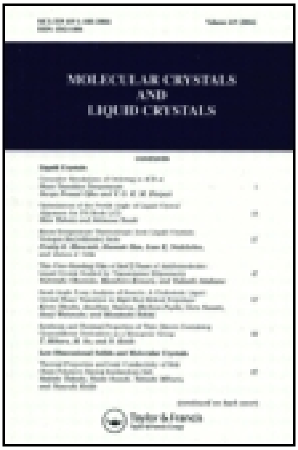

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Phase Rebuilding of α-Cinnamic Acid in Tail Irradiations

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To cite this article: Gerd Kaupp & Michael Haak (1998): Phase Rebuilding of α-Cinnamic Acid in Tail Irradiations, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 193-198

To link to this article: http://dx.doi.org/10.1080/10587259808044274

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp.193–198
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Phase Rebuilding of α-Cinnamic Acid in Tail Irradiations

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Irradiation of α-cinnamic acid crystals at their absorption tail at 365 and 405 nm and with filtered daylight gives surface features due to long-range molecular movements and phase rebuilding similar to the features in the shorter wavelength irradiations. AFM measurements indicate that the molecular migrations are guided by the crystal structure. Features such as walls, fences and trenches all follow the direction of the cleavage planes at 39° to the *c*-axis. Volcano-like features also require upward molecular transport. The visibly detectable disintegration of the crystals at low conversions in all cases is studied in some detail. A topotactic reaction is not observed.

Keywords: α-cinnamic acid; tail irradiation; AFM; SNOM; surface features; phase rebuilding

INTRODUCTION

Atomic force microscopy (AFM) measurements revealed that non-topotactic solid-state reactions give rise to characteristic surface features due to long-range molecular movements[1,2]. These processes are strictly guided by the crystal structures according to three-stage sequences of i) phase rebuilding, ii) phase transformation and iii) crystal disintegration.[1,2] The new evidence is at variance with Schmidt's topochemistry.[3] The conclusions from the occurance of face dependent surface features have been independently secured by scanning near-field optical microscopy SNOM that provides spectroscopic information[1,4] and by depth resolved grazing incidence X-ray diffraction GID that differentiates the processes at the surface and in the crystal bulk.[5]) Thus, phase rebuilding and phase

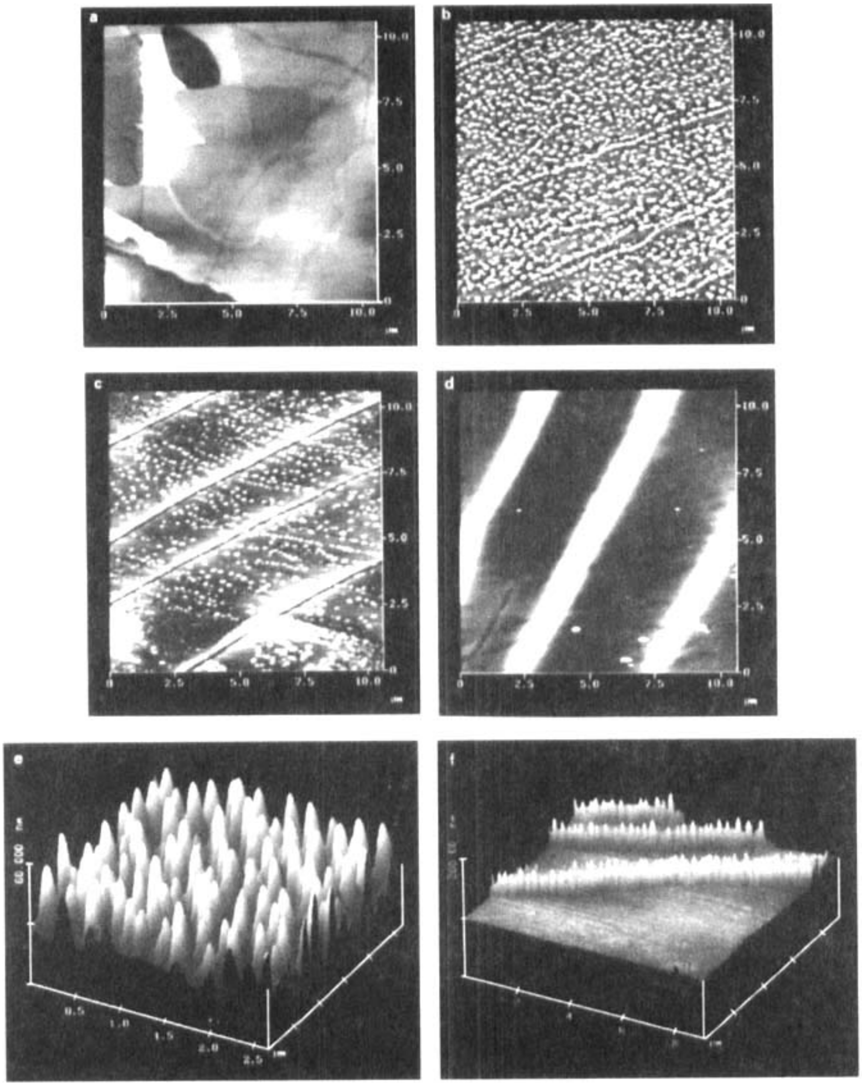
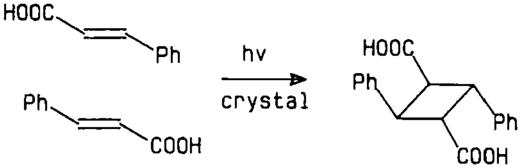


FIGURE 1 AFM topography of α-1 on its dominant (010) face; a) fresh with terraces; b), e) after 30 min irradiation at 365 nm (I_0 = 6.0 mW/cm^2) ; c) after 45 + 45 min irradiation (delay of 40 min); d) after 90 min continuous irradiation; f) after 6 months daylight; the contrast in a) covers 10 nm height, the one in b), c), d) 100 nm.

(See Color Plate I).

transformation could be directly detected in the bulk.[5] The previous standard of topochemistry *α-trans*-cinnamic acid (α-1) gives very distinct anisotropic features on its photolyzed surface[6] at short and long wavelengths.[1,2,4] At long wavelengths the light penetrates more deeply into the crystal.[1,7] However, it has been claimed that in a so-called tail irradiation (filter with edge at 350 nm) a single crystal of α-1 had not disintegrated and was 100% transformed into dimer 2 although its reported X-ray data exhibit undiscussed unusual non-planar hydrogen pair arrays of the carboxylic acids (in two planes displaced by 68 pm) and several close contacts.[8] As no AFM studies were tried with that crystal, we used our solid-state absorption data[6] and extended our AFM and SNOM work to irradiations of α-1 at considerably longer wavelengths in order to get a deeper insight into the crystal disintegration processes.



α-1 2

EXPERIMENTAL

Instead of a continuous xenon source with an edge filter[8] we used the emission bands of a Hg super-pressure lamp on an optical bench with a grating monochromator at 365 or 405 nm (dispersion 3.2 nm/cm; bandpass 6.4 nm) in air. Test experiments under Ar, N_2, and vacuum gave the same features. Daylight experiments were done in a Pyrex flask under Ar on window benches on the north and south sides in Oldenburg during six months always with closed windows at room temperature. Other crystals from the same batch were stored in the dark for comparison.

The plates of α-1 from benzene were 0.3 - 1.0 mm long and 40 - 60 μm thick. Prisms from evaporating diethylether had poor surfaces and were rapidly disintegrated parallel to the largest pinacoid. A particular quality of the crystals was not essential. Freshly cleaved crystals from diethylether or hydrated (010) surfaces of α-1[6] also gave the same series of features. For the detection of conversions by ^{1}H-NMR monolayers of 40 - 60 μm thick plates of α-1 were irradiated at 365 nm until the same sizes of the various AFM features as in Fig. 1 were found. A Fieldmaster Model LM-2UV (Coherent) was used for intensity measurements. Contact or non-contact AFM, SNOM, imaging techniques, and special precautions have been described elsewhere.[1,2,4] Crystal packings: Schakal 92 for AIX-UNIX of E. Keller, Freiburg, on an IBM RS 6000.

RESULTS AND DISCUSSION

If α-1 is irradiated on (010) various surface features develop depending on the conditions. Both in very sharp tail irradiations (365 and 405 nm) and in extremely slow daylight photolyses the crystals became opaque and disintegrated at low overall conversions. It may be judged from the absorption characteristics,[6] that 90% of the light were absorbed by 1300 layers (0.56 μm) at 365 and 4400 layers (1.95 μm) at 405 nm. Daylight passed the completely colorless crystals almost unabsorbed.

The AFM topographies after four different tail irradiations of α-1 are shown in Fig. 1. Fig. 1b reveals 1520 thermally stable volcanoes with an average height of 18.8 nm (max. height 30 nm, see also Fig. 1e). At longer irradiation these decreased when parallel fissures cutting the *c*-axis at an angle of 40° were formed (Fig. 1c). The parallel ridges in Fig. 1d (oriented at 40° to *c*) upon uninterrupted irradiation have typical heights of 80 nm but may reach 200 nm at 150 min irradiation. The parallel fenced walls (typically 40 nm high) in Fig. 1f again cut the *c*-axes at 40° in the direction of the cleavage planes (crystal structure: 39°)[9].

Slowing down the reaction by decreasing the intensity or irradiating at 405 nm (thereby both volcanoes and craters) increases the number of volcanoes that disappear at higher conversions at the expense of trenches and walls. In Fig. 1f at extremely low rate and extreme distances for the migrations the rims grow from the fence elements when molecules come up along the glide planes. The molecular movements are not instantaneous. Clearly, the deeper light penetration slows down the feature formation and helps in the relaxation of the lattice but does not avoid the phase rebuilding, of course. All surfaces in Fig. 1 were chemically uniform as expected, because the photodimerization proceeded uniformly under the surface: No SNOM contrast that would have differentiated gradients on the surface was detectable.[4]

NMR estimates indicated overall conversions of less than 1% for Fig. 1b/e and c, 1% for Fig. 1d, and 30% for Fig. 1f. At 365 nm the crystals of α-1 turned opaque at 2% conversion and disintegrated at 15 - 20% conversion (disintegration occured also on 405 nm irradiation). The crystal disintegration upon daylight exposure starts around conversions of 30%. The right hand side microscopic image of a typical crystal in Fig. 2 exhibits cracks along glide planes and crystallites particularly at the side faces (100) and (001) where molecules can more easily move through the surface.

The unexposed crystal that was stored in the dark is fully transparent and has sharp edges. These properties are lost in the exposed crystal. The reason

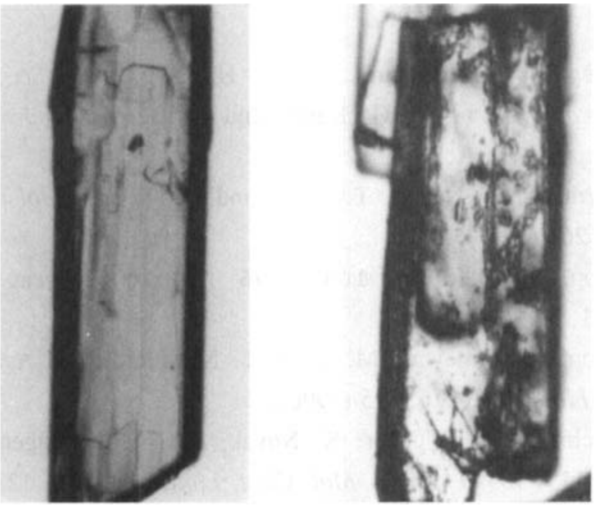


FIGURE 2 Micrographs of α-1; left: unirradiated; right: after 6 months exposure to filtered daylight; 200 fold enlarged

for its disintegration is mismatch of the molecules in the reacting crystal that enforces the movements and creates strain. The crystal cannot relax in topotactic transformations despite extremely slow reaction over six months and despite distribution of the strain over the whole crystal. The present system must optimize its hydrogen bonding at every stage of reaction and the more densely packed lattice of 2 (space group *Cc*[10]) cannot form in the bulk (highly diluted in 2) either. Thus, there is no other option to the crystal but long-range molecular movement forming surface features that are strictly governed by the crystal bulk also on tail irradiation. Multiple uses of the experimental mechanism have been demonstrated.[1,2]

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