

MS33-O2 Photomechanical actuation in organic crystals: expansion, bending, coiling, twisting and peelingRabih O. Al-Kaysi¹

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In some organic crystals light can be absorbed to trigger a topologically controlled photochemical reaction. In general the photochemical reaction inside the crystal generates forces that can shatter a large single crystal and turn it to photoproduct powder. The shape, size and chemistry of the material making up the crystal have a drastic effect on the way these internal forces affect the crystal during a photochemical reaction. For molecular crystal nanowires made from *tert*-butyl anthracene-9-carboxylate photoreaction leads to an anisotropic expansion by up to 15% along the long axis of the wire. When single crystalline microribbons of fluorinated-9-anthracene carboxylic acid are irradiated with UV light, the ribbons twist then untwist after the light is switched off. Crystalline microblocks made from *cis*-dimethyl-2(3-(anthracen-9-yl)allylidene)malonate tend to peel off photoreacted layers after a brief exposure to visible light (405 nm).

Keywords: Photomechanics, Light, Molecular Crystals.

MS33-O3 Solid-state photodimerization of *o*-ethoxy-cinnamic acidDemetrius C. Levendis¹, Manuel A. Fernandes²

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The complexity of this textbook example, where photodimerisation depends on the relative arrangement of molecules in each of the four polymorphs (α , β , γ and δ), has not yet been fully recognized. In this paper, we will discuss the intermolecular interactions that shape the polymorphs, crystal hopping, phase transformations and solid-state photodimerisation of *ortho*-ethoxy-cinnamic acid (*oetca*), all of which depend on the experimental conditions, crystallization method, and the history of the crystal.

On heating crystals of the α -form of *oetca* to 60 °C they hop, depending on the face that is in contact with the hot surface. Thereafter the crystals no longer hop, but undergo a reversible phase transformation from the α ($V = 499.5 \text{ \AA}^3$) to the δ (or α') form ($V = 1492.4 \text{ \AA}^3$). This is accompanied by a twisting of the molecules that may, at least in part, be the cause of the crystal hopping. The α and δ polymorphs undergo solid-state photodimerisation in different ways depending on whether it is carried out at room temperature or above 60 °C.

[1] Fernandes, M. A., Levendis, D. C., Schoening, F. R. L. (2004) A new polymorph of *ortho*-ethoxy-*trans*-cinnamic acid: single-to-single-crystal phase transformation and mechanism. *Acta Cryst. Section B-Structural Science*, **60**, 300-314.

[2] Fernandes, M. A., Levendis, D. C. (2004) Photodimerization of the α' -polymorph of *ortho*-ethoxy-*trans*-cinnamic acid in the solid state. 1. Monitoring the reaction at 293 K. *Acta Cryst. Section B-Structural Science*, **60**, 315-324.

[3] Fernandes, M. A., Levendis, D. C. (2015) Photodimerization of the α' Polymorph of *ortho*-Ethoxy-*trans*-cinnamic acid in the Solid State. Part2: Monitoring the Reaction at 343 K, *Acta Cryst. Section B (in preparation)*.

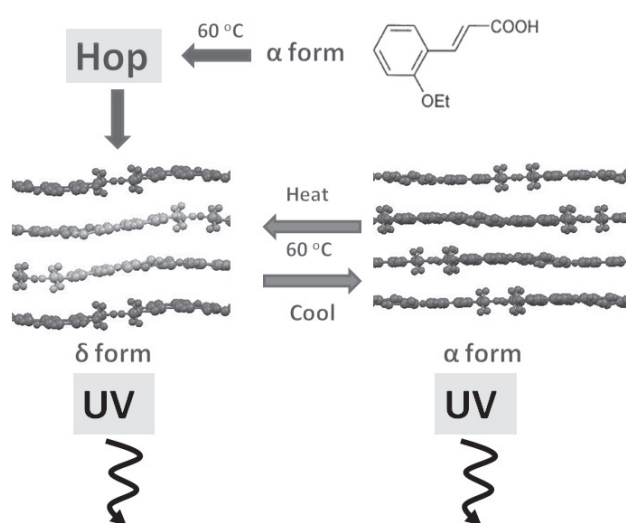


Figure 1. Schematic diagram showing the effect of heating and cooling the α and δ (or α') polymorphs of oetca

Keywords: solid-state reaction, photodimerisation, crystal hopping, thermal salient effect, single-crystal-to-single-crystal phase transformation, polymorph

MS33-O4 Identification of the cleavage planes in molecular crystals: topological and energetic aspects

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Thin films of organic semiconductors have a wide application in modern electronic devices. Until now we have used substrate surfaces for organic molecular beam epitaxy (OMBE) [1] provided by b-alanine crystal primary cleavage plane (010). Having a stake in different types and symmetries of substrate surfaces, we searched through the Cambridge Structural Database (release 5.35 Nov 2013) by means of the ToposPro program package [2] modified with a specially tailored procedure that determines possibility of the crystal to cleave along a given surface. This procedure is based on the analysis of the share of intermolecular interaction energy of molecules within the layer compared to the total energy of interaction.

As a result, we have extracted 546 structures of amino acids derivatives with 2-periodic hydrogen bonded network as the most probable candidates for easily cleavable crystals. We discarded the structures of solvates and hydrates as inappropriate in order to guarantee stability to ultra-high vacuum conditions needed for OMBE. For some selected key structures we calculated intermolecular interaction energies by means of the PIXEL method [3] trying to establish the structural features that can lead to the ability of molecular crystals to cleave. In addition, we proposed a quantitative descriptor of intermolecular interaction anisotropy – the X parameter.

To prove the validity of the proposed scheme we crystallized five crystals and seven co-crystals of amino acids. Unit cell parameters as well as face indexing procedure were carried out on a diffractometer. Subsequently we tested the crystals on the cleavage. For β -alanine crystals, during the squeezing between two glass plates, secondary cleavage planes along {111} faces were found that is in full agreement with our prediction.

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References:

- [1] S. Trabattoni, M. Moret, M. Campione, L. Raimondo, A. Sassella *Cryst. Growth Des.* **2013**, *13*, 4268.
- [2] V.A. Blatov, A.P. Shevchenko, D.M. Proserpio *Cryst. Growth Des.* **2014**, *14*, 3576.
- [3] A. Gavezzotti *J. Phys. Chem.* **2002**, *106*, 4145; A. Gavezzotti *J. Phys. Chem.* **2003**, *107*, 2344.