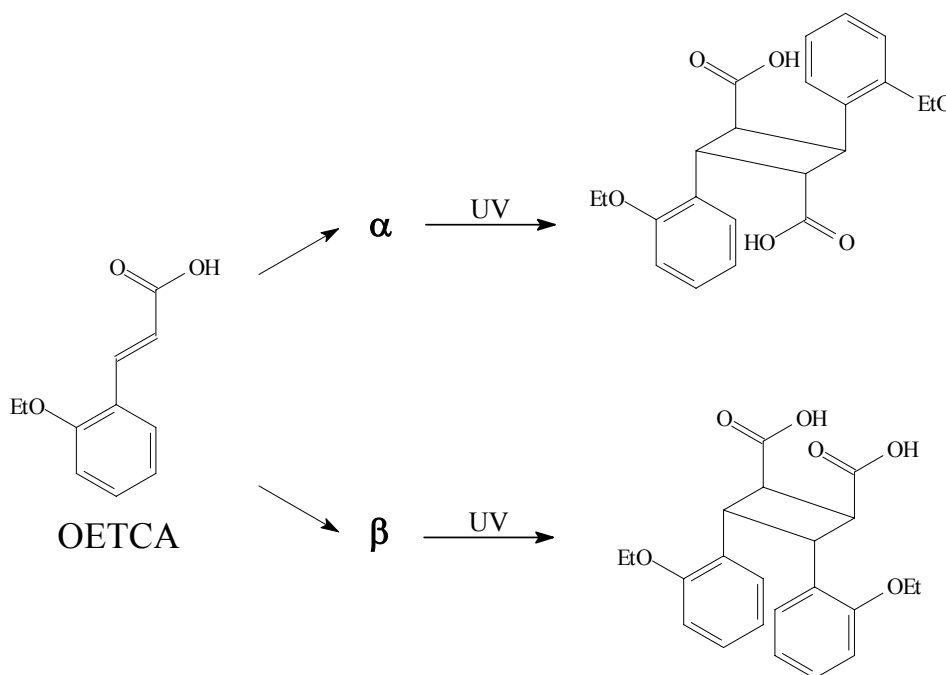


Chapter 4: Photodimerization Products of the α - and β -Polymorphs of *ortho*-Ethoxy-*trans*-cinnamic acid

4.1 Introduction

Having described in detail the structure of the various previously known polymorphs of OETCA, this chapter focuses on the crystal structures of the recrystallized photodimerization products obtained by the UV irradiation of the α - and β -polymorphs (Scheme 4.1). Four crystal structures are presented: the α -photodimer (2,2'-diethoxy- α -truxillic acid), β -photodimer (2,2'-diethoxy- β -truxinic acid), a solvate of the α -photodimer and a crystal containing the β -photodimer complexed to calcium. In addition to being interesting by themselves, the structures of the photodimers also provide significant insight into the reaction and phase transformation mechanism in the photodimerization of the various polymorphs, which will be covered in detail in the next few chapters. The nature and importance of C-H...O, C-H... π and π ... π interactions in these structures is also highlighted.



Scheme 4.1

4.1 Methods for Chapter 4

4.2.1 Crystal Growth

The α -polymorph was grown by slow evaporation from a saturated solution of OETCA in ethyl acetate at room temperature (25 °C) to yield prism-like crystals. A small amount (about 0.2 g) of the polymorph was then exposed to UV light ($\lambda = 350$ nm) using the TL09N fluorescent lamp until full conversion to the α -photodimer had occurred. Recrystallizing the photoproduct from DMF yielded very small crystals in a few days that were not quite good enough for a single crystal study. A subsequent attempt to recrystallise the photodimer from DMSO yielded crystals suitable for diffraction after a few months. Gopalan and Kulkari (2001) have also published the structure of the photodimer in which crystals were grown from hot acetic acid. It is not possible to dissolve the photoproduct in any other conventional solvent such as acetone, methanol or ethanol. In a serendipitous discovery, some crystals of the photodimer which had been dissolved in deuterated DMSO (DMSO-d₆) were discovered in an NMR tube that had been lying around for over a year. These were much larger and better formed than those that were grown intentionally from DMSO. Single crystal X-ray diffraction revealed that this was a pseudo polymorph or solvate of the α -photodimer.

A saturated solution of OETCA in benzene at 290 K was placed in a fume hood in order to evaporate the solvent off quickly. This yielded hexagonal needle like crystals of the β -benzene polymorph. A small amount of the polymorph was then exposed to UV light using the TL09N fluorescent lamp until full conversion to the β -photodimer had occurred. Crystals of the β -product were grown by slow evaporation from a saturated solution in ethyl acetate, to yield soft prism-like crystals. Crystals of the Calcium β -product salt were grown from fractions collected from a silica

column during a purification attempt. The Calcium was introduced into the mixture from an unknown source probably from the column itself.

4.2.2 X-ray Structural Analysis

Intensity data were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo K_{α} radiation (50kV, 30mA). The collection method involved ω -scans of width 0.3° . Data reduction was carried using the program *SAINT+* (Bruker, 1999a). Structures were solved by direct methods using *SHELXTL* (Bruker, 1999b). Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using *SHELXTL*.

With the exception of the carboxyl hydrogen atoms, all hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. When possible (structures RX, RXS and some hydrogen atoms in Ca-complex), the carboxyl hydrogen atoms were located from the difference map and allowed to ride on their parent atoms. All hydrogen atoms were refined isotropically.

The β -dimer (BRX) crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit. The two molecules exhibit a large amount of disorder which occurs around all the carboxylic acid groups and one of the ethoxy groups in each molecule. Each of these groups was refined over three positions using SADI and DFIX restraints. Attempts to collect a low temperature diffraction data set were unsuccessful as a phase transition occurs at about 253 K.

Data for the crystal structures are given in Table 4.1.

TABLE 4.1

Crystallographic Data

	RX (recrystallised α -photodimer)	RXS (α -photodimer DMSO-d6 solvate)	BRX (recrystallised β -photodimer)	Ca-complex (Calcium complexed with β -photodimer)
Chemical formula	$C_{22}H_{24}O_6$	$C_{22}H_{24}O_6 \cdot$ $2(C_2H_6OS)$	$C_{22}H_{24}O_6$	$C_{23.11}H_{27.22}Ca_{0.50}O_7$
Formula weight	384.41	540.67	384.41	437.24
Crystal system	Monoclinic	Triclinic	Triclinic	Tetragonal
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P4_2/n$
T, K	293(2)	173(2)	293(2)	173(2)
a, Å	8.3547(6)	7.5855(10)	9.9443(17)	20.562(2)
b, Å	8.4793(6)	8.5492(11)	14.671(2)	20.562(2)
c, Å	14.1958(11)	11.5069(15)	15.615(3)	10.2793(16)
α , deg	90	98.897(3)	115.082(3)	90
β , deg	106.810(2)	91.536(2)	93.380(3)	90
γ , deg	90	109.563(3)	90.175(3)	90
V , Å ³	962.69(12)	692.20(16)	2058.7(6)	4346.0(9)
Z	2	1	4	8
ρ_{calcd} , g cm ⁻³	1.326	1.297	1.240	1.336
R	0.054	0.045	0.073	0.040
Rw	0.125	0.123	0.248	0.124
S	1.100	1.056	1.060	1.095

4.3 Results and Discussion

The results and discussion is broken up into two sections. In section one the structures of the α -photodimer and its pseudo polymorph are discussed, while in section two the structures of the β -photodimer and a related calcium coordinated β -photodimer crystal are discussed.

4.3.1 Section 1 - Structure of the α -Photodimer and its Pseudo Polymorph

4.3.1.1 Crystal Growth and Molecular Structure

In 1964 the solid-state photochemical product of the α -polymorph (2,2'-diethoxy- α -truxillic acid) was discovered and described [Cohen & Schmidt, 1964; Cohen *et al.*, 1964; Schmidt, 1964]. The crystal structure was, however, not reported.

In this study the photodimerization reaction was carried out and several attempts were made to recrystallise the photoproduct. Recrystallizing the photoproduct from DMF yielded very small crystals in a few days that were not quite good enough for a single-crystal study. A subsequent attempt to recrystallise the photodimer from DMSO yielded crystals suitable for diffraction after a few months - referred to in this chapter as RX. Gopalan and Kulkari (2001) have also published the structure of the photodimer in which crystals were grown from hot acetic acid. An ORTEP diagram for this product as determined in this study is shown in Fig 4.1. Like the γ -polymorph of OETCA the carboxylic hydrogen atom is disordered about oxygen O11 and O12. The site occupancy factor for the carboxylic hydrogen was found to be about 60% at position H110 and 40% at position H120.

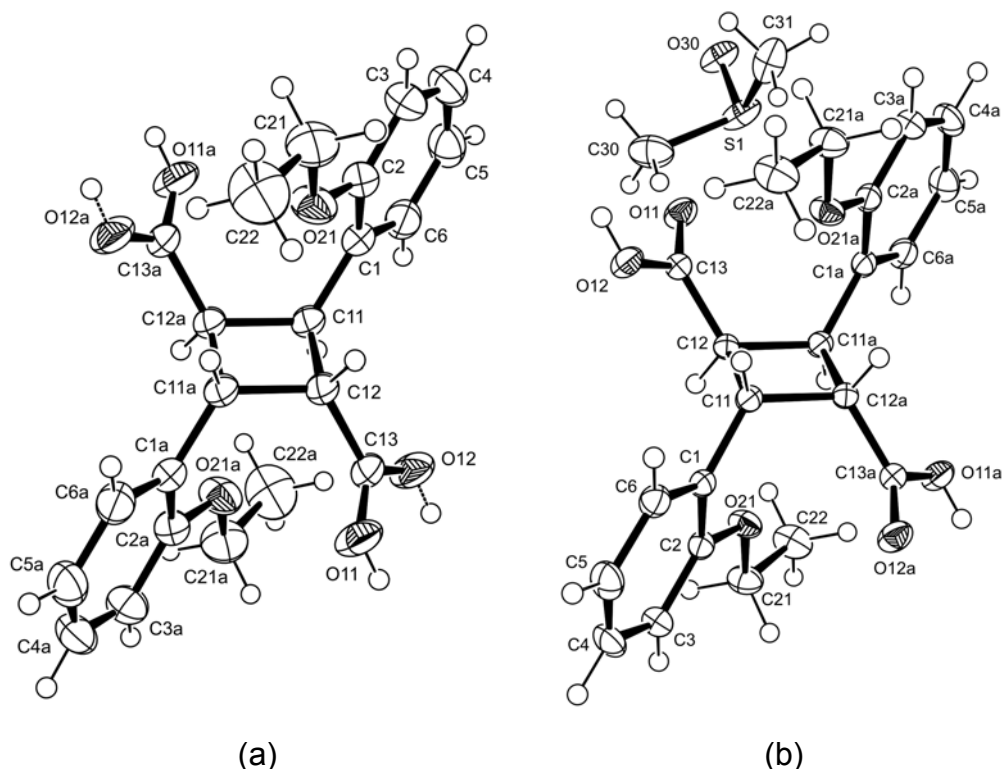


Figure 4.1: ORTEP diagram (50% probability level) of (a) the recrystallized photodimer product - RX - from the reaction of the α -polymorph (the α -photodimer), and (b) the α -photodimer solvate recrystallized from DMSO-d₆ in an NMR tube - RXS.

In a serendipitous discovery, some crystals of the photodimer which had been dissolved in deuterated DMSO (DMSO-d₆) were discovered in an NMR tube that had been lying around for over a year - referred to in this chapter as RXS. These were much larger and better formed than those that were grown intentionally from DMSO. Crystals from the NMR tubes were around 1 mm in size while the RX crystals (unsolvated α -photodimer) grown by slow evaporation from DMSO were around 0.3-0.5 mm in size. RX crystals grown from DMF were smaller than 0.1 mm in size. Crystals grown in the NMR tube are prismatic in shape and appear above the solution near the top of the tube (Fig. 4.2). The crystals are therefore most likely grown *via* a deposition process from the solvent vapor.

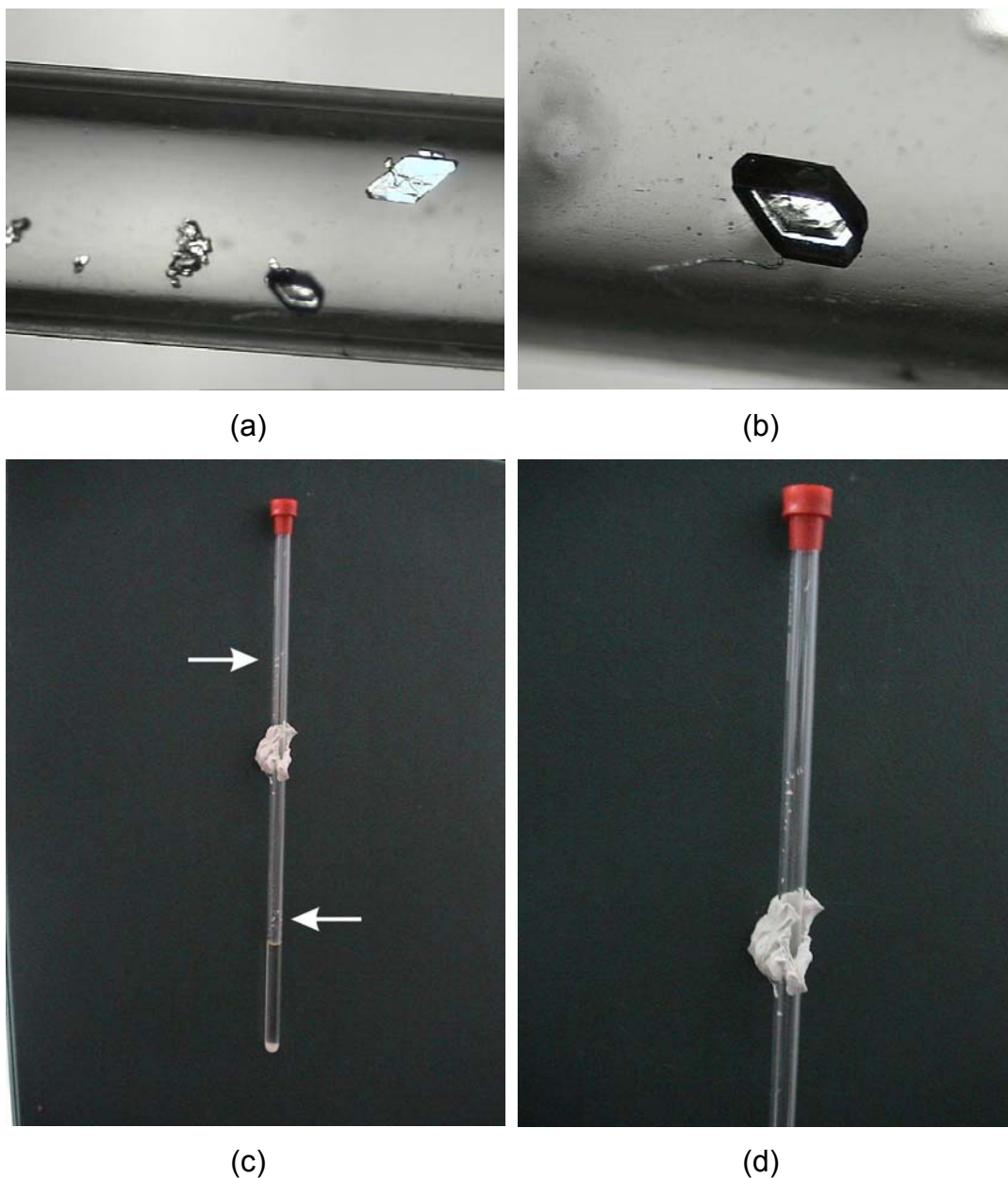


Figure 4.2: Photographs of crystals grown from DMSO-d₆ in an NMR tube. The white blob is Prestik[®] which was used to hold the NMR tube in place against a dark background. Arrows indicate the position of some of the crystals.

Examination *via* single crystal diffraction revealed that the crystals were composed of the photodimer which had co-crystallized with DMSO-d₆ molecule in a photodimer to DMSO-d₆ ratio of 1:2 (Fig. 4.1b).

Despite the molecules (dimers) in the pseudo polymorph having a completely different crystal environment, there are very few conformational differences between the two photodimer molecules (Fig. 4.3). Most of the differences occur around the carboxylic acid groups and this is presumably due to the different hydrogen bond pattern in the pseudo polymorph. The RX and GK [the α -photodimer structure grown from acetic acid and reported by Gopalan and Kulkari (2001)] photodimers have almost exactly the same conformation indicating the choice of solvent has not affected the final molecular conformation in these crystals. Ethoxy groups are arranged such that they lie above and below the plane of the cyclobutane ring. Also, the cyclobutane ring of both structures lies on a center of inversion in their respective crystal structures.

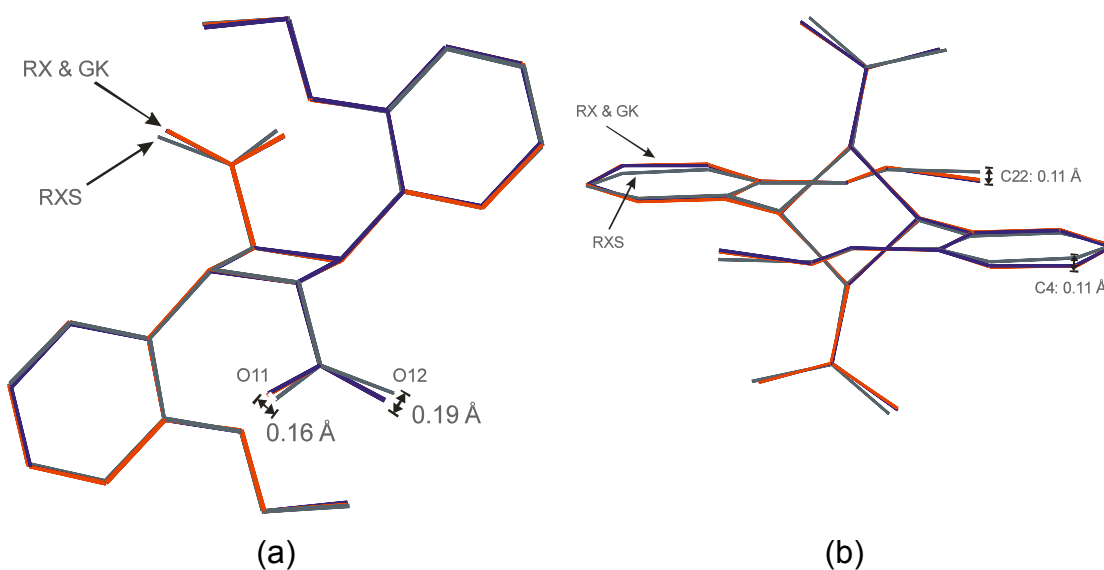


Figure 4.3: Superimposition of photodimer product recrystallized from DMSO (RX), acetic acid (GK) and the DMSO-d6 solvate (RXS).

4.3.1.2 Hydrogen Bonding, Weak Interactions and Crystal Packing

Examination of the hydrogen bond network for the unsolvated α -dimer (RX) revealed that molecules are hydrogen bonded to each other via the $R_2^2(8)$ rings derived from the parent monomer crystal. This leads to a polymeric type structure in which molecules are hydrogen bonded to each

other to form an infinite chain of molecules running parallel to the *a* axis (Fig. 4.4). The insolubility of the photodimer may be due to the inability of most solvents to break up the hydrogen bond network (see β -dimer in section two for a comparison). CH...O interactions play a relatively minor role in the stabilization of the structure.

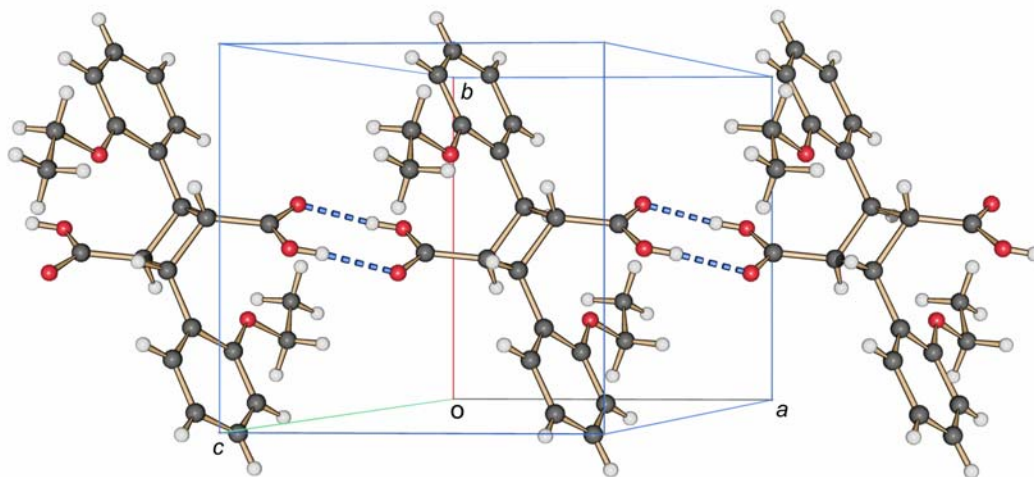


Figure 4.4: Hydrogen bonded carboxylic acid photodimer chain, running parallel to the *a* axis, chain identified in the RX crystal structure of 2,2'-diethoxy α -truxillic acid.

Photodimer molecules in RXS do not hydrogen bond to each other but are instead hydrogen bonded to two DMSO-*d*₆ molecules - one per carboxylic acid (Table 4.2 and Fig. 4.5). The first level graph set in this case is D, one for each strong (or classical) hydrogen bond, instead of the $R_2^2(8)$ rings of the RX polymorph (or every other structure reported in this thesis). In effect two strong O...O hydrogen bonds have been lost and these are instead compensated for by the presence of C-H...O interactions.

Table 4.2

Hydrogen bonding geometry in the α -dimer recrystallised from DMSO (RX), from acetic acid (GK; Gopalan & Kulkarni, 2001) and from deuterated DMSO-d₆ in an NMR tube (RXS). For comparison purposes the hydrogen bonding geometries in the α -, β - and γ -polymorphs are also included.

Structure	<i>D</i> -H... <i>A</i>	<i>D</i> -H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> -H... <i>A</i>
RX	O11-H110...O12 ⁱ	0.78(4)	1.86(4)	2.640(2)	174(3)
GK	O2-H1...O1 ⁱ	1.00(4)	1.63(4)	2.628(3)	176(4)
RXS	O12-H120...O30 ⁱⁱ	0.81(3)	1.81(3)	2.6135(19)	172(4)
α	O11-H11...O12 ⁱⁱⁱ	0.84	1.80	2.637(2)	172
β	O12-H110...O11 ^{iv}	0.84	1.78	2.618(2)	177
γ	O11-H110...O12 ^v	0.84	1.80	2.6249(17)	165

i) [2-x,-y,-z]; ii) [x,y,-1+z]; iii) [-x+2, -y, -z+1]; iv) [-x+1, -y, -z+3]; v) [-x+1/2, -y+7/2, -z]

C-H...O interactions between the DMSO-d₆ molecules and between the DMSO-d₆ molecule and photodimer molecule act to stabilize the structure (Fig. 4.5 and Table 4.3). O-H...O and C-H...O interactions are shorter in the RXS structure than in the RX and GK structures. C-H...O interactions are especially significant in the RXS structure with the shortest C...O distance being 3.352(3) Å compared to 3.489(3) Å in the GK structure. The RXS structure contains four structure reinforcing C-H...O interactions with a C...O distance less than 3.489(3) Å (Table 4.3). By comparison the α - and γ -polymorph structures both contain one C-H...O interaction with a C...O distance of 3.4 Å.

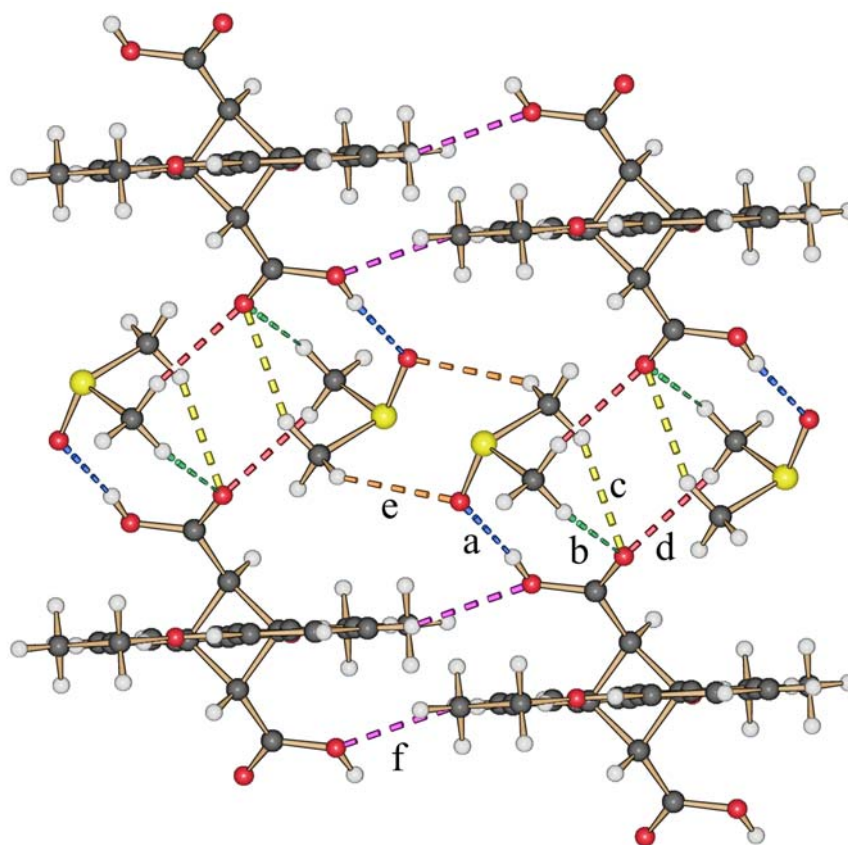


Figure 4.5: The extensive network of O-H...O and C-H...O hydrogen bonding in the RXS. The hydrogen bond network forms a layer of molecules parallel to the $[\bar{1} 1 0]$ plane. Labeled interactions represent various C-H...O interactions; (a): H120...O30 (blue), (b): H30A...O11 (green), (c): H31C...O11 (yellow), (d): H30B...O11 (red), (e): H31A...O30 (orange) and (f): H5...O12 (pink) - see Table 4.3 for details.

Table 4.3

C-H...O interaction geometry (less than sum of vdw radii) in the α -photodimer recrystallized from DMSO (RX), from acetic acid (GK; Gopalan & Kulkarni, 1990) and from deuterated DMSO in an NMR tube (RXS). For comparison purposes the C-H...O interaction geometries in the α -, β - and γ -polymorphs are also included.

Structure	D-H...A	D-H	H...A	D...A	D-H...A
RX	C5-H5...O11 ⁱ	0.93	2.76	3.556(3)	144
	C22-H22B...O12 ⁱⁱ	0.96	2.65	3.505(3)	149
GK	C4-H4...O2 ⁱⁱⁱ	0.93(3)	2.71(3)	3.500(4)	144(2)
	C11-H10...O1 ^{iv}	1.00(3)	2.60(3)	3.489(3)	148(3)
RXS	C30-H30A...O11 ^v	0.98	2.52	3.397(3)	149
	C30-H30B...O11 ^{vi}	0.98	2.42	3.352(3)	160
	C31-H31C...O11 ^v	0.98	2.53	3.413(3)	150
	C31-H31A...O30 ^{vii}	0.98	2.68	3.435(3)	135
	C5-H5...O12 ^{vii}	0.95	2.64	3.563(3)	163
α	C5-H5...O12 ^{viii}	0.95	2.76	3.645(3)	155
α	C6-H6...O11 ^{ix}	0.95	2.55	3.413(3)	151
γ	C5-H5...O12 ^x	0.95	2.76	3.665(2)	160
γ	C6-H6...O11 ^x	0.95	2.60	3.403(2)	143

i) $[-1/2+x, 1/2-y, -1/2+z]$; ii) $[-1/2+x, 1/2-y, 1/2+z]$; iii) $[x, 1/2-y, 1/2+z]$; iv) $[-1+x, 1/2-y, -1/2+z]$; v) $[x, y, 1+z]$; vi) $[1-x, 1-y, -z]$; vii) $[-x, -y, 1-z]$; viii) $[x, y-1, z]$; ix) $[-x+2, -y-1, -z+1]$; x) $[x-1/2, y-1/2, z]$

While the RX structure is related to the monomer crystal *via* its $R_2^2(8)$ hydrogen bonded dimers and hence to the direct photochemical product, the RXS structure can be thought of as being related to the dimer molecule when dissolved in DMSO solution, i.e. the hydrogen bonding pattern observed in the RXS crystal structure may be similar to that of the dimer when dissolved in DMSO.

One of the consequences of the loss of the extra O-H...O hydrogen bond, and in spite of all the extra C-H...O interactions, is that the RXS structure has a lower crystal density (1.297 g cm^{-3} at 173 K) when compared to that of the RX structure (1.326 g cm^{-3} at 293 K).

In addition to weak hydrogen bonding, other forces keeping both structures together are $\pi\cdots\pi$ and C-H... π interactions. Some examples of these interactions in the RX structure of the α -photodimer are shown in Fig. 4.6. Shortest centroid to centroid distances, between the phenyl rings involved in a $\pi\cdots\pi$ interaction, are 3.851(1) and 3.788(1) Å for the RX and RXS structures, respectively, while the closest H to centroid distance, between C-H hydrogens and phenyl rings involved in C-H... π interactions, is 3.200 (H22C... π) and 2.923 Å (H31B... π) for the RX and RXS structures, respectively.

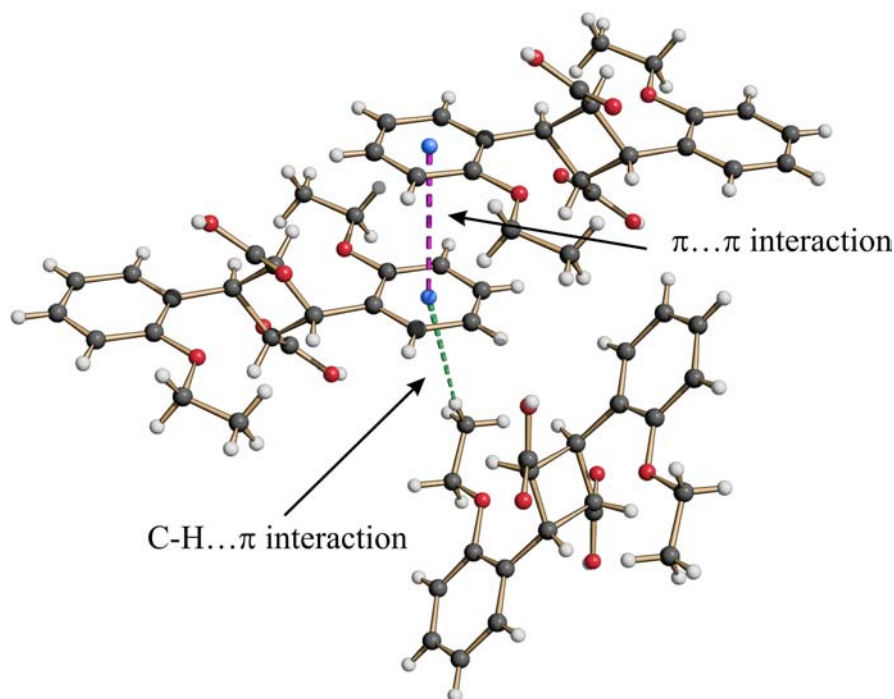


Figure 4.6: Weak interactions between α -photodimer molecules in the RX structure.

4.3.2.1 Molecular Structure

This deviation from planarity, in the β -photodimer, is probably due to phenyl and carboxylic acid groups lying in an eclipsed or *cis* position with respect to each other. In the α -photodimer, the phenyl and carboxylic acid groups are arranged in a staggered or *trans* position with respect to each other, thereby minimizing the ring strain. This might explain why attempts to carry out single-crystal-to-single-crystal solid-state photodimerization reactions in the β -solvates were unsuccessful. Though it was possible to maintain the crystal habit during the reaction process, the reacted crystals were never able to yield useful single-crystal diffraction patterns but yielded powder rings instead. While the closest inter C=C distance in the β -solvates is about 4 Å, which favors a solid-state reaction, these upon reacting and forming the β -photodimer may distort the local structure so that long range order is eventually lost but enough short range order is maintained to yield a powder pattern.

Table 4.4

RMS deviation from planarity values for the cyclobutane rings from various crystal structures

Structure	Deviation from mean plane (Å)
β photodimer (C11A-C12A-C11B-C12B)	0.1241
β photodimer (C11C-C12C-C11D-C12D)	0.1200
Ca- β photodimer (C11-C12-C11A-C12A)	0.1056
RX (C11-C12-C11-C12) ^a	0
RXS (C11-C12-C11-C12) ^a	0

a) The molecule lies on a center of inversion.

4.3.2.2 Hydrogen Bonding, Weak Interactions and Crystal Packing

The crystal structure of the β -dimer has two unique molecules (for convenience referred to here as molecule 1 and 2) in the asymmetric unit. Each of these molecules is hydrogen bonded, through $R_2^2(8)$ carboxylic acid linkages, to the other molecule in the asymmetric unit. This results in a hydrogen bonded chain, made up of an alternate arrangement of molecules 1 and 2, running parallel to the a axis of the unit cell (Fig. 4.8). Though this chain is similar to that in the α -photodimer, and the hydrogen bond distance is also very similar, about 2.7 Å in the β -photodimer (Table 4.5) and 2.63 Å in the α -photodimer, the β -photodimer is soluble in methanol, acetone and ethyl acetate amongst other solvents. By contrast the α -photodimer was only found to be soluble in DMF, DMSO and acetic acid. The fact that the α -photodimer is centrosymmetric and hence does not have a dipole moment suggests that it should be more soluble in relatively non-polar solvents. In comparison the non-centrosymmetric β -photodimer should be less soluble in non-polar solvents. That the opposite solubility trend is observed suggests that it is due to differences in the two crystal structures - most probably due to differences in the hydrogen bonding and crystal packing. The comparative instability of the hydrogen bond linkages in the β -photodimer (and hence increased solubility) may be due to the strain inherent in the molecular structure. Crystal densities for α - and β -photodimers are 1.326 and 1.240 g cm⁻³ (both at 293 K), respectively, indicating that crystal packing is less efficient in the β -photodimer. This extra space around the molecules may affect the solubility of the β -photodimer, as the structure is more accessible to solvent molecules due to increased porosity and possibly surface area. It also leads to the observed disorder. The location of the disordered ethoxy groups in the structure is shown in Figs. 4.8 and 4.9. The disordered ethoxy groups lie in between the carboxylic acid groups of neighbouring hydrogen bonded chains suggesting that the disorder in the ethoxy and carboxylic acid groups are linked. The ethoxy groups which are not

disordered can be found in a region of the structure which is further stabilized by C-H... π interactions between ethoxy and phenyl groups of neighboring hydrogen bonded chains (Fig. 4.9). Shortest phenyl ring centroid to centroid distances are 4.836(3) Å - more than 1 Å longer than in the two α -photodimer structures - indicating the absence of π ... π interactions. However, C-H... π interactions are prevalent in this structure, with H to phenyl ring centroid distances of 2.896 (H4D... π), 3.187 (H21A... π), 2.903 (H21B... π) and 3.241 Å (H4D... π). These distances are comparable to those in the α -photodimer structures.

Table 4.5

Hydrogen bond geometry in the β -photodimer (Å, °)

<i>D-H...A</i>	<i>D-H</i>	<i>H...A</i>	<i>D...A</i>	<i>D-H...A</i>
O11A-H1A...O12C ⁱ	0.82	1.87	2.670(14)	164.5
O11E-H1E...O12H ⁱ	0.82	1.89	2.69(3)	166.9
O11F-H1F...O12G ⁱ	0.82	1.85	2.662(15)	170.2
O11B-H1B...O12D ⁱⁱ	0.82	1.90	2.721(15)	176.5
O11I-H1I...O12L ⁱⁱ	0.82	1.85	2.67(2)	179.2
O11J-H1J...O12K ⁱⁱ	0.82	1.89	2.71(2)	176.4
O11C-H1C...O12A ⁱⁱⁱ	0.82	1.88	2.696(13)	174.6
O11G-H1G...O12F ⁱⁱⁱ	0.82	1.89	2.705(18)	178.5
O11H-H1H...O12E ⁱⁱⁱ	0.82	1.86	2.67(3)	176.3
O11D-H1D...O12B ^{iv}	0.82	1.86	2.661(16)	165.5
O11K-H1K...O12J ^{iv}	0.82	1.86	2.67(2)	168.8
O11L-H1L...O12I ^{iv}	0.82	1.92	2.73(2)	168.7

i) [x+1,y+1,z+1]; ii) [x,y+1,z+1]; iii) [x-1,y-1,z-1]; iv) [x,y-1,z-1]

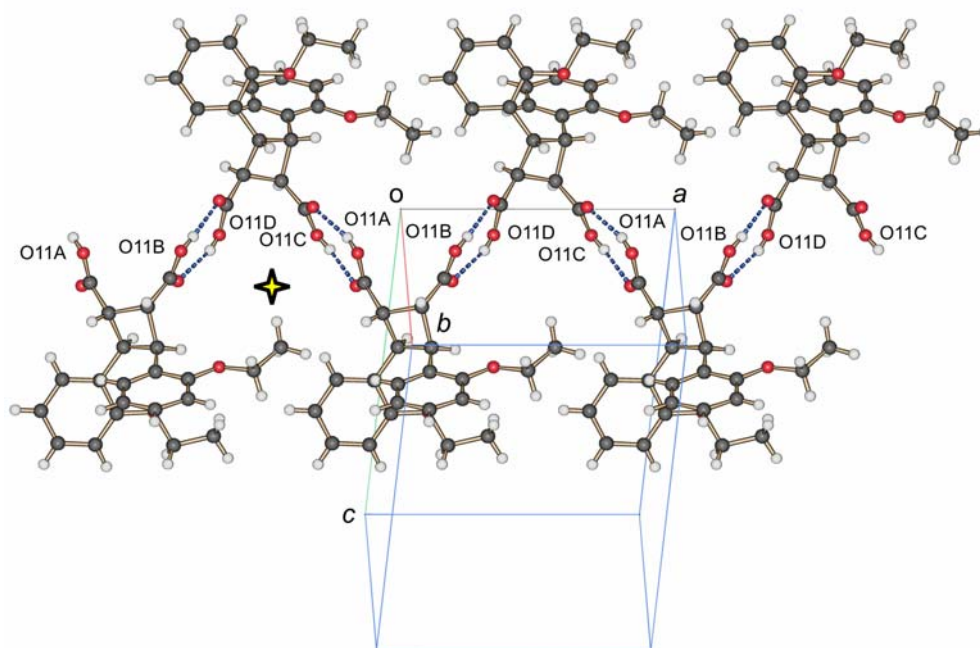


Figure 4.8: Hydrogen bonding in β -photodimer (BRX) showing the chain of alternating molecules running parallel to the a axis. The star indicates the position of the disordered ethoxy group on a neighboring photodimer chain. See Fig. 4.9.

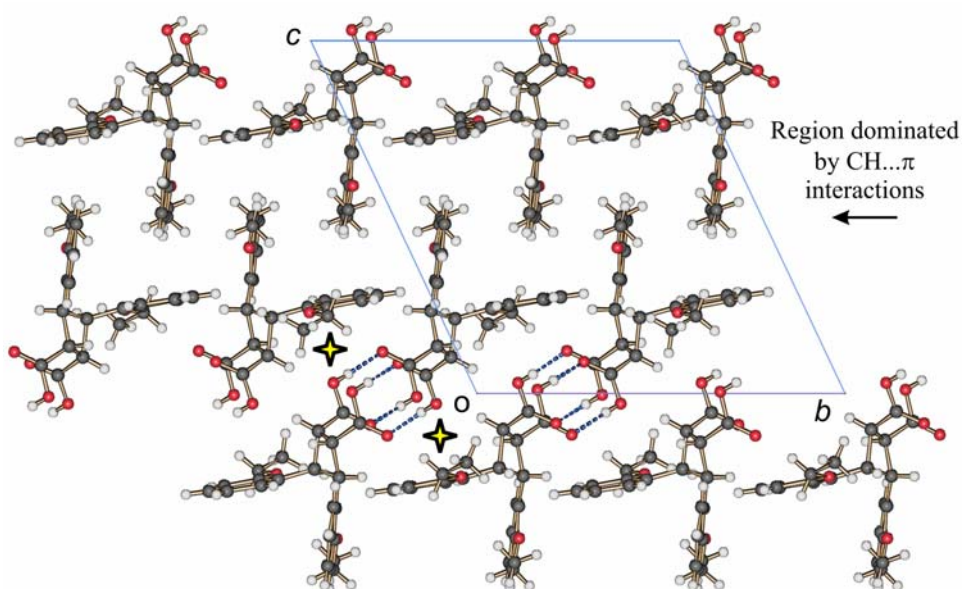


Figure 4.9: C-H... π interactions in the β -photodimer (BRX). The star indicates the position of the disordered ethoxy group on a neighboring photodimer chain. These lie in between the carboxylic acid groups of a neighboring hydrogen bonded chain. See Fig. 4.8.

4.3.2.3 Molecular Structure of a Ca Salt of the β -Photodimer

In another serendipitous discovery, a small number of crystals containing the β -photodimer coordinated to calcium were obtained during a purification process involving chromatography through a silica column (Fig. 4.10). This result reveals some interesting new avenues for future work (outside the scope of the current thesis) where metals could be used as directing agents for molecules to be involved in a photochemical reaction. The source of the calcium is unknown but may have come from the column itself. Attempts to repeat the synthesis were unsuccessful. The β -photodimer in this structure is ordered, with a carboxylate group (previously a carboxylic acid group) bound to the calcium atom through both oxygen atoms and a carboxylic acid group bound to a calcium atom through one of its oxygen atoms. The carboxylic acid group is also involved in a hydrogen bond to the carboxylate anion of a neighboring molecule (Fig. 4.11).

Though additional characterization was not possible (due to the small quantity of crystals obtained), the best structure solution was obtained using disordered water and ethanol molecules, both bound to the calcium atom. These were refined in partial occupancy in the same coordination site such that their occupancies summed up to unity. However, the shape and size of the ellipsoids around the ethanol molecule suggests that another solvent such as methanol may also be coordinated. With two carboxylate groups (total charge: 2-) bound to the calcium atom (charge: 2+), the complex is neutral. Like the β -photodimer, discussed above, the cyclobutane ring is also distorted from planarity (see Table 4.4)

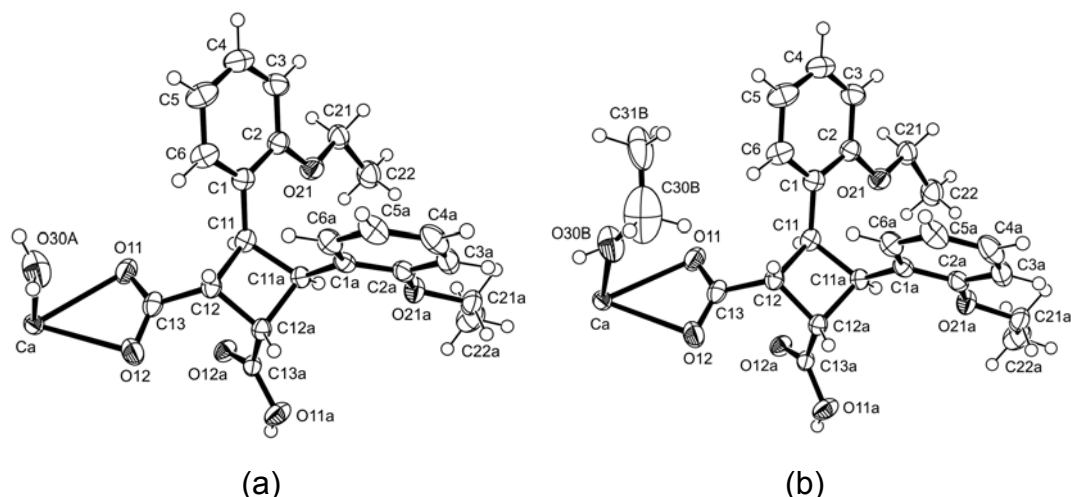


Figure 4.10: ORTEP (50% probability level) of the Ca-complex showing (a) the calcium atom coordinated to a water molecule and (b) the calcium atom coordinated to an ethanol molecule.

In the Ca-complex, pairs of calcium atoms are held together by photodimer molecules - one on the carboxylic acid end and one on the carboxylate end. Each calcium atom is coordinated to two carboxylate and two carboxylic acid groups such that four photodimer molecules are coordinated to each calcium atom. This produces an alternating chain of calcium atoms and photodimer molecules forming a polymeric chain parallel to the *c* axis of the structure (Fig. 4.10 and 4.11). One could view the two photodimer molecules connected at each end to equivalent calcium atoms as one 'link' in the chain.

Oxygen to calcium distances for the Ca-complex are listed in Table 4.6. The shortest distances are to the water (or ethanol) oxygen atom followed by the ketone oxygen of the carboxylic acid. A search for Ca-OH₂ distances¹ using the CSD (Version 5.25; Allen, 2002) and Vista indicates that the Ca to water distances in the Ca-complex structure are typical (Fig. 4.12).

¹ Structures containing the fragment Ca-OH₂ were searched for and the Ca...O distance recorded.

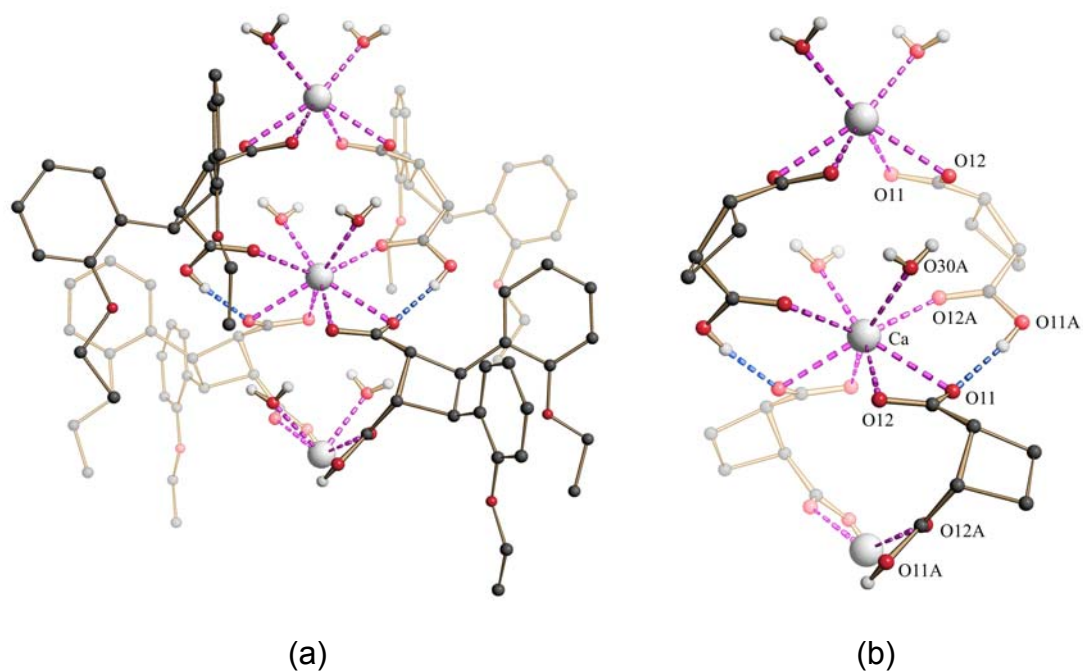


Figure 4.11: Diagram showing the coordination sphere around the calcium atom (ethanol molecule removed for clarity). Each β -photodimer molecule coordinates with two calcium atoms creating a chain of molecules running parallel to the c axis - see Fig. 4.13. The blue dotted line, between O11A and O11, indicates a hydrogen bond between neighboring dimer molecules. All the ethoxy groups point in the same direction along the chain.

Table 4.6

Oxygen to Ca distances

Bond	Distance
Ca-O11	2.546(2)
Ca-O12	2.497(2)
Ca-O12A ⁱ	2.442(1)
Ca-O30A	2.397(2)
Ca-O30B	2.397(2)

i) $[-y+1, x-1/2, z+1/2]$

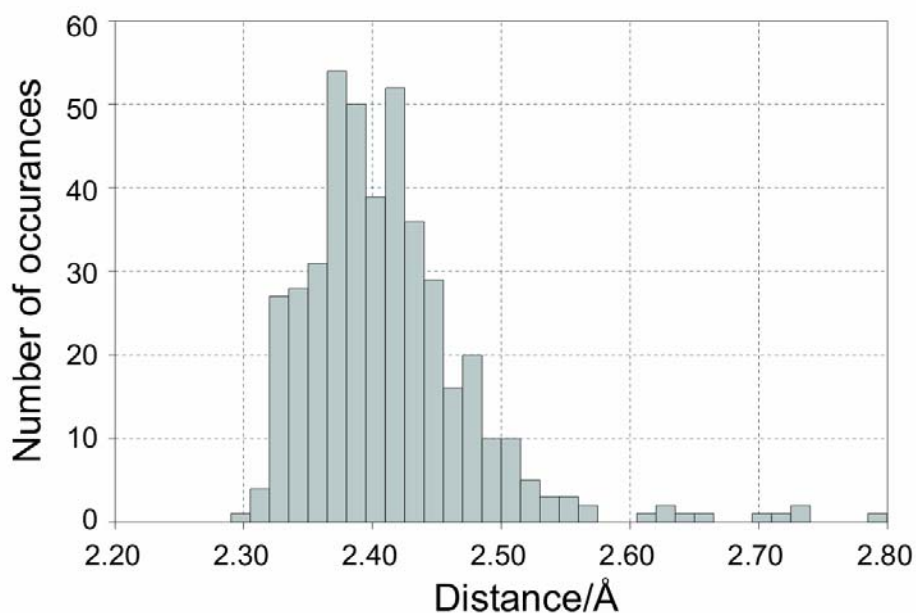


Figure 4.12: Distribution of Ca-OH₂ distances as extracted from the Cambridge Structural Database (CSD).

4.3.2.4 Hydrogen Bonding, Weak Interactions and Crystal Packing

The structure of the Ca-complex is unique amongst the structures reported here in that only intramolecular hydrogen bonding occurs, i.e. all hydrogen bonding occurs within the chain. A list of hydrogen bonds is given in Table 4.7. Only one hydrogen bond occurs between the two β -photodimer molecules (Fig. 4.11 and Table 4.7), the remaining hydrogen bonds occur between the water or ethanol molecules and the carboxylic and carboxylate groups of nearby photodimer molecules (Table 4.7).

Since no hydrogen bonding occurs between neighboring chains (Fig. 4.13), other interactions have to stabilize the structure. The shortest phenyl ring centroid to centroid distance is 4.808(1) indicating the absence of $\pi \cdots \pi$ interactions. Like the β -photodimer, the structure is instead dominated by C-H $\cdots\pi$ interactions with distances of 2.686 (H21B $\cdots\pi$), 2.859 (H21D $\cdots\pi$), 3.372 (H22C $\cdots\pi$) and 3.121 Å (H22D $\cdots\pi$), respectively.

Table 4.7

Hydrogen bond geometry in the Ca-complex ($\text{\AA}$, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O11A-H1A $\cdots$ O11 ⁱ	0.84	1.75	2.586(2)	171.0
O30A-H30B $\cdots$ O11 ⁱⁱ	0.84	2.30(4)	2.938(2)	132(5)
O30A-H30A $\cdots$ O12 ⁱⁱⁱ	0.84	2.11(3)	2.886(2)	154(6)
O30A-H30B $\cdots$ O12A ⁱⁱ	0.84	2.77(5)	3.047(2)	101(4)
O30B-H30C $\cdots$ O11 ⁱⁱ	0.84	2.20	2.938(2)	146.8
O30B-H30C $\cdots$ O12A ⁱⁱ	0.84	2.65	3.047(2)	110.7

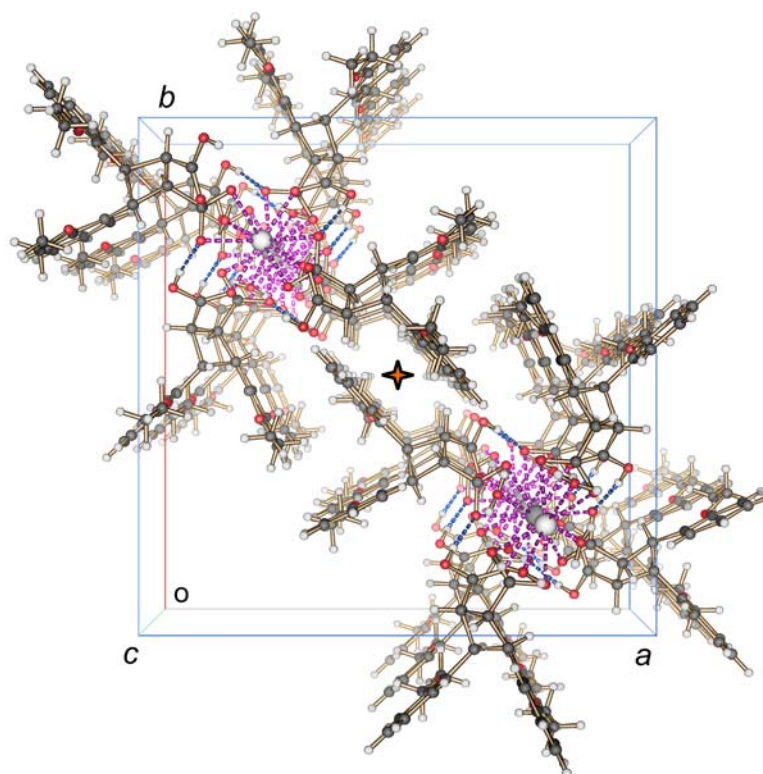
i) $[y+1/2, -x+1, z-1/2]$; ii) $[y+1/2, -x+1, z+1/2]$; iii) $[-y+1, x-1/2, z+1/2]$ 

Figure 4.13: Ca-complex chains running parallel to the c axis. The area indicated by the star is dominated by $C-H\cdots\pi$ interactions between phenyl and ethoxy groups from the neighboring chains. The blue dotted lines indicate intramolecular hydrogen bonds between H1A and O11 - see also Fig. 4.11 and Table 4.7.

4.4 Conclusion

In the pure α - and β -photodimer structures the common mode of hydrogen bonding is the $R_2^2(8)$ carboxylic acid linkage, forming a chain of hydrogen bonded molecules running parallel to one of the unit cell axes. In the α -photodimer, these hydrogen bonded linkages are extremely strong, such that the material is only soluble in very polar solvents, such as DMF and DMSO, but not in solvents such as acetone and ethanol. By contrast, the crystal structure of the β -photodimer is more open and the molecules under more strain. This results in the structure having a lower crystal density when compared to the α -photodimer and undergoes a solid-state phase transition when cooled below 253 K. The lower crystal density and the strain present in the β -photodimer may make this structure more soluble in solvents such as ethyl acetate and ethanol. The solubility of crystals of the β -photodimer may also relate to groups 'exposed' on the crystal faces. The pseudo polymorph or solvated α -photodimer, has a hydrogen pattern very different to that of the α -photodimer. In this case the α -photodimer molecule is hydrogen bonded on both sides to a DMSO molecule. The loss of two O-H...O interactions is compensated for by the presence of extra weak C-H...O interactions. The discovery of a calcium complex of the β -photodimer suggests that future work, where metals are used as directing agents for molecules involved in a photochemical reaction, might yield interesting results.