (20 ml) were refluxed for 24 h under nitrogen. The solution was then concentrated under reduced pressure and the resulting mixture was purified by silica gel column chromatography using 10% ether in hexanes (v/v) as eluent. The yellow solid obtained was recrystallized from ethanol to afford yellow prisms (1.40 g, 67% yield).

MP 172.5-173.5°C

IR (KBr disc) 3244 (broad, N-H stretch), 1202 (C=S stretch) cm\textsuperscript{-1}.

$^1$H NMR (CDCl\textsubscript{3}, 200 MHz) $\delta$ 2.12 (s, 6 H, OMe), 7.20-8.20 (m, 7H, arom), 8.60 (s, broad, 1 H, NH).

$^{13}$C NMR (CDCl\textsubscript{3}, 50 MHz) $\delta$ 17.92 (Me), 122.03 (arom, C-Br), 126.69, 128.67, 131.30, 131.60 (arom CH), 135.47, 137.82, 141.30 (arom C), 199.72 (C=S).

LRMS (El) $m/e$ (relative intensity) 321 (M$^+$+2, 14.2), 319 (M$^+$, 15.7), 306 (92.1), 304 (93.4), 288 (3.7), 266 (4.7), 225 (20.1), 207 (38.2), 137 (8.4), 121 (100), 112 (38.6), 104 (38.1), 77 (64.8). HRMS exact mass calcd for $C_{15}H_{14}NSBr$ 319.0030, found 319.0026.

Anal. Calcd for $C_{15}H_{14}NSBr$: C, 56.26; H, 4.41; N, 4.37; S, 10.01. Found: C, 56.29; H, 4.42; N, 4.30; S, 10.15.

Synthesis of $N$-(4-Bromophenyl)benzenecarbothioamide (73).

$N$-(4-Bromophenyl)benzamide (2.00 g, 7.3 mmol), Lawesson's reagent\textsuperscript{148} (2.05 g, 5.08 mmol) and toluene (20 ml) were refluxed for 24 h under nitrogen. The solution was then concentrated under reduced pressure and the resulting
mixture was purified by silica gel column chromatography using 15% ether in hexanes (v/v) as eluent. The yellow solid obtained was recrystallized from ethanol to afford yellow prisms (1.65 g, 78% yield).

MP 151.5-152.5°C, lit.\(^{149}\) 152°C

IR (KBr disc) 3143 (N-H stretch), 1214 (C= S stretch) cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.20-8.00 (m, 9 H, arom), 9.02 (s, broad, 1 H, NH).

\(^13\)C NMR (CDCl\(_3\), 50 MHz) \(\delta\) 119.88 (arom, CBr), 125.23, 126.68, 128.62, 131.40, 132.07 (arom CH), 137.94, 142.82 (arom C), 198.58 (C=S).

LRMS (El) \(m/ e\) (relative intensity) 293 (M\(^+\)+3, 13.3), 292 (M\(^+\)+2, 9.0), 291 (M\(^+\)+1, 13.7), 290 (M\(^+\)), 260 (6.8), 258 (7.3), 211 (3.7), 190 (13.3), 188 (13.7), 157 (2.3), 155 (2.5), 121 (100), 106 (13.7), 104 (22.3), 77 (28.3). HRMS exact mass calcd for C\(_{13}\)H\(_{10}\)NSBr 290.9717, found 290.9720.

Anal. Calcd for C\(_{13}\)H\(_{10}\)NSBr: C, 53.44; H, 3.45; N, 4.79; S, 10.97. Found: C, 53.70; H, 3.50; N, 4.74; S, 11.00.

**Synthesis of N-(4-Methoxyphenyl)benzenecarbothioamide (74).** N-(4-methoxyphenyl)benzamide (3.00 g, 13.2 mmol), Lawesson's reagent\(^{148}\) (3.74 g, 9.3 mmol) and toluene (30 ml) were refluxed for 24 h under nitrogen. The solution was then concentrated under reduced pressure and the resulting mixture purified by silica gel column chromatography using 15% ether in hexanes (v/v) as eluent. The yellow solid obtained was recrystallized from ethanol as yellow prisms (2.00 g, 61% yield).

MP: 130.0-131.0°C, lit.\(^{149}\) 133-135°C

IR (KBr disc) 3162 (N-H stretch), 1248 (C=S stretch) cm\(^{-1}\).
1H NMR (CDCl₃, 400 MHz) δ 3.82 (s, 3 H, OMe), 6.80-8.00 (m, 9 H, arom), 8.91 (s, broad, 1 H, NH).

13C NMR (CDCl₃, 75 MHz) δ 55.49 (Me), 114.19, 125.61, 126.68, 128.62, 131.20 (arom CH), 132.05, 142.93, 158.24 (arom C), 198.36 (C=S).

LRMS (EI) m/e (relative intensity) 243 (M⁺, 29.1), 210 (41.3), 140 (96.3), 121 (100), 104 (14.8), 77 (38.7). HRMS exact mass calcd for C₁₄H₁₃NOS 243.0718, found 243.0724.


Synthesis of N-PhenyI-N-(phenylthioxomethyl)benzenepropanamide (16). Triethylamine (0.71 g, 7.0 mmol) was added dropwise to a solution of N-phenylbenzenecarbothioamide (1.00 g, 4.7 mmol) and 3-phenylpropionyl chloride (1.19 g, 7.0 mmol) in dry benzene (60 ml) at room temperature under nitrogen. The reaction mixture was stirred for 2 h. It was then concentrated under reduced pressure and subjected to silica gel column chromatography (10% ether in hexanes (v/v) as eluent). The orange solid obtained was recrystallized from ethanol to afford orange prisms (0.70 g, 43% yield).

MP 71.0-72.0°C, lit.¹¹⁰ 67-68°C

IR (KBr disc) 1723 (C=O), 1217 (C=S stretch) cm⁻¹.

1H NMR (CDCl₃, 300 MHz) δ 2.73 (t, J = 10 Hz, 2 H, COCH₂), 2.95 (t, J = 10 Hz, 2 H, PhCH₂), 6.90-7.80 (m, 15 H, arom).

13C NMR (CDCl₃, 75 MHz) δ 31.37, 39.69 (CH₂), 119.10, 126.38, 127.48, 128.19, 128.35, 128.50, 128.54, 129.74, 131.22 (arom C-H), 140.01, 143.10, 144.86 (arom C), 174.57 (C=O), 212.08 (C=S).
LRMS (El) m/e (relative intensity) 346 (M⁺+1, 0.4), 345 (M⁺, 1.3), 313 (1.8), 312 (7.4), 213 (45.7), 212 (59.8), 180 (75.6), 132 (40.4), 121 (100), 104 (34.9), 91 (20.0), 77 (72.4). HRMS exact mass calcd for C₂₂H₁₉NOS 345.1187, found 345.1192.

**Synthesis of N-Phenyl-N-(phenylthioxomethyl)benzenepropanamide-2,2-d₂ (16-d₂).** Hydrocinnamic methyl ester (200 mg, 1.2 mmol) was refluxed with sodium methoxide (132 mg, 2.44 mmol) in MeOD (10 ml) for 96 h under anhydrous nitrogen. D₂O (5 ml) was then carefully added and the reaction mixture was refluxed for another 30 minutes. The reaction mixture was acidified with dilute HCl. The deuteriated hydrocinnamic acid formed was extracted with diethyl ether (3 x 25 ml), dried over anhydrous MgSO₄ and the solvent was removed by rotary evaporation. The product was then treated with thionyl chloride (5 ml) according to a known procedure¹⁵ without modification. The acid chloride formed (170 mg, 85% yield) was used for reaction with thiobenzanilide (see previous section) to give 16-d₂. The proton NMR of 16-d₂ showed 96% deuterium incorporation at the α-position.

**Synthesis of N-[(4-Methoxyphenyl)thioxomethyl]-N-phenylbenzenepropanamide (17).** The procedure of Sakamoto *et al.* was followed.¹¹⁰ Triethylamine (1.06 g, 10.5 mmol) was added dropwise to a solution of 4-methoxy-N-phenylbenzenecarbathioamide (1.70 g, 7.0 mmol) and 3-phenylpropionyl chloride (1.77 g, 10.5 mmol) in dry benzene (60 ml) at room temperature under nitrogen. The reaction mixture was stirred for 2 h. It was then concentrated under reduced pressure and subjected to silica gel column chromatography (10% ether
in hexanes (v/v) as eluent). The orange solid obtained was recrystallized from ethanol to afford orange prisms (1.50 g, 57% yield).

**MP 83.5-84.5°C**

**IR (KBr disc) 1727 (C=O), 1192 (C=S stretch) cm⁻¹.**

**¹H NMR (CDCl₃, 300 MHz) δ 2.76 (t, J = 10 Hz, 2 H, COCH₂), 2.98 (t, J = 10 Hz, 2 H, PhCH₂), 3.82 (s, 3 H, OMe), 6.70-7.70 (m, 14 H, arom).**

**¹³C NMR (CDCl₃, 50 MHz) δ 31.64, 39.56 (CH₂), 55.46 (Me), 113.62, 126.34, 128.14, 128.20, 128.48, 128.60, 129.52, 130.49 (arom C-H), 137.65, 140.21, 143.39, 162.97 (arom C), 174.78 (C=O), 210.80 (C=S).**

**LRMS (El) m/e (relative intensity) 375 (M⁺, 0.9), 342 (18.7), 284 (4.4), 243 (17.5), 242 (16.1), 210 (100), 151 (66.5), 135 (13.4), 105 (13.6), 91 (29.1), 77 (52.1), 65 (11.4), 51 (24.8). HRMS exact mass calcd for C₂₃H₂₁NO₂S 375.1293, found 375.1282.**

**Anal. Calcd for C₂₃H₂₁NO₂S: C, 73.57; H, 5.64; N, 3.73; S, 8.54. Found: C, 73.45; H, 5.67; N, 3.58; S, 8.44.**

**Synthesis of N-(4-Bromo-2,6-dimethylphenyl)-N-(phenylthioxomethyl)benzenepropanamide (18).** The procedure of Sakamoto et al. was followed. Triethylamine (0.70 g, 6.9 mmol) was added dropwise to a solution of N-(4-bromo-2,6-dimethylphenyl)benzenecarbothioamide (1.40 g, 4.6 mmol) and 3-phenylpropionyl chloride (0.78 g, 4.6 mmol) in dry benzene (30 ml) at room temperature under nitrogen. The reaction mixture was stirred for 2 h. It was then concentrated under reduced pressure and subjected to silica gel column chromatography (10% ether in hexanes (v/v) as eluent). The red solid obtained was recrystallized from ethanol to afford red prisms (1.30 g, 62% yield).
MP 87.0-88.0°C

IR (KBr disc) 1724 (C=O), 1191 (C=S stretch) cm⁻¹.

$^1$H NMR (CDCl₃, 300 MHz) $\delta$ 2.13 (s, 6 H, CH₃), 2.48 (t, $J = 9$ Hz, 2 H, COCH₂), 2.88 (t, $J = 9$ Hz, 2 H, PhCH₂), 6.90-7.70 (m, 12 H, arom).

$^{13}$C NMR (CDCl₃, 50 MHz) $\delta$ 17.93 (CH₃), 30.59, 39.40 (CH₂), 122.79 (arom CBr), 126.54, 127.19, 128.13, 128.56, 128.70, 130.83, 132.18 (arom C-H), 138.19, 139.86, 140.01, 144.81 (arom C), 173.31 (C=O), 208.90 (C=S).

MS (El) $m/e$ (relative intensity) 453 (M⁺+2, 1.0), 451 (M⁺, 0.9), 420 (0.3), 418 (0.4), 321 (9.7), 319 (9.4), 288 (18.0), 286 (18.1), 225 (18.8), 207 (47.7), 133 (37.1), 132 (65.1), 131 (45.7), 121 (88.7), 105 (62.5), 104 (82.0), 103 (62.5), 91 (50.7), 78 (57.4), 77 (100), 51 (58.3). HRMS exact mass calcd for C$_{24}$H$_{22}$NOSBr 451.0605, found 451.0601.

Anal. Calcd for C$_{24}$H$_{22}$NOSBr: C, 63.72; H, 4.90; N, 3.10; S, 7.09. Found: C, 63.82; H, 4.97; N, 3.12; S, 7.01.

**Synthesis of N-(4-Bromophenyl)-N-(phenylthioxomethyl)benzenepropanamide (19).** The procedure of Sakamoto et al. was followed. Triethylamine (0.83 g, 8.2 mmol) was added dropwise to a solution of N-(4-bromophenyl)benzenecarbothioamide (1.60 g, 5.5 mmol) and 3-phenylpropionyl chloride (1.38 g, 8.2 mmol) in dry benzene (30 ml) at room temperature under nitrogen. The reaction mixture was stirred for 2 h. It was then concentrated under reduced pressure and subjected to silica gel column chromatography (10% ether in hexanes (v/v) as eluent). The orange solid obtained was recrystallized from ethanol to afford orange prisms (1.30 g, 69% yield).
MP 126.5-127.5°C
IR (KBr disc) 1702 (C=O), 1207 (C=S stretch) cm⁻¹.
¹H NMR (CDCl₃, 200 MHz) δ 2.75 (t, J = 8 Hz, 2 H, COCH₂), 2.95 (t, J = 8 Hz, 2 H, PhCH₂), 6.70-8.00 (m, 14 H, arom).
¹³C NMR (CDCl₃, 50 MHz) δ 31.55, 39.80 (CH₂), 122.43 (arom CBr), 126.52, 127.74, 128.36, 128.59, 128.62, 129.91, 131.65, 132.93 (arom CH), 139.90, 142.09, 144.55 (arom C), 174.67 (C=O), 208.90 (C=S).
MS (El) m/e (relative intensity) 425 (M⁺+2, 0.1), 423 (M⁺, 0.1), 392 (0.6), 390 (0.7), 293 (10.1), 291 (11.1), 260 (15.1), 258 (15.4), 190 (13.5), 188 (14.0), 132 (31.7), 131 (25.3), 121 (100), 105 (29.0), 104 (47.7), 103 (27.5), 91 (17.6), 77 (63.2), 51 (34.2). HRMS exact mass calcd for C₂₂H₁₈NOSBr 423.0292, found 453.0288.
Anal. Calcd for C₂₂H₁₈NOSBr: C, 62.27; H, 4.28; N, 3.30; S, 7.56. Found: C, 62.43; H, 4.20; N, 3.30; S, 7.56.

Synthesis of N-(4-Methoxyphenyl)-N-(phenylthioxomethyl)benzenepropanamide (20). The procedure of Sakamoto et al. was followed.¹¹⁰ Triethylamine (1.68 g, 16.7 mmol) was added dropwise to a solution of N-(4-methoxyphenyl)benzenecarbothioamide (2.70 g, 11.11 mmol) and 3-phenylpropionyl chloride (2.81 g, 16.7 mmol) in dry benzene (50 ml) at room temperature under nitrogen. The reaction mixture was stirred for 2 h. It was then concentrated under reduced pressure and subjected to silica gel column chromatography (10% ether in hexanes (v/v) as eluent). The orange solid obtained was recrystallized from ethanol to afford orange prisms (3.10 g, 74% yield).
Synthesis of N-Phenyl-N-(phenylthioxomethyl)benzamide (49). The procedure of Sakamoto et al. was followed. Triethylamine (0.70 g, 7.0 mmol) was added dropwise to a solution of N-phenylbenzenecarbothioamide (1.00 g, 4.7 mmol) and benzoyl chloride (0.99 g, 7.0 mmol) in dry benzene (30 ml) at room temperature under nitrogen. The reaction mixture was stirred for 2 h. It was then concentrated under reduced pressure and subjected to silica gel column chromatography (10% ether in hexanes (v/v) as eluent). The orange solid obtained was recrystallized from ethanol to afford orange prisms (0.95 g, 64% yield).

MP 113.0-114.0°C, lit. 108-109°C
IR (KBr disc) 1696 (C=O), 1214 (C=S stretch) cm⁻¹.
**Synthesis of Phenyl[2,4,6-tris(1-methylethyl)phenyl]methanone (75).** The procedure of Ito et al. was followed. Into a solution containing 1,3,5-triisopropylbenzene (1.10 g, 5.3 mmol) and AlCl₃ (0.71 g, 5.3 mmol) in 15 ml of carbon disulphide was added dropwise a solution containing benzoyl chloride (0.50 g, 3.6 mmol) and 1,3,5-triisopropylbenzene (0.40 g, 1.8 mmol) in 5 ml of carbon disulphide. The mixture was refluxed for 12 h and then poured into an ice-hydrochloric acid mixture. The product was extracted with ether and the organic layer was washed successively with water, 5% NaOH solution, and water. After drying with anhydrous MgSO₄ and removing solvent by rotary evaporation, the product was recrystallized from methanol to afford colorless prisms (1.00 g, 91% yield).

MP 96-98°C, lit. 97-99°C

IR (KBr disc) 1665 (C=O) cm⁻¹.

H NMR (CDCl₃, 200 MHz) δ 6.04 (d, J = 8 Hz, 6 H, o-i-Pr CH₃), 1.06 (d, J = 8 Hz, 6 H, o-A-Pr CH₃), 1.38 (d, J = 8 Hz, 6 H, p-APr CH₃), 2.61 (septet, J = 8 Hz, 2
H, α-Pr CH), 2.61 (septet, J = 8 Hz, 1 H, p-Pr CH), 7.05 (s, 2 H, arom), 7.30-
7.90 (m, 5 H, arom).

$^{13}$C NMR (CDCl$_3$, 100 MHz) δ 23.28, 23.94, 24.79, 30.95, 34.29 (aliphatic),
120.89, 128.46, 129.41, 133.35 (arom CH), 135.01, 138.18, 144.91, 149.64
(arom C), 201.07 (C=O).

LRMS (El) m/e (relative intensity) 309 (M$^+$+1, 15.5), 308 (M$^+$, 74.3), 293 (28.5),
278 (14.7), 265 (26.3), 250 (27.2), 231 (39.9), 217 (8.4), 202 (8.2), 178 (6.3), 165
(5.2), 141 (5.9), 129 (13.9), 128 (11.2), 115 (14.5), 105 (71.1), 91 (26.3), 77
(74.2), 51 (11.2). HRMS exact mass calcd for C$_{22}$H$_{28}$O 308.2140, found
308.2137.

Synthesis of 4-Methoxyphenyl[2,4,6-tris(1-methylethyl)phenyl]methanone
(76). The procedure of Ito et al. was followed.$^{153}$ Into a solution containing 1,3,5-
triisopropylbenzene (1.00 g, 4.9 mmol) and AlCl$_3$ (0.65 g, 4.9 mmol) in 15 ml of
carbon disulphide was added dropwise a solution containing 4-methoxybenzoyl
chloride (0.56 g, 3.3 mmol) and 1,3,5-triisopropylbenzene (0.33 g, 1.63 mmol) in
5 ml of carbon disulphide. The mixture was refluxed for 12 h and then poured
into an ice-hydrochloric acid mixture. The product was extracted with ether and
the organic layer was washed successively with water, 5% NaOH solution, and
water. After drying with anhydrous MgSO$_4$ and removing solvent by rotary
evaporation, the product was recrystallized from methanol to afford colorless
prisms (0.78 g, 47% yield).

MP 111.0-111.5°C, lit.$^{156}$ 111-112°C
IR (KBr disc) 1655 (C=O) cm$^{-1}$. 

127
1H NMR (CDCl₃, 400 MHz) δ 1.04 (d, J = 8 Hz, 6 H, o-Pr CH₃), 1.17 (d, J = 8 Hz, 6 H, o-Pr CH₃), 1.28 (d, J = 8 Hz, 6 H, p-i-Pr CH₃), 2.62 (septet, J = 8 Hz, 2 H, o-Pr CH), 2.91 (septet, J = 8 Hz, 1 H, p-APr CH), 3.85 (s, 3 H, OMe), 6.90 (d, J = 10 Hz, 2 H, MeOCCH, arom), 7.03 (s, 2 H, arom), 7.79 (d, broad, J = 10 Hz, 2 H, COCCH, arom).

13C NMR (CDCl₃, 100 MHz) δ 23.50, 24.04, 24.88, 30.95, 34.35 (aliphatic), 55.46 (OMe), 113.69, 120.91, 131.88 (arom CH), 131.53, 135.32, 144.84, 149.47, 163.79 (arom C), 199.77 (C=O).

LRMS (El) m/e (relative intensity) 339 (M⁺+1, 18.5), 338 (M⁺, 79.3), 337 (39.3), 323 (100), 308 (46.2), 307 (93.1), 295 (22.1), 281 (26.2), 280 (36.4), 265 (21.9), 250 (13.5), 231 (24.2), 215 (21.5), 202 (16.3), 187 (14.3), 178 (11.8), 169 (17.4), 157 (27.4), 135 (67.8), 121 (36.5), 107 (21.9), 91 (20.6), 77 (36.0), 51 (11.5).

HRMS exact mass calcd for C₂₃H₃₀O₂ 338.2246, found 338.2250.

Synthesis of Phenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione (14).
Phenyl[2,4,6-tris(1-methylethyl)phenyl]methanone (0.50 g, 1.6 mmol), Lawesson's reagent (0.46 g, 1.1 mmol) and toluene (20 ml) were refluxed for 5 days under nitrogen. The solution was then concentrated under reduced pressure and the resulting mixture was purified by silica gel column chromatography using hexanes as eluent. The blue solid obtained was recrystallized from methanol to afford blue prisms (0.33 g, 63% yield).

MP 97.5-98.5°C

IR (KBr disc) 1215 (C=S stretch) cm⁻¹.

1H NMR (CDCl₃, 200 MHz) δ 1.02 (d, J = 8 Hz, 6 H, o-Pr CH₃), 1.10 (d, J = 8 Hz, 6 H, o-Pr CH₃), 1.30 (d, J = 8 Hz, 6 H, p-i-Pr CH₃), 2.73 (septet, J = 8 Hz, 2 H, COCCH, arom).
H, o-Pr CH₃), 2.94 (septet, J = 8 Hz, 1 H, p-Pr CH₃), 7.05 (s, 2 H, arom), 7.30-8.05 (m, 5 H, arom).

¹³C NMR (CDCl₃, 100 MHz) δ 23.59, 24.04, 24.61, 30.51, 34.13 (aliphatic), 121.19, 128.31, 128.51, 133.50 (arom CH), 143.28, 143.53, 144.63, 148.50 (arom C), 215.51 (C=S).

LRMS (El) m/e (relative intensity) 325 (M⁺+1, 10.0), 324 (M⁺, 38.9), 310 (25.0), 309 (100.0), 291 (9.9), 277 (17.7), 247 (16.3), 235 (14.2), 207 (16.4), 193 (11.1), 129 (20.3), 115 (11.0), 91 (19.8). HRMS exact mass calcd for C₂₂H₂₈S 324.1912, found 324.1909.

UV (CH₃CN) 604 nm (ε 58), 318 nm (ε 14000).

Anal. Calcd for C₂₂H₂₈S: C, 81.42; H, 8.70; S, 9.88. Found: C, 81.42; H, 8.76; S, 9.80.

**Synthesis of 4-Methoxyphenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione (15).** 4-Methoxyphenyl[2,4,6-tris(1-methylethyl)phenyl]methanone (0.30 g, 0.89 mmol), Lawesson's reagent¹⁴⁸ (0.25 g, 0.62 mmol) and toluene (10 ml) were refluxed for 6 days under nitrogen. The solution was then concentrated under reduced pressure and the resulting mixture was purified by silica gel column chromatography using hexanes as eluent. The blue solid obtained was recrystallized from methanol at 0°C to afford blue prisms (0.20 g, 64% yield).

MP 116.5-117.0°C
IR (KBr disc) 1161 (C=S) cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) δ 1.04 (d, J = 8 Hz, 6 H, o-Pr CH₃), 1.11 (d, J = 8 Hz, 6 H, o-Pr CH₃), 1.29 (d, J = 8 Hz, 6 H, p-Pr CH₃), 2.75 (septet, J = 8 Hz, 2 H, o-Pr CH), 2.92 (septet, J = 8 Hz, 1 H, p-Pr CH), 3.88 (s, 3 H, OMe), 6.84 (d,
\[ J = 10 \text{ Hz, } 2 \text{ H, MeOCCH, arom}, \] 7.04 (s, 2 H, arom), 7.98 (d, broad, \[ J = 10 \text{ Hz, } 2 \text{ H, COCCH, arom} \].

^13C NMR (CDCl\textsubscript{3}, 100 MHz) \[ \delta 23.70, 24.04, 24.65, 30.51, 34.19 \] (aliphatic), 55.55 (OMe), 113.65, 121.10, 131.00 (arom CH), 139.19, 143.11, 143.40, 148.23, 164.54 (arom C), 219.37 (C=S).

LRMS (EI) \[ m/e \] (relative intensity) 355 (M\textsuperscript{+}+1, 19.2), 354 (M\textsuperscript{+}, 62.8), 339 (100), 321 (64.3), 311 (18.9), 307 (23.6), 296 (13.1), 279 (14.3), 265 (14.4), 247 (11.2), 237 (29.0), 222 (9.4), 213 (16.3), 203 (11.1), 189 (10.7), 171 (15.3), 151 (30.2), 129 (35.4), 117 (10.1), 91 (15.4), 86 (45.3), 84 (65.8), 77 (90), 49 (20.9). HRMS exact mass calcld for C\textsubscript{23}H\textsubscript{30}OS 354.2017, found 354.2012.

UV (CH\textsubscript{3}CN) 591 nm (\( \varepsilon 68 \)), 363 nm (\( \varepsilon 17000 \)).

Anal. Calcd for C\textsubscript{23}H\textsubscript{30}OS: C, 77.92; H, 8.53; S, 9.04. Found: C, 77.81; H, 8.59; S, 9.02.

**Synthesis of 4-[2,4,6-Tris(1-methylethyl)benzoyl]benzonitrile (77).** The procedure of Ito et al. was followed.\textsuperscript{153} Into a solution containing 1,3,5-triisopropylbenzene (1.85 g, 9.1 mmol) and AlCl\textsubscript{3} (1.21 g, 9.1 mmol) in 15 ml of carbon disulphide was added dropwise a solution containing 4-cyanobenzoyl chloride (1.00 g, 6.0 mmol) and 1,3,5-triisopropylbenzene (0.62 g, 3.0 mmol) in 5 ml of carbon disulphide. The mixture was refluxed for 12 h and then poured into an ice-hydrochloric acid mixture. The product was extracted with ether and the organic layer was washed successively with water, 5% NaOH solution, and water. After drying with anhydrous MgSO\textsubscript{4} and removing solvent by rotary evaporation, the product was recrystallized from hexanes to afford a white powder (2.90 g, 96% yield).
Synthesis of 4-[2,4,6-Tris(1-methylethyl)benzoyl]benzoic Acid (21). A solution of 4-[2,4,6-tris(1-methylethyl)benzoyl]benzonitrile (1.00 g, 3.0 mmol) and 30% KOH (10 ml) in 2 ml ethanol was refluxed for 24 h. The mixture was then acidified with dilute HCl. The resulting white precipitate was filtered and recrystallized from methanol to afford white flakes (1.01 g, 96% yield).

MP 210.0-212.0°C, lit. 211.3°C
IR (KBr disc) 2963 (OH, broad), 1690, 1674 (C=O) cm⁻¹.
¹H NMR (CDCl₃, 400 MHz) δ 1.04 (d, broad, J = 8 Hz, 6 H, o-i-Pr CH₃), 1.14 (d, broad, J = 8 Hz, 6 H, o-i-Pr CH₃), 1.38 (d, J = 8 Hz, 6 H, p-i-Pr CH₃), 2.55 (septet, J = 8 Hz, 2 H, o-i-Pr CH), 2.92 (septet, J = 8 Hz, 1 H, p-i-Pr CH), 7.06 (s, 2 H, arom), 7.80-8.10 (AB, J = 10 Hz, 4 H, arom).
\[ ^{13}C\text{ NMR (CDCl}_3, 100\text{ MHz)} \delta 23.30, 23.98, 24.84, 31.16, 34.38\text{ (aliphatic), 121.15, 129.37, 130.49 (arom CH), 133.37, 134.35, 141.94, 145.05, 150.21 (arom C), 171.26 (COOH), 200.60 (C=O, ketone).} \]

LRMS (El) m/e (relative intensity) 353 (M\textsuperscript{+}+1, 11.2), 352 (M\textsuperscript{+}, 46.0), 337 (17.5), 319 (6.3), 307 (94.9), 292 (13.9), 281 (5.0), 268 (7.8), 250 (4.3), 231 (30.1), 149 (28.8), 121 (10.5), 105 (11.7), 91 (12.3), 77 (10.7), 65 (7.0). HRMS exact mass calcd for C\textsubscript{23}H\textsubscript{28}O\textsubscript{3} 352.2038, found 352.2038.

**Preparation of 4-[2,4,6-tris(1-methylethyl)benzoyl]benzoic Acid (R)-(+)-1-phenylethylamine Salt (36).** 4-[2,4,6-Tris(1-methylethyl)benzoyl]benzoic acid (51.5 mg, 0.15 mmol) and (R)-(+)-1-phenylethylamine (17.7 mg, 0.15 mmol) were dissolved in separate test-tubes, each with 10 ml of ethanol. The two solutions were then mixed together and the final solution was allowed to stand. Fine white needles were obtained on filtration (42.0 mg, 59% yield).

MP (decomposes at 180-190°C)
IR (KBr disc) 3422 (NH, broad), 1670 (C=O) cm\textsuperscript{-1}.

\[ ^1\text{H NMR (CDCl}_3, 400\text{ MHz)} \delta 1.04 \text{ (d, broad, } J = 8\text{ Hz, } 6\text{ H, o-Pr CH}_3\text{), 1.17 \text{ (d, broad, } J = 8\text{ Hz, } 6\text{ H, o-i-Pr CH}_3\text{), 1.30 \text{ (d, } J = 8\text{ Hz, } 6\text{ H, p-i-Pr CH}_3\text{), 1.49 \text{ (d, } J = 8\text{ Hz, } 3\text{ H, CH}_3\text{), 2.59 \text{ (septet, } J = 8\text{ Hz, } 2\text{ H, o-Pr CH}\text{), 2.92 \text{ (septet, } J = 8\text{ Hz, } 1\text{ H, p-Pr CH}\text{), 4.19 \text{ (d, broad, } J = 8\text{ Hz, } 1\text{ H, CH}\text{), 3.50 - 5.50 \text{ (s, broad, } 3\text{ H, } +\text{NH}_3\text{), 7.08 \text{ (s, } 2\text{ H, arom), 7.10-7.30 \text{ (m, } 5\text{ H, Ph}), 7.65-7.90 \text{ (AB, } J = 10\text{ Hz, 4 H, arom).}}\]

MS (FAB) m/e 474 (M\textsuperscript{+}+1), 335, 275, 231, 186, 149. [Matrix: 3-nitrobenzyl alcohol]
Anal. Calcd for C$_{31}$H$_{39}$NO$_3$: C, 78.61; H, 8.30; N, 2.96. Found: C, 78.26; H, 8.18; N, 2.80.

**Preparation of 4-[2,4,6-tris(1-methylethyl)benzoyl]benzoic Acid (S)-(−)-Proline Complex (37).** 4-[2,4,6-Tris(1-methylethyl)benzoyl]benzoic acid (50 mg, 0.14 mmol) and (S)-(−)-proline (16.3 mg, 0.14 mmol) were dissolved in two separate test tubes, each with 10 ml of ethanol. The two solutions were then mixed together and the final solution was allowed to stand. Colorless prisms were obtained on filtration (40.0 mg, 60% yield).

MP (decomposes at 180°C, completely melts at 208-209°C)
IR (KBr disc) 3210 (NH, broad), 1702, 1685, 1672 (C=O) cm$^{-1}$.
$^1$H NMR (CD$_3$OD, 400 MHz) δ 1.09 (d, broad, J = 8 Hz, 6 H, o-i-Pr CH$_3$), 1.15 (d, broad, J = 8 Hz, 6 H, o-i-Pr CH$_3$), 1.29 (d, J = 8 Hz, 6 H, p-i-Pr CH$_3$), 1.98 (m, 2 H), 2.11 (m, 1 H), 2.30 (m, 1 H), 2.56 (septet, J = 8 Hz, 2 H, o-i-Pr CH), 2.96 (septet, J = 8 Hz, 1 H, p-i-Pr CH), 3.18-3.46 (m, 2 H), 4.00 (m, 1 H), 7.15 (s, 2 H, arom), 7.75-7.20 (AB, J = 10 Hz, 4 H, arom).

$^{13}$C NMR (CD$_3$OD, 100 MHz) δ 23.43, 24.45, 25.10 (CH$_2$), 25.20, 30.35 (CH$_2$), 32.51, 35.75, 47.00 (CH$_2$), 62.53 (α-CH, proline), 122.24, 130.37, 131.20 (arom CH), 135.91, 137.11, 142.26, 146.36, 151.80 (arom C), 168.87, 173.88 (carboxylates), 202.47 (C=O, ketone).

MS (FAB) m/e 468 (M$^+$+1), 335, 251, 231, 215, 202, 189, 178, 165. [Matrix: 3-nitrobenzyl alcohol]

Anal. Calcd for C$_{28}$H$_{37}$NO$_5$: C, 71.92; H, 7.98; N, 3.00. Found: C, 71.83; H, 8.00; N, 2.94.
Synthesis of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol) Acetone Complex (22-acetone). Following the procedure Diel and Alder, mixture of anthracene (2.51 g, 14.1 mmol) and dimethyl acetylenedicarboxylate (2.00 g, 14.1 mmol) was heated to 170°C for 30 min in an oil bath. The reaction mixture was cooled to room temperature and the product obtained (dimethyl 9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate) was recrystallized from chloroform (4.20 g, 93% yield). The recrystallized product (1.00 g, 3.1 mmol) was then dissolved in 20 ml of anhydrous THF at 0°C. Phenyl lithium (1.8M solution in THF, 17.4 ml, 31.3 mmol) was added dropwise to the solution from a syringe. The mixture was stirred for 24 h at room temperature. The reaction was then carefully quenched with water and extracted with ether. After drying with anhydrous MgSO₄, the ethereal layer was concentrated by rotary evaporation. The mixture was then subjected to silica gel chromatography using 20% ether in hexanes (v/v) as eluent. The white solid obtained (Rf = 0.3, 20% ether in hexanes (v/v)) was recrystallized from acetone to afford colorless prisms (0.50 g, 25% yield).

DSC: loss of solvent at 104.7-119.9°C, melting at 220.1°C.
TGA: loss of mass -9.012% at 118.0°C (loss of acetone).
IR (KBr disc) 3298 (OH, broad), 1698 (C=O) cm⁻¹.
¹H NMR (CDCl₃, 400 MHz) δ 2.16 (s, 6 H, CH₃), 4.59 (s, 2 H, CH), 6.60-7.40 (m, 28 H, arom).
¹³C NMR (acetone-d₆, 50 MHz) δ 57.94 (CH), 84.26 (C-OH), 123.48, 124.88, 128.04, 128.33, 129.71 (arom CH), 146.89, 147.40, 150.36.
LRMS (EI) m/e (relative intensity) 568 (M+, 0.1), 550 (1.2), 534 (0.3), 473 (7.2), 445 (9.8), 414 (5.8), 368 (2.8), 267 (13.7), 178 (100), 105 (11.0). HRMS exact mass calcd for C_{42}H_{32}O_{2} 568.2402, found 568.2410.

Anal. Calcd for C_{45}H_{38}O_{3}: C, 86.23; H, 6.11. Found: C, 86.54; H, 5.99.

Synthesis of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol) Ethanol Complex (22*EtOH). Complex 22*acetone (100 mg, 0.16 mmol) was recrystallized from ethanol. Colorless prisms (75 mg, 76% yield) were obtained.

DSC: loss of solvent at 102.6-151.7°C, melting at 238.7°C.
TGA: loss of mass -7.409% at 129.1-153.0°C (loss of ethanol).
IR (KBr disc) 3384, 3154 (OH, broad) cm\(^{-1}\).
\(^{1}\text{H NMR (CDCl}_{3}, 400 \text{ MHz})\) \(\delta\) 1.22 (t, \(J = 8\) Hz, 3 H, CH\(_{3}\)), 3.60 (q, \(J = 8\) Hz, 2 H, CH\(_{2}\)), 4.60 (s, 2 H, CH), 6.60-7.40 (m, 28 H, arom).
UV (CH\(_{3}\)CN) 281 nm (\(\varepsilon\) 3200), 272 nm (\(\varepsilon\) 2200)
Anal. Calcd for C\(_{44}\)H\(_{38}\)O\(_{3}\): C, 85.96; H, 6.23. Found: C, 85.90; H, 6.16.

Synthesis of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol) Toluene Complex (22*toluene). Complex 22*acetone (100 mg, 0.16 mmol) was recrystallized from ethanol. Colorless prisms (80 mg, 76% yield) were obtained.

DSC: loss of solvent at 109.4-128.9°C, melting at 238.7°C.
TGA: loss of mass -13.85% at 128°C.
IR (KBr disc) 3404, 3306 (OH, broad) cm\(^{-1}\).
$^1$H NMR (CDCl$_3$, 200 MHz) δ 2.35 (s, 3 H, CH$_3$), 4.61 (2, 2 H, CH$_2$), 4.50-4.90 (s, broad, 2 H, OH), 6.60-7.40 (m, 33 H, arom).

Anal. Calcd for C$_{49}$H$_{40}$O$_2$: C, 89.06; H, 6.10. Found: C, 89.17; H, 6.12.

7.3. Photochemical Reactions

7.3.1. General Procedure

Light Sources
A 450 W Hanovia medium pressure mercury arc lamp housed in a Pyrex jacket was used for irradiation conducted at $\lambda \geq 290$ nm. For irradiation at 254 nm, a Rayonet photoreactor equipped with sixteen low pressure mercury discharge tubes was used. Irradiation at 337 nm was performed by using a Molelectron UV 22 pulsed nitrogen laser (330 mW average power).

Solid State Irradiations
Single crystal photolyses were performed by irradiating samples in quartz or Pyrex tubes under a nitrogen atmosphere or low vacuum. For polycrystalline powder irradiations, solid samples were sandwiched between two Pyrex or quartz plates and placed in a polythene bag sealed under nitrogen gas.

Solution Phase Irradiations
Solutions for photolyses were placed in Pyrex or quartz tubes and were degassed by at least three freeze-pump-thaw cycles before irradiation.
7.3.2. Photochemical Procedures and Spectral Characterization of Photoproducts

Solid State Photolysis of 1-(1,1-Dimethylethyl)-2,5-pyrrolidinedione (10). Compound 10 (100 mg, 0.65 mmol) was ground to fine powder and irradiated at 254 nm through a quartz filter. The reaction was complete in 12 h. The mixture was subjected to chromatography using 20% acetone in hexanes (v/v) as eluent. The white solid obtained (26) was recrystallized from acetone to afford colorless plates (79 mg, 79% yield).

Tetrahydro-7,7-Dimethyl-1H-azepine-2,5-dione (26).

MP 174.0-175.0°C, lit.\textsuperscript{158} 175-176°C

IR (KBr disc) 3202 (N-H stretch, lactam), 1705 (ketone C=O), 1654 (amide C=O) cm\textsuperscript{-1}.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) δ 1.38 (s, 6 H, CH\textsubscript{3}), 2.65, 2.72 (m, 4 H, CH\textsubscript{2}), 2.89 (s, 2 H, CH\textsubscript{2}CMe\textsubscript{2}), 6.40 (s, broad, 1 H, NH).

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 50 MHz) δ 30.78 (CH\textsubscript{3}), 31.83, 38.91, 55.31 (CH\textsubscript{2}), 52.00 (quaternary C), 173.99 (amide C=O), 208.05 (ketone C=O).

LRMS (El) m/e (relative intensity) 155 (M\textsuperscript{+}, 7.4), 140 (35.4), 138 (6.5), 123 (2.1), 113 (7.0), 112 (100), 99 (8.8), 98 (14.9), 97 (5.6), 84 (10.7), 70 (7.8), 58 (58.4), 57 (6.3), 56 (21.4), 55 (24.4). HRMS exact mass calcd for C\textsubscript{8}H\textsubscript{13}NO\textsubscript{2} 155.0946, found 155.0946.

Solid State Photolysis of 1-Cyclohexyl-2,5-pyrrolidinedione (11). Compound 11 (100 mg, 0.55 mmol) was ground to fine powder and irradiated at 254 nm through a quartz filter. After 3 h of photolysis, the mixture was subjected to
chromatography using 20% acetone in hexanes (v/v) as eluent. A white solid mass (27) (14 mg, 14% yield) was obtained.

**Mixture of cis & trans-Octahydro-1H-1-benzazepine-2,5-dione (27).**

IR (KBr disc) 3200 (N-H stretch, lactam), 1705 (ketone C=O), 1655 (amide C=O) cm⁻¹.

$^1$H NMR (CDCl₃, 200 MHz) $\delta$ 1.05-1.90 (m, 8 H, -(CH₂)₄-), 2.00-2.15 (m, 0.7 x 1 H, -COCH-), 2.25-2.40 (m, 0.3 x 1 H, -COCH-), 2.45-2.90 (m, 4H, (CH₂)₂), 3.30-3.40 (m, 0.3 x 1 H, NHCH), 4.00-4.15 (m, 0.7 x 1 H, NHCH), 5.50-5.80 (s, broad, 1 H, NH).

$^{13}$C NMR (CDCl₃, 50 MHz) $\delta$ 19.56, 23.56, 24.21, 24.47, 24.94, 26.18, 30.37, 30.80, 31.00, 33.10, 36.45, 38.65 (CH₂), 47.83, 52.39, 55.96, 56.78 (CH), 175.03 (amide C=O), 209.90, 210.42 (ketone C=O).

LRMS (EI) $m/e$ (relative intensity) 182 (M⁺+1, 14.3), 181 (M⁺, 100), 164 (17.0), 152 (10.1), 136 (15.8), 126 (24.4), 124 (20.1), 111 (67.3), 109 (30.9), 100 (41.1), 96 (37.6), 82 (86.6), 67 (45.7), 56 (98.5). HRMS exact mass calcd for C₁₀H₁₅NO₂ 181.1099, found 181.1099.

**Solid State Photolysis of 1-Cyclopentyl-2,5-pyrrolidinedione (12).** Compound 12 (100 mg, 0.60 mmol) was ground to fine powder and irradiated at 254 nm through a quartz filter. After 3 h of photolysis, the mixture was subjected to chromatography using 20% acetone in hexanes (v/v) as eluent. The white solid mass (28) was recrystallized from chloroform to afford prisms (11 mg, 11% yield).

**cis-Octahydrocyclopent[b]azepine-2,5-dione (28).**
MP 192.5-193.5°C, lit.\textsuperscript{158} 192.5-193.5°C

IR (KBr disc) 3209 (NH stretch, lactam), 1700 (ketone C=O), 1660 (amide C=O) cm\textsuperscript{-1}.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) \(\delta\) 1.55-2.30, (m, 6 H, -(CH\textsubscript{2})\textsubscript{3}-), 2.48-3.05, (m, 4 H, -(CH\textsubscript{2})\textsubscript{2}-), 3.15 (m, 1 H, COCH), 4.30 (m, 1 H, CHNH), 6.30 (s, broad, 1 H, NH).

\textsuperscript{13}C NMR (CDCl\textsubscript{3}, 50 MHz) \(\delta\) 23.36, 25.89, 30.49, 34.35, 39.39 (CH\textsubscript{2}), 54.03, 54.52 (CH), 175.52 (amide C=O), 208.02 (ketone C=O).

LRMS (El) \(m/e\) (relative intensity) 168 (M\textsuperscript{+}+1, 5.7), 167 (M\textsuperscript{+}, 47.2), 125 (9.2), 124 (100), 112 (11.0), 111 (20.3), 110 (5.4), 100 (24.0), 96 (35.0), 95 (24.9), 83 (16.7), 82 (57.1), 69 (14.8), 68 (30.7), 67 (25.2), 57 (9.8), 56 (38.6), 55 (27.9).

HRMS exact mass calcd for C\textsubscript{9}H\textsubscript{13}NO\textsubscript{2} 167.0946, found 167.0942.

Solid State Photolysis of 1-(1-Methylethyl)-2,5-pyrrolidinedione (13). Compound 13 (100 mg, 0.71 mmol) was ground to fine powder and irradiated at 254 nm through a quartz filter. After 3 h of photolysis, the mixture was subjected to chromatography using 20% acetone in hexanes (v/v) as eluent. The white solid mass (29) was recrystallized from chloroform to afford prisms (22 mg, 22% yield).

Tetrahydro-7-methyl-1H-azepine-2,5-dione (29).

MP 139.0-140.0°C, lit.\textsuperscript{158} 139.5-140.5°C

IR (KBr disc) 3224 (NH stretch, lactam), 1700 (ketone C=O), 1652 (amide C=O) cm\textsuperscript{-1}.

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 200 MHz) \(\delta\) 1.35 (d, \(J=9\) Hz, 3 H, CH\textsubscript{3}), 2.64, (m, 6 H, CH\textsubscript{2}), 3.81 (m, 1 H, CH), 7.21 (s, broad, 1 H, NH).
Solid State Photolysis of N-Phenyl-N-(phenylthioxomethyl)benzenepropanamide (16). Compound 16 (500 mg, 1.45 mmol) was ground to fine powder and irradiated at >290 nm through a Pyrex filter. No special attempts were made to exclude moisture. After 12 h of photolysis, the mixture was dissolved in 10 ml of ether. Half of the solution was subjected to chromatography using 10% ether in hexanes (v/v) as eluent. N-Phenylbenzenecarbothioamide (50) was isolated (28 mg, 9% yield). The spectral data of 50 are summarized in the previous section. The other half of the solution was extracted with 10% NaOH (4 x 10 ml). The aqueous solution was acidified with HCl and extracted with ether. After drying with MgSO₄, the solution was filtered and the solvent was removed by rotary evaporation. 3-Phenylpropanonic acid (51) was obtained (20 mg, 9% yield). A similar photolysis under anhydrous conditions gave no reaction.

3-Phenylpropanonic acid (51).
MP 48.0-49.0°C, lit¹⁵⁹ 47-49°C
IR (KBr disc) 2933 (broad, OH, acid), 1704 (C=O) cm⁻¹.
¹H NMR (CDCl₃, 200 MHz) δ 2.68 (t, J = 9 Hz, 2 H, COCH₂), 2.96 (t, J = 9 Hz, 2 H, PhCH₂), 7.05-7.20 (m, 5 H, arom), 10.80-12.20 (s, broad, 1 H, COOH).
¹³C NMR (CDCl₃, 50 MHz) δ 30.57, 35.59 (CH₂), 126.39, 128.26, 128.57 (arom CH), 140.14 (arom C), 179.15 (C=O).
MS (EI) m/e (relative intensity) 151 (M\(^{+}+1\), 4.1), 150 (M\(^{+}\), 42.1), 105 (15.5), 104 (47.7), 91 (100), 78 (14.3), 77 (14.0), 65 (11.8), 51 (11.5). HRMS exact mass calcd for C\(_9\)H\(_{10}\)O\(_2\) 150.0681, found 150.0685.

**Solution Phase Photolysis of \(N\)-Phenyl-\(N\)-(phenylthioxomethyl)benzene-propanamide (16) in Benzene.** The general procedure for solution phase photolysis was followed with compound 16 (150 mg, 0.43 mmol) in 20 ml of benzene. No special attempts were made to exclude moisture. The solution was irradiated at \(\geq 290\) nm through a Pyrex filter for 24 h. Following a workup procedure similar to that of the solid state photolysis, compound 50 (19 mg, 20% yield) and 3-Phenylpropanionic acid (12 mg, 19% yield) were obtained. A similar photolysis using anhydrous benzene gave no reaction.

**Solution Phase Photolysis of \(N\)-Phenyl-\(N\)-(phenylthioxomethyl)benzene-propanamide (16) in 10% Methanol in Benzene (v/v).** The general procedure for solution phase photolysis at \(\geq 290\) nm was followed with compound 16 (167 mg, 0.48 mmol) in 20 ml of 10% methanol in benzene (v/v). After 6 h of photolysis, the mixture was subjected to chromatography using 10% ether in hexanes (v/v) as eluent. \(N\)-Phenylbenzenecarbothioamide (50) (85 mg, 82% yield) and methyl 3-phenylpropanoate (52) (66 mg, 83% yield) were isolated.

**Methyl 3-Phenylpropanoate (52).**

IR (KBr disc) 1740 (C=O) cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 2.64 (t, \(J = 8\) Hz, 2 H, COCH\(_2\)), 2.96 (t, \(J = 8\) Hz, 2 H, PhCH\(_2\)), 3.69 (s, 3 H, OMe), 7.10-7.40 (m, 5 H, arom).
$^{13}$C NMR (CDCl$_3$, 50 MHz) $\delta$ 30.94, 35.70 (CH$_2$), 51.61 (OMe), 126.27, 128.27, 128.51 (arom CH), 140.51 (arom C), 173.34 (C=O).

MS (El) $m/e$ (relative intensity) 165 (M$^++$1, 9.7), 164 (M$^+$, 67.2), 133 (23.6), 121 (2.6), 105 (85.9), 104 (100), 91 (89.5), 79 (17.6), 78 (19.5), 77 (27.1), 65 (10.7), 59 (2.3), 51 (7.8). HRMS exact mass calcd for C$_{10}$H$_{12}$O$_2$ 164.0837, found 164.0841.

Solution Phase Photolysis of $N$-Phenyl-$N$-(phenylthioxomethyl)benzene-propanamide (16) in 10% MeOD in Benzene (v/v). The general procedure for solution phase photolysis was followed with compound 16 (20 mg, 0.06 mmol) in 3 ml of 10% MeOD in benzene (v/v). The solution was irradiated at $\geq$290 nm through a Pyrex filter. After 6 h of photolysis, the mixture was analysed by GC/LRMS and GC/HRMS. These spectra were identical to those from non-deuterated 52.

Sensitized Photolysis of $N$-Phenyl-$N$-(phenylthioxomethyl)benzene-propanamide (16) in 10% Methanol in Benzene (v/v). The general procedure for solution phase photolysis at $\geq$ 290 nm was followed. Two samples were prepared and each of them contained compound 16 (0.02M) in 2 ml of 10% methanol in benzene (v/v). In one of the samples was dissolved Michler's ketone (0.12M). The two samples were irradiated at 337nm with a nitrogen laser beam (96% of the radiation was absorbed by sensitizer). After 6 h of photolysis, the samples were analysed by GC. The same conversions were observed for both samples.
Solid State Photolysis of N-Phenyl-N-(phenylthioxomethyl)benzenepropanamide-$d_2$ (16-$d_2$). Compound 16-$d_2$ (500 mg, 1.45 mmol) was ground to a fine powder and irradiated at $\geq$290 nm through a Pyrex filter. No special attempts were made to exclude moisture. After 12 h of photolysis, the mixture was dissolved in 5 ml of ether and extracted with 10% NaOH (4 x 10 ml). The aqueous layer was acidified with HCl and then extracted with ether. After drying with MgSO$_4$, the solution was filtered and the solvent was removed by rotary evaporation. 3-Phenylpropanonic acid was obtained (15 mg, 7% yield). Comparison of the proton NMR spectrum with that of 16-$d_2$ indicates that there was no deuterium loss during photolysis.

Solution Phase Photolysis of N-Phenyl-N-(phenylthioxomethyl)benzenepropanamide-$d_2$ (16-$d_2$) in 10% Methanol in Benzene (v/v). A procedure similar to that used for photolysis of compound 16 in 10% methanol in benzene (v/v) was followed except compound 16-$d_2$ (100 mg, 0.29 mmol) in 10 ml of 10% methanol in benzene (v/v) was used. The solution was irradiated at $\geq$290 nm through a Pyrex filter. After 6 h of photolysis, the mixture was subjected to chromatography using 10% ether in hexanes (v/v) as eluent. The methyl 3-phenylpropanoate obtained (35 mg, 70% yield) was analysed by proton NMR. Comparison of the proton NMR spectrum with that of 16-$d_2$ indicates no deuterium loss during photolysis.

Solid State Photolysis of N-[(4-Methoxyphenyl)thioxomethyl]-N-phenylbenzenepropanamide (17). The general procedure for solid state photolysis at $\geq$290 nm was followed with compound 17 (200 mg, 0.53 mmol). No special attempts were made to exclude moisture. After 12 h of photolysis, the sample
was subjected to chromatography using 12% ether in hexanes (v/v) as eluent. Compound 71 was isolated (13 mg, 10% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 71 are summarized in the previous section.

**Solution Phase Photolysis of N-[(4-Methoxyphenyl)thioxomethyl]-N-phenylbenzenepropanamide (17) in Benzene.** The general procedure for solution phase photolysis was followed with compound 17 (150 mg, 0.40 mmol) in 20 ml of benzene. No special attempts were made to exclude moisture. The solution was irradiated at ≥290 nm through a Pyrex filter. After 24 h of photolysis, the mixture was subjected to chromatography using 12% ether in hexanes (v/v) as eluent. Compound 71 was isolated (24 mg, 25% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 71 are summarized in the previous section.

**Solid State Photolysis of N-(4-Bromo-2,6-dimethylphenyl)-N(phenylthioxomethyl)benzenepropanamide (18).** Following a procedure similar to that used for solid state photolysis of 17, compound 18 (150 mg, 0.33 mmol) was photolysed. Compound 72 was isolated (5 mg, 5% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 72 are summarized in the previous section.

**Solution Phase Photolysis of N-(4-Bromo-2,6-dimethylphenyl)-N(phenylthioxomethyl)benzenepropanamide (18) in Benzene.** Compound 18 (100 mg, 0.22 mmol) in 10 ml of benzene was photolysed using a procedure similar to that used for 17. Compound 72 was isolated (11 mg, 16% yield). 3-Phenylpropanonic
acid was detected by GC. Spectral data for 72 are summarized in the previous section.

**Solid State Photolysis of \( N\)-(4-Bromophenyl)-\( N\)-(phenylthioxomethyl)-benzenepropanamide (19).** Following a procedure similar to that used for solid state photolysis of 17, compound 19 (100 mg, 0.24 mmol) was photolysed. Compound 73 was isolated (5 mg, 7% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 73 are summarized in the previous section.

**Solution Phase Photolysis of \( N\)-(4-Brom\'o-2,6-dimethylphenyl)-\( N\)-(phenylthioxomethyl)benzenepropanamide (19) in Benzene.** Compound 19 (100 mg, 0.24 mmol) in 10 ml of benzene was photolysed using a procedure similar to that used for 17. Compound 73 was isolated (10 mg, 14% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 73 are summarized in the previous section.

**Solid State Photolysis of \( N\)-(4-Methoxyphenyl)-\( N\)-(phenylthioxomethyl)-benzenepropanamide (20).** Following a procedure similar to that used for solid state photolysis of 17, compound 20 (100 mg, 0.27 mmol) was photolysed. Compound 74 was isolated (5 mg, 8% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 74 are summarized in the previous section.

**Solution Phase Photolysis of \( N\)-(4-Methoxyphenyl)-\( N\)-(phenylthioxomethyl)-benzenepropanamide (20) in Benzene.** Compound 20 (100 mg, 0.27 mmol) in 10 ml of benzene was photolysed using a procedure similar to that used for 17.
Compound 74 was isolated (9 mg, 14% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 74 are summarized in the previous section.

**Solid State Photolysis of N-Phenyl-N-(phenylthioxomethyl)benzamide (49).** Following a procedure similar to that used for solid state photolysis of 17, compound 49 (200 mg, 0.63 mmol) was photolysed. Compound 50 was isolated (5 mg, 4% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 50 are summarized in the previous section.

**Solution Phase Photolysis of N-Phenyl-N-(phenylthioxomethyl)benzamide (49) in Benzene.** Compound 49 (100 mg, 0.32 mmol) in 10 ml of benzene was photolysed using a procedure similar to that used for 17. Compound 50 was isolated (7 mg, 10% yield). 3-Phenylpropanonic acid was detected by GC. Spectral data for 50 are summarized in the previous section.

**Solution Phase Photolysis of N-Phenyl-N-(phenylthioxomethyl)benzamide (49) in 10% Methanol in Benzene (v/v).** Compound 49 (100 mg, 0.32 mmol) in 10 ml of 10% methanol in benzene (v/v) was photolysed using a procedure similar to that used for 17. Compound 50 was isolated (51 mg, 76% yield). Methyl benzoate was detected by GC. Spectral data for 50 are summarized in the previous section.

**Solution Phase Photolysis of Phenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione (14) in Benzene.** Compound 14 (100 mg, 0.31 mmol) in 10 ml of benzene (v/v) was photolysed using a procedure similar to that used for 17. The reaction was complete in 48 h. No starting material 14 was left. The mixture
was subjected to chromatography using hexanes as eluent. A pale yellow liquid (43) was isolated (70 mg, 70% yield).

8,8-Dimethyl-3,5-bis(1-methylethyl)-7-phenylbicyclo[4.2.0]octa-1,3,5-trien-7-thiol (43).

IR (KBr disc) 2964 (C-H) cm\(^{-1}\).

\(^1\)H NMR (CDCl\(_3\), 300 MHz) \(\delta\) 0.83 (s, 3 H, CH\(_3\)), 1.20-1.40 (m, 12 H, i-Pr CH\(_3\)), 1.60 (s, 3 H, CH\(_3\)), 2.31 (s, 1 H, SH), 2.90 (septet, \(J = 9\) Hz, 1 H, i-Pr CH), 3.13 (septet, \(J = 9\) Hz, 1 H, i-Pr CH), 6.79 (s, 1 H, arom), 7.08 (s, 1 H, arom), 7.15-7.50 (m, 5 H, arom).

\(^1^3\)C NMR (CDCl\(_3\), 50 MHz) \(\delta\) 22.60, 24.33, 24.60, 25.58, 26.11, 29.32, 34.99 (aliphatic CH/CH\(_3\)), 55.10, 63.57 (quaternary C), 115.83, 123.39, 126.79, 127.23, 127.91 (arom CH), 140.44, 143.53, 144.29, 150.24, 150.64 (arom C).

LRMS (El) \(m/e\) (relative intensity) 325 (M\(^+\)+1, 7.1), 324 (M\(^+\), 25.9), 323 (28.8), 310 (23.4), 309 (100), 292 (7.0), 277 (12.8), 266 (12.4), 247 (13.0), 235 (19.6), 215 (7.3), 203 (10.9), 193 (17.4), 178 (6.8), 129 (14.6), 115 (6.7), 101 (6.8), 91 (16.0), 86 (35.1), 84 (55.9), 51 (20.6), 49 (65.8). HRMS exact mass calcd for C\(_{22}\)H\(_{28}\)S 324.1912, found 324.1913.

Anal. Calcd for C\(_{22}\)H\(_{28}\)S: C, 81.42; H, 8.70; S, 9.88. Found: C, 81.18; H, 8.73; S, 9.74.
Solid State Photolysis of Phenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione (14). Single crystals of 14 (200 mg, 0.62 mmol) were photolysed at $\lambda \geq 290$ nm for 24 h according to the general procedure. Proton NMR (CDCl$_3$, 400 MHz) of the mixture indicated the presence of compound 43 (9 % conversion). Attempts to separate 43 from 14 by either GC or HPLC were not successful.

Solution Phase Photolysis of 4-Methoxyphenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione (15) in Benzene. Compound 14 (100 mg, 0.28 mmol) in 10 ml of benzene (v/v) was photolysed using a procedure similar to that used for 17. The reaction was complete in 48 h. The mixture was subjected to chromatography using hexanes as eluent. A pale yellow liquid (44) was isolated (72 mg, 72% yield).

8,8-Dimethyl-3,5-bis(1-methylethyl)-7-(4-methoxyphenyl)bicyclo[4.2.0]octa-1,3,5-trien-7-thiol (44).
IR (KBr disc) 2960 (C-H) cm$^{-1}$.
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 0.83 (s, 3 H, CH$_3$), 1.15-1.40 (m, 12 H, i-Pr CH$_3$), 1.58 (s, 3 H, CH$_3$), 2.39 (s, 1 H, SH), 2.89 (septet, $J = 9$ Hz, 1 H, i-Pr CH), 3.12 (septet, $J = 9$ Hz, 1 H, i-Pr CH), 3.78 (s, 3 H, OMe), 6.70-7.30 (m, 6 H, arom).
$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 22.60, 24.32, 24.59, 25.55, 26.06, 29.28, 34.96 (aliphatic CH/CH$_3$), 55.10 (quaternary C), 55.20 (OMe), 63.13 (quaternary C), 113.18, 115.85, 123.33, 128.35 (arom CH), 135.70, 140.75, 144.15, 150.23, 150.54, 158.36 (arom C).
LRMS (EI) m/e (relative intensity) 355 (M$^+$+1, 3.0), 354 (M$^+$, 9.5), 353 (21.3), 352 (48.5), 351 (46.1), 337 (100), 318 (21.8), 294 (14.2), 275 (16.0), 263 (18.4), 245 (13.6), 229 (10.4), 215 (13.9), 202 (13.2), 189 (9.1), 168 (10.9), 151 (15.1),
Anal. Calcd for C_{23}H_{30}SO: C, 77.92; H, 8.53; S, 9.04. Found: C, 77.71; H, 8.22; S, 8.92.

Solid State Photolysis of 4-Methoxyphenyl[2,4,6-tris(1-methylethyl)phenyl]-methanethione (15). Single crystals of 15 (200 mg, 0.56 mmol) were photolysed at λ ≥ 290 nm for 24 h. Proton NMR (CDCl₃, 400 MHz) of the mixture showed the presence of compound 44 (12 % conversion). Attempts to separate 44 from 15 by either GC or HPLC were not successful.

Solid State Photolysis of 4-[2,4,6-Tris(1-methylethyl)benzoyl]benzoic Acid (R)-(+-) Phenylethylamine Salt (36). Crystals of compound 36 (200 mg, 0.42 mmol) were ground to a fine powder and photolysed at λ ≥ 290 nm at -40°C for 3 days. The reaction mixture was then dissolved in ethanol, acidified with dilute HCl and treated with diazomethane. The product was chromatographed using 10% ether in hexanes (v/v) as eluent. Tiny colorless plates (38) were obtained (3 mg, 2% yield). Chiral HPLC (Chiracel OD, 10% i-propanol in hexane (v/v)) analysis shows 66% ee. A similar photolysis with the same amount of starting material at 20°C for 24 h gave 38 (15 mg, 10% yield) in 17% ee. A solution phase photolysis (50 mg, 0.11 mmol) in ethanol (5 ml) for 4 h gave no ee.

Methyl 4-[7-Hydroxy-8,8-dimethyl-3,5-bis(1-methylethyl)bicyclo[4.2.0]octa-1,3,5-trien-7-yl]benzoate (38).
MP 160.5-161.5°C, lit.66 161.5-162°C
IR (KBr disc) 3430 (OH, broad), 1719 (C=O) cm⁻¹.

¹H NMR (CDCl₃, 400 MHz) δ 0.80 (s, 3 H, CH₃), 1.13 (d, J = 9 Hz, 3 H, 5-i-Pr CH₃), 1.18 (d, J = 9 Hz, 3 H, 5-i-Pr CH₃), 1.27 (d, J = 9 Hz, 6 H, 3-i-Pr CH₃), 1.44 (s, 3 H, CH₃), 2.61 (s, 1 H, OH), 2.82 (septet, J = 9 Hz, 1 H, i-Pr CH), 2.91 (septet, J = 9 Hz, 1 H, i-Pr CH), 3.88 (s, 3 H, OMe), 6.89 (s, 1 H, arom), 7.07 (s, 1 H, arom), 7.41 (d, J = 11 Hz, 2 H, arom), 7.96 (d, J = 11 Hz, 2 H, arom).

¹³C NMR (CDCl₃, 100 MHz) δ 22.73, 24.11, 24.22, 24.27, 24.32, 24.53, 30.50, 35.01 (aliphatic CH/CH₃), 51.99 (OMe), 54.80 (quaternary C), 85.60 (C-OH), 116.15, 124.17, 126.70, 129.03 (arom CH), 128.81, 139.40, 145.05, 147.85, 151.64, 152.72 (arom C), 167.11 (C=O, ester).

LRMS (El) m/e (relative intensity) 367 (M⁺+1, 2.7), 366 (M⁺, 7.3), 351 (17.9), 336 (3.6), 323 (2.9), 307 (45.4), 292 (9.0), 265 (6.4), 246 (40.8), 231 (87.3), 213 (15.6), 203 (9.0), 185 (8.4), 152 (39.5), 121 (100), 105 (7.6), 93 (29.9). HRMS exact mass calcd for C₂₄H₃₀O₃ 366.2195, found 366.2197.

Solid State Photolysis of 4-[2,4,6-tris(1-methylethyl)benzoyl]benzoic Acid (S)-(−)-Proline Complex (37). Crystals of compound 37 (200 mg, 0.43 mmol) were ground into fine powder and were photolysed at λ ≥290 nm at -40°C for 24 h. The reaction mixture was then dissolved in ethanol, acidified with dilute HCl and treated with diazomethane. The product was chromatographed using 10% ether in hexanes (v/v) as eluent. Compound 38 were obtained (9 mg, 6% yield).
Chiral HPLC analysis shows 26% ee ([α]₀ = -24.2). A similar photolysis with the same amount of starting material at 20°C for 12 h gave racemic 38 (24 mg, 16% yield). A solution phase photolysis (50 mg, 0.11 mmol) in ethanol (5 ml) for 4 h also gave racemic 38.

**Solid State Photolysis of 9,10-Dihydro-9,10-ethanoanthracene-11,12-bis(diphenylmethanol) Acetone Complex (22·acetone).** Compound 22·acetone (200 mg, 0.32 mmol) was ground to a fine powder and photolysed at λ ≥290 nm according to the general procedure. After 24 h of irradiation, the reaction mixture was subjected to chromatography using hexanes as eluent. Colorless crystals of 67 were isolated (26 mg, 15% yield).

9,10-Dihydro-12,12,14,14-tetraphenyl-9,10[3',4']furanoanthracene (67)

MP 277.0-278.0°C
IR (KBr disc) 3059,3034 (CH) cm⁻¹.
¹H NMR (CDCl₃, 400 MHz) δ 5.13 (s, 2 H, CH), 6.60-7.30 (m, 28 H, arom).
¹³C NMR (CDCl₃, 100 MHz) δ 50.45 (CH), 94.81 (quaternary C), 123.07, 124.65, 127.08, 127.51, 127.70 (arom CH), 143.69, 146.65, 153.18.
LRMS (El) m/e (relative intensity) 551 (M⁺+1, 5.7), 550 (M⁺, 12.4), 474 (39.7), 473 (100), 446 (34.1), 445 (90.1), 295 (28.0), 267 (90.0), 178 (73.5), 105 (36.4).
HRMS exact mass calcd for C₄₂H₃₀O 550.2297, found 550.2301.
UV (CH$_3$CN) 333 nm ($\varepsilon$ 7700), 281 nm ($\varepsilon$ 6100).

Anal. Calcd for C$_{42}$H$_{30}$O: C, 91.60; H, 5.49. Found: C, 91.60; H, 5.37.

Photolysis of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol) Acetone Complex (22-acetone) in Acetone Solution. Compound 22-acetone (200 mg, 0.32 mmol) was dissolved in 10 ml of acetone and was photolysed with $\geq$290 nm according to the general procedure. After 6 h of irradiation, the reaction mixture was subjected to chromatography using 15% ether in hexanes (v/v) as eluent. Colorless crystals of photoproduct 68 were isolated (78 mg, 43% yield).

4b,8b,8c,8d-Tetrahydro-dibenzo[a,f]cyclopropa[cd]pentalene-8b,8c-bis(diphenylmethanol) (68).

MP 145-148°C

IR (KBr disc) 3323 (OH, broad) cm$^{-1}$.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 4.21 (s, 1 H, CH), 4.59 (s, 1 H, CH), 6.35-7.60 (m, 28 H, arom).

$^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 43.05 (CH), 60.83 (quaternary C), 61.39 (CH), 74.55 (quaternary C), 79.67, 80.65 (C-OH), 51.99 (OMe), 54.80 (quaternary C), 85.60 (C-OH), 120.22, 121.23, 124.72, 125.63, 126.12, 126.25, 126.35, 127.03,
127.12, 127.17, 127.62, 127.88, 127.94, 128.12, 128.33, 128.47, 128.55 (arom
CH), 137.78, 138.12, 144.33, 145.49, 146.13, 149.19, 148.12, 151.88 (arom C).
LRMS (El) m/e (relative intensity) 568 (M+, 0.0), 550 (7.4), 534 (8.9), 532 (3.8),
473 (1.0), 445 (7.0), 383 (9.8), 369 (100), 291 (27.9), 289 (44.0), 277 (6.2), 267
(13.9), 182 (31.4), 165 (21.9), 144 (10.2), 105 (86.7), 77 (46.8), 71 (14.7), 57
(19.5), 51 (12.5). HRMS exact mass calcd for C_{42}H_{32}O_{2} 568.2402, found
568.2406.
Anal. Calcd for C_{45}H_{38}O_{3} (1:1 complex with acetone): C, 86.23; H, 6.11. Found:
C, 86.69; H, 5.97.

Solid State Photolysis of 9,10-Dihydro-9,10-ethenoanthracene-11,12-
bis(diphenylmethanol) Ethanol Complex (22*EtOH). Compound 22*EtOH
(200 mg, 0.33 mmol) was ground to fine powder and was photolysed at \( \lambda \geq 290 \)
nm according to the general procedure. After 24 h of irradiation, the reaction
mixture was subjected to chromatography using hexanes as eluent. Colorless
crystals of photoproduct 67 were isolated (18 mg, 10% yield).

Photolysis of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenyl-
methanol) Ethanol Complex (22*EtOH) in Ethanol Solution. Compound 22*EtOH
(100 mg, 0.16 mmol) was dissolved in 10 ml of ethanol and photolysed
at \( \lambda \geq 290 \) nm according to the general procedure. After 12 h of irradiation, the
reaction mixture was analysed by proton NMR (CDCl_{3}, 400 MHz). Compound 68
was detected (20% conversion) as the only major product.

Photolysis of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenyl-
methanol) Ethanol Complex (22*EtOH) in Benzene Solution. Compound
22•EtOH (100 mg, 0.16 mmol) was dissolved in 10 ml of benzene and was photolysed with ≥290 nm according to the general procedure. After 12 h of irradiation, the reaction mixture was analysed by proton NMR (CDCl₃, 200 MHz) and silica gel TLC (30% ether in hexanes (v/v) as eluent). Compound 68 was detected as the only product in both analyses.

**Solid State Photolysis of 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol) Toluene Complex (22•toluene).** Compound 22•toluene (200 mg, 0.30 mmol) was ground into fine powder and photolysed at λ ≥290 nm according to the general procedure. After 24 h of irradiation, the reaction mixture was subjected to chromatography using hexanes as eluent. Colorless crystals of compound 67 were isolated (20 mg, 12% yield).
Chapter 8 EXPERIMENTAL (CRYSTALLOGRAPHIC)

8.1. General Considerations

Data Collection

All structures reported in this thesis were obtained by using intensity measurement from a Rigaku AFC6 diffractometer equipped with a sealed tube X-ray source. In a typical experiment, the crystal used for X-ray diffraction study was chosen from its external appearance under an optical microscope. It was then mounted on an AFC6 goniometer (glued to a glass fiber) and centered in the X-ray beam. The incident beam collimator was 1 mm in diameter and the crystal to detector distance was 285 mm. Both horizontal and vertical aperatures of the detector were fixed at 6.0 mm by manually insertable slits. Data collection procedures were controlled by the TEXPAY software supplied by Molecular Structure Corporation. At that point, AUTO mode of data collection was initiated. This AUTO mode includes various steps. First, the reciprocal lattice was searched systematically for up to 25 reflections. It then proceeded to the next routine of indexing the reflections in the working list. A primitive unit cell and the orientation matrix were calculated. If indexing was unsuccessful, a different crystal would be chosen and the whole process would be restarted. The next routine, DELAUNAY, reduced and transformed the primitive cell to highest possible symmetry. Laue symmetry was determined by the measurement of equivalent reflections (skipped for triclinic cells).

Data collection parameters were then selected. Data collection limits for the indices were selected based on the Laue group. Three standard reflections were chosen based on their intensity and spatial distribution in \( \chi \). Scan width in \( \omega \)
was determined by scanning the standard reflections. (Scan width was expressed as \( A + B \tan \theta \); the first part is dependent on the mosaic spread of the crystal, while the second is dependent on variation in \( K_{\alpha 1} - K_{\alpha 2} \) splitting of the radiation used which is in turn \( \theta \)-dependent.) The default scan mode was \( \omega-2\theta \) but in cases of unit cells with large cell dimensions, \( \omega \) scan mode would be used in order to avoid overlapping of reflections. The scan speed was chosen by the software based on the average intensity of the reflections present in the working list and was fixed at 8, 16 or 32° min\(^{-1} \) in \( \omega \).

Data were collected in four shells of 2θ. Weak reflections with \( I < 40.0\sigma(I) \) were rescanned up to 8 rescans and the counts were accumulated to improve the counting statistics. Reflections were tagged unobserved if \( I < 3.0\sigma(I) \). Stationary background measurements were made at the beginning and end of each scan with the scan-to-background counting time in the ration of 2:1. Three standard reflections were monitored every 200 reflections collected, for crystal orientation and decay correction. In cases where the deviation in any of the angular settings were greater than preset deviation values, all the reflections in the working list were recentered and a new orientation matrix was calculated.

At the end of the data collection, more accurate cell dimensions were calculated using the positions of strong reflections with high 2θ values. Up to 25 reflections from the data collected satisfying the requirement for \( F_{\text{obs}} \geq 50.0 \) were centered accurately and used. Finally, three strong reflections with \( \chi \) near 90° were selected for \( \psi \)-scans.

**Data Reduction**

The raw intensity data were then processed using the TEXSAN software provided by the Molecular Structure Corporation.\(^{161} \) Intensities were corrected for
background, and the standard deviations, $\sigma(I)'s$, are calculated by the following expressions:

$$I = C - 2(b_1 + b_2)$$
$$\sigma^2(I) = [C + 4(b_1 + b_2) + (pI)^2]$$

where $C$ is the total scan counts, $b_1$ and $b_2$ are background counts, and $p$ is a factor used to correct for the underestimation of $\sigma(I)'s$ for the strong reflections. The corrected intensities were then used to calculate observed structure factor amplitude, $|F_0|$. 

$$|F_0| = \sqrt{I/L_p}$$

where $L_p$ stands for Lorentz-polarization factors.

A Wilson analysis\textsuperscript{162} of the intensities was also performed to estimate an overall temperature factor and a scale factor which would be used as the starting value for the scale factor in the least-squares refinement of the trial structure. By using the $N(Z)$ test, systematic absences and the Laue group, a space group was then selected. If the space group was in a non-standard setting, the data would be transformed with the transformation matrix provided. In addition, an average $\psi$-scan curve was calculated which was used in calculating transmission factors for an empirical absorption correction.

**Structure Solution**

Most of the structures reported in this thesis are solved by direct methods using MITHRIL.\textsuperscript{163} Therefore, a brief outline of solving a structure with direct methods is presented here.

MITHRIL (Multan with Interactive facilities, Triplet checking, Higher invariants, Random phasing, Intelligent control of flow and options and Linear
equations phasing) is a series of computer programs designed to derive the phases for each reflection and to calculate an E-map for peak interpretation.

The first step of this procedure is to normalize the observed structure factor amplitudes to give $|\text{EI}|$'s, the normalized structure factor amplitude for each reflection by the equation:

$$|\text{EI}|^2 = k^2 |F|^2 / \varepsilon \sum_i f_i^2$$

where $k$ is a scale factor, $\varepsilon$ is an integer and $f_i$ is the scattering factor for atom $i$ corrected for thermal motion. At this stage, it is assumed that all atoms have an isotropic thermal motion, i.e.

$$f_i = f_i^0 \exp \left( -B \sin^2 \theta / \lambda^2 \right)$$

where $B$ is the isotropic temperature factor which is equal to $8\pi^2 \overline{u^2}$, and $\overline{u^2}$ is the mean-square amplitude of vibration of the atom under consideration. The $\varepsilon$ value is normally 1 except for some special class of reflections in some space group (e.g. in $P2_1/c$, $\varepsilon = 2$ for $h0l$ and $0k0$ reflections and 1 for all others).

A statistical analysis called E-statistics was then performed to estimate whether the space group is centric or acentric. After that, the program proceeded to make a list of "triplets" using a number of reflections above a preset minimum value of $|\text{EI}|$. A "triplet", in this case, is a set of three reflections whose indices sum to zero, such as,

$$h_1 + h_2 + (\overline{h_1} + \overline{h_2}) = 0$$

where $h_1 = h_1, k_1, l_1$ and $h_2 = h_2, k_2, l_2$. The corresponding phase relationship, called the $\Sigma_2$ relationship, is

$$\phi h_1 + \phi h_2 + \phi(\overline{h_1} + \overline{h_2}) = \phi(h_1, h_2)$$
where $\phi(h_1, h_2)$ is the phase of the relationship which is constant regardless of the choice of the "origin" to which the individual phases are being referred and is usually zero. Each of these relationships is given a weight $\kappa(h_1, h_2)$ which is, in general, proportional to the product of the $\text{IE}^i$'s that make up the relationship.

A special case of the above relationship, called the $\Sigma_1$ relationship, arises when two of the three reflections involved are the same. In such cases, the phase of a reflection can be estimated directly from the intensity data with a given probability that the assigned phase is correct.

After a complete list of $\Sigma_2$ relationships was assembled, the program focused on a set of reflections that participate in a large number of $\Sigma_2$ relationships. Based on the number of $\Sigma_2$ relationships and their corresponding $\kappa$ values, a weight $a_{h_1}$ can be calculated which is an estimation of how reliable the assigned phase is.

Three strong reflections with high $a_{h_1}$ values were then used to define the origin, and for non-centrosymmetric space groups, an additional reflection may be used to fix the enantiomorph. In addition, reflections developed from the $\Sigma_1$ relationships as well as a few more reflections (usually 4 - 6) were chosen as a "starting set". All reflections in the starting set were assigned a phase, and the phases for the other reflections in the data set were derived from the "weighted tangent formula":

$$
\tan \phi_{h_1} = \frac{\Sigma h_2 w_{h_2} w(h_1 + h_2) \kappa(h_1, h_2) \sin (\phi_{h_2} + \phi(h_1 + h_2))}{\Sigma h_2 w_{h_2} w(h_1 + h_2) \kappa(h_1, h_2) \cos (\phi_{h_2} + \phi(h_1 + h_2))}
$$

where $w_i$ is the weight with which each phase $\phi_i$ is estimated.

In this way, a complete set of phases, known as a phase set was obtained. The process then went back to the starting set and some of the phases
were permuted between the possible values. For each permutation, a new phase set is obtained. Among these phase sets, one of them might be the correct solution to the phase problem. In cases of non-centrosymmetric structures, since an infinite number of possible permutations exists, a procedure known as the magic integer method was used to assign the initial phases in the starting set.

Each of these phase sets was evaluated in terms of $R_{\text{Karle}}$ (reliability index), $\psi_0$ (psi-zero) test and the "absolute figure of merit" for internal consistency. These results were appropriately weighted and a combined figure of merit (CFOM) was calculated for every phase set. The program took the phase set with the best CFOM as the default solution.

Finally, an E-map of the unit cell was obtained by Fourier synthesis.

$$\rho(x,y,z) = (V^{-1}) \sum \sum \sum |E| \exp (i\alpha) \exp [-2\pi i(hx+ky+lz)]$$

where $\rho(x,y,z)$ is the electron density at $(x,y,z)$; $\alpha$ is the phase taken from the best phase set and $V$ is volume of the unit cell. A meaningful solution is said to be obtained if some (or all) of the peaks correspond to the molecule under investigation.

Quite often only a partial structure can be located in the E-map from MITHRIL. In these cases, another program called DIRDIF was used to expand the "trial structure". DIRDIF is a direct methods phase refinement and extension program which utilizes the starting phases from the known partial structure to calculate the difference structure factors. It is followed by a Fourier synthesis from which an electron density map is obtained. Additional atoms were located and the procedure was repeated until all or most of the non-hydrogen atoms were available for refinement.
Structure Refinement

The various variables describing the trial structure from MITHRIL or DIRDIF are then refined at this stage in order to obtain a better fit between the observed structure factors and those calculated for the model structure. All structures reported in this thesis are refined by full-matrix least-squares method.\textsuperscript{165} and the function minimized is:

\[ \Sigma w (|F_0| - k|F_c|)^2 \]

where \( w \) is the weight given to each reflection and is derived from the counting statistics:

\[ w = 1 / \sigma^2(F_0) \]

and \( k \) is a factor used to scale the calculated structure factors to match the observed structure factors.

The variables normally refined are the positional and thermal parameters for each atom and the scale factor. All non-hydrogen atoms are refined with anisotropic thermal parameters. The scattering factor for anisotropic thermal motion is expressed as:

\[ f = f_0 \exp (-2\pi^2 \sum \sum U_{ij} h_i h_j a_i^* a_j^*) \]

Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms are taken from the International Tables for X-ray crystallography.\textsuperscript{168} A secondary extinction coefficient \((g)\) may also be refined if necessary.

\[ |F_{o \text{corrected}}| = |F_{o \text{extinction}}| (1 + g |F|^2 Lp) \]
A difference Fourier map is computed after a certain number of refinement cycles. It is an electron density map based on the difference in structure factors between the observed and calculated values.

\[ \rho_o(x,y,z) - \rho_c(x,y,z) = (V^{-1}) \sum \sum \sum (|F_o| - |F_c|) \exp(i\alpha) \exp[-2\pi i (hx + ky + lz)] \]

where \( \alpha \) is the phase of \( F_c \). At this stage, any missing atoms in the model structure (including hydrogen) can hopefully be located from difference maps. Hydrogen atoms may also be calculated and fixed in idealized positions (C-H = 0.95Å or 0.99Å, B_H = 1.2 B_{bonded} atom). In some cases, hydrogen atoms are refined with isotropic thermal parameters.

The refinement is considered converged when the shift in any of the parameters being refined is negligible compared to its standard deviation. The reliability of the model structure can be estimated by some derived quantities:

1. The R-factor, \( R = [\sum |F_o| - |F_c|] / [\sum |F_o|] \).
2. The weighted R-factor, \( R_w = [\sum w (|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} \)
3. The goodness of fit, \( S = [\sum w (|F_o| - |F_c|)^2 / (m-n)]^{1/2} \)

where \( m \) and \( n \) are the number of observations and variables, respectively.
4. The residual peaks in the final difference map.

The closer the R-values to zero, the better the model structure describes the "real" structure, while \( S \) is ideally equal to 1. The residual peaks represent the electron density not accounted for by the model structure.
Treatment of Disorder

A minor disorder in a structure is normally included in the model as split atoms with distributed occupancies. The disordered atoms are then refined isotropically at two or more different positions. The occupancies are normally not refined but are adjusted manually such that the $B_{eq}$ values for these positions are roughly equal. The model is then further refined with anisotropic thermal parameters. The model may have to be further adjusted until a reasonable geometry is reached.

Structure Completion

After the refinement is converged, all bond lengths and angles are derived from the final atomic positions and their standard deviations are estimated from the errors associated with the corresponding parameters used. Molecular structures are drawn using ORTEP with 50% probability ellipsoids.

8.2. 1-(1,1-Dimethylethyl)-2,5-pyrrolidinedione (10)

A crystal of approximate dimensions of 0.15 x 0.15 x 0.20 mm size was chosen for data collection. Crystallographic data of 10 appear in Table 8.1. A monoclinic cell with $Z = 8$ (assuming a density of 1.182 gcm$^{-1}$) was indicated by preliminary measurements. 2631 Reflections were collected of which 2477 were unique and 938 observed ($\geq 3\sigma(I)$). The final unit-cell parameters were obtained by least-squares on the setting angles for 23 reflections with $2\theta = 7.9$ - 19.8°. The data for 10 were processed and corrected for Lorentz and polarization effects. No absorption or decay correction was applied.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2$_1$/n. The structure was solved
by direct methods. The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All hydrogen atoms were fixed in idealized positions (C-H = 0.95Å, B_H = 1.2 B_{bonded atom}). A secondary extinction correction was applied (final coefficient = 7.39 x 10^{-7}). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography. The refinement converged at R = 0.049, R_w = 0.062 for 200 variables (GOF = 1.70; including zeros: R = 0.186, R_w = 0.080), with the largest parameter shift in the final cycle being 0.02σ. The final difference map showed electron density between -0.14 and 0.17 eÅ^{-3}. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.2 - 8.4, respectively.

Table 8.1. Crystallographic Data of 10 and 26

<table>
<thead>
<tr>
<th></th>
<th>10</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_8H_{13}NO_2</td>
<td>C_8H_{13}NO_2</td>
</tr>
<tr>
<td>fw</td>
<td>155.20</td>
<td>155.20</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2_1/n</td>
<td>P2_1/c</td>
</tr>
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<td>a, Å</td>
<td>10.551(4)</td>
<td>9.868(2)</td>
</tr>
<tr>
<td>b, Å</td>
<td>8.342(3)</td>
<td>7.725(1)</td>
</tr>
<tr>
<td>c, Å</td>
<td>19.992(3)</td>
<td>10.963(2)</td>
</tr>
<tr>
<td>β (deg)</td>
<td>97.65(2)</td>
<td>98.78(2)</td>
</tr>
<tr>
<td>V</td>
<td>1743.9(9)</td>
<td>825.8(3)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
<td>ρ_{calc}, g/cm^3</td>
<td>1.182</td>
<td>1.248</td>
</tr>
<tr>
<td>F(000)</td>
<td>672</td>
<td>336</td>
</tr>
<tr>
<td>Radiation</td>
<td>Mo-K_α (λ=0.71069 Å)</td>
<td>Cu-K_α (λ=1.54178 Å)</td>
</tr>
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<td>μ, cm^{-1}</td>
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<td>6.94</td>
</tr>
<tr>
<td>Crystal size, mm</td>
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<td>0.05 x 0.30 x 0.40</td>
</tr>
<tr>
<td>Transmission factors</td>
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<td>0.85-1.00</td>
</tr>
<tr>
<td>Scan type</td>
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<td>ω-29</td>
</tr>
<tr>
<td>Scan range, deg in ω</td>
<td>1.10 + 0.35 tan θ</td>
<td>1.05 + 0.20 tan θ</td>
</tr>
<tr>
<td>Scan speed, deg/min</td>
<td>32</td>
<td>16</td>
</tr>
<tr>
<td>Data collected</td>
<td>+h, +k, ±l</td>
<td>+h, +k, ±l</td>
</tr>
<tr>
<td>2θ_{max}, deg</td>
<td>45</td>
<td>155</td>
</tr>
<tr>
<td>Crystal decay</td>
<td>Negligible</td>
<td>-2.1%</td>
</tr>
<tr>
<td>Total reflections</td>
<td>2631</td>
<td>1913</td>
</tr>
<tr>
<td>Total unique reflections</td>
<td>2477</td>
<td>1813</td>
</tr>
</tbody>
</table>
$R_{\text{merge}}$ & 0.058 & 0.030 \\
No. of reflections with /$\geq 3\sigma$(/) & 938 & 1354 \\
No. of variables & 200 & 105 \\
p-factor & 0.02 & 0.05 \\
$R$ & 0.049 & 0.043 \\
$R_w$ & 0.062 & 0.061 \\
Goodness of fit (gof) & 1.70 & 3.07 \\
Max $\Delta/\sigma$ (final cycle) & 0.02 & 0.00 \\
Residual density $e/\text{Å}^3$ & -0.14 to +0.17 & -0.16 to +0.21 \\

Table 8.2.  
Final atomic coordinates (fractional) and $B_{\text{eq}}$ ($\text{Å}^2$) of compound 10.  

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$B_{\text{eq}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)</td>
<td>0.8492(5)</td>
<td>0.2982(6)</td>
<td>0.5009(2)</td>
<td>10.0(3)</td>
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<tr>
<td>O(2)</td>
<td>0.9258(5)</td>
<td>0.2769(6)</td>
<td>0.7285(2)</td>
<td>9.3(3)</td>
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<td>O(3)</td>
<td>0.2883(4)</td>
<td>0.0619(7)</td>
<td>0.8100(3)</td>
<td>10.1(3)</td>
</tr>
<tr>
<td>O(4)</td>
<td>-0.0855(4)</td>
<td>0.0909(6)</td>
<td>0.8953(2)</td>
<td>7.4(3)</td>
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<td>N(1)</td>
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<td>0.2436(6)</td>
<td>0.6156(2)</td>
<td>4.1(2)</td>
</tr>
<tr>
<td>N(2)</td>
<td>0.1130(4)</td>
<td>0.0319(5)</td>
<td>0.8660(2)</td>
<td>3.9(2)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.8629(6)</td>
<td>0.3416(9)</td>
<td>0.5584(4)</td>
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</tr>
<tr>
<td>C(2)</td>
<td>0.8818(5)</td>
<td>0.5122(8)</td>
<td>0.5814(4)</td>
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<tr>
<td>C(3)</td>
<td>0.8963(5)</td>
<td>0.5075(9)</td>
<td>0.6561(4)</td>
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<td>C(4)</td>
<td>0.8979(6)</td>
<td>0.3334(9)</td>
<td>0.6732(3)</td>
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<td>C(5)</td>
<td>0.8526(5)</td>
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<td>C(6)</td>
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<tr>
<td>C(7)</td>
<td>0.7669(7)</td>
<td>0.0098(8)</td>
<td>0.5507(4)</td>
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<td>C(8)</td>
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<td>0.0107(9)</td>
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</tr>
<tr>
<td>C(9)</td>
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</table>

Table 8.3.  
Bond lengths ($\text{Å}$) of compound 10 with estimated standard deviations.  

<table>
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<th>atom</th>
<th>atom</th>
<th>distance</th>
<th>atom</th>
<th>atom</th>
<th>distance</th>
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<td>C(2)</td>
<td>C(3)</td>
<td>1.481(8)</td>
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<td>1.201(7)</td>
<td>C(3)</td>
<td>C(4)</td>
<td>1.492(9)</td>
</tr>
<tr>
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<td>1.205(6)</td>
<td>C(5)</td>
<td>C(6)</td>
<td>1.499(8)</td>
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<tr>
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<td>C(12)</td>
<td>1.202(6)</td>
<td>C(5)</td>
<td>C(7)</td>
<td>1.521(8)</td>
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<tr>
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<td>C(5)</td>
<td>C(8)</td>
<td>1.525(8)</td>
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<td>C(10)</td>
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<td>1.492(8)</td>
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<tr>
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8.3. Tetrahydro-7,7-dimethyl-1H-azepine-2,5-dione (26)

A crystal of approximate dimensions of 0.05 x 0.30 x 0.40 mm size was chosen for data collection. Crystallographic data of 26 appear in Table 8.1. A monoclinic cell with Z = 4 (assuming a density of 1.248 g cm\(^{-1}\)) was indicated by preliminary measurements. 1913 Reflections were collected of which 1813 were unique and 1354 observed (\(\geq 3\sigma(I)\)). The final unit-cell parameters were obtained by least-squares on the setting angles for 17 reflections with 2\(\theta = 89.7 \text{ to } 105.8^\circ\). The data for 26 were processed,\(^\text{161}\) and corrected for Lorentz and polarization effects. A linear decay correction was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.85 to 1.00).
Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2\(1/c\). The structure was solved by direct methods.\(^{163}\) The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. The amide hydrogen atom, H(13), was refined with isotropic thermal parameters. All the other hydrogen atoms were fixed in idealized positions (C-H = 0.95\(\text{Å}\), \(B_{\text{H}} = 1.2\) \(B_{\text{bonded \ atom}}\)). A secondary extinction correction was applied (final coefficient = 1.37 \(\times\) 10\(^{-5}\)). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography.\(^{168}\) The refinement converged at \(R = 0.043\), \(R_w = 0.061\) for 105 variables (GOF = 3.07; including zeros: \(R = 0.059\), \(R_w = 0.070\)), with the largest parameter shift in the final cycle being 0.00\(\sigma\). The final difference map showed electron density between -0.16 and 0.21 \(\text{e\(\text{Å}^{-3}\)}\). Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.5 - 8.7, respectively.

**Table 8.5.** Final atomic coordinates (fractional) and \(B_{\text{eq}}\) (\(\text{Å}^2\)) of compound 26.

<table>
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<th>(z)</th>
<th>(B_{\text{eq}})</th>
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<tr>
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Table 8.6. Bond lengths (Å) of compound 26 with estimated standard deviations.

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Table 8.7. Bond angles (deg) of 26 with standard deviations

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<td>109.7(1)</td>
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8.4. N-Phenyl-N-(phenylthioxomethyl)benzenepropanamide (16)

A crystal of approximate dimensions of 0.15 x 0.15 x 0.30 mm size was chosen for data collection. Crystallographic data of 16 appear in Table 8.8. An orthorhombic cell with Z = 4 (assuming a density of 1.264 g cm⁻¹) was indicated by preliminary measurements. 2144 Reflections were collected of which 1860 were observed (≥ 3σ(I)). The final unit-cell parameters were obtained by least-squares on the setting angles for 24 reflections with 2θ = 88.6 - 108.6°. The data for 16 were processed and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.81 to 1.00). No decay correction was applied.
Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2₁2₁2₁. The structure was solved by direct methods. The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All the hydrogen atoms were fixed in idealized positions (C-H = 0.95Å, B_H = 1.2 B_{bonded atom}). A secondary extinction correction was applied (final coefficient = 5.68 x 10⁻⁶). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography. The refinement converged at R = 0.029, R_W = 0.039 for 227 variables (GOF = 2.05; including zeros: R = 0.038, R_W = 0.040), with the largest parameter shift in the final cycle being 0.03σ. (The refinement of the other enantiomorph converged at R = 0.040, R_W = 0.053) The final difference map showed electron density between -0.19 and 0.24 eÅ⁻³. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.9 - 8.11, respectively.

**Table 8.8. Crystallographic Data of 16 and 17.**

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</table>

**Table 8.9.**

| Residual density E/\(\AA\)^3 | -0.27 to +0.24 | -0.19 to +0.24 | Max./\(\\sigma\) (final cycle) | goodness of fit (gof) | R-factor | | p-factor | No. of variables | No. of reflections with /2\(\sigma\)(I) | Total reflections | Crystal decay |
|-------------------------------|----------------|----------------|-------------------------------|-------------------|-----------|----------------|---------------|-----------------|----------------|----------------|
| 0.00                          | 0.03           | 0.03           |                               |                   |           |                |               |                 |                |                |
| 1.68                          | 2.05           | 2.05           |                               |                   |           |                |               |                 |                |                |
| 0.049                        | 0.098          | 0.098          |                               |                   |           |                |               |                 |                |                |
| 0.045                        | 0.090          | 0.090          |                               |                   |           |                |               |                 |                |                |
| 0.03                        | 0.02           | 0.02           |                               |                   |           |                |               |                 |                |                |
| 0.02                         | 0.01           | 0.01           |                               |                   |           |                |               |                 |                |                |
| 227                          | 227            | 227            |                               |                   |           |                |               |                 |                |                |
| 1603                          | 1600           | 1600           |                               |                   |           |                |               |                 |                |                |
| 6488                          | 244            | 244            |                               |                   |           |                |               |                 |                |                |
| -1.0%                         | Negligible     | Negligible     |                               |                   |           |                |               |                 |                |                |
| 60                            | 65             | 65             |                               |                   |           |                |               |                 |                |                |
| -1h + k, +l                  | +h, +k, +l     | +h, +k, +l     |                               |                   |           |                |               |                 |                |                |
| 35                            | 35             | 35             |                               |                   |           |                |               |                 |                |                |
| 1.45 ± 0.35° a, e             | 1.31 ± 0.20° a, e | 1.31 ± 0.20° a, e |                               |                   |           |                |               |                 |                |                |

Note: The table provides final atomic coordinates (fractional) and (b(\text{deg}) A^2(\text{g})) of compound 16.
### Table 8.11. Bond angles (deg) of 16 with standard deviations

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<th>Atom 15</th>
<th>Atom 16</th>
<th>Atom 17</th>
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### Table 8.10. Bond lengths (Å) of compound 16 with estimated standard deviations.

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8.5. $N$-[(4-Methoxyphenyl)thioxomethyl]-$N$-phenylbenzenepropanamide (17)

A crystal of approximate dimensions of 0.15 x 0.30 x 0.30 mm size was chosen for data collection. Crystallographic data of 17 appear in Table 8.8. An orthorhombic cell with $Z = 8$ (assuming a density of 1.271 gcm$^{-1}$) was indicated by preliminary measurements. 6498 Reflections were collected of which 1603 were observed ($\geq 3\sigma(I)$). The final unit-cell parameters were obtained by least-squares on the setting angles for 17 reflections with $2\theta = 20.3 - 37.8^\circ$. The data for 17 were processed$^{161}$ and corrected for Lorentz and polarization effects. A linear decay correction was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as Pbca. The structure was solved by direct methods.$^{163}$ The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All the hydrogen atoms were fixed in idealized positions (C-H = 0.95Å, B$_H$ = 1.2 B$_{bonded\ atom}$). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography$^{168}$. The refinement converged at $R = 0.045$, $R_W = 0.049$ for 244 variables (GOF = 1.68; including zeros: $R = 0.273$, $R_W = 0.070$), with the largest parameter shift in the final cycle being 0.00$\sigma$. The final difference map showed electron density between -0.27 and 0.24 eÅ$^{-3}$. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.12 - 8.14, respectively.
Table 8.12. Final atomic coordinates (fractional) and B(eq) (Å²) of compound 17.

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Table 8.13. Bond lengths (Å) of compound 17 with estimated standard deviations.

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Table 8.14. Bond angles (deg) of 17 with standard deviations.

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8.6. \(\text{N-(4-Bromo-2,6-dimethylphenyl)}\)-\(\text{N-(phenylthioxomethyl)}\)benzenepropanamide (18)

A crystal of approximate dimensions of 0.20 x 0.20 x 0.30 mm size was chosen for data collection. Crystallographic data of 18 appear in Table 8.15. An orthorhombic cell with \(Z = 4\) (assuming a density of 1.3874 gcm\(^{-1}\)) was indicated by preliminary measurements. 3119 Reflections were collected of which 1303 were observed (\(\geq 3\sigma(I)\)). The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with \(2\theta = 25.1 - 32.6^\circ\). The data for 18 were processed\(^{161}\) and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.97 to 1.00). A linear decay correction

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was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as Pca2₁. The structure was solved by direct methods. The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All the hydrogen atoms were fixed in idealized positions (C-H = 0.95Å, B>H = 1.2 Bbonds atom). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography. The refinement converged at R = 0.031, R_W = 0.029 for 252 variables (GOF = 1.59; including zeros: R = 0.160, R_W = 0.036), with the largest parameter shift in the final cycle being 0.000. (The refinement of the other polarity converged at R = 0.038, R_W = 0.043) The final difference map showed electron density between -0.23 and 0.38 eÅ⁻³. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.16 - 8.18, respectively.

**Table 8.15. Crystallographic Data of 18 and 19.**

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**Table 8.16.** Final atomic coordinates (fractional) and B(eq) (Å²) of compound 18.

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Table 8.16. Bond angles (deg) of 18 with standard deviations

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Table 8.17. Bond lengths (Å) of compound 18 with estimated standard deviations.
8.7. *N*(4-Bromophenyl)-*N*(phenylthioxomethyl)benzenepropanamide (19)

A crystal of approximate dimensions of 0.30 x 0.40 x 1.00 mm size was chosen for data collection. Crystallographic data of 19 appear in Table 8.15. An monoclinic cell with Z = 4 (assuming a density of 1.406 gcm⁻¹) was indicated by preliminary measurements. 4584 Reflections were collected of which 4569 were unique and 3685 were observed (≥ 3σ(I)). The final unit-cell parameters were obtained by least-squares on the setting angles for 23 reflections with 2θ = 111.3 - 113.9°. The data for 19 were processed,¹⁶¹ and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.54 to 1.00). A linear decay correction was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2₁/a. The structure was solved by direct methods.¹⁶³ The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All the hydrogen atoms were fixed in idealized positions (C-H = 0.95Å, B_H = 1.2 B_bonded_atom). A secondary extinction correction was applied (final coefficient = 8.97 x 10⁻⁶). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography.¹⁶⁸ The refinement converged at R = 0.042, R_w = 0.058 for 236 variables (GOF = 4.12; including zeros: R = 0.053, R_w = 0.059), with the largest parameter shift in the final cycle being 0.00σ. The final difference map showed electron density between -0.65 and 0.69 eÅ⁻³. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.19 - 8.21, respectively.
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Table 8.20. Bond lengths (Å) of compound 19 with estimated standard deviations.

Table 8.19. Final atomic coordinates (fractional) and B(eq) (Å²) of compound 19.
Table 8.21. Bond angles (deg) of 19 with standard deviations.

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<td>C17</td>
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<td>C21</td>
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8.8. N-Phenyl-N-(phenylthioxomethyl)benzamide (49)

A crystal of approximate dimensions of 0.20 x 0.10 x 0.40 mm size was chosen for data collection. Crystallographic data of 49 appear in Table 8.22. An orthorhombic cell with Z = 4 (assuming a density of 1.259 g/cm³) was indicated by preliminary measurements. 1953 Reflections were collected of which 1624 were observed (≥ 3σ(I)). The final unit-cell parameters were obtained by least-squares on the setting angles for 23 reflections with 2θ = 75.3 - 88.7°. The data for 49 were processed, and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.88 to 1.00). A linear decay correction was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.
Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as \( P2_12_12_1 \). The structure was solved by direct methods. The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All the hydrogen atoms were fixed in idealized positions (C-H = 0.95\(\AA\), B\(_H\) = 1.2 \(\text{B}_{\text{bonded atom}}\)). A secondary extinction correction was applied (final coefficient = 5.42 \(\times\) 10\(^{-6}\)). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography. The refinement converged at \( R = 0.036, R_W = 0.052 \) for 209 variables (GOF = 2.45; including zeros: \( R = 0.053, R_W = 0.057 \)), with the largest parameter shift in the final cycle being 0.000. (The refinement of the other enantiomorph converged at \( R = 0.045, R_W = 0.062 \)) The final difference map showed electron density between -0.15 and 0.12 e\(\AA\)^{-3}. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.23 - 8.25, respectively.

### Table 8.22. Crystallographic Data of 49 and 37.

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<td>Cu-K(_\alpha) ((\lambda=1.54178\ \AA))</td>
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<td>6.07</td>
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<td>0.25 x 0.10 x 0.50</td>
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Table 8.23. Final atomic coordinates (fractional) and B(eq) (Å²) of compound 49.

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Table 8.24. Bond lengths (Å) of compound 49 with estimated standard deviations.

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Table 8.25. Bond angles (deg) of 49 with standard deviations.

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<th>atom</th>
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<td>C9</td>
<td>C10</td>
<td>119.1(4)</td>
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<tr>
<td>C1</td>
<td>N1</td>
<td>C14</td>
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<td>C10</td>
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<tr>
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<td>C14</td>
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<td>S1</td>
<td>C1</td>
<td>N1</td>
<td>123.0(2)</td>
<td>C11</td>
<td>C12</td>
<td>C13</td>
<td>120.0(4)</td>
</tr>
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<td>C8</td>
<td>C13</td>
<td>C12</td>
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<td>C14</td>
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8.9. 4-[2,4,6-tris(1-methylethyl)benzoyl]benzoic Acid (S)-(-)-Proline Complex (37)

A crystal of approximate dimensions of 0.25 x 0.10 x 0.50 mm size was chosen for data collection. Crystallographic data of 37 appear in Table 8.22. An monoclinic cell with Z = 4 (assuming a density of 1.175 gcm⁻¹) was indicated by preliminary measurements. 5859 Reflections were collected of which 5564 were unique and 3640 were observed (≥ 3σ(I)). The final unit-cell parameters were
obtained by least-squares on the setting angles for 21 reflections with \(2\theta = 46.8 - 59.0^\circ\). The data for 37 were processed,\(^{161}\) and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.94 to 1.00). A linear decay correction was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as \(P2_1\). The structure was solved by direct methods.\(^{163}\) The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. The two carboxylic acid hydrogen atoms, H(73) and H(74), were fixed in positions determined from difference Fourier syntheses. All the other hydrogen atoms were fixed in idealized positions (\(C-H = 0.95\AA\), \(B_H = 1.2 B_{\text{bonded atom}}\)). A secondary extinction correction was applied (final coefficient = 8.09 x 10\(^{-7}\)). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography.\(^{168}\) The refinement converged at \(R = 0.058\), \(R_W = 0.056\) for 613 variables (GOF = 3.73; including zeros: \(R = 0.111\), \(R_W = 0.058\)), with the largest parameter shift in the final cycle being 0.49\(\sigma\). The absolute configuration of 37 was based on the (S)-proline auxiliary. The final difference map showed electron density between -0.21 and 0.23 e\(\AA^{-3}\). Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.26 - 8.28, respectively.

**Table 8.26.** Final atomic coordinates (fractional) and \(B(\text{eq})\) (\(\AA^2\)) of compound 37.

<table>
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Table 8.27.  Bond lengths (Å) of compound 37 with estimated standard deviations.

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*Table 8.28: Bond angles (deg) of 37 with standard deviations.*
8.10. Phenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione (14)

A crystal of approximate dimensions of 0.40 x 0.30 x 0.60 mm size was chosen for data collection. Crystallographic data of 14 appear in Table 8.29. An monoclinic cell with Z = 4 (assuming a density of 1.059 g cm\(^{-3}\)) was indicated by preliminary measurements. 6476 Reflections were collected of which 6135 were unique and 2062 were observed (\(\geq 3\sigma(I)\)). The final unit-cell parameters were obtained by least-squares on the setting angles for 24 reflections with \(2\theta = 29.9 - 36.2^\circ\). The data for 14 were processed,\(^{161}\) and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.93 to 1.00). A linear decay correction was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as \(P2_1/n\). The structure was solved by direct methods.\(^{163}\) The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All the hydrogen atoms were fixed in idealized positions (\(C-H = 0.95\AA, B_H = 1.2\) \(B_{bonded\ atom}\)). A secondary extinction correction was applied (final coefficient = \(3.09 \times 10^{-7}\)). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography.\(^{168}\) The refinement converged at \(R = 0.051, R_W = 0.067\) for 209 variables (GOF = 2.06; including zeros: \(R = 0.197, R_W = 0.081\)), with the largest parameter shift in the final cycle being 0.000\(\sigma\). The final difference map showed electron density between -0.17 and 0.24 e\(\AA^{-3}\). Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.30 - 8.32, respectively.
Table 8.29. Crystallographic Data of 14 and 15.

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Table 8.30. Final atomic coordinates (fractional) and B(eq) (Å{2}) of compound 14.

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### Table 8.32: Bond angles (deg) of 14 with standard deviations.

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### Table 8.33: Bond lengths (Å) of compound 14 with estimated standard deviations.

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8.11. 4-Methoxyphenyl[2,4,6-tris(1-methylethyl)phenyl]methanethione (15)

A crystal of approximate dimensions of 0.20 x 0.15 x 0.30 mm size was chosen for data collection. Crystallographic data of 15 appear in Table 8.29. An monoclinic cell with Z = 4 (assuming a density of 1.118 gcm\(^{-1}\)) was indicated by preliminary measurements. 4777 Reflections were collected of which 4546 were unique and 2736 were observed (≥ 3σ(I)). The final unit-cell parameters were obtained by least-squares on the setting angles for 3 reflections with 2θ = 76.4 - 76.5°. The data for 15 were processed,\(^{161}\) and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.91 to 1.00). No decay correction was applied.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2\(_1\)/n. The structure was solved by direct methods (SHELXS86).\(^{169}\) The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All the hydrogen atoms were refined isotropically. A secondary extinction correction was applied (final coefficient = 2.86 x 10\(^{-6}\)). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography.\(^{168}\) The refinement converged at R = 0.045, R\(_W\) = 0.048 for 347 variables (GOF = 2.83; including zeros: R = 0.094, R\(_W\) = 0.052), with the largest parameter shift in the final cycle being 0.15σ. The final difference map showed electron density between -0.19 and 0.25 eÅ\(^{-3}\). Final
atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.33 - 8.35, respectively.

Table 8.33. Final atomic coordinates (fractional) and B(eq) (Å²) of compound 15.

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Table 8.34. Bond lengths (Å) of compound 15 with estimated standard deviations.

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Table 8.35. Bond angles (deg) of 15 with standard deviations.

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8.12. 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylphosphine oxide) ethanol complex (64·EtOH)

A crystal of approximate dimensions of 0.20 x 0.20 x 0.40 mm size was chosen for data collection. Crystallographic data of 64·EtOH appear in Table 8.36. An orthorhombic cell with Z = 4 (assuming a density of 1.238 g·cm⁻¹) was indicated by preliminary measurements. 4024 Reflections were collected of which 3275 were observed (≥ 3σ(I)). The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 57.1 - 81.7°. The data for 64·EtOH were processed, and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.91 to 1.00). A
linear decay correction was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2₁2₁2₁. The structure was solved by direct methods.¹⁶³ The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. The hydrogen atom of the ethanol OH group was not located. All the other hydrogen atoms were fixed at idealized positions (C-H = 0.95Å, B_H = 1.2 B_bonded_atom). A secondary extinction correction was applied (final coefficient = 5.07 x 10⁻⁶). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography ¹⁶⁸. The refinement converged at R = 0.038, R_W = 0.040 for 425 variables (GOF = 2.57; including zeros: R = 0.060, R_W = 0.041), with the largest parameter shift in the final cycle being 0.00σ. (The refinement of the other enantiomorph converged at R = 0.046, R_W = 0.048) The final difference map showed electron density between -0.23 and 0.30 eÅ⁻³. The ethanol molecule is found to be highly disordered. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.37 - 8.39, respectively.

Table 8.36. Crystallographic Data of 64•EtOH and 64•iPrOH.

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Table 8.36: Bond lengths (Å) of compound 64+ EtOH with estimated standard deviations.
Table 8.39. Bond angles (deg) of 64•EtOH with standard deviations.

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8.13. 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylphosphine oxide) 2-propanol complex (64·iPrOH)

A crystal of approximate dimensions of 0.10 x 0.10 x 0.10 mm size was chosen for data collection. Crystallographic data of 64·iPrOH appear in Table 8.36. An orthorhombic cell with Z = 4 (assuming a density of 1.239 g cm⁻¹) was indicated by preliminary measurements. 4110 Reflections were collected of which 2616 were observed (> 3σ(I)). The final unit-cell parameters were obtained by least-squares on the setting angles for 24 reflections with 2θ = 25.3 - 48.0°. The data for 64·iPrOH were processed, and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.96 to 1.00). No decay correction was applied.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2₁2₁2₁. The structure was solved by direct methods (SHELX86). The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses. The iso-propanol molecule is found to be highly disordered. One of the methyl groups of the iso-propanol molecule was modelled by splitting the total population into two different positions, C(41a) and C(41b), with occupancies 72.2% and 27.8% respectively. C(41a) and C(41b) were refined isotropically. All the other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom of the iso-propanol OH group was not located. All the other hydrogen atoms were fixed at idealized positions (C-H = 0.95Å, B_H = 1.2 B_bonded atom). The populations of the hydrogen atoms attached to C(41a) and C(41b) were given the same value as the carbon atom they are attached. A secondary extinction correction was applied (final coefficient = 9.49 x 10⁻⁷). Neutral atom scattering
factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography. The refinement converged at $R = 0.047$, $R_w = 0.051$ for 433 variables (GOF = 2.56; including zeros: $R = 0.108$, $R_w = 0.055$), with the largest parameter shift in the final cycle being $0.02\sigma$. (The refinement of the other enantiomorph converged at $R = 0.051$, $R_w = 0.054$) The final difference map showed electron density between -0.23 and 0.24 eÅ$^{-3}$. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.40 - 8.42, respectively.

**Table 8.40.** Final atomic coordinates (fractional) and $B$(eq) (Å$^2$) of compound 64-IPrOH.

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**Table 8.4.** Bond lengths (Å) of compound 64.147.0 with estimated standard deviations.
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8.14. 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylphosphine oxide) Ethyl Acetate complex (64•EtOAc)

A crystal of approximate dimensions of 0.15 x 0.05 x 0.30 mm size was chosen for data collection. Crystallographic data of 64•EtOAc appear in Table 8.43. An monoclinic cell with Z = 4 (assuming a density of 1.254 gcm⁻³) was indicated by preliminary measurements. 8247 Reflections were collected of which 8001 were unique and 5327 were observed (≥ 3σ(I)). The final unit-cell parameters were obtained by least-squares on the setting angles for 21 reflections with 2θ = 86.0 - 101.8°. The data for 64•EtOAc were processed, and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.80 to 1.00). No decay correction was applied.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2₁/c. The structure was solved by Patterson methods (DIRDIF92 PATTY). The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All the hydrogen atoms were fixed in idealized positions (C-H = 0.95Å, B_H = 1.2 B_bonded atom). A secondary extinction correction was applied (final coefficient = 1.45 x 10⁻⁶). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography. The refinement converged at R = 0.049, R_w = 0.058 for 452 variables (GOF = 2.98; including zeros: R = 0.120, R_w = 0.085), with the largest parameter shift in the final cycle being 0.02σ. The final difference map showed electron density between -0.41 and 0.27 eÅ⁻³. Final atomic coordinates and
equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.44 - 8.46, respectively.

Table 8.43. Crystallographic Data of 64*EtOAc and 22*acetone

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Table 8.44. Final atomic coordinates (fractional) and B(eq) (Å²) of compound 64*EtOAc.

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<tr>
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<td>0.3600(4)</td>
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<td>0.006(2)</td>
<td>0.3160(5)</td>
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</tr>
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<td>Atom</td>
<td>Atom</td>
<td>Atom</td>
<td>Atom</td>
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<td>------</td>
<td>------</td>
</tr>
<tr>
<td>O1</td>
<td>O2</td>
<td>O3</td>
<td>O4</td>
<td>O5</td>
</tr>
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<tr>
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<td>C40</td>
<td>C39</td>
<td>C38</td>
<td>C37</td>
</tr>
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<td>C33</td>
<td>C32</td>
<td>C31</td>
<td>C30</td>
</tr>
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<td>C24</td>
<td>C23</td>
<td>C22</td>
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<td>C18</td>
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<td>1.39(2)</td>
<td>1.40(2)</td>
</tr>
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</table>

Table 8.46: Bond angles (deg) of 6+6 and 6+4 with standard deviations.
8.15. 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol)

Acetone complex (22\textsuperscript{acetone})

A crystal of approximate dimensions of 0.30 x 0.20 x 0.50 mm size was chosen for data collection. Crystallographic data of 22\textsuperscript{acetone} appear in Table 8.43. A monoclinic cell with Z = 4 (assuming a density of 1.177 g\textpercm\textsuperscript{3}) was indicated by preliminary measurements. 7883 Reflections were collected of which 7449 were unique and 4831 were observed (≥ 3σ(I)). The final unit-cell parameters were obtained by least-squares on the setting angles for 24 reflections with 2θ = 88.2 - 102.9°. The data for 22\textsuperscript{acetone} were processed,\textsuperscript{161} and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.95 to 1.00). A linear decay correction was applied based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2\textsubscript{1}/n. The structure was solved
by Patterson methods. The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. The acetone molecule is found to be disordered and the non-hydrogen atoms on it were refined at two different positions with populations of 60.6% and 39.4%. All hydrogen atoms on the diol molecule were refined with isotropic thermal parameters. Hydrogen atoms on the disordered acetone were fixed in idealized positions (C-H = 0.95Å, B_H = 1.2 B_bonded atom). A secondary extinction correction was applied (final coefficient = 2.69 x 10^-6). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography. The refinement converged at R = 0.043, R_w = 0.046 for 599 variables (GOF = 2.81; including zeros: R = 0.081, R_w = 0.052), with the largest parameter shift in the final cycle being 0.31σ. The final difference map showed electron density between -0.15 and 0.15 eÅ^-3. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.47 - 8.49, respectively.

Table 8.47. Final atomic coordinates (fractional) and B(eq) (Å^2) of compound 22-acetone.

<table>
<thead>
<tr>
<th>atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>B(eq)</th>
</tr>
</thead>
<tbody>
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<td>0.2962(1)</td>
<td>0.21001(7)</td>
<td>0.20797(9)</td>
<td>4.07(6)</td>
</tr>
<tr>
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<td>0.4399(1)</td>
<td>0.12036(7)</td>
<td>0.27571(8)</td>
<td>4.48(6)</td>
</tr>
<tr>
<td>O(3a)</td>
<td>1.4397(6)</td>
<td>0.0541(2)</td>
<td>0.4201(3)</td>
<td>9.1(2)</td>
</tr>
<tr>
<td>O(3b)</td>
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<td>0.0583(4)</td>
<td>0.3970(5)</td>
<td>12.9(6)</td>
</tr>
<tr>
<td>C(1)</td>
<td>0.8535(2)</td>
<td>0.2628(1)</td>
<td>0.1497(1)</td>
<td>4.9(1)</td>
</tr>
<tr>
<td>C(2)</td>
<td>0.9761(2)</td>
<td>0.2342(2)</td>
<td>0.1632(1)</td>
<td>6.1(1)</td>
</tr>
<tr>
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<tr>
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<td>0.1337(1)</td>
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<tr>
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<tr>
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Table 8.48. Bond lengths (Å) of compound 22-acetone with estimated standard deviations.

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<th>distance</th>
<th>atom</th>
<th>atom</th>
<th>distance</th>
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<td>C(20)</td>
<td>1.389(3)</td>
</tr>
<tr>
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<td>C(19)</td>
<td>C(24)</td>
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</tr>
<tr>
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<td>C(20)</td>
<td>C(21)</td>
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<tr>
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<td>C(43b)</td>
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<td>C(21)</td>
<td>C(22)</td>
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</tr>
<tr>
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<td>C(2)</td>
<td>1.389(3)</td>
<td>C(22)</td>
<td>C(23)</td>
<td>1.370(4)</td>
</tr>
<tr>
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<td>C(13)</td>
<td>1.384(3)</td>
<td>C(23)</td>
<td>C(24)</td>
<td>1.385(3)</td>
</tr>
<tr>
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<td>C(3)</td>
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</tr>
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<tr>
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</tr>
<tr>
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<td>C(15)</td>
<td>1.379(3)</td>
<td>C(28)</td>
<td>C(29)</td>
<td>1.367(3)</td>
</tr>
<tr>
<td>C(6)</td>
<td>C(7)</td>
<td>1.375(4)</td>
<td>C(29)</td>
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<tr>
<td>C(7)</td>
<td>C(8)</td>
<td>1.392(3)</td>
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<td>C(32)</td>
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Table 8.4. Bond angles (deg) of 22-actone with standard deviations.

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<td>1.59 (2)</td>
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<td>1.51 (2)</td>
<td>1.52 (2)</td>
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<td>1.50 (2)</td>
<td>1.51 (2)</td>
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<td>1.51 (2)</td>
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<td>1.51 (2)</td>
<td>1.52 (2)</td>
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<td>1.51 (2)</td>
<td>1.52 (2)</td>
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8.16. 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol)

   Ethanol complex (22*EtOH)

   A crystal of approximate dimensions of 0.15 x 0.20 x 0.40 mm size was chosen for data collection. Crystallographic data of 22*EtOH appear in Table 8.50. A monoclinic cell with Z = 4 (assuming a density of 1.191 g cm$^{-3}$) was indicated by preliminary measurements. 7575 Reflections were collected of which 7261 were unique and 4799 were observed ($\geq 3\sigma(I)$). The final unit-cell parameters were obtained by least-squares on the setting angles for 22 reflections with $2\theta = 90.0 - 108.5^\circ$. The data for 22*acetone were processed$^{161}$ and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.91 to 1.00). No decay correction was applied.

   Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2$_1$/n. The structure was solved by direct methods (SHELX86)$^{169}$ The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. All hydrogen atoms on the diol molecule were refined with isotropic thermal parameters. Hydrogen atoms on the disordered ethanol molecule were fixed in idealized positions (C-H = 0.99Å, B$_H =$
1.2 Bonded atom. A secondary extinction correction was applied (final coefficient = 2.69 x 10^{-6}). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray crystallography \superscript{168}. The refinement converged at $R = 0.056$, $R_w = 0.060$ for 557 variables (GOF = 3.80; including zeros: $R = 0.090$, $R_w = 0.061$), with the largest parameter shift in the final cycle being 0.04$\sigma$. The final difference map showed electron density between -0.35 and 0.34 eÅ$^{-3}$. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.51 - 8.53, respectively.

Table 8.50. Crystallographic Data of 22*EtOH and 22*toluene.

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<td>fw</td>
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<td>Monoclinic</td>
</tr>
<tr>
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<td>P2$_1$/c</td>
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<td>10.703(2)</td>
</tr>
<tr>
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<tr>
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</tr>
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<td>3679(1)</td>
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<td>4</td>
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<td>1400</td>
</tr>
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<td>Cu-K$_\alpha$ ($\lambda$=1.54178 Å)</td>
</tr>
<tr>
<td>$\mu$, cm$^{-1}$</td>
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<td>5.15</td>
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<td>0.94 + 0.20 tan $\theta$</td>
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<td>$+h$, $+k$, $\pm l$</td>
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<td>Total unique reflections</td>
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<td>3414</td>
</tr>
<tr>
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<td>$R_w$</td>
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</table>

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Table 8.51.  Final atomic coordinates (fractional) and B(eq) (Å²) of compound 22-EtOH.

<table>
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<th>x</th>
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</tr>
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</tr>
<tr>
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8.17. 9,10-Dihydro-9,10-ethenoanthracene-11,12-bis(diphenylmethanol)

Toluene complex (22\textsuperscript{toluene})

A crystal of approximate dimensions of 0.10 x 0.10 x 0.20 mm size was chosen for data collection. Crystallographic data of 22\textsuperscript{toluene} appear in Table 8.50. A monoclinic cell with \(Z = 4\) (assuming a density of 1.193 g cm\(^{-1}\)) was indicated by preliminary measurements. 8395 Reflections were collected of which 7980 were unique and 3414 were observed \((\geq 3\sigma(I))\). The final unit-cell parameters were obtained by least-squares on the setting angles for 22 reflections with \(2\theta = 50.8 - 85.9^\circ\). The data for 22\textsuperscript{toluene} were processed,\textsuperscript{161} and corrected for Lorentz and polarization effects. Absorption correction (empirical, based on azimuthal scans for three reflections) was also applied (transmission factors: 0.85 to 1.00). A polynomial decay correction was applied.

| C(9) | C(11) | C(12) | 112.8(2) | C(26) | C(25) | C(30) | 118.2(3) |
| C(9) | C(11) | C(17) | 115.6(2) | C(25) | C(26) | C(27) | 121.6(3) |
| C(12) | C(11) | C(17) | 131.4(2) | C(28) | C(27) | C(28) | 119.7(3) |
| C(10) | C(12) | C(11) | 112.1(2) | C(27) | C(28) | C(29) | 120.0(3) |
| C(10) | C(12) | C(18) | 117.8(2) | C(28) | C(29) | C(30) | 120.0(3) |
| C(11) | C(12) | C(18) | 130.0(2) | C(25) | C(30) | C(29) | 120.5(3) |
| C(1) | C(13) | C(9) | 127.5(2) | C(18) | C(31) | C(32) | 122.2(2) |
| C(1) | C(13) | C(14) | 119.7(2) | C(18) | C(31) | C(36) | 120.1(3) |
| C(9) | C(13) | C(14) | 112.8(2) | C(32) | C(31) | C(36) | 117.7(3) |
| C(4) | C(14) | C(10) | 127.6(2) | C(31) | C(32) | C(33) | 121.9(3) |
| C(4) | C(14) | C(13) | 120.9(2) | C(32) | C(33) | C(34) | 119.6(4) |
| C(10) | C(14) | C(13) | 111.5(2) | C(33) | C(34) | C(35) | 120.0(4) |
| C(10) | C(15) | C(10) | 127.2(2) | C(34) | C(35) | C(36) | 120.1(4) |
| C(10) | C(15) | C(16) | 112.6(2) | C(31) | C(36) | C(35) | 120.5(4) |
| C(8) | C(16) | C(9) | 127.8(2) | C(18) | C(37) | C(38) | 122.8(2) |
| C(8) | C(16) | C(15) | 120.9(3) | C(18) | C(37) | C(42) | 118.8(2) |
| C(9) | C(16) | C(15) | 111.3(2) | C(38) | C(37) | C(42) | 118.3(3) |
| O(1) | C(17) | C(11) | 112.0(2) | C(37) | C(38) | C(39) | 121.1(3) |
| O(1) | C(17) | C(19) | 104.8(2) | C(38) | C(39) | C(40) | 119.6(3) |
| O(1) | C(17) | C(25) | 107.5(2) | C(39) | C(40) | C(41) | 120.3(3) |
| C(11) | C(17) | C(19) | 105.9(2) | C(40) | C(41) | C(42) | 119.9(3) |
| C(11) | C(17) | C(25) | 112.5(2) | C(37) | C(42) | C(41) | 120.8(3) |
| C(19) | C(17) | C(25) | 113.9(2) | O(3) | C(43) | C(44) | 147.5(8) |
| O(2) | C(18) | C(12) | 107.5(2) |
based on the intensities of three standard reflections, measured every 200 reflections throughout the data collection.

Based on E-statistics and subsequent successful structure solution and refinement, the space group was determined as P2_1/c. The structure was solved by direct methods (SHELX86). The non-hydrogen atoms were determined from E-maps or from subsequent difference Fourier syntheses and were refined with anisotropic thermal parameters. The two hydroxyl hydrogen atoms, H(1) and H(2), were refined with isotropic thermal parameters. All the other hydrogen atoms were fixed in idealized positions (C-H = 0.95 Å, B_H = 1.2 B_bonded atom). A secondary extinction correction was applied (final coefficient = 4.93 x 10^{-7}). Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for X-ray Crystallography. The refinement converged at R = 0.052, R_w = 0.069 for 469 variables (GOF = 2.10; including zeros: R = 0.147, R_w = 0.080), with the largest parameter shift in the final cycle being 0.01σ. The final difference map showed electron density between -0.20 and 0.30 eÅ^{-3}. Final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, and bond angles appear in Tables 8.54 - 8.56, respectively.

Table 8.54. Final atomic coordinates (fractional) and B(eq) (Å^2) of compound 22-toluene.

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Table 8.55. Bond lengths (Å) of compound **22·toluene** with estimated standard deviations.

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