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Probing Polymorphism and Reactivity in the Organic Solid State Using ^{13}C NMR Spectroscopy: Studies of p-Formyl-*trans*-cinnamic Acid

KENNETH D. M. HARRIS* AND JOHN M. THOMAS†

Department of Physical Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EP, United Kingdom; and †Davy Faraday Research Laboratory, The Royal Institution, 21 Albemarle Street, London W1X 4BS, United Kingdom

p-Formyl-*trans*-cinnamic acid (p-FCA) is known to exist in two different crystal phases (denoted β and γ). When crystals of the β phase of p-FCA are exposed to UV radiation, a solid state dimerization reaction occurs to produce 4,4′-diformyl-β-truxinic acid. In contrast, crystals of the γ phase of p-FCA are photostable. It is shown in this paper that high resolution solid state ^{13}C NMR spectroscopy is a sensitive technique for distinguishing the β and γ phases of p-FCA, and can be used to investigate, in detail, the chemical transformation that occurs upon UV irradiation of the β phase. Specifically, the ^{13}C NMR spectra presented here were recorded using the TOSS (total suppression of sidebands) pulse sequence; this is based upon the standard ^{13}C CPMAS (cross polarization/magic angle sample spinning/high power ^{1}H decoupling) method, but has the additional feature that all orders of spinning sidebands are eliminated from the spectrum.

The photoproduct obtained from UV irradiation of β-p-FCA contains a significant noncrystalline component (assessed via powder X-ray diffraction), and our NMR studies suggest that this noncrystalline component of the photoproduct contains some amount of the γ phase of the monomer p-FCA. A mechanism is proposed to explain the fact that UV irradiation of β-p-FCA can generate, in addition to the expected photodimer, an impurity amount of the γ phase of p-FCA. © 1991 Academic Press, Inc.

The topochemical principle (*1*) has been applied widely to rationalize the course of chemical transformations within organic molecular crystals (*2–9*). Reactions that are under topochemical control follow the pathway involving the minimum amount of molecular movement, and hence for a topochemical reaction between a pair of adjacent molecules within a crystal, the stereochemistry of the reaction product should be governed primarily by the relative positions and orientations of the two precursor molecules in the reactant crystal. In topochemical dimerization reactions, for

* To whom correspondence should be addressed at present address: Department of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, Scotland.

example, the molecular structure of the dimer should "reflect" the relative positioning of pairs of adjacent molecules in the monomer crystal. The [2 + 2] photodimerization reactions of *trans*-cinnamic acid and its derivatives (*10–12*) represent perhaps the classic example of a set of reactions that conform to the topochemical principle. (Note: we subsequently use the term *trans*-cinnamic acid in the general sense to refer collectively to *trans*-cinnamic acid and its derivatives.) Crystals of the *trans*-cinnamic acids can be assigned to one of three types (designated α, β, and γ) according to their behavior upon exposure to UV radiation (see Fig. 1a). Thus, UV irradiation of α-type crystals leads to the formation of a centrosymmetric (α-truxillic acid) dimer, whereas UV irradiation of β-type crystals generates a mirror-symmetric (β-truxinic acid) dimer. In contrast, no reaction occurs within crystals of the γ-type when they are exposed to UV radiation. Single-crystal X-ray diffraction studies (*13*) have demonstrated that clear correlations exist between the crystal structure and the photoreactivity of *trans*-cinnamic acid crystals, with crystals of the α-, β-, and γ-types each possessing a characteristic mode of molecular packing (Fig. 1a). Furthermore, these structure–reactivity correlations indicate clearly that the photodimerization reactions in *trans*-cinnamic acid crystals are under topochemical control.

Two further aspects of these systems are noteworthy. First, *trans*-cinnamic acid and many of its derivatives exhibit polymorphism; i.e., a particular *trans*-cinnamic acid can exist in more than one type of a crystal structure (α, β, or γ). Second, dimerization of *trans*-cinnamic acids is a solid state phenomenon; UV irradiation of these compounds in solution generally results in *trans* $\rightleftarrows$ *cis* isomerization rather than dimerization (*10*).

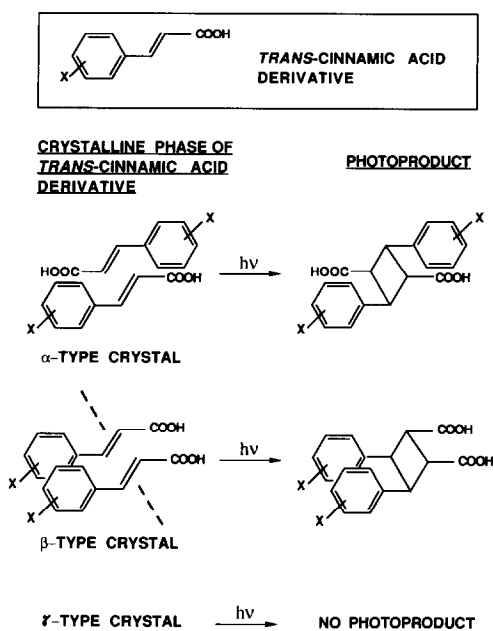Some solid state reactions are known to

FIG. 1a. Classification of crystals of *trans*-cinnamic derivatives according to their behaviour upon UV irradiation. Note that, as shown, potentially dimerizable monomer molecules in α-type crystals are related across a crystallographic center of symmetry, whereas potentially dimerizable monomer molecules in β-type crystals are related crystallographically by translation. This results in the production of an α-truxillic acid following topochemical dimerization in α-type crystals, and the production of a β-truxinic acid following topochemical dimerization in β-type crystals.

occur in a single crystal $\rightarrow$ single crystal manner from pure reactant (e.g., monomer) crystal to pure product (e.g., dimer) crystal, and it is possible to follow directly the course of such reactions by single-crystal X-ray diffraction (*14–16*). Many chemical reactions within crystalline solids, however, do not conform to this ideal behavior, and in these cases the reaction is associated with a considerable loss of crystallinity; in extreme cases, an amorphous product may be obtained (*17*). This fact clearly limits the usefulness of diffraction-based methods for probing directly the course of such reactions, and the aim of the work described in
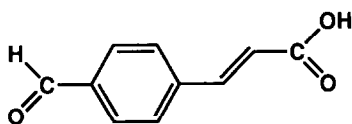
FIG. 1b. Structural formula of p-formyl-trans-cinnamic acid (p-FCA).

this paper was to assess the feasibility of employing high resolution solid state ^{13}C NMR spectroscopy as an alternative approach to follow chemical transformations within organic crystals. It is shown clearly that this technique can indeed probe such reactions in a direct and nondestructive manner, even when the reaction is associated with an appreciable loss of crystallinity within the system. The question of polymorphism is also relevant for the systems investigated here, and it is shown that high resolution solid state ^{13}C NMR spectroscopy can serve as a sensitive means of distinguishing different crystal phases of a given molecular species. (It has indeed been demonstrated previously (18) that this technique can provide detailed information on the structural changes accompanying phase transformations within organic solids.)

The solid state photodimerization of p-formyl-trans-cinnamic acid (abbreviated p-FCA; see Fig. 1b) was chosen for our investigations. p-FCA is known to exist in two different crystal phases: crystallization from ethanol gives a photoreactive β phase, whereas a photostable γ phase is obtained upon crystallization from acetone (19). Henceforth, the abbreviations β-p-FCA and γ-p-FCA are used to denote the β and γ phases of p-FCA respectively. Powder X-ray diffraction (Figs. 2a and 2b) confirms the different identities of these crystal phases.

^{13}C NMR spectra of the β and γ phases of p-FCA, recorded using the TOSS pulse sequence, are shown in Figs. 3a and 3b, and, before discussing the results, we mention briefly some salient features of the NMR

techniques employed. High resolution ^{13}C NMR spectra of organic solids are generally recorded by combining (20) the cross polarization (21, 22) and magic angle sample spinning (23, 24) techniques together with high power ^{1}H decoupling. We refer subsequently to this combined technique as the ^{13}C CPMAS method. The TOSS (total suppression of sidebands) pulse sequence (25, 26), a variant of the conventional ^{13}C CPMAS method, was used to record the ^{13}C NMR spectra discussed in this paper. With the TOSS technique, isotropic peaks are retained in the spectrum but all orders of spinning sidebands are eliminated. This is a particular advantage in the study of trans-cinnamic acids and their photoproducts, in
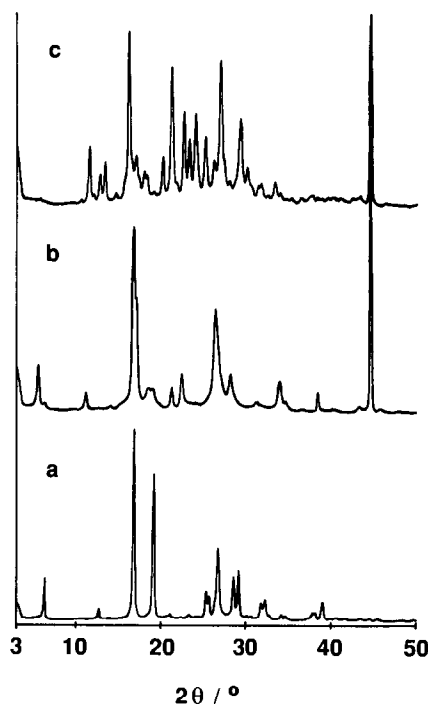

FIG. 2. Powder X-ray diffractograms (CuKα radiation) recorded for (a) γ-p-FCA, (b) β-p-FCA, and (c) the β-photoproduct (obtained following UV irradiation of β-p-FCA). (Note: the aluminum sample holder used to record diffractograms (b) and (c) gives rise to peaks at $2\theta \approx 38.4°$ and $44.6°$).
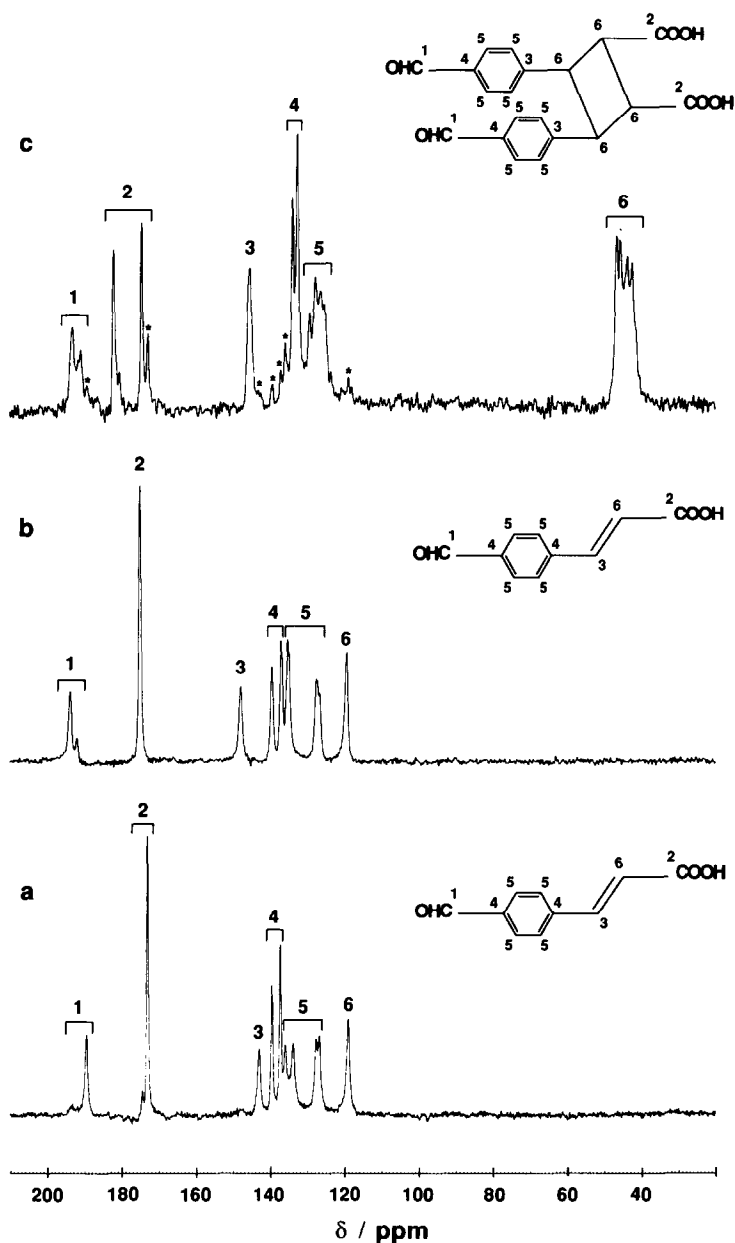
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FIG. 3. Solid state ^{13}C NMR spectra recorded at 75.47 MHz, using the TOSS pulse sequence, for (a) γ-p-FCA, (b) β-p-FCA, and (c) the β-photoproduct (obtained following UV irradiation of β-p-FCA). Chemical shifts (δ) are given relative to the ^{13}C resonance in tetramethylsilane. Spectral assignments are based, in part, on results obtained from nonquaternary suppression (NQS) experiments and from reference to the solution NMR literature. Peaks marked * in spectrum (c) probably arise from an impurity amount of the γ phase of the monomer p-FCA.

view of the fact that they possess large ^{13}C chemical shift anisotropies. The nonquaternary suppression (NQS) technique (27–29) (another variant of the conventional ^{13}C CPMAS experiment) has served as a valuable aid for spectral assignment in this work (although no NQS spectra are actually shown here) since, under appropriate circumstances, it allows resonances due to quaternary carbons to be distinguished from those due to nonquaternary carbons.

Comparison of Figs. 3a and 3b demonstrates clearly that the β and γ phases of p-FCA can be readily distinguished by solid state ^{13}C NMR spectroscopy; i.e., the differences in molecular packing between these crystal phases are sufficiently large to give rise to appreciable differences in isotropic chemical shift. In particular, the most significant difference (and therefore potentially the most diagnostic indicator of the identity of the crystal phase) is for the olefinic (C=C) carbon adjacent to the benzene ring (peaks labelled 3 in Figs. 3a and 3b). The pattern of chemical shifts for the benzene ring also differs appreciably in the two cases. Comparison of Figs. 3a and 3b suggests that the sample of β-p-FCA does not contain any significant impurity amount of γ-p-FCA, and also that the sample of γ-p-FCA does not contain any significant impurity amount of β-p-FCA (i.e., neither spectrum contains a low intensity subspectrum characteristic of the other phase). The latter conclusion, regarding the phase purity of our γ-p-FCA sample, is consistent with conclusions from powder X-ray diffraction (compare Figs. 2a and 2b). There is a possibility, on the other hand, that the peak at $2\theta \approx 6.3°$ in the diffractogram of β-p-FCA *might* indicate the presence of an impurity amount of γ-p-FCA within our sample of β-p-FCA. This evidence, however, is considered to be far from conclusive since: (i) several peaks with significant intensity in the diffractogram of γ-p-FCA are clearly absent from the diffractogram of our β-p-FCA sam-

ple (the absence of the peaks at $2\theta \approx 29.1°$, $32.2°$, and $39.0°$ is particularly noteworthy; the absence of the other peaks characteristic of γ-p-FCA can not be concluded with certainty, since their positions coincide with peaks due to β-p-FCA); (ii) the crystal structure of β-p-FCA is not known,[1] and we can therefore not rule out, at this stage, the possibility that the peak at $2\theta \approx 6.3°$ could indeed be a genuine low-intensity diffraction maximum from β-p-FCA.

It is relevant to note that, under certain circumstances, solid state NMR spectroscopy may be a better method than powder X-ray diffraction for assessing the phase purity of a sample. In particular, diffraction-based methods can only be used profitably for the identification of crystalline impurities with particle size greater than a certain limiting value. Later in this paper we report an example in which solid state NMR spectroscopy has been used successfully to determine the identity of an impurity phase for which there is no direct evidence from powder X-ray diffraction. Finally, it is important to stress that the relative intensities of peaks in the ^{13}C CPMAS NMR spectrum (or the corresponding TOSS spectrum) of a particular crystal phase will depend on the choice of cross-polarization contact time, and it is therefore important to compare spectra recorded using the same contact time when considering the relative peak intensities and chemical shifts as a "fingerprint" of the phase in question.

It is apparent from Figs. 3a and 3b that the –CHO group in β-p-FCA, the –COOH group in γ-p-FCA, and possibly also the –CHO group in γ-p-FCA each give rise to two isotropic ^{13}C resonances (of unequal in-

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[1] Despite extensive attempts, we have not been able to prepare β-p-FCA crystals of sufficient size and quality for single crystal X-ray diffraction experiments. Note that a reported crystal structure determination of β-p-FCA (30) is actually believed (31) to be the structure of γ-p-FCA.

tensities). The underlying reason for this is not clear, although crystallographic disorder is one possible explanation (for example, the –CHO group and the –COOH group in the p-FCA molecule can each be oriented in two different ways while still maintaining the planarity of the molecule). In the absence of further crystallographic information, however, we make no attempt to put forward a definitive explanation for this observation.

Exposure of the γ-p-FCA sample to UV radiation did not give rise to any change in its solid state ^{13}C NMR spectrum nor any change in its powder X-ray diffractogram, as expected for a photostable γ phase.

UV irradiation of the β-p-FCA sample, on the other hand, results in a marked change in the powder X-ray diffractogram (compare Figs. 2b and 2c), indicating the generation of a new crystalline phase. (Note: (i) the UV irradiation was carried out with the crystals of β-p-FCA dispersed in water; (ii) the polycrystalline sample obtained from this reaction is subsequently denoted the β-photoproduct). Moreover, it is clear from the powder X-ray diffractogram (Fig. 2c) that the β-photoproduct contains an appreciable noncrystalline component. The solid state ^{13}C NMR spectrum (Fig. 3c), on the other hand, is not affected significantly by this loss of crystallinity, and shows direct evidence for the chemical change that has taken place. In particular, resonances associated with olefinic (C=C) carbons in the monomer p-FCA (peaks labelled 3 and 6 in Fig. 3b) are replaced, as a function of reaction progress, by resonances characteristic of carbons in the cyclobutane ring of the photodimer (peaks labelled 6 in Fig. 3c). The main set of peaks in the NMR spectrum of the β-photoproduct (i.e., the peaks not marked by an asterisk in Fig. 3c) is consistent with the major component of the β-photoproduct being 4,4'-diformyl-β-truxinic acid (see the numbered peak assignments in Fig. 3c). (Note: the fact that the photoreactive phase

is of the β-type and not the α-type has been determined by dissolving the photoproduct in DMSO-d$_6$ and measuring conventional solution ^{1}H and ^{13}C NMR spectra of this solution; this has shown clearly that the dimer present in the β-photoproduct is 4,4'-diformyl-β-truxinic acid and not 4,4'-diformyl-α-truxillic acid).

The solid state ^{13}C NMR spectrum of the β-photoproduct contains a low intensity subspectrum (peaks marked with an asterisk in Fig. 3c) which is assigned as the γ phase of the monomer p-FCA (compare Figs. 3a and 3c). (Note: although some of the aromatic resonances in this low-intensity subspectrum could equally be attributed to the β phase of p-FCA, the absence of a resonance at ~148 ppm is particularly good evidence for the absence of any β-p-FCA in the β-photoproduct). Solution ^{1}H NMR spectroscopy of the β-photoproduct dissolved in DMSO-d$_6$ confirms the presence of some monomer p-FCA in the β-photoproduct and indicates a monomer-to-dimer conversion of about 91%. (Note: (i) the proportion of monomer varied somewhat in the photoproducts obtained in different experiments, and many contained a significantly higher monomer-to-dimer conversion than this; (ii) unless studied as a careful function of cross-polarization contact time, solid state ^{13}C NMR spectra of the type reported here can not strictly be interpreted in a quantitative manner—solution ^{1}H NMR of the dissolved photoproduct is considered here to be a more reliable indication of the monomer-to-dimer conversion in the photoproduct.)
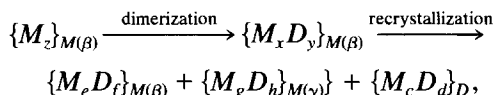
It is perhaps surprising that the photoproduct obtained from UV irradiation of our sample of β-p-FCA should contain an impurity amount of the γ phase of p-FCA. This observation could be explained readily if an impurity amount of γ-p-FCA were present in the starting material, but the presence of such an impurity was ruled out earlier on the basis of the solid state ^{13}C NMR results

for our β-p-FCA sample. Furthermore, the powder X-ray diffractogram of the β-photoproduct does not provide any strong evidence to suggest the presence of a crystalline monomer phase (note that the low intensity peak at $2\theta \approx 5.8°$, superimposed on the broad background scattering, does not occur exactly in the position of the low-angle peak in the diffractogram of either the β phase or the γ phase of p-FCA). These powder X-ray diffraction and solid state NMR results can be reconciled by suggesting that the γ-p-FCA present in the β-photoproduct is of a sufficiently small crystallite size that it is part of the "noncrystalline" portions of the β-photoproduct (the presence of a noncrystalline component within the β-photoproduct was inferred earlier from its powder X-ray diffractogram (Fig. 2c)).

In the light of these conclusions, it is relevant to consider how it might be possible for some amount of γ-p-FCA to be present in the β-photoproduct, when the sample of β-p-FCA used to obtain this photoproduct did not itself contain any γ-p-FCA. The most plausible explanation arises from the accepted notion (32, 33) that photodimerization in many β phase *trans*-cinnamic acids occurs according to a dimerization-followed-by-recrystallization mechanism, and there is indeed some direct experimental evidence that this mechanism operates in the photodimerization of β-p-FCA (34). In summary, this mechanism proceeds as follows. Dimerization within the monomer crystal will produce a dimer/monomer solid solution, and after a certain extent of dimerization (when the concentration of dimer in this crystal has reached its solubility limit), phase separation will occur to give a monomer-rich (or pure monomer) phase and a dimer-rich (or pure dimer) phase:

$$\{M_z\}_M \xrightarrow{\text{dimerization}} \{M_xD_y\}_M \xrightarrow{\text{recrystallization}}$$
$$\{M_aD_b\}_M + \{M_cD_d\}_D,$$
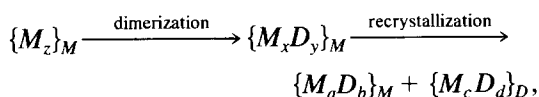
where M and D represent monomer and dimer, respectively, $\{ \ \}_M$ and $\{ \ \}_D$ denote the monomer and dimer crystal structures, respectively, $a/b > x/y > c/d$ (possibly with $b = 0$ and/or $c = 0$), $z = x + 2y$, $x = a + c$, and $y = b + d$. In the knowledge that there are two different monomer phases of p-FCA (denoted $\{ \ \}_{M(\beta)}$ and $\{ \ \}_{M(\gamma)}$), this general reaction scheme should be modified to

$$\{M_z\}_{M(\beta)} \xrightarrow{\text{dimerization}} \{M_xD_y\}_{M(\beta)} \xrightarrow{\text{recrystallization}}$$
$$\{M_eD_f\}_{M(\beta)} + \{M_gD_h\}_{M(\gamma)}\} + \{M_cD_d\}_D,$$

where $x = e + g + c$, and $y = f + h + d$. The important question here concerns the identity of the monomer phase produced following the recrystallization step. If the β phase is generated, then further dimerization can proceed within this phase, and clearly by repeating such dimerization-followed-by-recrystallization steps, the monomer-to-dimer conversion in the system as a whole will progressively increase. If, on the other hand, the monomer recrystallizes out as the γ phase, then this monomer can not take part in further reaction; moreover, if the γ-p-FCA recrystallized in this way has a sufficiently small crystallite size, the presence of this phase in the β-photoproduct might not be apparent from powder X-ray diffraction. We do not claim that our results provide definitive proof for the occurrence of this mechanism (more crystallographic data would be required first), but the explanation proposed above is certainly consistent with the observations from our experiments.

In conclusion, the experiments reported here demonstrate that it is possible to distinguish the different crystal phases of p-FCA by comparing their high resolution ("isotropic") solid state ^{13}C NMR spectra. Moreover, such spectra can be used to monitor directly the conversion of monomer to dimer in the photodimerization of the reactive β phase of p-FCA despite the fact that the product phase contains a substantial non-

crystalline component (thus limiting the usefulness of diffraction-based methods for following this reaction). In addition, solid state NMR spectroscopy is a nondestructive probe of the reaction system (in contrast, for example, to solution NMR spectroscopy), and, moreover, is capable of revealing some amount of crystallographic information, notably in relation to phase identification and to the presence of crystallographic inequivalences and/or disorder.

The approach adopted here could clearly be extended to monitor, in a controlled manner, the progress of the photodimerization reaction, allowing, *inter alia,* kinetic aspects of the reaction to be investigated. There is also much still to be discovered about photodimerization reactions in *trans*-cinnamic acid crystals, and of particular interest is the fact that, in many cases (including p-FCA (*35, 36*)), the reaction is associated with uptake of water by crystals of the photoproduct. Work is in progress, using solid state NMR spectroscopy and other techniques, to extend further our understanding of this and other facets of the photoreactivity of these crystalline solids.

In view of the large number of known photochemical transformations in organic solids (*37–39*), much progress is expected in the future application of solid state NMR spectroscopy in their investigation, particularly in those cases for which diffraction-based methods can not be used for the characterization of the product phase.

Acknowledgements

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