

The Rôle of Powder Diffraction in Establishing Structure–Property Relationships for Crystalline Solids: a New Structural Assignment of the Photoreactive and Photostable Phases of *p*-Formyl-*trans*-cinnamic Acid

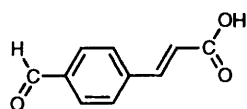
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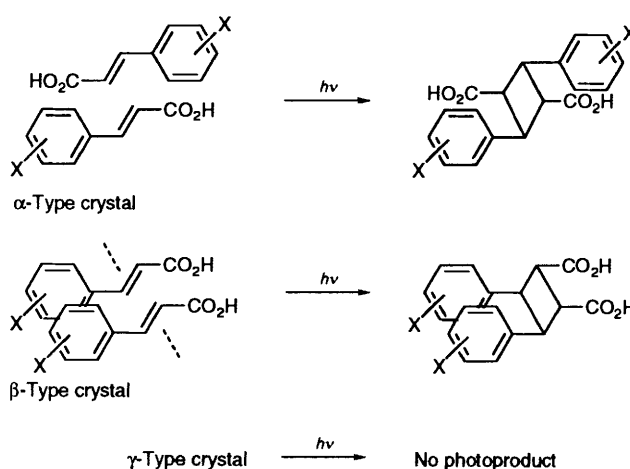
It has been reported previously that the photoreactive β phase of *p*-formyl-*trans*-cinnamic acid represents an exception to the well-established correlation between structural and photochemical properties of crystalline *trans*-cinnamic acid derivatives. However, it is shown in this paper that the crystal structure reported previously to be the β phase of *p*-formyl-*trans*-cinnamic acid is actually the photostable γ phase. In a wider context, the work reported here highlights the necessity of carrying out powder diffraction investigations in the determination of structure–property relationships for crystalline solids.

[2 + 2] Photodimerization reactions in crystalline *trans*-cinnamic acid and its derivatives^{1–3} represent the classic example of a set of solid-state reactions which conform to the topochemical principle.^{3–12} One consequence of this principle is that the course of certain solid-state reactions can be understood completely from a knowledge of the spatial arrangement of molecules in the crystal structure of the 'reactant' crystal. Crystals of *trans*-cinnamic acid and its derivatives can be classified as α -, β - or γ -types according to their behaviour upon exposure to UV radiation. UV irradiation of α -type crystals produces a centrosymmetric (α -truxillic acid) dimer, whereas UV irradiation of β -type crystals produces a mirror-symmetric (β -truxinic acid) dimer. In contrast, no reaction occurs when γ -type crystals are exposed to UV radiation. The single-crystal X-ray diffraction studies of Schmidt¹³ demonstrated well-defined correlations between crystal structure and photoreactivity in these materials, with the α -, β - and γ -type crystals each having a characteristic mode of molecular packing. Furthermore, it has been noted that, in all photoreactive (α - and β -type) crystals, the distance between the C=C bonds of potentially reactive monomer molecules is less than *ca.* 4.2 Å, whereas the corresponding distance in all photostable (γ -type) crystals is greater than *ca.* 4.7 Å.



p-Formyl-*trans*-cinnamic acid (*p*-FCA) exists in two different crystalline phases.¹⁴ Crystallization from ethanol produces a photoreactive β phase (yielding 4,4'-diformyl- β -truxinic acid upon UV irradiation), whereas crystallization from acetone produces a photostable γ phase.

The crystal structure has been reported¹⁵ for a crystal of *p*-FCA grown by vacuum sublimation techniques, and has been claimed to represent the crystal structure of the β phase of *p*-FCA. If this claim were correct, this crystal structure would be particularly interesting amongst β phase *trans*-cinnamic acid derivatives since the shortest distance between the C=C bonds of potentially reactive *p*-FCA molecules in this structure is 4.825 Å; as noted above, the corresponding distance in all photoreactive (α - and β -type) *trans*-cinnamic acid crystals of



known structure is less than *ca.* 4.2 Å. The crystal structure reported to be the β phase of *p*-FCA has been widely accepted^{12,16–23} as a structurally-anomalous β -type *trans*-cinnamic acid derivative, possessing an unprecedentedly (and uniquely) large value for the shortest distance between the C=C bonds of potentially reactive molecules in the crystal.

Experimental

Samples of *p*-FCA were crystallized from ethanol and acetone by cooling warm solutions of *p*-FCA in these solvents, and allowing the solutions to stand at room temp. for 3 weeks.

UV irradiation of these *p*-FCA samples was carried out with the sample (0.1 g) dispersed in distilled water (10 cm³) inside a pyrex vessel with a synthetic quartz cover sealed using vacuum grease. The vessel was flushed out with nitrogen gas for 30 min before commencing the irradiation experiment. UV irradiation (through the quartz cover) was carried out using a 100 W high pressure mercury discharge lamp (UVP 'Blak-Ray' model B-100AP). During UV irradiation, the dispersant was stirred continuously to ensure uniform irradiation of all crystallites in the sample. Samples extracted from the reaction vessel were filtered and dried under vacuum. UV irradiation of the sample of *p*-FCA crystallized from ethanol for 40 min was sufficient to give complete conversion of monomer to dimer (assessed from the UV absorption spectrum of a solution containing a portion of the material extracted from the reaction vessel dissolved in methanol). UV irradiation of the sample of *p*-FCA crystallized

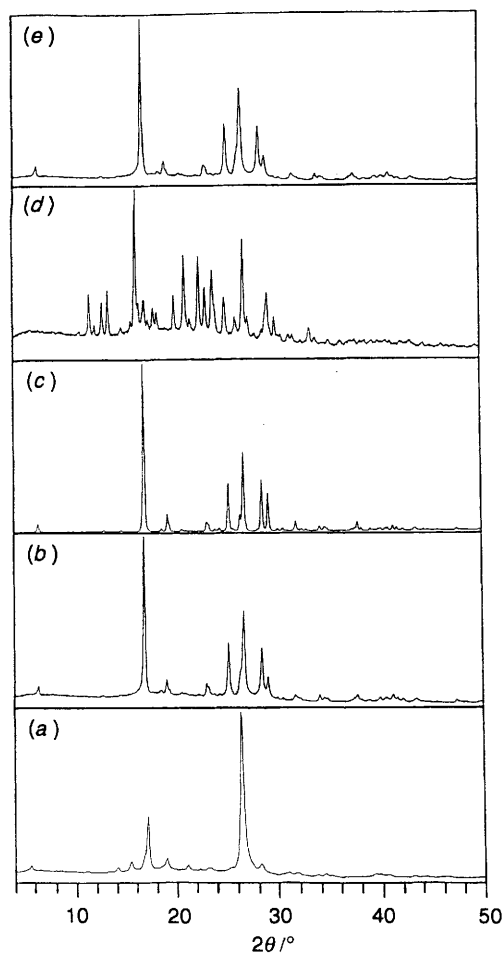


Fig. 1 (a) Powder X-ray diffractogram recorded for a sample of *p*-FCA crystallized from ethanol (β phase); (b) powder X-ray diffractogram recorded for a sample of *p*-FCA crystallized from acetone (γ phase); (c) powder X-ray diffractogram simulated on the basis of the crystal structure reported in ref. 15; (d) powder X-ray diffractogram recorded for the sample of *p*-FCA crystallized from ethanol (β phase) following UV irradiation; (e) powder X-ray diffractogram recorded for the sample of *p*-FCA crystallized from acetone (γ phase) following UV irradiation

from acetone gave no detectable conversion of monomer to dimer (for irradiation times substantially longer than 40 min).

Powder X-ray diffractograms were measured in transmission mode on a Stoe STADI/P high-resolution powder X-ray diffractometer, using Ge-monochromatized Cu-K α radiation and a linear position-sensitive detector covering 6° in 2θ . For these experiments, the polycrystalline samples were ground and mounted between two layers of transparent tape.

Results and Discussion

Powder X-ray diffraction [see Figs. 1(a) and (b)] confirms that different crystalline phases of *p*-FCA are produced by crystallization from ethanol and acetone—this fact has also been established by high-resolution solid state ^{13}C NMR spectroscopy.²⁴ UV irradiation of the sample of *p*-FCA crystallized from ethanol produces a new crystalline phase, as indicated by powder X-ray diffraction [Fig. 1(d)]. Solid-state ^{13}C NMR and solution-state ^{13}C and ^1H NMR spectroscopy have shown that this new crystalline phase is the photodimer (4,4'-diformyl- β -truxinic acid) expected for reaction in a β -type crystal. Powder X-ray diffraction [Fig. 1(e)] and high-resolution solid-state ^{13}C NMR spectroscopy²⁴ indicate that there is no reaction when the sample of *p*-FCA crystallized from

acetone is exposed to UV radiation—this sample is assigned as the γ phase of *p*-FCA.

The powder X-ray diffractogram simulated using the crystal structure reported previously¹⁵ to be the β phase of *p*-FCA is shown in Fig. 1(c). It is clear that this diffractogram is in excellent agreement with the experimental powder X-ray diffractogram [Fig. 1(b)] of the photostable phase of *p*-FCA. It is therefore clear that the crystal structure that has been claimed to be the β phase of *p*-FCA is actually the crystal structure of the γ phase of *p*-FCA. As noted above, the shortest distance (4.825 Å) between the C=C bonds of potentially reactive *p*-FCA molecules within this crystal structure is entirely consistent with its revised assignment as a γ -type *trans*-cinnamic acid derivative, according to the rules and generalizations established by Schmidt.¹³

The powder X-ray diffractogram of the β phase of *p*-FCA can be indexed on the basis of the following approximate unit cell with monoclinic metric symmetry: $a = 6.32$, $b = 4.26$, $c = 31.80$ Å, $\beta = 93.5^\circ$. The shortest axis (4.26 Å) in this unit cell is consistent with Schmidt's generalizations for β -type *trans*-cinnamic acids (although this actually represents a comparatively large value for the shortest axis in a β -type *trans*-cinnamic acid). (The low intensity peak at 2θ ca. 6.3° in the diffractogram of the β phase of *p*-FCA was omitted in determination of the lattice parameters reported above—this peak probably arises from a small impurity amount of the γ phase of *p*-FCA.) Despite extensive attempts, we have not been able to grow crystals of the β phase of *p*-FCA that are of suitable size and quality for crystal structure determination *via* single crystal X-ray diffraction.

In conclusion, this work has shown that the crystal structure reported previously¹⁵ to represent the β phase of *p*-FCA is actually the crystal structure of the photostable γ phase of *p*-FCA, and therefore does not represent a structurally-anomalous photoreactive *trans*-cinnamic acid derivative. It is not clear on what basis the single crystal used in the X-ray diffraction study reported in ref. 15 was assigned as the photoreactive β phase.

In more general terms, the work reported here emphasizes the necessity of utilizing powder diffraction techniques when establishing correlations between: (i) solid-state properties (in this case photoreactivity) deduced for a polycrystalline sample; and (ii) structural properties deduced from single crystal X-ray diffraction data. A single crystal selected [as in (ii)] from a polycrystalline sample is only representative of the bulk polycrystalline sample if the powder X-ray diffractogram simulated using the structure determined from the single crystal X-ray diffraction data matches the experimental powder X-ray diffractogram of the polycrystalline material. Valid structure-property relationships between (i) and (ii) can, and should, be derived only once this test has been satisfied.

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