



A single-crystal-to-single-crystal Diels-Alder reaction with mixed topochemical and topotactic behaviour

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A single-crystal-to-single-crystal Diels-Alder reaction with mixed topochemical and topotactic behaviour.

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Electron donor/acceptor (EDA) interactions have been found to be very useful in engineering reactive heteromolecular crystals but few examples have been reported in literature. By utilising EDA interactions, crystals of charge transfer (CT) complexes were formed with bis(*N*-allylimino)-1,4-dithiin as the electron acceptor and 9-bromoanthracene as electron donor. The CT crystallised in monoclinic $P2_1/n$ with the crystal structure consisting of stacks of alternating electron donor and acceptor molecules in 1:1 ratio. These crystals are able to undergo a solid-state Diels-Alder reaction with bis(*N*-allylimino)-1,4-dithiin as the dienophile and 9-bromoanthracene as diene. Examination of close contacts indicate that the diene can theoretically react with the dienophile above or below it within a stack as the reaction distances are less than 3.5 Å in both directions. A single crystal was selected and allowed to react at 30°C, analysed at various states of conversion by single-crystal X-ray diffraction, and was found to react by approximately 10% every 6 days, with the reaction occurring in a single direction along the CT stack axis. The solid-state reaction creates void space which leads to a molecular conformational change within the crystal. Consequently, the single crystal started to show significant signs of deterioration after approximately 28% conversion but remained intact upon further reaction, and was found to anneal as 100% conversion was approached, leading to the formation of new intermolecular interactions not present in the starting crystal. The solid-state reaction occurs topochemically when fewer than 28% or more than 80% of the molecules have reacted, with minimal motion during the reaction. In the conversion range of 28-80% the reaction occurs in an almost topotactic manner with significant molecular motion and associated crystal deterioration.

Introduction

Organic reactions such as photochemical dimerisations and Diels-Alder cycloadditions can take place in solid-state constrained environments such as in organic crystals, or in porous crystals or cavitands or 'molecular flasks'. In porous crystals the bulk of the crystal is essentially unchanged as the host provides a scaffold around which the reactions occur.¹ Thermally induced topochemical reactions in the solid state were reviewed in detail by Paul and Curtin as far back as 1973.² In addition, Toda has described numerous efficient thermal and photochemical reactions in the solid-state that were studied in their research group between 1999 and 2004. Some stereo- and enantioselective reactions in crystalline inclusion compounds were also described, together with their mechanisms, which were studied by spectroscopic and X-ray diffraction techniques.³ More recently the strategies used to design or 'engineer' crystal structures (including charge-

transfer crystals) in preparation for possible topochemical solid-state reactions were reviewed by Biradha and Santra.⁴

In the original formulation of the topochemical principle Schmidt and his co-workers⁵ suggested that solid-state reactions occur with minimal motion, and that in solid-state photochemical reactions the atoms involved in the reaction have to be within 4.2 Å of each other; the distance and orientation criteria have since been referred to as Schmidt's criterion. There has over the last 20 years been some debate on what exactly minimal motion actually means. Kaupp^{6,7} has suggested that solid-state reactions occur with maximal motion that sometimes occur when the reaction is heterogeneous rather than homogeneous.⁸ For a heterogeneous reaction it has been suggested that the surface behaviour of all such reactions should be examined via AFM to determine if the solid-state reaction indeed involves minimal motion.⁶ Since the tail-end absorbed radiation (sample irradiated with the lowest energy wavelength able to drive the reaction) technique pioneered by Enkelmann⁹ and co-workers in 1994, single-crystal-to-single-crystal (SCSC) photochemical reactions have become more common. The use of tail-end radiation results in a crystal being reacted more evenly and in many cases allows photochemical reactions that would usually not occur as SCSC reactions to be studied as SCSC reactions.^{10,11} The study of SCSC reactions (both thermal and photochemical) has led to some interesting reaction

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† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: Crystal coordinates as CIF files for all the structures reported in Tables 1 and 2 have been deposited as a compressed file. The CIF files can also be obtained from the Cambridge Crystallographic Data Centre (CCDC). See DOI: 10.1039/x0xx00000x

mechanism discoveries for some of these reactions, and allowed the mechanism of reaction cooperativity to be identified in a few solid-state reactions.¹²⁻¹⁴ Even so, there is still some debate as to whether reactions occur with minimal motion and whether this view is perhaps limiting progress in the field of solid-state chemistry. Reactions that are influenced by the starting coordinates of the parent crystal are currently classified as either topochemical or topotactic.¹⁵ Reactions that occur as SCSC reactions are typically regarded as topochemical reactions and viewed as occurring with minimal motion, while reactions that lead to significant loss of crystal quality (and usually crystal disintegration), but where the structure of the product is influenced by the starting coordinates of the reagents are classified as topotactic reactions and occur with significant molecular motion resulting in crystal disintegration. A topotactic pathway is taken by most solid-state reactions where the starting coordinates of the reagents determine the structure of the resulting product. The solid-state dimerisation of nitrosobenzene derivatives recently reported by Varga, K., *et al* were carried out in different topochemical environments,¹⁶ which allowed them to propose different possible theoretical explanations of the thermal organic reaction mechanisms in the solid state.

The study of SCSC solid-state reactions by conventional 'slow' diffraction techniques only allows us to see the average picture of what is happening in the crystal, compared to the vast array of ever increasing new technologies and spectroscopies becoming available in structural dynamics and photocrystallography.¹⁷ However, considerable mechanistic and other information can be gleaned by the careful analysis of this data.^{8,18-22}

Materials and methods

Materials

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

Synthesis

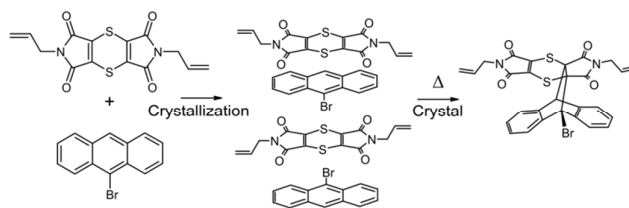
Bis(*N*-Allylimino)-1,4-dithiin was synthesised in a two-step procedure. 1g of dichloromaleic anhydride (5.99mmol) and 0.34g of allylamine (5.96mmol) were dissolved in tetrahydrofuran. The tetrahydrofuran was removed in *vacuo* and the resulting mixture dissolved in acetic acid in a 50ml round bottom flask. This mixture was heated under reflux at 140°C for 1.5 hours. The solvent was then removed in *vacuo* to yield yellow orange crystals, which were then purified by silica gel column chromatography (20% ethyl acetate/hexane) to yield 1.105g (5.36mmol) of yellow crystals of *N*-allyldichloromaleimide (Yield = 90 %).

Into a 20ml round bottom flask 0.200g of *N*-allyldichloromaleimide (0.972mmol) was added, dissolved in ethanol, and heated for five minutes at 80°C. 0.074g of

thiourea (0.972mmol) was dissolved in ethanol and added to the flask. The solution was then heated under reflux for 2 hours during which green crystals began precipitating out of the orange yellow solution. The ethanol was then removed in *vacuo* and the product dissolved in dichloromethane. The organic layer was washed with dichloromethane, water and brine in order to thoroughly extract the product from the aqueous layer after which the dichloromethane solution was dried with anhydrous magnesium sulfate and filtered. The solvent was removed in *vacuo* with bis(*N*-allylimino)-1,4-dithiin crystallising out as green crystals with a yield of 0.162g (76%).

Crystallisation and solid-state reaction

Bis(*N*-allylimino)-1,4-dithiin (0.010g, 0.03mmol) and 9-bromoanthracene (0.008g, 0.03mmol) were dissolved in about 3ml dichloromethane each in separate vials. The donor 9-bromoanthracene solution was then added to acceptor bis(*N*-allylimino)-1,4-dithiin solution and a colour change from purple to brown was observed. Co-crystallisation was induced through vapour diffusion with hexane, which after twenty four hours led to the concomitant crystallisation of brown plate and fine needle like charge transfer crystals. Only the crystal structures and solid-state reactivity of the plate crystals are reported here, as the fine crystals of the second polymorph were too small to study by SCSC reaction. Diffraction quality crystals were selected under a microscope. The first of these were reacted at 40°C and 50°C but found to disintegrate after about 20% conversion. Reaction at 75°C for 24 hours resulted in the crystal maintaining its shape (habit), but which no longer diffracted X-rays. Consequently the data reported here were taken from a crystal which was reacted thermally at 30 °C and analysed after various reaction times by single-crystal X-ray diffraction. The crystal was kept at -20°C after harvesting, and when not reacting or being analysed. The reaction being studied is shown in Scheme 1. Photographs of the crystal before reaction, and at 91% conversion (49 days reaction) are shown in Fig. 1.



Scheme 1

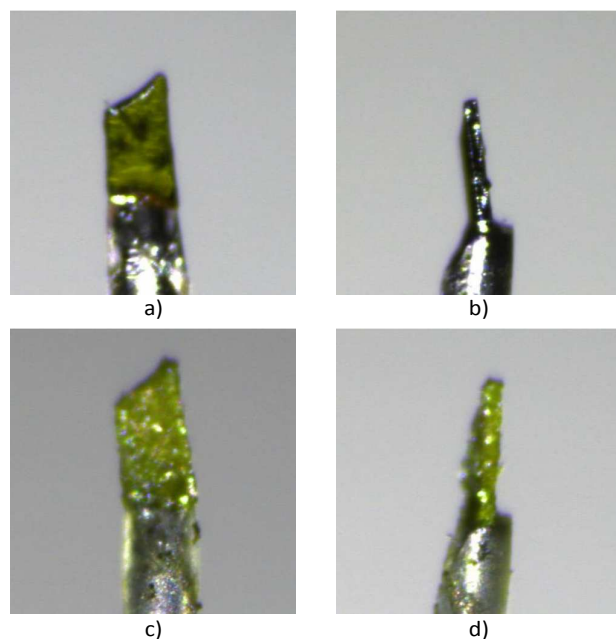


Fig. 1 Photographs of the crystal (a and b) before reaction (CT), and (c and d) after 49 days of reaction (91% conversion). Small fragments due to partial disintegration can be seen on the surface of the crystal as well as on the glass mount after 49 days of reaction. The colour of the crystal is angle dependent, with the colour of the CT being orange in most viewing angles, while it becomes yellow at the reaction proceeds. The angle as mounted on the diffractometer makes this crystal appear green both before and after reaction.

Crystals of the recrystallized product were prepared by reacting 0.020 g of the CT at 130 °C, followed by recrystallization from dichloromethane by slow evaporation, which resulted in a solvated crystal form and non-solvated crystal form.

Crystal structure solution and refinement

Intensity data were collected on a Bruker Venture Photon 100 CCD area detector diffractometer with graphite monochromated Mo K α radiation (50kV, 30mA). The collection method involved ω - and ϕ -scans of width 0.5° and 1024x1024 bit data frames. All crystal structures were solved by direct methods. Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement for most atoms by full matrix least-squares calculations based on F^2 . Atoms for the CT and product components in the reacting crystals were placed from the Fourier difference map to build the initial model if necessary, or by using coordinates of other solved structures as starting coordinates. *SHELXL-2014*²³ restraints such as SIMU, DELU, SADI and DFIX were used during and in the final refinements as required. Reaction conversions were taken as the relative occupancies of the reactant and product molecules in each crystal structure. As a side note, it was not possible to place the CT components in the structure solution for the crystal after 84 days of reaction due to the weak

diffraction data. However, examination of the residual peaks indicated the presence of a peak of about 1.04 eÅ³ at the expected position for the bromine atom of the CT 9-bromoanthracene molecule, which indicated that a small amount of the reagents was still present after 84 days reaction. (See refine_special_details section in the CIF file of the 84 day reacted crystal included in the ESI for more information).

For the two recrystallised product structures it was found that the bromine atom was disordered over two positions due to full molecule disorder, with the remaining atoms approximately in the same position as the dominant structure. While the bromine atom was refined over two positions, it was not possible to place an alternative position for the second orientation for the molecule. Consequently the *R*-factors for the recrystallised products are high. Analysis using *PLATON*²⁴ did not indicate the presence of twinning in both cases. 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: *APEX2*,²⁵ cell refinement and data reduction: *SAINT*,²⁶ program suite used to solve and refine structures: *SHELX-2014*,²³ molecular graphics: *ORTEP-3* for Windows,²⁷ *SCHAKAL-99*²⁸ and *CrystalExplorer-3.1*,²⁹ software used to prepare material for publication: *WinGX-2014.1*³⁰ and *PLATON*.²⁴ Crystallographic information for the CT before and at various stages of conversion can be found in Table 1, while the crystallographic information for the recrystallized product can be found in Table 2. The atom numbering scheme for the CT and product structures can be found in Fig. 2. The same numbering scheme has used for the recrystallised product crystals.

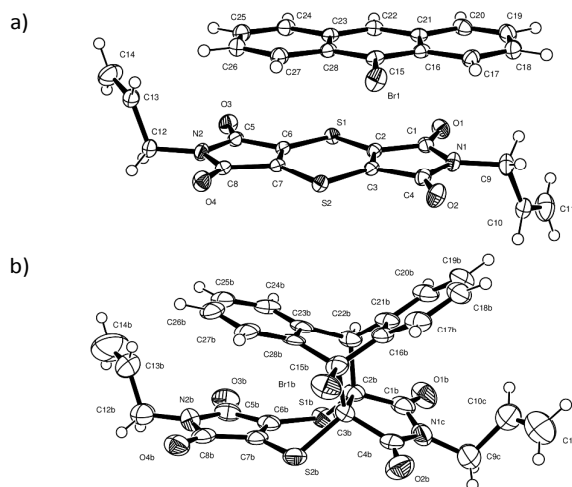


Fig. 2 ORTEP diagrams drawn at the 50% probability level for (a) the CT structure, and (b) for the reaction product (CT components and minor disorder removed for clarity) in a

crystal after 93% conversion (54 days reaction) showing the labelling scheme used in both.

Calculations

Lattice and molecule...molecule interaction energies were calculated using *PIXEL*³¹ as incorporated in the August 2012 version of the *CLP*³² package. The calculations were carried out as prescribed within the *CLP* manual. The calculation was initialized by geometrically normalizing bonds involving *H* to neutron distances within *CLP*, followed by the calculation of an *ab initio* MP2/6-31G(*d,p*) molecular electron density using *Gaussian-09*.³³ This molecular electron density description was then used as input by *PIXEL* to carry out the calculations.

Hirshfeld surfaces were generated using CrystalExplorer-3.1.²⁹

Results and discussion

Charge-transfer crystal and solid-state reaction

Charge transfer crystals of the plate polymorph of bis(*N*-allylimino)-1,4-dithiin (AD) and 9-bromoanthracene (9BrA) were found to crystallise in the space group $P2_1/n$ in a 1:1 donor to acceptor ratio. Crystal packing diagrams are shown in Fig. 3 with crystallographic details given in Table 1.

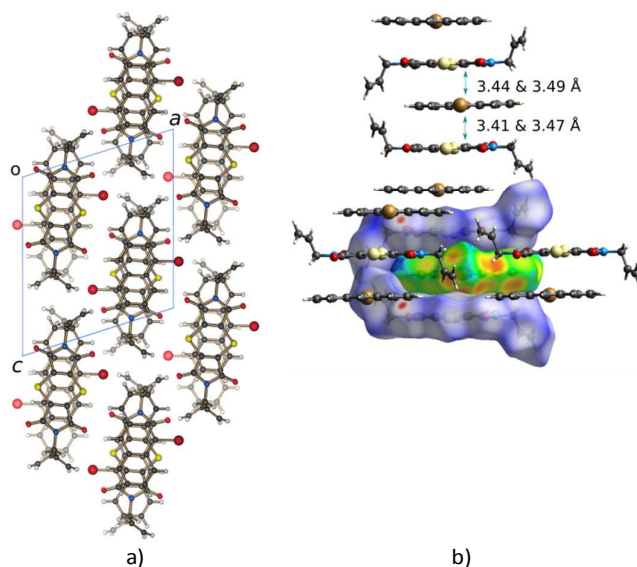


Fig. 3 (a) Packing in the crystal structure of AD:9BrA in which the donor and acceptor molecules alternate in the CT stack formed along the *b* axis. Consequently the bromine atoms also alternate along the CT axis, and point into an area occupied by the allyl groups of two neighbouring stacks. The allyl groups are arranged *trans* to each other in the acceptor molecule as can be seen in (b).

Molecules in the CT structure arrange in stacks where donor and acceptor molecules alternate. The allyl groups on the

acceptor molecules are arranged *trans* to each other. Each allyl group on an acceptor points towards the allyl group on the next acceptor within a stack, with the donor molecule located between them. This results in the donor molecule within a stack effectively being surrounded on three sides by a pocket formed by two acceptor molecules as shown by the blue *d-norm* Hirshfeld surfaces in Fig. 3b which surround the green *de* surface of a bromoanthracene. The solid-state reaction discussed in this paper occurs at the open end of this pocket. Also visible in Fig. 3b is that the bromine atom of the bromoanthracene molecule is surrounded by the allyl groups from acceptor molecules in two neighbouring CT stacks. An unusual feature of this stack - compared to such stacks in previously reported dithiin charge-transfer crystals^{12,34} - is that the dienophiles are pseudo related through a mirror plane defined by the anthracene molecule, which means that the diene interacts with the opposite sides of the same double bond in the dienophile above it and below it. The usual situation is that the dienophiles are related (or pseudo related) by an inversion centre located on the central ring of the anthracene. Distances between the reacting atoms are between 3.41 and 3.49 Å at -100 °C, and therefore well within Schmidt's criterion (< 4.2 Å).⁵ The reaction can therefore theoretically occur in either direction but at 30 and 50 °C occurs along the longer direction indicated in Fig. 3b. This too is unusual, as all other solid-state reactions involving dithiin derivatives with anthracene have been found to occur in both directions along the CT stack, though there is evidence suggesting that there is a lot cooperatively in the process, and that the reaction once initiated occurs to some extent in a single direction before changing direction again.^{12,34} In the case of the AD:9BrA crystal, the reaction seems to be completely cooperative as the reaction only occurs in one direction despite the two distances being approximately equal (differ less than 0.08 Å) to each other. It is likely that this may be a consequence of asymmetry in the local packing environment; this asymmetry being indicated by the previously mentioned pseudo mirror symmetry around the anthracene molecules.

The CT stack after about 20% and 93% conversion (monomers deleted for clarity in this case) to the Diels-Alder product are shown in Fig. 4. A distinctive feature of the reaction is the rotation of one of the allyl groups from a *trans* position (with respect to the other allyl group) to a *cis* position. From a crystal quality point of view, the consequence of this motion is that it leads to crystal degradation after about 20% conversion has occurred. In our first attempt to carry out a SCSC reaction at 30 °C the crystal disintegrated, while the second attempt resulted in the work reported here. Reaction at 75 °C for 24 hours resulted in a crystal that had maintained its crystal habit (though mostly opaque) but no longer diffracted suggesting that at this temperature the reaction is more random, and the molecular motions (the rotation of the allyl group being one of these) more significant.

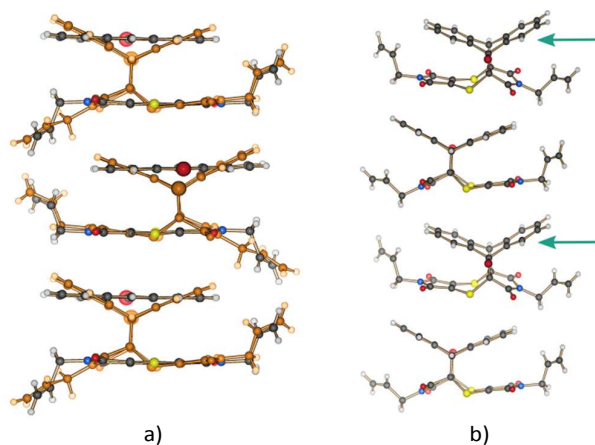


Fig. 4 Molecules in the charge-transfer stack of (a) the crystal at 20% conversion (product in orange), and (b) after 93% conversion (CT monomers deleted for clarity) to the Diels-Alder cycloadduct. Note the position of the allyl groups in the final product which are orientated *trans* with respect to each other initially (a; see also Fig. 3b), but orientated *cis* with respect to each other in the final product crystal (b). Note also that the orientation of the allyl group in the 20% reacted crystal is similar to that of the starting material. It is only after 28% conversion that conformation of this allyl group starts resembling that of the final product. In addition, the product molecules tilt slightly off the original CT stacking axis in the SCSC product crystal as highlighted by the arrows in (b).

While the crystal may experience a significant amount of stress due to the rotation of the allyl group, the process is required as the formation of the Diels-Alder product itself leads to some space (a void) being created between the anthracene and dithiin rings, which bend away from each other during the reaction as shown in Fig. 5a. This space is filled by the allyl group rotating towards the void as the reaction proceeds beyond 20% conversion.

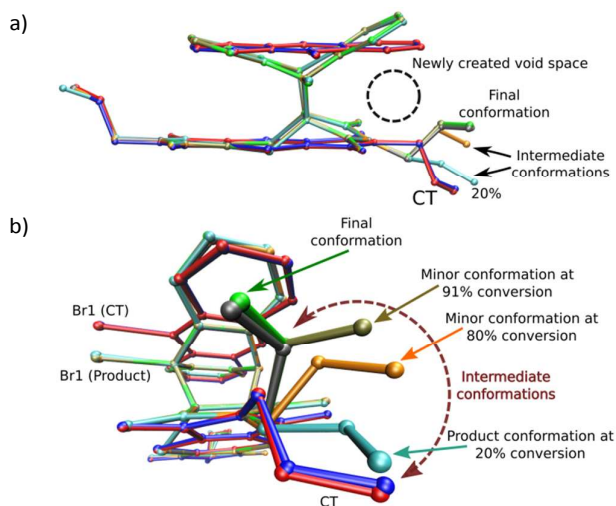
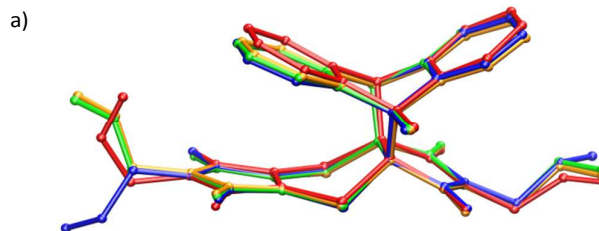


Fig. 5 Overlay by least squares fit of N and S atoms of the unreacted CT structure (blue), the CT molecules in the 28% reacted crystal (red), the product conformation after about 80% conversion [major conformation in grey (65%), minor conformation in orange (15%)], and the product conformation after about 91% conversion [major conformation in green (83%), minor conformation in tan (8%)]. The presence of the minor components indicates the probable path taken by the allyl group during the rotation assuming it is the intermediate allyl conformation. The sole conformation of the product at 20% conversion (orange in Fig. 4a) is also shown. In this conformation the allyl group lies in the same plane as the imide group it is bonded to. In addition, only the major (final) conformation is present in the crystal after 70 days (97% conversion) or more reaction.

Analysis of the allyl conformation in the starting CT structure, the product conformation at 20% conversion, and two almost completely reacted crystals also indicates the path taken by the allyl group during the reaction (Fig. 5b). This concerted motion probably also leads to the slight tilt of the product molecules relative to the CT axis visible in Fig. 4b. The tilt alternates between $+5$ to -5° relative to the *b* axis for each successive product molecule, with the rotation occurring parallel to the *c* axis (see Fig. 3a for axes). In order to determine the most stable allyl conformation likely to be adopted by the product, some reacted product was recrystallized by slow evaporation from dichloromethane leading to two crystal forms: non-solvated product crystals, and dichloromethane solvate product crystals. The resulting product conformation from the recrystallised product structures, and the product from the 91% and 93% reacted crystal structures are shown in Fig. 6. Ironically, the allyl group that does not undergo rotation during the SCSC reaction is the one that shows the most variation in the molecules from the various structures. However, the allyl group that does undergo rotation during the solid-state reaction does adopt approximately the same conformation in all these structures. This suggests that one of the driving forces for the molecular rotation is minimisation of the intramolecular energy, with the creation of void space during the reaction allowing the process to occur. In the case of the allyl group that does not move, the conformation in both the CT and the reacted product is about the same but different from the recrystallized structures. C-H...O interactions involving this allyl group increase in strength as the crystal anneals near the end of reaction, and may hold it in place during the reaction (see H-bonds C14-H14B...O3 and C14B-H14D...O3B in Table 3).



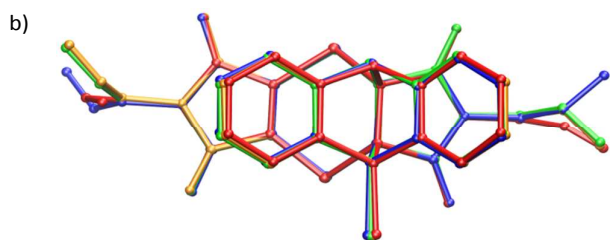


Fig. 6 Overlay by least squares fit of Br, N, O and S atoms of the recrystallised product crystal (red), recrystallised product dichloromethane solvate crystal (blue), solid-state reaction product after 91% (orange) and 93% (green) conversion.

The mobile allyl group also forms new weak interactions as it changes position as can be seen by examining close contacts involving the affected allyl group before and after the reaction. While the strongest interactions in the CT and reaction product structures are dominated by charge-transfer and $\pi\cdots\pi$ interactions, the structure is also stabilised by C-H...O and C-H...Br interactions. The weakening of some of these present in the CT structure followed by the strengthening of other hydrogen bonds, and the appearance of a new one in the reacted crystal can be seen in the Hirshfeld surfaces in Fig. 7 and the H-bond list in Table 3. The Hirshfeld surfaces for the CT before reaction (Fig. 7a and c) indicate that the carbonyl groups are involved in strong C-H...O interactions with the aromatic hydrogen atoms of the anthracene molecules from neighbouring stacks. One of these – C22-H22...O1 – lengthens dramatically as C22 is directly involved in the reaction, changing from an aromatic sp^2 carbon, to an alkyl sp^3 carbon in the process; the C22...O1 distance which is 3.350 Å before reaction, lengthens to 3.762 Å at 97%, and is therefore absent in the Hirshfeld surface of the product

At the beginning of the reaction there are no significant C-H...O or C-H...Br interactions involving either of the allyl groups as can be seen in Table 3, where hydrogen bonds involving C11 or C14 with O or Br are either long or non-existent. However, after 80% conversion very significant C-H...O interactions appear, involving both allyl groups now interacting with the carbonyl groups on molecules in neighbouring stacks. In the case of the conformationally stable allyl group, strong C-H...O interactions involving C14 are formed in the direction of a nearby carbonyl group, presumably due to the relaxation (annealing) of the structure near the end of the reaction. In this case the C14...O3 distance shortens from 3.602 Å in the CT, to 3.331 Å in the reaction product (Table 3). No conformational change is required by this allyl group to bring about the interaction, and the C-H...O interaction is centrosymmetric resulting in the formation of a molecular dimer that can be seen in Fig. 7d. On the other hand, the allyl group that does undergo conformational change forms two new interactions which are not present in the original CT structure: a weak C-H...Br (C11C-H11F...Br1B) interaction indicated in Fig. 7b, and a C-H...O interaction (C11C-H11E...O3B) visible in Fig. 7d. These can only form if the allyl group rotates into the correct position as can be seen by

comparing the allyl groups in Figs. 6c and d. The overall effect of the conformational change is the optimisation of the intramolecular energy of the molecule as well as the intermolecular energy of the crystal. The geometrical parameters of these hydrogen bonds are listed in Table 3. In addition to changes in the hydrogen bonding, there is also a short contact involving S1 and O4 which shortens from 3.487 Å (C8-O4...S1) in the CT, to 3.302 Å (C8B-O4B...S1B) at 97% conversion.

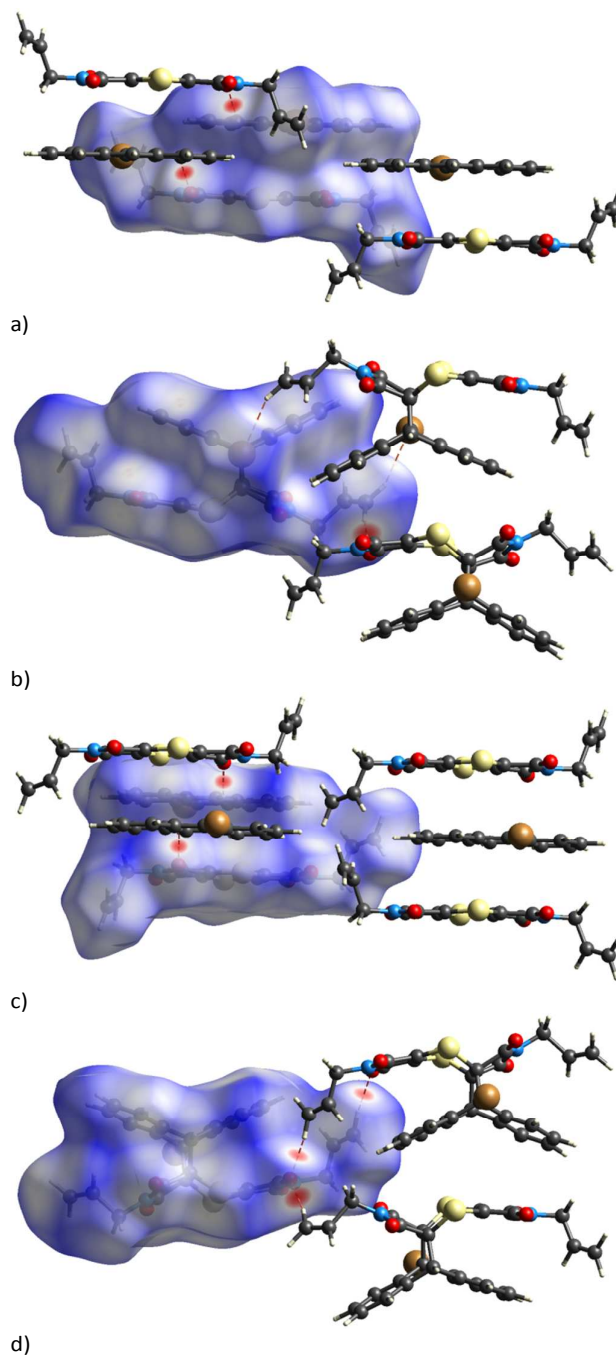


Fig. 7 Hirshfeld surfaces around the reacting molecules with bromine atom pointing out of the page before (a) and after (b)

the reaction, as well as with the bromine pointing into the page before (c) and after (d) the reaction. Hirshfeld surfaces of the product phase for crystals reacted to 91% or more display the same features.

Table 3 Hydrogen bond geometries in the CT structure before reaction, at 93% conversion, and at 97% conversion (\AA , $^\circ$). Symmetry codes for acceptor atoms: (i) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (ii) $-x, 1-y, 1-z$; (iii) $-x, 1-y, -z$; (iv) $1-x, 1-y, 1-z$; (v) $1-x, 1-y, -z$; (vi) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

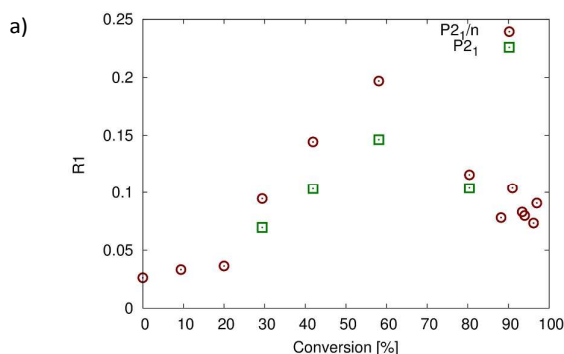
D-H...A	D-H	H...A	D...A	<D-H...A
CT				
C11-H11...O3 ⁱ	Not possible in this orientation			
C14-H14B...O3 ⁱⁱ	0.95	2.76	3.602(2)	148
C22-H22*...O1ⁱⁱⁱ	0.95	2.54	3.350(2)	144
C27-H27...O4 ^{iv}	0.95	2.48	3.239(2)	136
C11-H11B...Br1 ^v	Not possible in this orientation			
C8-O4...S1 ^{vi}			3.487(1)	145.8(1)
54 Days (93%) Product structure				
C11C-H11E...O3B ⁱ	0.95	2.33	3.270(13)	171
C14B-H14D...O3B ⁱⁱ	0.95	2.48	3.330(16)	149
C22B-H22B*...O1Bⁱⁱⁱ	1.00	2.97	3.765(10)	137
C27B-H27B...O4B ^{iv}	0.95	2.62	3.204(10)	120
C11C-H11F...Br1B ^v	0.95	3.02	3.849(12)	147
C8B-O4B...S1B ^{vi}			3.297(6)	145.3(6)
70 Days (97%) Product structure				
C11C-H11E...O3B ⁱ	0.95	2.36	3.308(14)	178
C14B-H14D...O3B ⁱⁱ	0.95	2.48	3.331(16)	149
C22B-H22B*...O1Bⁱⁱⁱ	1.00	2.98	3.762(9)	136
C27B-H27B...O4B ^{iv}	0.95	2.63	3.205(9)	120
C11C-H11F...Br1B ^v	0.95	3.03	3.846(13)	145
C8B-O4B...S1B ^{vi}			3.302(5)	145.2(5)

*converted from aromatic to methine hydrogen in reaction

Crystallographic details related to the solid-state reaction

Crystallographic and refinement details are listed in Table 1. The crystal structures of the reacting crystal were initially solved in $P2_1/n$ which result in R -factor values (SHELX $R1$ index for all data with $I > 2\sigma$) less than 4% when reaction conversion was 20% or less. Beyond this point the crystal starts to degrade with the R -factor increasing to 9.6% at about 28% conversion, reaching a maximum of 19.7% at about 60% conversion when solved in $P2_1/n$ (Fig. 8a). Solving the structure in $P2_1$ - structure treated as two reaction sites related by a pseudo inversion centre - results in significantly lower R -factor values that are anywhere from 3-5% lower than in the $P2_1/n$ solution, as well as probably providing more accurate occupancy values for the reacting crystal between 30% and 80% conversion, even

though the data to parameter ratio for these solutions is low (Fig. 8a). While the average structure at this stage can still be described as $P2_1/n$, the structure is best described at a local level using a $P2_1$ model after 20% conversion. After 80% conversion the R -factor values for models in the two space groups are similar suggesting that the average structure can be adequately (from an R -factor perspective) described by a $P2_1/n$ model. The reaction therefore seems to occur in stages, with the product formed during the first stage of solid-state reaction adopting a conformation compatible with the starting (or parent) CT crystal (see 20% product conformation in Figs. 4a and 5b). The reaction can probably be described as occurring topochemically (minimal atomic motion) during this stage. After more than 20% conversion the product starts to influence the overall structure of the crystal with significant molecular motions involving one of the allyl groups occurring in order to stabilise this intermediate structure by adopting a more favourable geometry from an intramolecular energy point of view. This stage coincides with the high R -factor values in the range of 28-80% conversion in Fig. 8a. The structure appears to be an intermediate between the starting CT crystal and the final product crystal at this stage. Whether the reaction should be described as topochemical at this stage is debatable as very significant motions are occurring within the crystal at this point, but the crystal remains essentially intact. In the final stage (after 80% conversion) the crystal is dominated by the product, and anneals towards the product crystal structure, with the formation or optimization of the C-H...O and C-H...Br interactions involving the rotating allyl group, and the tilting of the product molecules off the original CT axis mentioned previously. The R -factor decreases to more reasonable values at this stage as the crystal anneals. The three stages of reaction probably also account for the sigmoidal look of the conversion versus time plot shown Fig. 8b. The reaction starts relatively slowly initially as it is held back by the structure of the CT crystal, then speeds up in the intermediary stages as the reaction creates void space, then slows down again as the crystal anneals towards the product crystal structure. It is likely that the annealing crystal does not allow the movements required for easy further reaction as the reaction nears completion in the final stage, slowing the reaction down.



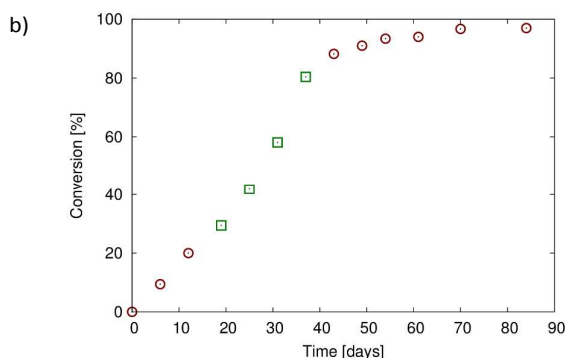


Fig. 8 (a) Plot of $R1$ (R -factor) values for structures at different states of conversion solved in $P2_1/n$ (all structures) and in $P2_1$ for conversions between 28% and 80%. The structures solve in $P2_1/n$ with R -factor values less than 5% up to 20% conversion, but after these solve with much higher R -factors reaching a maximum of 19.7% at 60% conversion. Solving the structures at 28–80% conversion in $P2_1$ instead leads to significantly lower R -factor values. (b) Plot of percent conversion against reaction time. Points 4–6 (28 – 80% conversion) are from the $P2_1$ structure solutions [green points in (a)], with the remainder from the $P2_1/n$ structure solutions. The graphs in Fig. 10 are plotted with respect to the conversion values shown in (b).

The deterioration of crystal quality due the solid-state reaction can also be seen in the diffraction patterns of the sample. Reconstructions of the $h0l$ layer are shown in Fig. 9. As can be seen the diffraction range of the crystal decreases from diffracting beyond 0.75 \AA resolution at 10 seconds exposure in the starting CT (Fig. 9a), to barely diffracting to 1.0 \AA resolution after more than 90% conversion at 60 seconds of exposure on the same instrument (Fig. 9c). Also visible in Fig. 9c is a broad powder ring around the beam stop which indicates that the crystal exterior is also undergoing a phase change (or becoming amorphous) while still maintaining the crystal habit as the reaction continues.

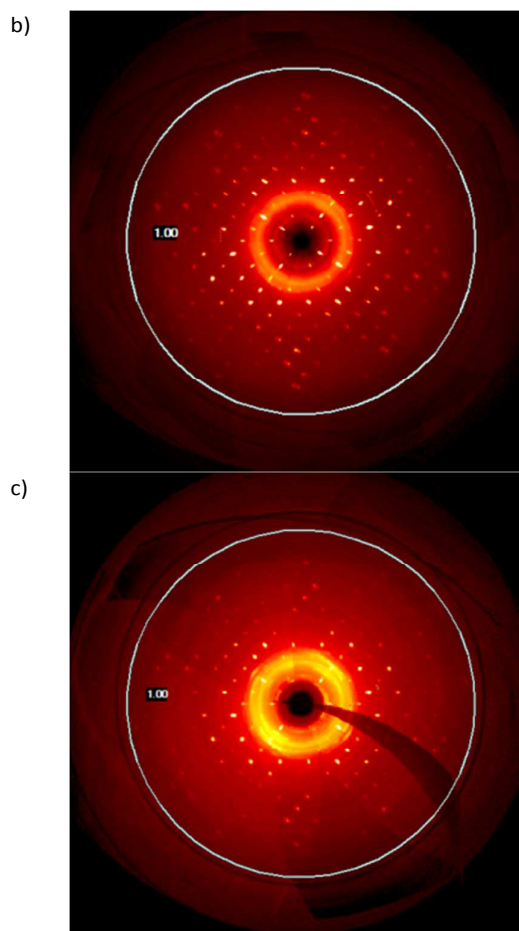
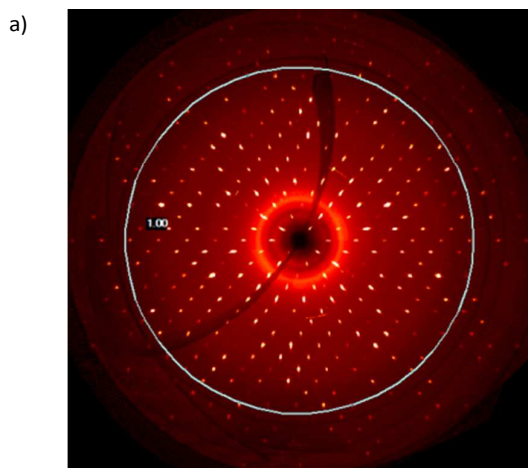


Fig. 9 Reconstructions of the $h0l$ diffraction layer at various degrees of conversion; (a) CT crystal before reaction, (b) after 31 days reaction (58% conversion), and (c) after 49 days reaction (91% conversion).

Despite the large change in R -factor during intermediate stages of the reaction (about 28–80% of conversion), the unit cell parameters do not change very much. The changes in unit cell parameters, as well as the percent change in unit cell parameters with reaction conversion are shown in Fig. 10. The a unit cell parameter decreases slightly [about $\sim 0.22 \text{ \AA}$ ($\sim 1.7\%$)] over the course of the reaction. The c unit cell parameter decreases by about $\sim 0.26 \text{ \AA}$ ($\sim 1.7\%$) until 80% conversion is reached. At this point c starts to lengthen and at 97% conversion is $\sim 0.11 \text{ \AA}$ (0.78%) longer than in the CT. These axes are orientated perpendicular to the reacting stack axis (CT stack is parallel to b) and would therefore not be expected to change much. The b axis increases by $\sim 0.64 \text{ \AA}$ ($\sim 4.7\%$). This large change is probably due to the Diels-Alder cycloadduct being formed in this direction within the stack axis. The molecules expand along the b axis, and the movement of the allyl groups also occurs along the stack axes. The β angle increases by $\sim 3.0^\circ$ ($\sim 2.8\%$) as the CT stacks relax (anneal) into new positions with respect to each other near the end of the reaction. While the volume data in Fig. 10c are erratic due to

the weak data, the overall trend is an increase of cell volume of $\sim 41 \text{ \AA}^3$ ($\sim 1.7\%$).

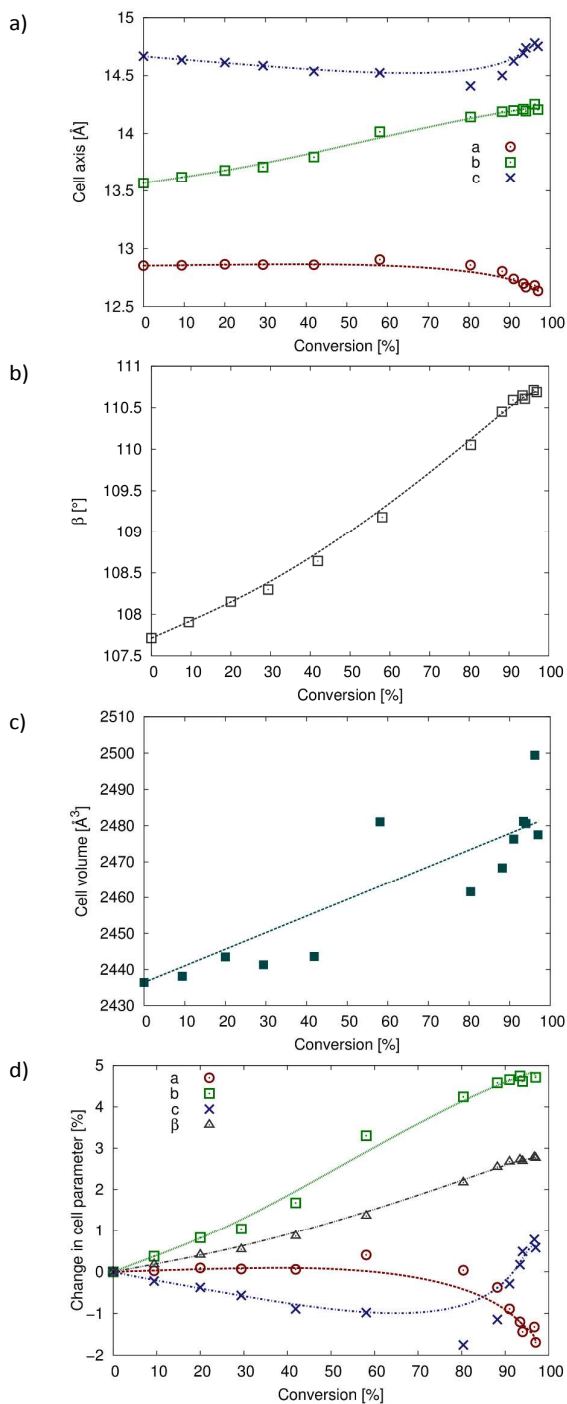


Fig. 10 Changes in unit cell parameters with degree of conversion. (a) Changes in *a*, *b* and *c*; (b) change in β angle; (c) change in cell volume; (d) percent change in cell parameters with percent conversion.

Comparison between solid-state and solution recrystallized products

The non-solvated recrystallized product crystallises in $P2_1/c$ with one molecule in the asymmetric unit (Fig. 11a), while the solvated recrystallized product crystallizes in $P-1$ with one product molecule and one dichloromethane molecule in the asymmetric unit (Table 2). The bromine atom is disordered in both structures over the two sides of the ex-anthracene part of the molecule indicating the presence of full molecule disorder in both structures. While it was not possible to place the minor alternate position for the lighter elements in both structures, the bromine atom was refined over two position in both structures with an occupancy ratio of 0.862(2):0.138(2) in the non-solvated crystal, and an occupancy ratio of 0.908(4):0.092(4) in the dichloromethane solvate. In addition, one of the allyl groups in the non-solvated structure is rotationally disordered over two sites in a ratio of 0.781(14):0.219(14). A unique feature of the product molecule in the non-solvated crystal is that one of the allyl groups is orientated upwards such that it is wedged between two carbons of an ex-anthracene benzene ring in a conformation reminiscent of a scorpion tail (Fig. 11a).

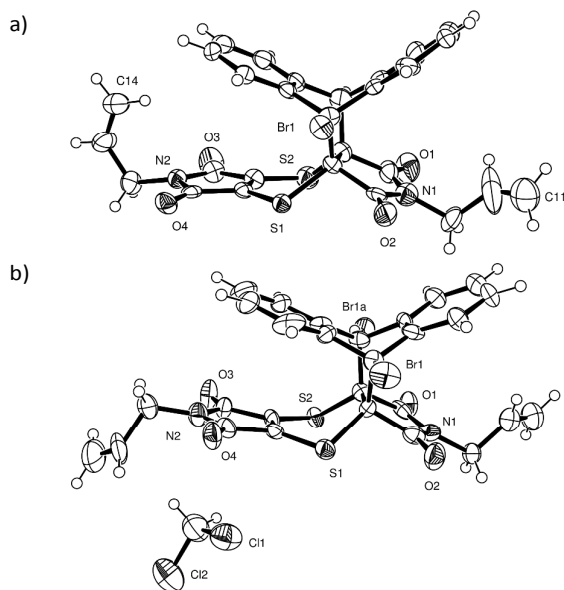


Fig. 11 ORTEP diagrams drawn at the 50% probability level for (a) the non-solvated recrystallized product (alternate disordered bromine atom and alternate disordered position of the allyl group around C11 removed for clarity), and (b) for the dichloromethane solvate of the reaction product with alternate bromine position (Br1a) which is present in both the solvated and non-solvated structures also indicated.

Unlike the solid-state reacted crystal where molecules stack on each other, and where electron poor (ex-dithiin) regions of the product molecules interface with the electron rich (ex-anthracene) regions of neighbouring molecules within a stack

(Fig. 4b), molecules in the non-solvated recrystallized product first overlap on each other on the ex-anthracene regions to form π ... π dimers which then pack in an edge-to-face manner to form a zig-zag or herring bone type structure (Fig. 12a). In the solvated product crystal, the molecules arrange in stacks similar to those in the solid-state reaction product. However, while the molecules are vertically arranged on top of each other in the SCSC product – this being a consequence of the starting CT structure – the product molecules in the solvated crystal structure are displaced relative to each other, with an allyl group sitting over the aromatic rings of the product below it in the stack, and with dichloromethane molecules filling up the space between the product molecules (Fig. 12b).

Lattice energy calculations carried out with *PIXEL*³¹ involving only the dominant conformation in the non-solvated recrystallized product crystal yields an energy of -213.4 kJ/mol. Carrying out the same calculation for only the product (dominant conformation) in the SCSC reacted crystals which have reacted 91% or more, yields energies of about -195(1) kJ/mol. Ignoring the difference in the intramolecular energies (which may be significant), the solution grown product is clearly more stable from an intermolecular point of view. The solid-state reaction has, however, resulted in a very different crystal from those obtained from solution and provides a method for producing metastable crystals.

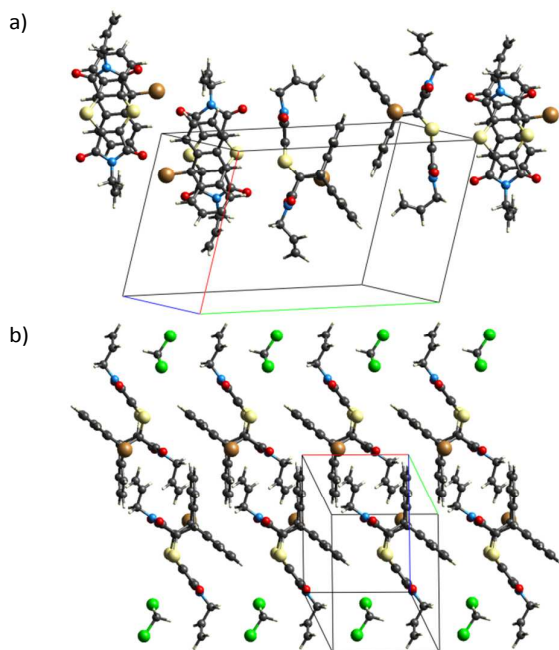
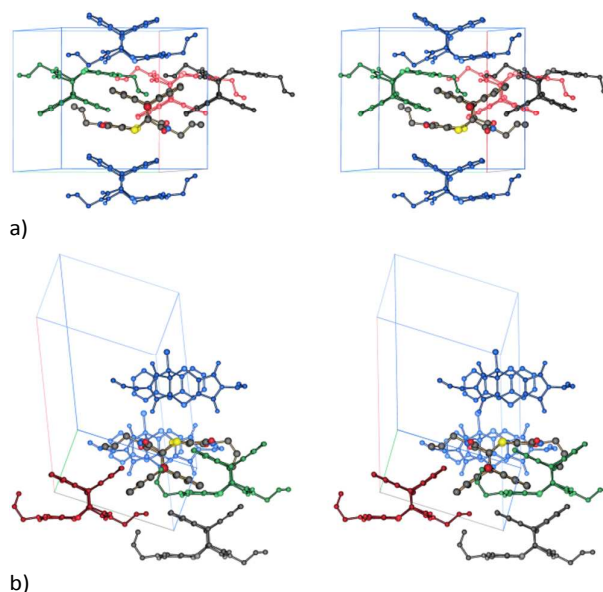


Fig. 12 Crystal packing in (a) the non-solvated recrystallized product (molecules interacting in a π ... π manner, and in an edge-to-face manner clearly visible), and (b) for the dichloromethane solvate where product molecules pack in stacks similar to the stacks found in the SCSC product, but with the allyl group over the benzene ring, and the

dichloromethane molecules filling up the gap between the product molecules.

For comparison, molecule...molecule interactions stronger than -35 kJ/mol present in each of the three product crystals (SCSC derived and both recrystallized forms) are shown in Fig. 13. For the SCSC product, the strongest interactions are with molecules in neighbouring stacks related by an inversion axis [data from 54 day reacted (93% conversion) crystal, lattice energy 195.7 kJ/mol]; all contribute -55 kJ/mol or more, with the strongest interaction contributing -60.2 kJ/mol (Fig. 13a). Molecules along the stacking (ex-CT axis) contribute to the fourth strongest interaction at -50.6 kJ/mol. The molecule...molecule interaction bringing the centrosymmetric C-H...O interaction shown in Fig. 7d into alignment contributes -26.7 kJ/mol in this structure, while the molecule...molecule interaction associated with the new C-H...O hydrogen bond contributes -18.7 kJ/mol. The molecule...molecule interaction associated with the S1...O4 interaction listed in Table 3 contributes -15.1 kJ/mol, with the energy contributions due to Coulombic, polarization, dispersion and repulsive forces being -4.1, -3.5, -18.8 and 11.4 kJ/mol respectively, indicating that the S...O interaction is attractive in this case, though these numbers are for the full molecule...molecule interaction.

In the non-solvated recrystallized product, the strongest interaction is between the π ... π interacting dimers discussed previously at -71.0 kJ/mol, while the edge-to-face interaction contributes about -42.9 kJ/mol (Fig. 13b). For the solvated recrystallized product, the strongest interaction is with a molecule related by an inversion centre in a neighbouring stack at -69.6 kJ/mol, while molecules along the stack discussed previously have a molecule...molecule interaction energy of -50.7 kJ/mol (Fig. 12c). Interactions involving the dichloromethane contribute less than -25 kJ/mol each to the lattice energy.



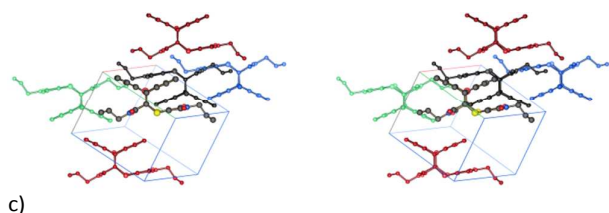


Fig. 13 Stereo diagrams showing molecule...molecule interaction energies (kJ/mol) stronger than -35 kJ/mol between a central reference product molecule (drawn with larger atomic radii and standard atom colours) and surrounding molecules (colour coded according to energy) for (a) the SCSC reaction product (black: -60.2; red: -56.4; green: -55.4; blue: -50.6), (b) the non-solvated recrystallized product (black: -71.0; red: -53.1; green: -46.6; blue: -42.9), and (c) for the dichloromethane solvate (black: -69.6; red: -40.5; green: -39.8; blue: -38.5). Cell axis colours are as follows: *a* in grey, *b* in red, and *c* in green.

Conclusions

This work shows that SCSC reactions do not necessarily occur *via* a completely topochemical pathway. In the reaction studied here, an allyl group rotates by almost 180° to fill a void created by the solid-state reaction. The process occurs in stages, during which good crystallinity is observed until about 20% conversion. The crystal structure of the CT dominates the reaction and the conformation of the product at this point. After about 28% conversion, the *R*-factor increases dramatically, reaching about 19% after about 50% conversion. Molecular movements dominate the structure at this time, and the reaction can, to some extent, be regarded as occurring topotactically. However, once 80% conversion is reached, the crystal starts to anneal, with new C-H...O interactions involving the rotating allyl group being formed, and others being strengthened in the process. In addition, the product molecules tilt slightly relative to the original CT axis. Consequently, the driving force for the conformational change is a combination of minimizing the intramolecular energy of the molecule and the intermolecular energy of the crystal. When the reaction product is recrystallized from dichloromethane a non-solvated crystal form, as well as a dichloromethane solvate form is obtained. Both contain considerable full molecule disorder. This work shows that a more ordered single crystal of the product can be obtained by SCSC synthesis, provided one can wait more than two months for the reaction to complete (for reaction at 30°C), and provided one can stop the SCSC product crystal from undergoing a phase change to a more stable form during and after the reaction.

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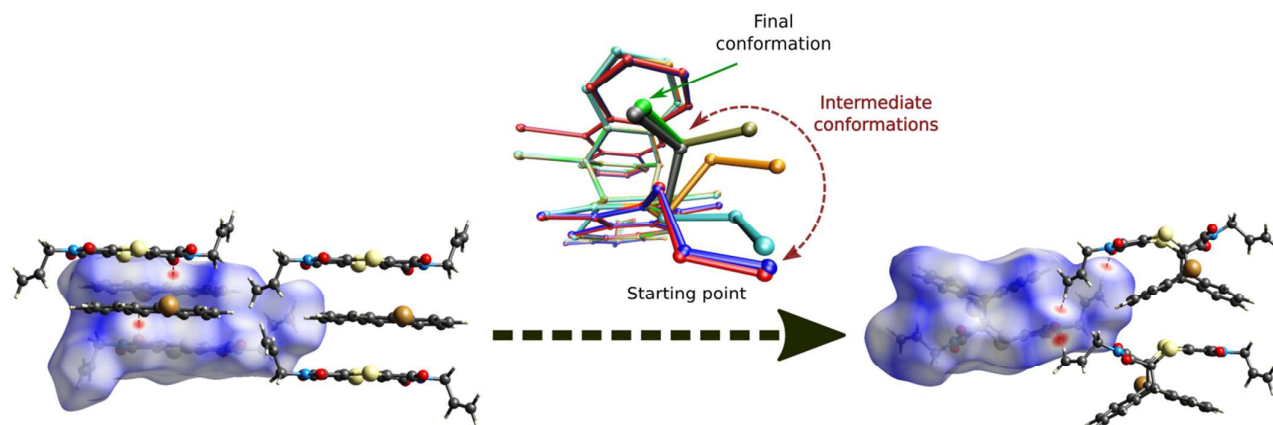
Table 1 Crystallographic and refinement data for reacted CT crystals (molecular formula: $C_{14}H_{10}N_2O_4S_2$, $C_{14}H_9Br$; Formula weight: 591.48). Data for crystals which have undergone up to 20% conversion, or more than 80% conversion were solved in space group $P2_1/n$. Data for crystals which have undergone between 20-80% conversion were found to solve best in $P2_1$ and have been included here instead of the $P2_1/n$ refinements. See text for details.

Conversion/%	0 (starting CT)	9.4 (6 days)	20.1 (12 days)	29.4 (19 days)	41.9 (25 days)	58.1 (31 days)	80.4 (37 days)	88.2 (43 days)	91.0 (49 days)	93.4 (54 days)	94.0 (61 days)	96.7 (70 days)	97 (84 days)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
a/Å	12.8529(5)	12.8561(4)	12.8650(6)	12.8617(8)	12.8605(14)	12.905(2)	12.8578(11)	12.8049(10)	12.7386(12)	12.6987(10)	12.668(2)	12.6830(16)	12.6357(10)
b/Å	13.5669(4)	13.6180(4)	13.6783(6)	13.7077(8)	13.7943(15)	14.015(2)	14.1427(12)	14.1886(9)	14.1989(11)	14.2111(11)	14.193(3)	14.2527(17)	14.2062(11)
c/Å	14.6676(5)	14.6351(5)	14.6129(7)	14.5846(9)	14.5372(16)	14.524(3)	14.4105(13)	14.4999(11)	14.6254(12)	14.6928(12)	14.740(3)	14.782(2)	14.7531(12)
β /°	107.7130(10)	107.9060(10)	108.152(2)	108.297(2)	108.642(4)	109.180(4)	110.053(4)	110.453(3)	110.594(4)	110.648(3)	110.608(5)	110.713(4)	110.689(4)
Unit cell volume/Å ³	2436.40(15)	2438.12(13)	2443.5(2)	2441.3(3)	2443.6(5)	2481.1(7)	2461.6(4)	2468.3(3)	2476.3(4)	2481.2(3)	2480.6(8)	2499.4(6)	2477.5(3)
Temperature/K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Density (Calc.)/ g cm ⁻³	1.613	1.612	1.608	1.609	1.608	1.583	1.596	1.592	1.587	1.583	1.584	1.572	1.586
Z	4	4	4	4	4	4	4	4	4	4	4	4	4
Radiation type	MoK α	MoK α	MoK α	MoK α	MoK α	MoK α	MoK α	MoK α	MoK α	MoK α	MoK α	MoK α	MoK α
Absorption coefficient, μ /mm ⁻¹	1.899	1.898	1.894	1.895	1.893	1.865	1.880	1.874	1.868	1.865	1.865	1.851	1.868
Absorption correction	Integration	Integration	Integration	Integration	Integration	Integration	Integration	Integration	Integration	Integration	Integration	Integration	Integration
No. of reflections measured	85876	86184	62425	61508	56880	96915	42789	65093	34735	62291	23758	32098	53951
No. of independent reflections	5873	5879	5888	8587	8583	8691	8630	4346	4364	4369	4336	4396	3888
R_{int}	0.0479	0.0613	0.0512	0.0829	0.1335	0.2648	0.2129	0.3217	0.3077	0.2943	0.2266	0.2398	0.3034
Final R_1 ($I > 2\sigma(I)$)	0.0263	0.0333	0.0364	0.0696	0.1032	0.1463	0.1038	0.0781	0.1037	0.0830	0.0799	0.0725	0.0907
Final $wR(F^2)$ ($I > 2\sigma(I)$)	0.0667	0.0756	0.0906	0.1632	0.2494	0.3412	0.2351	0.1613	0.1538	0.1447	0.1465	0.1200	0.1432
Final R_1 (all data)	0.0349	0.0526	0.0554	0.1057	0.1724	0.2358	0.2224	0.1656	0.2066	0.1621	0.1864	0.1588	0.1502
Final $wR(F^2)$ (all data)	0.0715	0.0836	0.1018	0.1880	0.2982	0.4108	0.2969	0.1988	0.1942	0.1747	0.1909	0.1482	0.1663
Goodness of fit on F^2	1.032	1.020	1.042	1.062	1.043	1.039	1.045	1.016	1.040	1.030	1.019	1.027	1.128
CCDC number	1409360	1409361	1409362	1409363	1409364	1409365	1409366	1409367	1409368	1409369	1409370	1409371	1417564

Table 2 Crystallographic and refinement data for recrystallised product crystals.

	Non-solvated	Dichloromethane solvate
Molecular formula	C ₂₈ H ₁₉ BrN ₂ O ₄ S ₂	C ₂₈ H ₂₀ BrN ₂ O ₄ S ₂ · CH ₂ Cl ₂
Formula Mass	591.48	677.41
Crystal system	Monoclinic	Triclinic
a/Å	12.7053(8)	8.2573(9)
b/Å	23.1346(14)	12.5878(13)
c/Å	8.5162(5)	14.5411(16)
α/°	90	110.120(6)
β/°	103.246(4)	90.583(7)
γ/°	90	99.971(6)
Unit cell volume/Å ³	2436.6(3)	1393.8(3)
Temperature/K	-100	-50
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1
Density (Calc.)/g cm ⁻³	1.612	1.614
Z	4	2
Radiation type	MoKα	MoKα
Absorption coefficient, μ/mm ⁻¹	1.899	1.856
Absorption correction	Integration	Integration
No. of reflections measured	22108	21563
No. of independent reflections	5878	5449
<i>R</i> _{int}	0.0861	0.1251
Final <i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0664	0.1111
Final <i>wR</i> (<i>F</i> ²) (<i>I</i> > 2σ(<i>I</i>))	0.1549	0.3219
Final <i>R</i> 1 (all data)	0.1324	0.1864
Final <i>wR</i> (<i>F</i> ²) (all data)	0.1709	0.3543
Goodness of fit on <i>F</i> ²	1.029	1.075
CCDC number	1409373	1409372

Graphical abstract



During a SCSC solid-state Diels-Alder reaction, voids are created, followed by conformational change and crystal annealing that leads to the formation of new weak interactions.