Photodimerization of the α'-polymorph of *ortho*-ethoxy-*trans*-cinnamic acid in the solid state. I. Monitoring the reaction at 293 K

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Structural changes that occur during the [2 + 2] photodimerization of the metastable α'-polymorph of *ortho*-ethoxy-*trans*-cinnamic acid at 293 K are presented here. Crystals of the α'-polymorph were first stabilized by exposing the α-polymorph to UV light for a short period of time at 343 K. The photodimerization reaction was then carried out at 293 K and observed *in situ* by single-crystal X-ray diffraction. The α'-polymorph contains three molecules in the asymmetric unit, labelled A, B and C, which are arranged to form two potential reaction sites. The intermolecular distance between the C=C bonds of molecules A and B (making up the AB site) is 3.6 Å, and these were observed to undergo photodimerization at 293 K. The corresponding distance between centrosymmetrically related C=C bonds in the CC site (made up of C molecules) is 4.6 Å, and these remain unreacted even after 60 h irradiation at 293 K. The crystal of the final product, which corresponds to a 66.7% conversion (only two out of three molecules in the asymmetric unit take part in the photodimerization reaction at 293 K), contains an ordered arrangement of the photodimer and unreacted monomer. The crystal retains many structural features of the original monomer crystal, including carboxylic acid hydrogen bonds and C—H$\cdots$O interactions. Single-crystal X-ray diffraction was used to monitor changes in the unit-cell parameters, reacting molecules and molecular conformations as the reaction progressed. The conformation of the photodimer obtained from the solid-state reaction differs from that of the photodimer obtained by recrystallization from solution.

1. Introduction

Although solid-state photodimerization reactions have been intensely studied over the last 40 years there has been a renewed interest in reactions of this type (Ito *et al.*, 2003; Busse *et al.*, 2002; Tanaka & Toda, 2000; Ohba & Ito, 2003; Hosomi *et al.*, 2000; Turowska-Tyrk, 2003). In more recent studies there has been an emphasis on trying to carry out photodimerization reactions in a single-crystal-to-single-crystal fashion through the use of tail-end absorbed UV light – a technique first used by Enkelmann and co-workers (Enkelmann *et al.*, 1993). Although relatively rare, single-crystal-to-single-crystal photodimerization studies have been successfully carried out in cinnamic acid (Enkelmann *et al.*, 1993), chloro-, methoxy- and nitro- derivatives of *trans*-

cinnamic acid (using vibrational microspectroscopy; Atkinson *et al.*, 2002), 4-chlorocinnamoyl-*O*,*O'*-dimethyldopamine (Ohba & Ito, 2003) and 5-benzylidene-2-(4-chloro-benzyl)cyclopentanone (Turowska-Tyrk, 2003) amongst other compounds. The hope is that through this process some understanding and control over reaction pathways in the solid state, and hence over the products obtained, will be achieved.

In an earlier paper we reported the existence of a fourth *ortho*-ethoxy-*trans*-cinnamic acid (OETCA) polymorph, the α'-polymorph which, although related to its parent α-polymorph, presents new possibilities in the study of photo-dimerization reactions in the solid state (Fernandes *et al.*, 2004). The other three previously known polymorphs (Schmidt, 1964), α-OETCA (triclinic, $P\bar{1}$), β-OETCA (a solvate, hexagonal, $R\bar{3}$) and γ-OETCA (monoclinic, $C2/c$), were recently fully characterized (Fernandes *et al.*, 2001). The relationship between the α- and α'-polymorph is shown in (I). The α'-polymorph with two different reaction environments (as defined by the closest C=C distances between neigh-boring molecules) provides an opportunity to study the effect of UV light on these different environments. As mentioned in the previous paper, it is possible to stabilize the α'-polymorph by irradiaton with UV light at high temperature (in this case 343 K) for a short period of time (conversion of *ca* 8% of the OETCA monomer to the dimer being sufficient). It is there-fore possible to study the behavior of this polymorph, in spite of the reversible 333 K phase transition, under photo-dimerizing conditions at room temperature (and lower) as well as at elevated temperatures. We have found that the solid-state photochemistry of this polymorph is temperature dependent [see (I)]. The effect of temperature on photo-dimerization pathways in organic crystals has also been observed in 1,4-dicinnamoylbenzene (Hasegawa *et al.*, 1985).
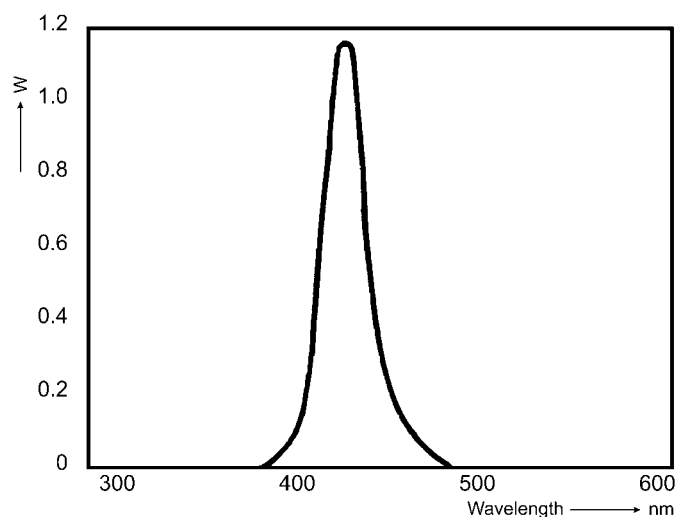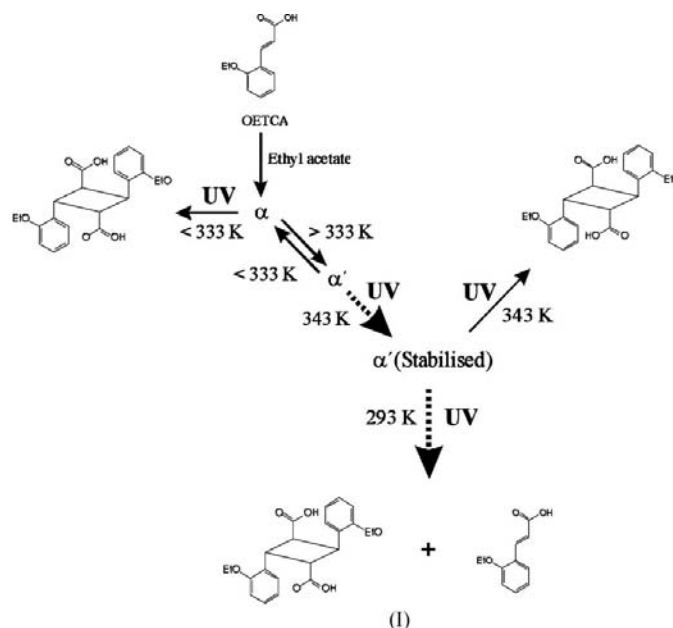
(I)

Here we report the effect on the α'-polymorph on irra-diating with UV light at 293 K after stabilization at 343 K [shown by the dotted arrows in (I)].

2. Experimental

2.1. Crystal growth

Crystals of the α-polymorph were grown by slow evapora-tion from a saturated solution of OETCA in ethyl acetate at room temperature (298 K) to yield prism-like crystals. The melting point of these crystals as determined by DSC was 407.9–408.9 K.

2.2. Photodimerization

A sample of the α'-polymorph was kept on a Kofler hot stage at 343 (3) K and exposed to UV light from a Philips TL03 UV lamp (the emission spectrum is given in Fig. 1). Crystals were extracted from the device after 6 and 12 h of UV exposure and analysed by single-crystal X-ray diffraction. The 12 h crystals were then exposed to UV light at 293 K and analysed at 12 h intervals (data sets were collected from the same crystal after 24, 36, 48 and 60 h of UV exposure time). No changes were observed after 48 h of exposure.

2.3. X-ray structural analysis

Intensity data for crystals at various time intervals were collected at 173 K on a Bruker SMART 1K CCD area-detector diffractometer with graphite-monochromated Mo $K\alpha$ radiation (50 kV, 30 mA). The collection method involved ω scans of width 0.3°. Data reduction was carried using the program *SAINT*+ (Bruker, 1999*a*). Structures were solved by direct methods using *SHELXTL* (Bruker, 1999*b*) and refined

Figure 1
Emission spectrum of the Philips TL03 fluorescent UV lamp.

Table 1
Experimental details.

	6 h	12 h	24 h	36 h	48 h
Crystal data					
Chemical formula	$C_{33}H_{36}O_9$	$C_{33}H_{36}O_9$	$C_{33}H_{36}O_9$	$C_{33}H_{36}O_9$	$C_{33}H_{36}O_9$
Chemical formula weight	576.62	576.62	576.62	576.62	576.62
Cell setting, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a, b, c (Å)	8.6452 (13), 10.8577 (17), 17.262 (3)	8.6164 (10), 10.8765 (14), 17.292 (2)	8.4919 (13), 10.9148 (17), 17.372 (3)	8.3863 (13), 10.9711 (18), 17.427 (3)	8.3099 (12), 11.0026 (16), 17.471 (3)
α, β, γ (°)	92.470 (3), 92.102 (3), 112.563 (3)	93.157 (2), 92.001 (2), 112.657 (3)	96.027 (3), 91.772 (3), 111.956 (3)	98.323 (3), 91.809 (3), 111.336 (3)	99.768 (3), 91.912 (3), 110.392 (3)
V (Å³)	1492.4 (4)	1490.4 (3)	1480.8 (4)	1471.6 (4)	1468.1 (4)
Z	2	2	2	2	2
D_x (Mg m^{-3})	1.283	1.285	1.293	1.301	1.304
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
No. of reflections for cell parameters	728	923	864	1002	794
θ range (°)	2.37–26.28	2.36–24.08	2.59–27.20	2.62–26.99	2.53–28.07
μ (mm^{-1})	0.093	0.093	0.094	0.094	0.095
Temperature (K)	173 (2)	173 (2)	173 (2)	173 (2)	173 (2)
Crystal form, color	Irregular, white	Irregular, white	Irregular, white	Irregular, white	Irregular, white
Crystal size (mm)	$0.38 \times 0.33 \times 0.24$	$0.45 \times 0.24 \times 0.14$	$0.45 \times 0.24 \times 0.14$	$0.45 \times 0.24 \times 0.14$	$0.45 \times 0.24 \times 0.14$
Data collection					
Diffractometer	Bruker SMART 1K	Bruker SMART 1K	Bruker SMART 1K	Bruker SMART 1K	Bruker SMART 1K
Data collection method	ω scans with 0.3 ° steps at $\chi = 57.4$ °	ω scans with 0.3 ° steps at $\chi = 57.4$ °	ω scans with 0.3 ° steps at $\chi = 57.4$ °	ω scans with 0.3 ° steps at $\chi = 57.4$ °	ω scans with 0.3 ° steps at $\chi = 57.4$ °
Absorption correction	None	None	None	None	None
No. of measured, independent and observed reflections	8177, 5500, 3167	8551, 5499, 2989	8447, 5471, 2825	8385, 5439, 3015	8381, 5409, 3394
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.022	0.023	0.030	0.028	0.028
θ_{max} (°)	25.5	25.5	25.5	25.5	26
Range of h, k, l	$-10 \Rightarrow h \Rightarrow 8$ $-13 \Rightarrow k \Rightarrow 13$ $-20 \Rightarrow l \Rightarrow 20$	$-10 \Rightarrow h \Rightarrow 10$ $-13 \Rightarrow k \Rightarrow 8$ $-20 \Rightarrow l \Rightarrow 18$	$-10 \Rightarrow h \Rightarrow 10$ $-13 \Rightarrow k \Rightarrow 7$ $-21 \Rightarrow l \Rightarrow 19$	$-10 \Rightarrow h \Rightarrow 10$ $-13 \Rightarrow k \Rightarrow 7$ $-21 \Rightarrow l \Rightarrow 19$	$-10 \Rightarrow h \Rightarrow 10$ $-13 \Rightarrow k \Rightarrow 7$ $-21 \Rightarrow l \Rightarrow 19$
Refinement					
Refinement on	F^2	F^2	F^2	F^2	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.053, 0.136, 1.03	0.053, 0.142, 1.00	0.062, 0.172, 1.03	0.054, 0.140, 0.99	0.046, 0.116, 1.01
No. of reflections and parameters used in refinement	5500, 390	5499, 418	5471, 409	5439, 395	5409, 397
H-atom treatment	Not refined	Not refined	Not refined	Not refined	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0572P)^2 + 0.0749P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0620P)^2 + 0.0626P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0700P)^2 + 0.1699P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0627P)^2$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0523P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$	<0.000	<0.000	<0.000	<0.000	<0.000
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.14, -0.21	0.16, -0.22	0.19, -0.35	0.19, -0.26	0.18, -0.22
Extinction method	None	None	None	None	None

Computer programs used: *SMART-NT* (Bruker, 1998), *SAINT+* (Bruker, 1999*a*), *SHELXTL* (Bruker, 1999*b*), *PLATON* (Spek, 2003), *SCHAKAL*-97 (Keller, 1997), *ORTEP*3 (Johnson *et al.*, 1997).

using a combination of restraints on bonds lengths and angles (*DFIX*, *SADI*, *SIMU* and *FLAT*), and rigid bodies taken from refinements on data sets at other reaction times. Non-H atoms were first refined isotropically and then by anisotropic refinement with full-matrix least-squares calculations based on F^2 using *SHELXTL*. With the exception of the carboxyl H atoms in the final product crystal (after 48 h of exposure to UV light), all H atoms were positioned geometrically and

allowed to ride on their respective parent atoms. The carboxyl H atoms were located from the difference map and allowed to ride on their parent atoms. All H atoms were refined isotropically. The labelling system used in the structure solution of the α'-polymorph has been retained (see Fernandes *et al.*, 2004). In crystals where the *AB* predimer pair (made up of molecules *A* and *B*) has photodimerized, the photodimer has been labelled as the *DE* product where *D* and *E* were the

Table 2
Root-mean square deviations from planarity for the C molecule from the various structures.

Exposure time (h)	Dimer site occupancy factor	Deviations from planarity (Å)
6 h	0.124 (2)	0.065
12 h	0.219 (3)	0.061
24 h	0.680 (4)	0.074
36 h	0.912 (3)	0.103
48 h	1.000	0.118

original A and B molecules, respectively (Fig. 2). Data for crystals at various reaction times are given in Table 1.[1]

3. Results and discussion

3.1. Reaction by UV radiation

The overall photodimerization reaction scheme studied in this paper is shown in Fig. 3.

An α'-polymorph crystal was reacted with UV light for 12 h at 343 K, resulting in the photodimerization of *ca* 22% of the monomer molecules in the AB reaction site (or 15% for the whole crystal). At this point the crystal was cooled down to room temperature (293 K) and irradiated further. After an additional 36 h (48 h total) of radiation all the monomer molecules in the AB site had reacted, while those in the CC site remained unchanged (Fig. 4). Irradiating the crystal for another 12 h (60 h total) produced no further changes in the crystal structure.

Plots showing the variation of the site occupancy of molecules in the AB reaction site, and changes in the unit-cell parameters and volume with time are shown in Fig. 5. The reaction in the AB site follows first-order kinetics. Changes in the cell axes over the reaction range (12–48 h) are uniform with the changes being *ca* −0.31, 0.13 and 0.18 Å or −3.6, 1.2 and 1.0% for the a, b and c axes, measured at 173 K, respectively. The a axis therefore contracts significantly, while both b and c expand slightly. Unit-cell angles change significantly over the course of the reaction (12– 48 h): 6.611, −0.089 and −2.265° or 7.10, −0.10 and −2.01% for α, β and γ, as measured at 173 K, respectively. The cell volume decreases gradually as the reaction proceeds. The gradual change in unit-cell parameters is the result of the crystal adapting to the shape of the photoproduct as the reaction proceeds. One would expect that the geometry of the AB reaction site would also be affected. Monitoring the predimer ('pre-photodimer') C=C to C=C distances in the AB and CC sites shows that the molecules in the AB site stay at an approximately constant contact distance of 3.6 Å between double bonds. Molecules in the CC site, which are initially at a very unfavorable predimer C=C contact distance (> 4.6 Å), move closer to each other (but never reach a distance less than 4.6 Å), then move apart as the reaction in the AB site reaches completion (Fig. 6). So while photodimerization occurs in the AB site, molecules in

the CC site never become closer than 4.6 Å to each other and hence never react.

It is unlikely that the C=C contact distance in the AB site would become much closer than 3.6 Å as this is close to the sum of the van der Waals radii (Bondi, 1964). However, one would expect the relative orientations of the molecules in the AB site to gradually change as a result of the AB reaction site adapting to the shape of the photoproduct as the reaction proceeds. This was found to be the case for 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone (Turowska-Tyrk, 2003) and 5-benzylidene-2-benzylcyclopentanone (Turowska-Tyrk, 2001). The intermolecular C1B—C11B···C12A and C12A···C11B—C12B (see Fig. 7) angles change from 87.95 and 105.93°, respectively, after 12 h of UV irradiation (22% conversion in the AB site) to 88.93 and 104.18 °, respectively, after 36 h (91% conversion in the AB site). The tendency for these intermolecular angles to reach 90°, leading to improved π–π interactions as the reaction proceeds, has also been noted in 5-benzylidene-2-(4-chlorobenzyl)cyclopentanone (Turowska-Tyrk, 2003). The intermolecular torsion angle C11A—C12A···C11B—C12B stays approximately constant at *ca* −1.3° throughout the reaction process (12–36 h of UV exposure), indicating that molecules A and B do not rotate relative to each other.
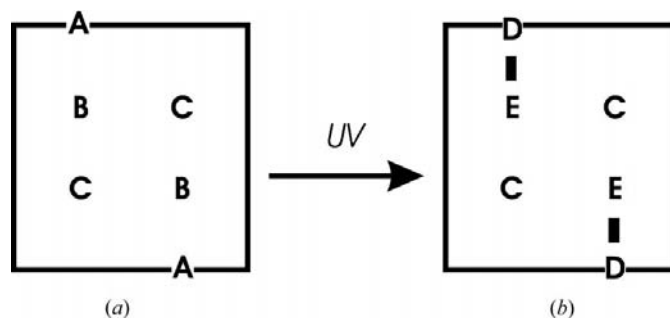
Figure 2
Convention used for the naming of molecules in the monomer crystal (*a*) structure and its product (*b*). Upon photodimerization the AB predimer pair is labelled as the DE molecule (where D and E were the original A and B molecules, respectively).
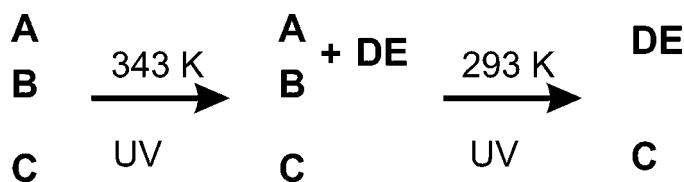
Figure 3
The overall reaction scheme for the photodimerization of the α'-polymorph at room temperature. Crystals of the α'-polymorph (Fig. 4a) were irradiated initially for 12 h at 343 K to stabilize them. This resulted in a crystal that contained a mixture of the DE product and monomer A and B molecules in the AB reaction site (Fig. 4b). The crystal was then further exposed to UV light at 293 K, leading to more DE product until all A and B molecules were consumed. At this stage the product crystal is composed of the DE dimer in the AB reaction site and the C molecule (Fig. 4c). No further reaction occurs at 293 K.

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: WS5010). Services for accessing these data are described at the back of the journal.
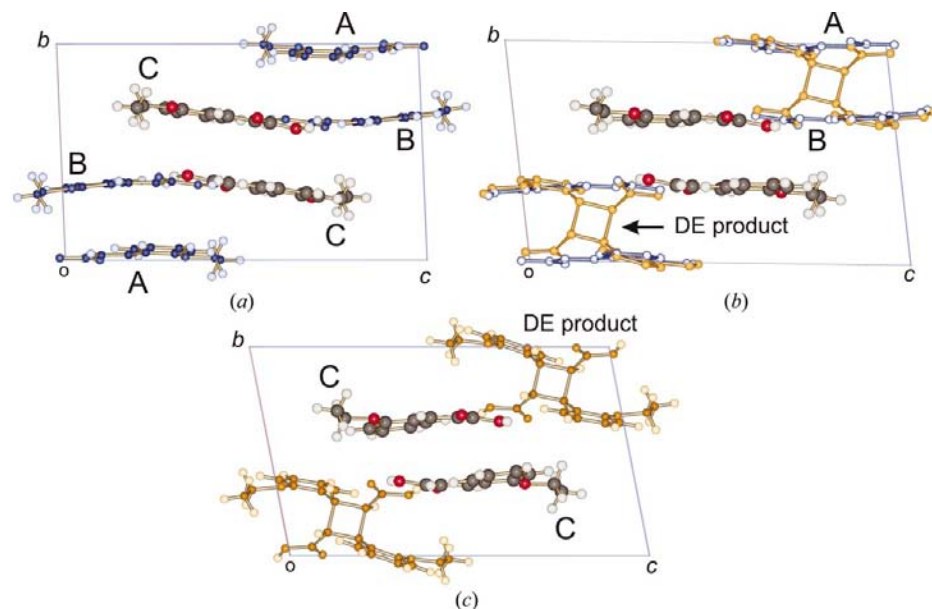
Table 3
Selected torsion angles t_1 and t_2 for the solid-state reaction product and the solution-grown dimers (see Fig. 9 for definition).

	t_1 (°)	t_2 (°)
48 h-D	−171.42	−157.81
48 h-E	−179.94	−165.29
GK	54.20	160.77

3.2. Molecular structure

ORTEP diagrams for molecules in the α'-polymorph after 24 and 48 h of exposure to UV light are shown in Fig. 7. Owing to the α'-polymorph having two reaction sites, one photo-reactive and one photo-stable at 293 K, it is possible to monitor the change in conformation of molecule C as a result of stresses caused by the reaction process. Measuring the RMS (root mean square) deviation from planarity for C molecules at various reaction times indicates that it increases steadily from 0.065 to 0.118 Å, after 6 and 48 h of UV exposure, respectively (Table 2). The deviation from planarity is due to slight changes in the conformation of the carboxylic and ethoxy groups of OETCA (Fig. 8). Superimposing the dimer molecule from 24, 36 and 48 h, where the DE molecule was refined freely in all three structures, shows very little conformational change as the reaction proceeds. Most of the changes occur around C3D (the difference between 24 and 48 h being 0.07 Å) and C22D (the difference between 24 and 48 h being 0.11 Å).

The dimerization product of OETCA, 2,2′-diethoxy-α-truxillic acid, can occur as two different conformational polymorphs, depending on whether the product was obtained directly from the solid-state photodimerization or by recrystallization of the dimer. Comparing the conformation of the dimer molecule from the solid-state reaction (48 h) with that obtained from solution growth (GK; Gopalan & Kulkarni, 2001; see also Fernandes *et al.*, 2001) indicates that there are differences in the orientation of the ethoxy and carboxylic acid groups (Fig. 9). The solution-grown dimer (GK) sits on a crystallographic centre of inversion with the ethoxy groups lying above and below the plane of the cyclobutane ring. In contrast, the solid-state reaction structure (48 h) has its ethoxy groups pointing away from the cyclobutane ring and does not sit on a centre of inversion; as a consequence each half of the molecule is slightly different from the other. The torsion angles t_1 and t_2 (Fig. 9; Table 3) in the two halves of 48 h differ by *ca* 8.5 and 7.5°, respectively. The difference in t_1 and t_2 angles between the 48 h and GK structures is *ca* 144 and 35°, respectively. A reason for these differences is that the solid-state reaction (48 h) structure derives its conformation from that of its parent monomer. In contrast, the solution-grown dimer has had no such restraints on its conformation during its growth and adopts the conformation best suited to create a stable crystal.

3.3. Hydrogen bonding

Hydrogen-bond details are listed in Table 4. Molecules in the 48 h structure are kept together by classical carboxylic hydrogen bonds to form a string of molecules made up of two dimer and two monomer molecules (Fig. 10a and b). Molecule C is hydrogen bonded, in a non-centrosymmetric fashion, to a dimer molecule through two different hydrogen bonds (O11C—H1$C\cdots$O12E and O11E—H1$E\cdots$O12C; Fig. 10b and Table 4). Using a graph-set notation (Etter, 1990; Bernstein *et al.*, 1995) the first-level graph set for the hydrogen-bond system is DD (where each carboxylic acid hydrogen bond is unique owing to the lack of an inversion centre) and the graph set $R_2^2(8)$ is obtained only when the second-level graph sets are examined. This accounts for two of the three carboxylic hydrogen bonds. The photodimers are hydrogen bonded to each other in a centrosymmetric fashion, which is described by the first-level graph set $R_2^2(8)$(O11D—H$\cdots$O12D). The hydrogen-bond pattern is directly derived from that of the parent monomer α'-crystal, where the non-centrosymmetric hydrogen bonds were originally the non-centrosymmetric BC (the molecule label B becomes E in the product crystal) hydrogen dimers and the centrosymmetric hydrogen bonds were originally the centrosymmetric

Figure 4
The α'-polymorph (a) before and (b) after stabilization at 343 K. Upon further exposure to UV light at 293 K a final product crystal containing only the C molecule and DE product is obtained (c). Molecules in the CC site do not undergo photodimerization. Letters A and B define the AB reaction site while C defines the CC reaction site.

AA (the molecule label *A* becomes *D* in the product crystal) hydrogen-bonded dimers (see Fernandes *et al.*, 2004).

The hydrogen bond defined by O11*D*—H1*D*···O12*D* has a *D*···*A* distance of 2.714 (2) Å, which is at least 0.07 Å longer than any such bond in the α-, γ- and β-polymorphs and more than 0.10 Å longer than in the O11*A*···O12*A* (the original monomer) distance in the α'-polymorph (measured in 6 h – necessary as this was the only way to determine the α'-poly-
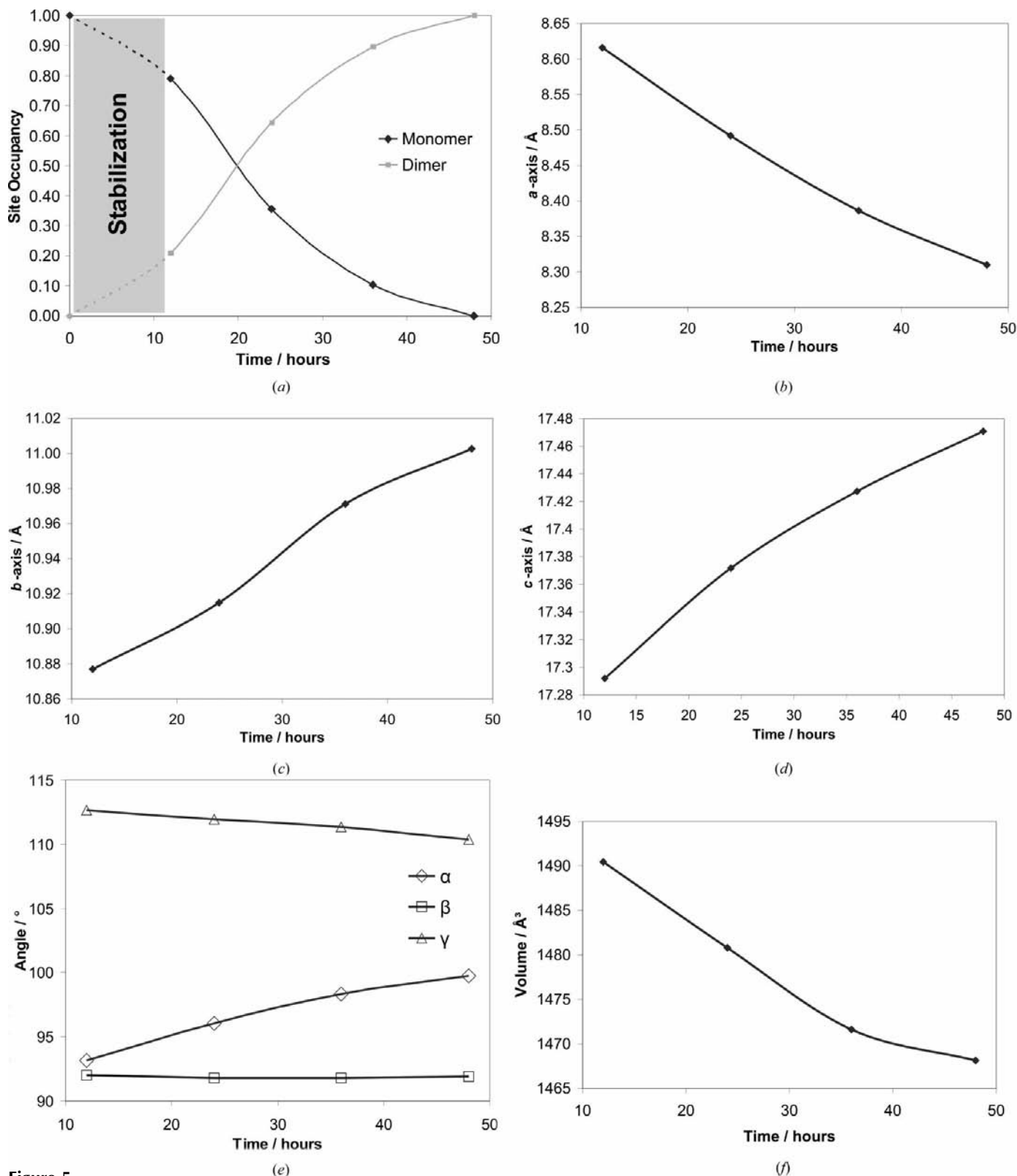

Figure 5
Plots of site occupancy in the *AB* site and changes in unit-cell parameters and volume *versus* irradiation time (at 293 K).

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morph structure at 173 K; see Fernandes *et al.*, 2004; Table 4). This is presumably a consequence of the contraction of the monomer molecules on converting to the dimer in the solid-state reaction. The photodimer molecules are smaller than the original substrate molecules and as a result when the reaction occurs the carboxylic atoms are pulled away from the original carboxylic hydrogen-bond centre. This leads to a slight
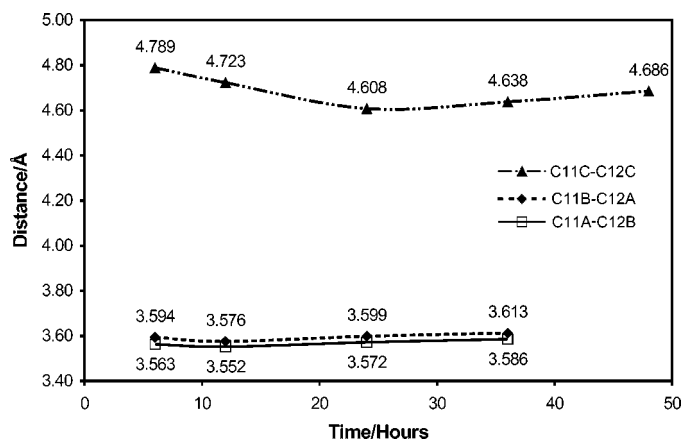

Figure 6
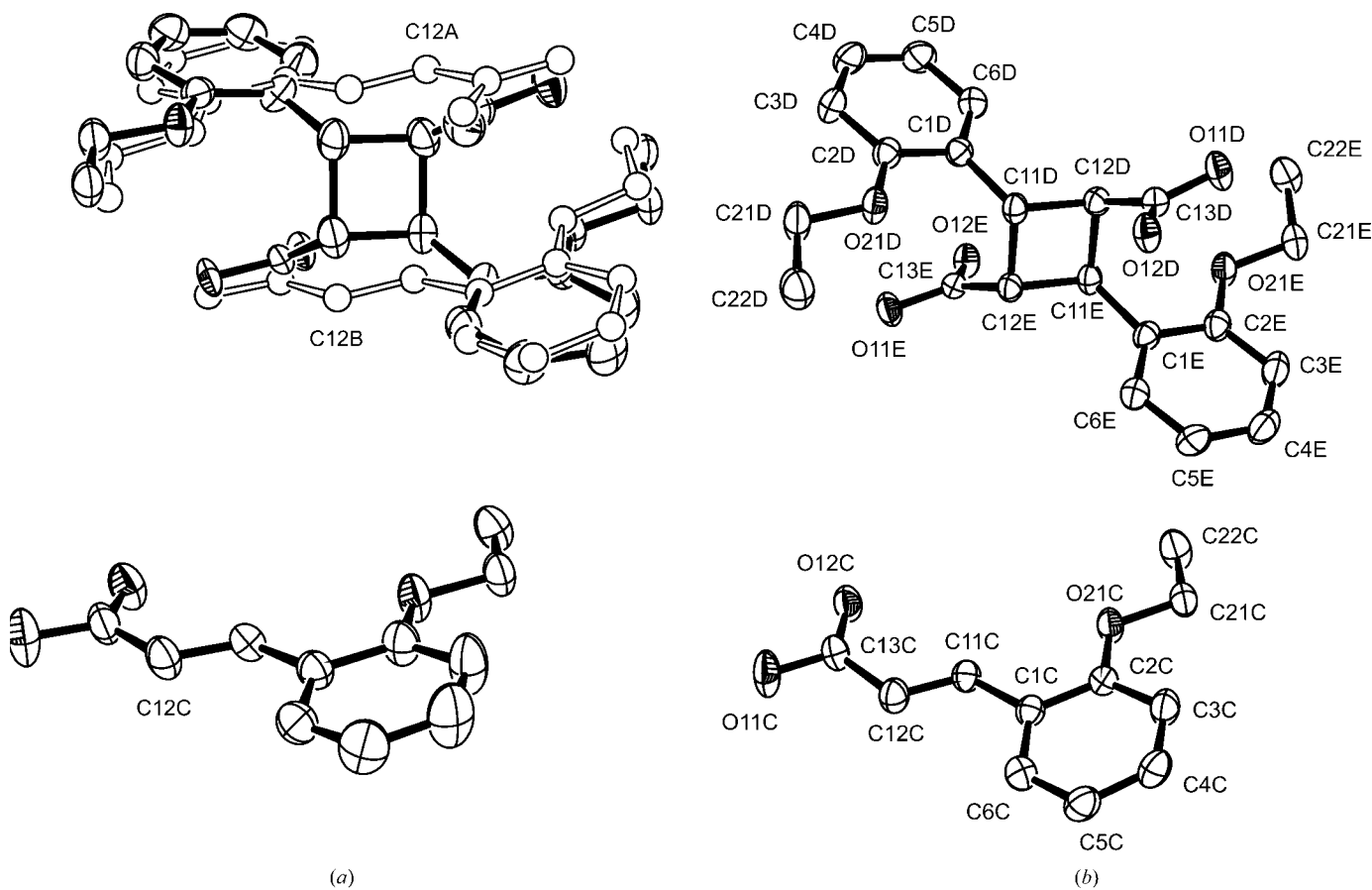Predimer distances in the *AB* and *CC* sites at various irradiation times.

increase in the $D\cdots A$ distances in the product crystal when compared with the monomer crystal. In addition, the O11D—H1$D\cdots$O12D hydrogen bond appears to have an unusual 'step' geometry (Fig. 10a). This is also a consequence of the solid-state reaction.

The C—H$\cdots$O distances for various structures are listed in Table 5. In general, for the monomer structures (6 h in the α'-polymorph as measured after 6 h irradiation, and in the α- and γ-polymorphs) the C5—H5$\cdots$O12 interaction tends to have a longer $D\cdots A$ distance and a more linear D—H$\cdots A$ angle than the C6—H6$\cdots$O11 interaction. In general, the difference in the two distances is *ca* 0.2 Å. In contrast, the product crystal (48 h) has almost equivalent C5$\cdots$O12 and C6$\cdots$O11 distances, with the exception of C5$E\cdots$O12E and C6$E\cdots$O11C, which have distances resembling those of the monomer crystals. The average C$\cdots$O distance 48h is 3.453 Å while in 6h and α- and γ-polymorphs it is 3.470, 3.529 and 3.534 Å, respectively. The average C$\cdots$O distance is shorter in 48 h than in the other structures. The consistency of these C—H$\cdots$O interactions in all these structures – even after a solid-state reaction – is interesting as it shows how important this interaction is to the stability of these various structures. An example of the C—H$\cdots$O interaction contribution to the structure after 48 h is shown in Fig. 10c.

Figure 7
ORTEP (50% probability level; H atoms omitted for clarity) diagrams of the asymmetric unit at (*a*) 173 K after 24 h UV exposure (the two monomer molecules, with empty bonds and open spheres, and superimposed dimer molecule, with solid bonds and shaded ellipsoids) and (*b*) after 48 h of UV exposure (100% conversion in the *AB* site).

Table 4
Hydrogen-bond geometry in 48 h, 6 h (in the α'-polymorph as measured after 6 h irradiation), the α- and γ-polymorph (Fernandes *et al.*, 2001), and the α-dimer (Gopalan & Kulkarni, 2001).

Structures 48 h, 6 h, α, β and γ were determined at 173 (2) K. The α-dimer was determined at 130 (2) K.

Structure	$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
48 h	O11D—H1$D\cdots$O12D^{i}	0.92 (2)	1.80 (2)	2.7138 (18)	169 (2)
48 h	O11C—H1$C\cdots$O12E^{ii}	0.87 (2)	1.80 (2)	2.6619 (18)	176 (2)
48 h	O11E—H1$E\cdots$O12C^{ii}	1.00 (2)	1.64 (3)	2.6350 (18)	169(2)
6 h	O12A—H1$A\cdots$O11A^{i}	0.84	1.73	2.566 (3)	170.4
6 h	O11C—H1$C\cdots$O12B^{ii}	0.84	1.80	2.622 (3)	166.0
6 h	O11B—H1$B\cdots$O12C^{ii}	0.84	1.76	2.591 (2)	167.7
α	O11—H11$a\cdots$O12$^{\mathrm{iii}}$	0.84	1.80	2.637 (2)	172
β	O12—H11O$\cdots$O11$^{\mathrm{iv}}$	0.84	1.78	2.618 (2)	177
γ	O11—H11O$\cdots$O12$^{\mathrm{v}}$	0.84	1.80	2.6249 (17)	165
α-dimer (GK)	O2—H2$a\cdots$O1$^{\mathrm{vi}}$	0.96 (2)	1.67 (2)	2.627 (3)	174 (5)

Table 5
C—H...O interaction geometry in 48 h, 6 h (in the α'-polymorph as measured after 6 h irradiation), the α- and γ-polymorph (Fernandes *et al.*, 2001).

All structures were determined at 173 (2) K.

Structure	$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
48 h	C5D—H5$D\cdots$O12D^{i}	0.95	2.53	3.421 (2)	157
48 h	C6D—H6$D\cdots$O11D^{ii}	0.95	2.77	3.464 (2)	131
48 h	C5C—H5$C\cdots$O12C^{iii}	0.95	2.62	3.447 (2)	146
48 h	C6C—H6$C\cdots$O11E^{iv}	0.95	2.50	3.401 (2)	158
48 h	C5E—H5$E\cdots$O12E^{iii}	0.95	2.63	3.536 (2)	159
48 h	C6E—H6$E\cdots$O11C^{iv}	0.95	2.65	3.446 (2)	142
6 h	C5A—H5$A\cdots$O12A^{i}	0.95	2.68	3.545 (4)	151
6 h	C6A—H6$A\cdots$O11A^{ii}	0.95	2.52	3.346 (4)	146
6 h	C5C—H5$C\cdots$O12C^{iii}	0.95	2.67	3.556 (3)	154
6 h	C6C—H6$C\cdots$O11B^{iv}	0.95	2.49	3.349 (3)	150
6 h	C5B—H5$B\cdots$O12B^{iii}	0.95	2.71	3.594 (4)	156
6 h	C6B—H6$B\cdots$O11C^{iv}	0.95	2.57	3.435 (3)	151
α	C5—H5$\cdots$O12$^{\mathrm{v}}$	0.95	2.76	3.645 (3)	155
α	C6—H6$\cdots$O11$^{\mathrm{vi}}$	0.95	2.55	3.413 (3)	151
γ	C5—H5$\cdots$O12$^{\mathrm{vii}}$	0.95	2.76	3.665 (2)	160
γ	C6—H6$\cdots$O11$^{\mathrm{vii}}$	0.95	2.60	3.403 (2)	143

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+2, -y, -z$; (iii) $x-1, y, z$; (iv) $-x+1, -y+1, -z+1$; (v) $x, y-1, z$; (vi) $-x+2, -y-1, -z+1$; (vii) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

3.4. Crystal packing

The similarity between the structure after 48 h and its parent crystal, the α'-polymorph, is obvious (Figs. 4a and c). The corrugated sheet structure and the boundaries of the original 'ribbons' in the α'-polymorph can still be seen in the structure after 48 h. As a consequence, the structure and crystal packing after 48 h can be viewed entirely as derived from its parent crystal. Whereas the hydrogen-bonded OETCA dimer is the basic building block of the α'-polymorph, the hydrogen-bonded set of molecules is composed of two C molecules and two dimer molecules (Figs. 10a and b; see §3.3)

can be viewed as the basic building block of the 48 h structure. These hydrogen-bonded units are further assembled *via* C—H$\cdots$O interactions (derived from the monomer crystal) to form a new 'ribbon' running down the a axis. The 'new ribbons' are then held together by other weak interactions to form a 'slab' of molecules. The upper and lower parts of the hydrogen-bonded units can be thought of as defining the limits of a molecular 'slab' (Fig. 11). The stacking of these 'slabs' along the b axis completes the structure.

4. Conclusion

At 293 K only molecules making up the AB reaction site photodimerize, while molecules in the CC site are left unreacted. The final product crystal, containing the photodimer in the AB reaction site, retains much of the structure of the original monomer crystal. In addition, the carboxylic acid hydrogen bonds and C—H$\cdots$O interactions, present in the monomer crystal, are retained in the product crystal. During the reaction, the a axis contracts, while the b and c axes expand, and the cell volume decreases with time. Molecules in the AB site remain at a constant distance from each other during the whole reaction, while molecules in the CC site initially move closer to each other, but are never close enough to react. Molecules in the AB site do not rotate, with respect to each other, during the reaction. During the reaction the C molecule deviates more from planarity owing to conformational changes in the ethoxy and carboxylic acid groups. In addition, the solid-state product obtained has a conformation different to that obtained from solution growth.

At 293 K only two molecules out of three in the asymmetric unit take part in the photodimerization reaction and the reaction therefore stops at 66.7% conversion. Solid-state reactivity at 343 K (above the phase transition temperature) differs remarkably from the 293 K case: photodimerization at
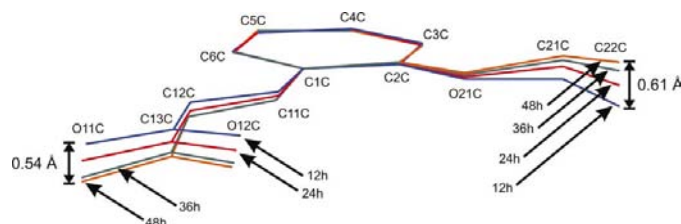
Figure 8
Superimposition of the C molecules from the 12, 24, 36 and 48 h structures from a least-squares fit of the corresponding C1C, C2C, C3C, C4C, C5C and C6C atoms. The C molecule does not undergo photodimerization at 293 K, but does show some conformational change around the ethoxy (C22C) and carboxylic acid groups (C13C) as the reaction proceeds.

343 K goes to 100% completion in two distinct stages. Details will be discussed in a separate paper (Fernandes & Levendis, 2004).
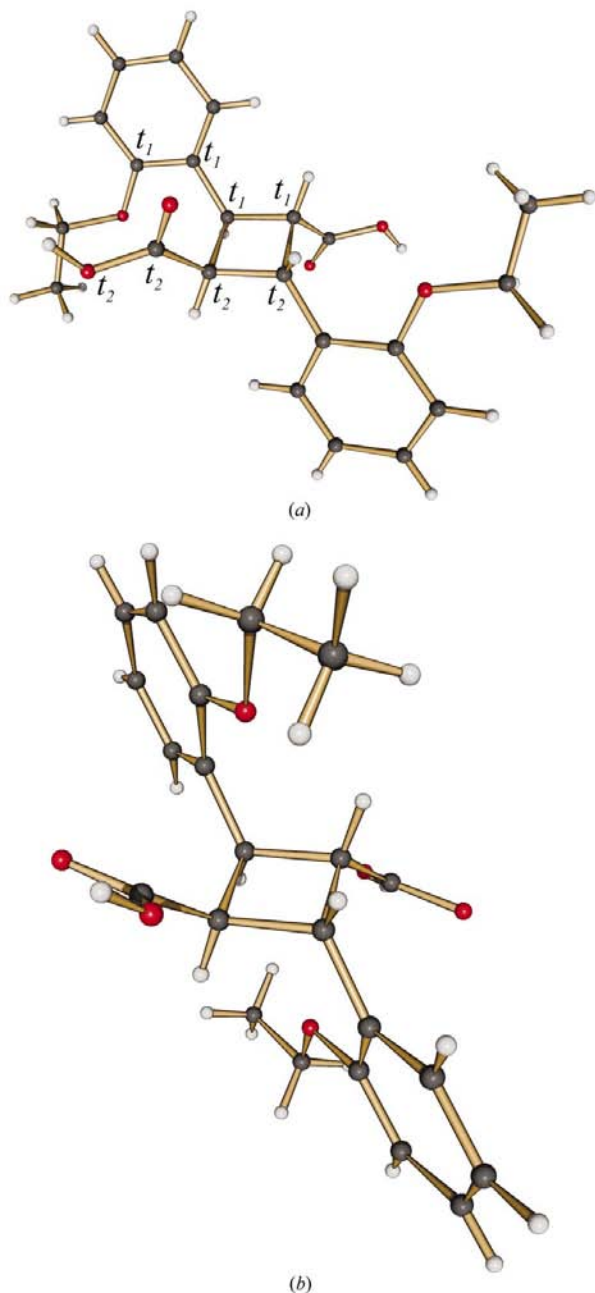
Figure 9
Comparison of the geometry of 2,2′-diethoxy α-truxillic acid molecules from (a) the solid-state reaction (48 h) and (b) from solution growth (Gopalan & Kulkarni, 2001). The relative orientation of the carboxylic acid and ethoxy groups differ between the two structures. Values for the torsion angles t_1 and t_2 in the two structures are given in Table 3.
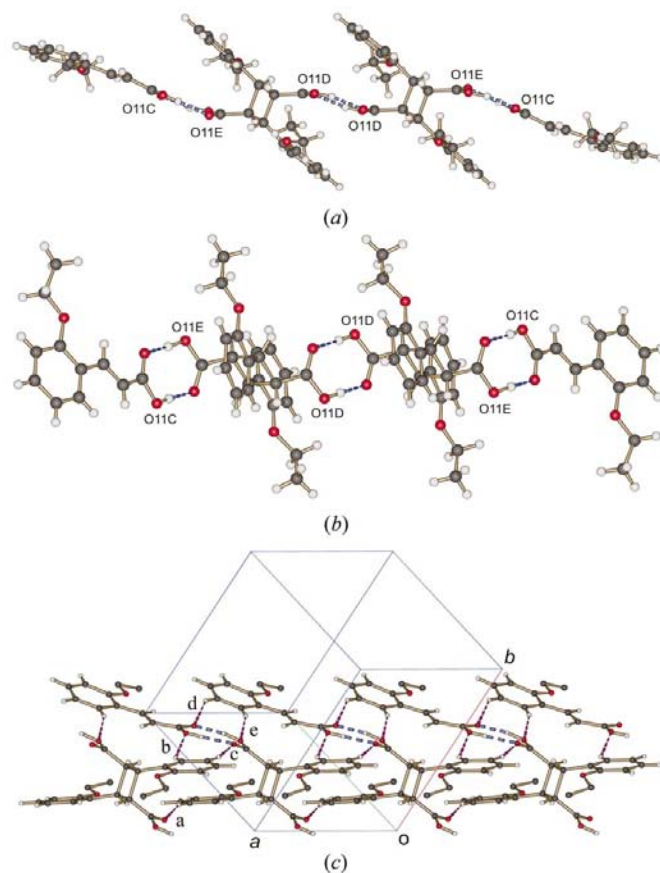

Figure 10
Hydrogen bonding in the solid-state reaction product crystal (48 h). Molecules in the 48 h structure are kept together by three $R_2^2(8)$ carboxylic hydrogen bonds to form a string of molecules composed of two dimer and two monomer molecules (a) and (b). These are further assembled through C—H$\cdots$O interactions to form a 'ribbon' of molecules running down the a axis, part of which is shown in (c) [ethoxy H atoms have been deleted for clarity; (a) H5D$\cdots$O12D, (b) H6E$\cdots$O11C, (c) H5E$\cdots$O12E, (d) H5C$\cdots$O12C and (e) H6C$\cdots$O11E].
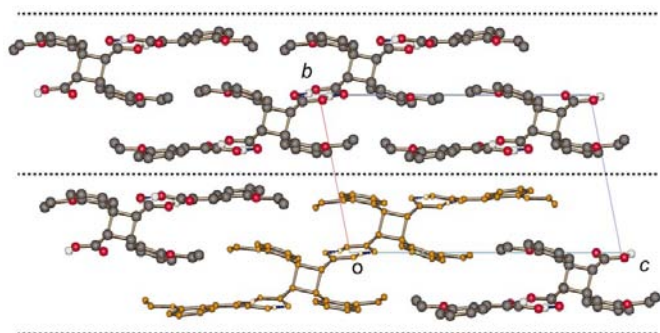

Figure 11
Crystal packing after 48 h (the product crystal), as viewed down the a axis. The hydrogen-bonded unit, composed of two C and two dimer molecules shown around the origin, is the basic building component of the crystal structure (see text). These are held together by C—H$\cdots$O interactions down the a axis. The upper and lower parts of these hydrogen-bonded molecule units can be thought of as defining the limits of a molecular 'slab' (marked with dotted lines). Stacking of these 'slabs' along the b-axis completes the structure.

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