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Supplementary information for:

Photodimerisation of the α´-polymorph of *ortho*-ethoxy-*trans*-cinnamic acid occurs *via* a two-stage mechanism at 343 K yielding 100% α-truxillic acid.

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1. Supplementary information associated with the materials and methods section

Materials

Reagents were purchased from Sigma Aldrich and used as received. Solvents used in syntheses and recrystallisation were purchased from Merck SA.

Crystallisation and solid-state reaction

OETCA was synthesized according to a previously reported method.[28] Crystals of the *α*-polymorph were grown by slow evaporation from a saturated solution of OETCA in ethyl acetate at room temperature (293 K) to yield prism-like crystals of the *α*-polymorph (melting point as determined by DSC was 407.9-408.9 K). A sample of these was then placed on a Kofler hot stage at 343(3) K leading to a single-crystal-single-crystal phase transformation to the *α*´-polymorph which was then exposed to UV light from a Philips TL03 UV lamp. Crystals were then extracted from the hot stage at 6 hour intervals and analyzed by single-crystal X-ray diffraction. Data sets were collected after 6, 12, 18, 24, 36, 48, 60, 72 and 120 hours of UV exposure (all on different crystals).

Crystal structure solution and refinement

Where possible, crystals were chosen according to their behaviour under a polarizing microscope, i.e., their ability to uniformly polarize light, and then examined using single-crystal diffraction. This approach was successful for crystals which had been exposed for 24 hours or less. The surfaces of crystals which had been exposed for longer periods of time became white with longer reaction times - presumably due to reaction and phase transition (Stage 2) at the surface in competition with SCSC reaction in the body of the crystals. These were also examined under a polarizing microscope but had to be cut in order to extract fragments suitable for single crystal diffraction study. Intensity data for crystals, at various UV exposure time intervals, were collected at 173 K on a Bruker SMART 1K CCD area detector diffractometer with graphite monochromated Mo Kα radiation (50kV, 30mA). The collection method involved *ω* scans of width 0.3°. Data reduction was carried out using the program *SAINT+*.[31] Structures were solved by direct methods and refined 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-hydrogen atoms were first refined isotropically followed by anisotropic refinement full matrix least-squares calculations based on F^2 using *SHELXL-2014*.[32] All hydrogen atoms were first located in the difference-Fourier map then positioned geometrically and allowed to ride on their respective parent atoms. Particular details for the final refinements for all structures in the form of *SHELXL-2014 RES* files can be found in the CIF file associated with the structure in the supporting information. Software used in this work were as follows: Data collection: *SMART*;[30] cell refinement and data reduction: *SAINT*;[31] program suite used to solve and refine structures: *SHELX-2014*;[32] molecular graphics: *ORTEP-3* for Windows,[33] *SCHAKAL-99*,[34] VMD-1.91,[35] and *CrystalExplorer-3.1*;[36] software used to prepare material for publication: *WinGX-2014.1*[37] and *PLATON*.[38]

The labelling system used in our two previous papers involving the α´ polymorph - namely on the formation of α´ polymorph by phased transition from the α polymorph,[29] and the photodimerisation of the α´ polymorph at 293 K[15] - has been retained (Fig. 1 in main document). In crystals where the *AB* predimer pair (made up of molecules *A* and *B*) has photodimerised, the photodimer has been labelled as the *DE* product where *D* and *E* were the original *A* and *B* molecules respectively (Figs. 1 and 3). Structure solutions of the α´-polymorph exposed for more than 24 h (67%

conversion of *AB* predimer) indicate that the *DE* product molecule changes conformation during the course of the reaction to an alternative conformation that we have labelled as the *FG* conformer. Here the *F* and *G* labelled atoms were the original *A* and *B* molecules, respectively (Figs 1 and 3). Crystallographic data for crystals at various reaction times are given in Table S1.

Powder diffraction studies

Powder diffraction patterns were collected on a Philips PW1820 powder diffractometer with X-rays generated from a copper tube set at 40kV and 20mA. Samples of the α polymorph were prepared by lightly grinding the sample in an agate mortar and pestle and sprinkling the powder on silicon disks coated with a thin layer of silicone grease. The sample was then kept on a Kofler hot stage at 343(3) K in air and exposed to UV light from a Philips TL03 UV lamp.

Calculations

Intramolecular energies for *DE*, *FG* and *C* molecules were calculated with the *M06-2X*[39] DFT functional and *6-311G(d,p)* basis set, using *Gaussian-09*.[40] In the calculations, the molecular geometry (angles and torsion angles) derived from the crystal coordinates for all atoms except hydrogens were kept frozen but bond lengths allowed to optimise, while H atom positions were allowed to fully optimize. This was done because the presence of disorder introduces small errors to the bond lengths of a structure due to the overlap of the disordered molecules. The energy penalty for slightly incorrect bond lengths is very high leading to large energy differences between apparently similar conformations, while the energy penalty for slightly incorrect angles and bond lengths is much lower. To be able to compare the energies of the molecular conformations from different structures the bond lengths were optimised (corrected) while at the same time keeping the angles and torsion angles fixed in the calculations. In addition, H atoms in crystal structures determined by X-ray diffraction methods are geometrically and not experimentally placed, requiring the position of these to be fully optimised.

Lattice and molecule…molecule interaction energies were calculated using the August 2014 version of *AA-CLP*.[41] The calculation was initialized by geometrically normalizing bonds involving *H* to neutron distances followed by the addition of EHT charges on all atoms as prescribed within the *CLP* manual, before calculating the lattice energy.

Hirshfeld surfaces were generated using *CrystalExplorer-3.1*.[36]

Table S1 Crystallographic and refinement data. Conversion values are based on the occupancy values of the product molecule (sum *DE* and *FG* occupancies) in the *AB* reaction site while molecules in the *CC* site remain unreacted in Stage 1. Structures 6 h and 12 h are the same data sets reported in reference 15 but re-refined using *SHELXL-2014*.

Time reacted (Conversion in *AB* site)	6 h (12.4 %)	12 h (21.9 %)	18 h (46.8 %)	24 h (66.9 %)	36 h (82.8 %)	48 h (89.9 %)	60 h (100 %)	72 h (100 %)	120 h (100 %)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
a/Å	8.6452(13)	8.6164(10)	8.5451(15)	8.4820(16)	8.440(2)	8.370(3)	8.3738(14)	8.3766(14)	8.435(6)
b/Å	10.8577(17)	10.8765(14)	10.8805(19)	10.894(2)	10.918(3)	10.992(4)	11.2351(19)	11.2383(18)	11.431(8)
c/Å	17.262(3)	17.292(2)	17.346(3)	17.360(3)	17.372(4)	17.276(6)	17.064(3)	17.082(3)	17.048(12)
α/°	92.470(3)	93.157(2)	94.925(3)	96.558(3)	98.412(4)	101.552(5)	106.059(3)	106.072(4)	105.141(14)
β/°	92.102(3)	92.001(2)	91.831(3)	91.831(4),	92.041(4)	92.358(6)	92.617(4)	92.601(3)	92.907(18)
γ/°	112.563(3)	112.657(3)	111.868(3)	111.203(4)	109.825(5)	107.262(6)	104.502(3)	104.599(3)	104.043(16)
Unit cell volume/Å^3	1492.4(4)	1490.4(3)	1487.6(4)	1481.1(5)	1483.6(6)	1478.5(8)	1482.2(4)	1483.8(4)	1527.8(19)
Temperature/K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	293(2)
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
Density (Calc.)/ g cm^{-3}	1.283	1.285	1.287	1.293	1.291	1.295	1.292	1.291	1.253
Z	2	2	2	2	2	2	2	2	2
Radiation type	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα	MoKα
Absorption coefficient, μ/mm^{-1}	0.093	0.093	0.093	0.094	0.094	0.094	0.094	0.094	0.091
No. of reflections measured	8177	8551	7956	8103	7781	7775	7951	8147	5034
No. of independent reflections	5500	5499	5173	5469	5157	5403	5392	5480	2827
R_{int}	0.022	0.023	0.022	0.022	0.029	0.031	0.038	0.032	0.205
ϑ_{max} /°	25.24	25.24	25.0	25.24	25.0	25.24	25.24	25.24	20.0
Data / restraints / parameters	5500/ 0/ 390	5499/ 0/ 418	5173/ 0/ 536	5469/ 450/ 561	5157/ 56/ 439	5403/ 146/ 606	5392/ 62/ 587	5480/ 50/ 557	2827/ 153/ 165
Final R_1 ($I > 2\sigma(I)$)	0.052	0.052	0.057	0.059	0.071	0.076	0.059	0.056	0.138
Final $wR(F^2)$ ($I > 2\sigma(I)$)	0.117	0.117	0.136	0.135	0.170	0.191	0.146	0.123	0.301
Final $R1$ (all data)	0.108	0.114	0.0891	0.116	0.150	0.165	0.133	0.134	0.367
Final $wR(F^2)$ (all data)	0.137	0.142	0.1535	0.162	0.202	0.229	0.177	0.155	0.422
Goodness of fit on F^2	1.023	1.002	1.057	1.004	1.038	1.027	0.982	0.990	0.912
CCDC number	1472995	1472989	1472990	1472991	1472992	1472993	1472994	1472996	1472988

2. Supplementary information associated with the results and discussion section

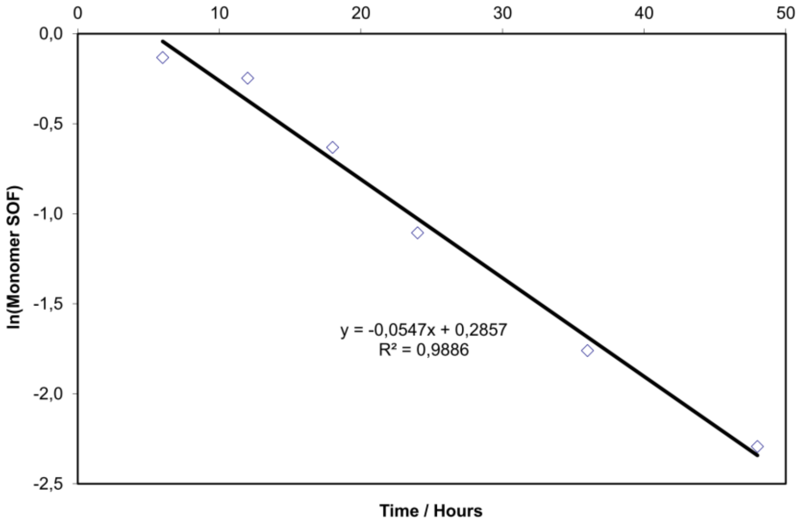
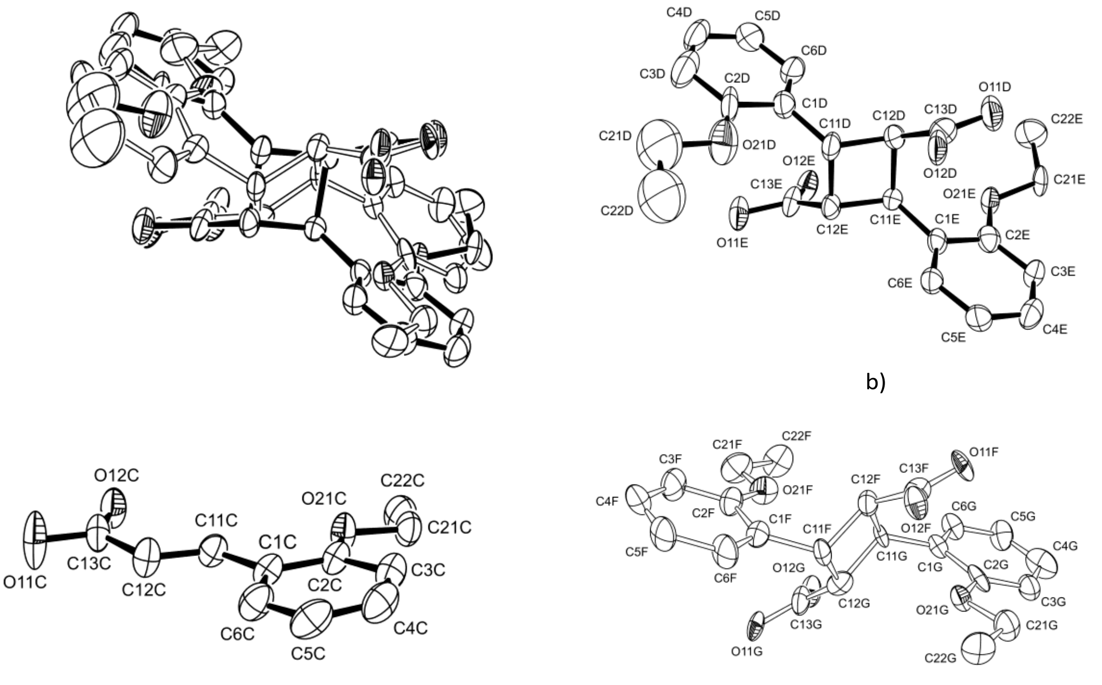


Fig. S1 Plot of ln(SOF) versus time for monomer molecules in the *AB* reaction site indicating that the reaction follows approximately first order kinetics.



b)

a)

c)

Fig. S2 ORTEP (50% probability level; Hydrogen atoms omitted for clarity) diagrams of the Stage 1 343 K crystal product; (a) the asymmetric unit showing the *C* molecule, and the disordered *DE* (solid bonds) and *FG* (open bonds) conformations of the photoproduct; (b) the *DE* conformation of the photoproduct; (c) the *FG* conformation of the photoproduct.

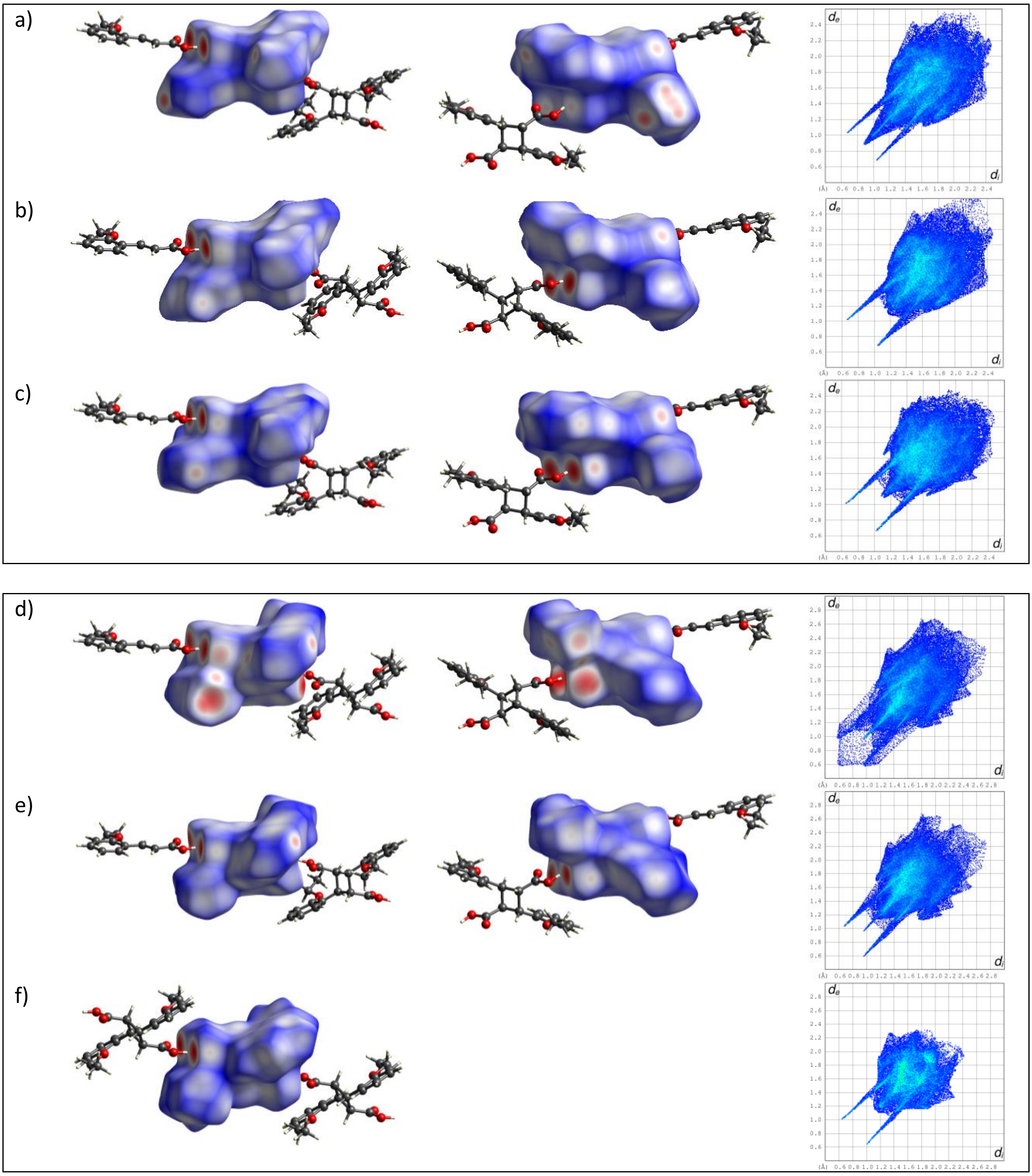


Fig. S3 Hirshfeld surfaces and fingerprint plots for *DE* (upper panel) and *FG* (lower panel) molecules from reacted and recrystallized crystals; (a) *DE* Hirshfeld surface from 60 h considering a hypothetical crystal containing only *C…DE…DE…C* which shows very close contacts around the ethoxy groups. (b) *DE* molecule from the disentangled *DE…FG* arrangement shown in Fig. 16 in the main text. The only remaining close contacts are due to C-H…O interactions which are present in all the structures. (c) *DE* molecule from the *α´*-polymorph reacted at 298 K (r48 h) showing stronger C-H…O contacts and tighter crystal packing due to the ordered nature of the reaction at this temperature. (d) *FG* Hirshfeld surface from 60 h considering a hypothetical crystal containing only *C…FG…FG…C* which shows very close contacts around the ethoxy and carboxylic acid groups. (e) *FG* molecule from the disentangled *DE…FG* arrangement shown in Fig. 16 in the main text where most of these close contacts have been resolved. (f) *FG* molecule (one side only as the structure is centrosymmetric) after recrystallization (CSD refcode *XOSKEV*; Gopalan & Kulkarni, 2001).[42]

Detailed description of the geometrical changes occurring in the *AB* and *CC* reaction sites during stage 1 of the photodimerisation reaction

As mentioned in the main document, the large changes in the unit cell parameters (see Fig. 6 in main document) can be viewed as being a consequence of changes in the *AB* reaction site. The molecules in the *AB* site have to adapt to the shape of the photoproduct and its conformer as the reaction proceeds in order to maintain crystal integrity. In addition the geometry of the *CC* site will also be affected by changes in the *AB* site. Monitoring the predimer ("pre-photodimer") distances between the C=C distances in neighbouring molecule in the non-centrosymmetric *AB* and centrosymmetric *CC* sites as the reaction proceeds (Fig. S4), shows that the molecules in the *AB* site stay at an approximately constant C=C contact distance of about 3.55 Å from each other. These distances are almost identical to the distances at 293 K. Molecules in the *CC* site, which are initially at an unfavourable predimer C=C contact distance (>4.2 Å – based on Schmidt's criteria) initially move closer to each other, but never reach a distance less than 4.6 Å, then move away as the reaction in the *AB* site proceeds beyond 80% conversion (Fig. S4). As a consequence of the conformational changes in the *AB* reaction site, the final predimer C=C contact distance (4.804 Å) for stage 1 of the reaction at 343 K is much further than the equivalent distance (4.686 Å) in the final product from the reaction at 293 K. At both temperatures molecules in the *CC* site never get close enough to react.

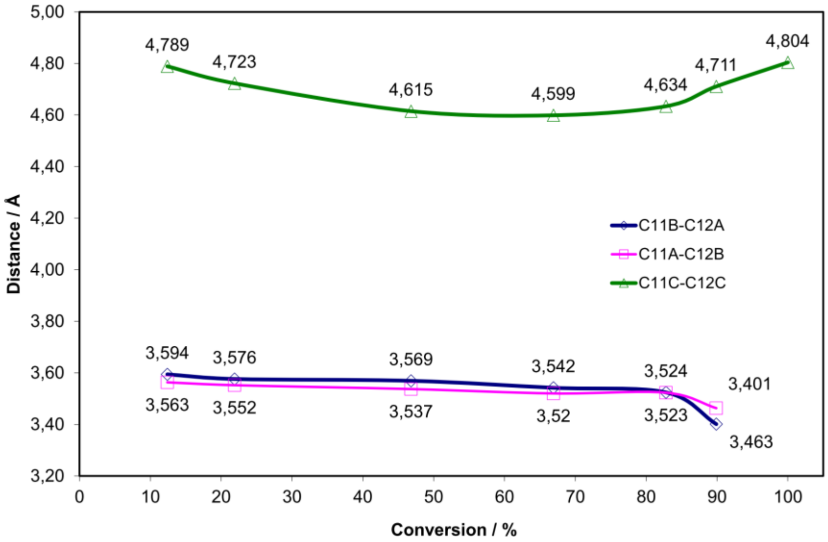


Fig. S4 Predimer distances in the *AB* and *CC* sites as stage 1 of the reaction at 343 K proceeds.

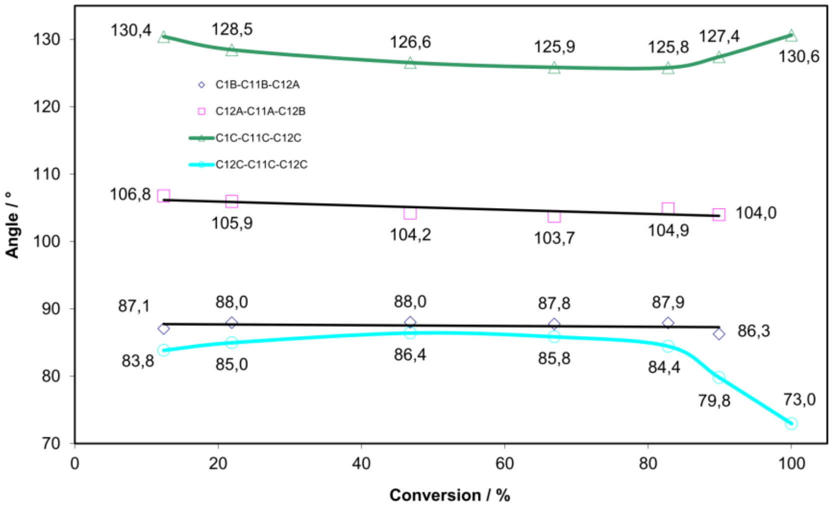


Fig. S5 Changes in molecular geometry in the *AB* site; intermolecular angles (C1B-C11B...C12A and C12A...C11B-C12B) and *CC* site (C1C-C11C...C12C and C12C...C11C-C12C) at different degrees of conversion (in the *AB* site) during the photodimerisation of the α´ polymorph at 343 K.

In addition to changes in the predimer distances, 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 (Fig. S5). Monitoring the intermolecular C1B-C11B…C12A and C12A…C11B-C12B angles (see Fig. S2 for the numbering scheme in *DE* product which was adapted from molecules *A* and *B*) shows that they change from 87.1 and 106.8°, respectively, after 6 hours (structure 6 h; 12% conversion) of UV exposure to 86.3 and 104.0°, respectively, after 48 hours (structure 48 h; 90% conversion in the *AB* site) of UV exposure. The amount of movement involved is almost identical to the reaction at 293 K. The C11A-C12A…C11B-C12B torsion angle remains approximately constant at about -1.4° throughout the reaction process indicating that molecules *A* and *B* do not rotate relative to each other. Monitoring the equivalent intermolecular angles in the *CC* site (C1C-C11C…C12C and C12C…C11C-C12C) indicates that they initially tend to 90° but then move abruptly away after about 80% conversion. The initial and final C1C-C11C…C12C angle for the molecules in the *CC* site are 130.4 and 125.9°, respectively, at 293 K, and 130.4 and 130.6°, respectively, at 343 K – a difference of about 5° in the two final product crystals. The initial and final C12C…C11C-C12C angle for the molecules in the *CC* site are 83.8 and 82.4°, respectively, at 293 K, and 83.8 and 73.0°, respectively, at 343 K – a difference of about 9.5° between the two final product crystals. This strong response of molecules in the *CC* site to changes in the *AB* site is not just a consequence of steric (or packing) effects, but probably also due to the fact that molecules are linked to molecules in the *AB* site via hydrogen bonds. Consequently, a big change in the *AB* site (in the form of the *DE* to *FG* conformation change) is transmitted directly to molecules in the *CC* site via the hydrogen bonds as well as indirectly through packing effects to surrounding molecules. At 343 K, the crystal also seems to be flexible enough to absorb these changes allowing a SCSC reaction to take place.