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The photodimerisation of the chloro-, methoxy- and nitro-derivatives of *trans*-cinnamic acid: a study of single crystals by vibrational microspectroscopy †

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Received (in Cambridge, UK) 27th May 2002, Accepted 15th July 2002

The techniques of infrared and Raman microscopy have been used to monitor the photochemical dimerisation reactions of β-2-chloro-*trans*-cinnamic acid, β-3-chloro-*trans*-cinnamic acid, β-4-chloro-*trans*-cinnamic acid, α-2-methoxy-*trans*-cinnamic acid, β-2-nitro-*trans*-cinnamic acid, β-3-nitro-*trans*-cinnamic acid and β-4-nitro-*trans*-cinnamic acid. In this way the *topotactic* nature of the reactions has been confirmed. These reactive derivatives have been compared with the unreactive γ-forms of these and related compounds.

Introduction

Solid state organic reactions are attracting increased attention at the current time because of the possibility that the crystal lattice in a solid reactant may direct the course of a reaction and determine the stereochemical nature of products. This has led to the concept of so-called "Crystal Engineering"[1,2] in which asymmetric synthesis in solid crystals,[3–6] cascade reactions[7] and reactions between components in co-crystals[8–12] are possible. The potential for such methods is high but they have been held back by a poor understanding of the reaction mechanism resulting from the lack of suitable methods for monitoring reactions within single crystals. X-Ray diffraction is often inappropriate because the crystals typically degrade during the course of the reactions making it impossible to determine the structures of the products.[13] Atomic Force Microscopy has also been employed and while this allows the progress of a reaction to be monitored it gives no information regarding the *structures* of intermediates or products of the reactions.[14–17] Infrared and Raman microscopy overcome many of these problems because the methods yield structural information while, at the same time, allowing small fragments (down to area limits of approximately 20 μm × 20 μm for infrared; 2 μm × 2 μm for Raman) to be studied.

Our aim in the current work was to utilise the techniques of infrared and Raman microscopy to follow photochemical reactions within single crystals. In an earlier paper we have reported a study of the photochemical dimerisation of the α (head-to-tail) and β (head-to-head) forms of *trans*-cinnamic acid.[18] This process, which has been well-known since the early years of the 20th century,[19,20] was selected as a paradigm of such reactions. In the current work we have extended our investigation to cover a range of derivatives of *trans*-cinnamic acid. We have studied the photodimerisation reactions of the β-forms of 2-, 3- and 4-chloro-*trans*-cinnamic acids, the α-form of 2-methoxy-*trans*-cinnamic acid and the β-forms of 2-, 3- and 4-nitro-*trans*-cinnamic acids. In each case a comparison of infrared and Raman spectra of the products has allowed us to confirm the nature of the product and hence to demonstrate the *topotactic* nature of these reactions. We have compared the reactivity of the α- and β-crystal forms with that of the unreactive γ-forms of the same derivatives. This work extends our use of infrared and Raman spectroscopy to a wide range of solid-state organic photochemical reactions.

Experimental

Infrared spectra were recorded using a Bruker Equinox 55 FTIR and IRscope II microscope. A medium-band liquid nitrogen-cooled detector was used to monitor the spectral range 600–4000 cm^{-1} with a typical resolution of 4 cm^{-1}. Most of the Raman spectra reported were obtained at Reading using a Renishaw (model 1000) laser Raman spectrometer with a Leica microscope attachment and equipped with frequency-doubled Nd-YAG (532 nm) and diode (785 nm) laser sources. Some spectra (those of γ-3-chloro-*trans*-cinnamic acid, α-2-methoxy-*trans*-cinnamic acid and the 2-, 3- and 4-nitro derivatives) were recorded at Auckland using a similar spectrometer equipped with an Ar^+ ion laser ($\lambda = 514$ nm) in place of the Nd-YAG laser on the Reading instrument. All spectra reported in this work were recorded using the 514 or 532 nm sources. Spectra were recorded in the range 200–3200 cm^{-1} with a typical resolution of 4 cm^{-1}.

Samples

All samples of *trans*-cinnamic acid derivatives were obtained from Aldrich with stated purities of 97–99%. The following crystal forms of the derivatives studied were prepared by recrystallisation from the solvents listed, adopting the procedure of Schmidt *et al.*:[21] β-2-chloro-*trans*-cinnamic acid, recrystallised from an ethanol–water mixture; β-3-chloro-*trans*-cinnamic acid, ethanol; γ-3-chloro-*trans*-cinnamic acid, acetic acid; β-4-chloro-*trans*-cinnamic acid, acetic acid; β-2-nitro-*trans*-cinnamic acid, ethanol; γ-2-nitro-*trans*-cinnamic acid, no recrystallisation—used as supplied; β-3-nitro-*trans*-cinnamic acid, acetic acid–water mixture; γ-3-nitro-*trans*-cinnamic acid, no recrystallisation; β-4-nitro-*trans*-cinnamic acid, acetic acid; γ-4-nitro-*trans*-cinnamic acid, no recrystallisation; α-2-methoxy-*trans*-cinnamic acid, methanol; γ-3-methoxy-*trans*-cinnamic acid, benzene; γ-4-methoxy-*trans*-cinnamic acid, ethanol. All samples were photolysed using a medium-pressure,

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† Electronic supplementary information (ESI) available: infrared and Raman spectroscopic data. See http://www.rsc.org/suppdata/p2/b2/b205116h/

DOI: 10.1039/b205116h

water-cooled mercury lamp (Photochemical Reactors Ltd.) for a period of 3–4 h.

Crystallography

Suitable crystals were prepared as described above.

α-2-Methoxy-*trans*-cinnamic acid $C_{10}H_{10}O_3$, M = 178.18, monoclinic, a = 7.171(13), b = 17.69(3), c = 8.092(14) Å, β = 117.77(1), U = 908 Å^3, space group $P2_1/a$, D_c = 1.303 g cm^{-3}, Z = 4.

γ-3-Methoxy-*trans*-cinnamic acid, $C_{10}H_{10}O_3$, M = 178.18, monoclinic, a = 8.655(12), b = 4.919(7), c = 21.97(2) Å, β = 97.86(1), U = 927 Å^3, space group $P2_1/n$, D_c = 1.277 g cm^{-3}, Z = 4.

Data were measured with MoKα radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the image plate. 100 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program[22] to provide 1668 and 1720 independent reflections respectively. The structures were solved using direct methods with the SHELXS86 program.[23] Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. The structures were refined on F^2 using SHELXL[24] to R_1 0.0840, wR_2 0.2252 and R_1 0.0693, wR_2 0.2064; for 751 and 1340 reflections respectively with $I > 2\sigma(I)$. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 186690 and 186691. See http://www.rsc.org/suppdata/p2/b2/b205116h/ for crystallographic files in .cif or other electronic format.

Spectral data

All numbers are wavenumbers measured in cm^{-1}. Where no intensities are given the band may be assumed to have medium intensity. The assignments in the region below 1500 cm^{-1} are tentative because of vibrational coupling and overlap of spectral bands. There was no change in the spectra of the γ-forms after irradiation. Raman spectra have not been recorded for all samples where no changes were observed in the infrared spectra upon photolysis. Frequencies of infrared and Raman bands for γ-3-chloro-*trans*-cinnamic acid, γ-3-methoxy-*trans*-cinnamic acid, γ-4-methoxy-*trans*-cinnamic acid, β-2-nitro-*trans*-cinnamic acid, γ-2-nitro-*trans*-cinnamic acid, γ-3-nitro-*trans*-cinnamic acid, β-4-nitro-*trans*-cinnamic acid and γ-4-nitro-*trans*-cinnamic acid are listed as supplementary material available in the RSC Electronic Supplementary Information Service.†

β-2-Chloro-*trans*-cinnamic acid. Before photolysis, infrared: 1692 (vs) (ν(C=O)), 1632 (s) (ν(C=C) aliphatic), 1591 (w), 1567 (w) (ν(C=C) aromatic), 1474, 1427 (s), 1340 (s), 1312, 1279 (s), 1229 (s), 1160 (w), 1120 (w), 1050 (w), 1039 (w), 984 (s), 920 (br), 876, 853 (δ(C–H), ν(C–C) and ν(C–O)), 758, 736, 722 (w) (ring vibration). **Raman:** 3078, 3053 (ν(C–H)), 1638 (vs) (ν(C=C) aliphatic), 1591 (vs) (ν(C=C) aromatic), 1473 (vw), 1442 (w), 1292, 1278 (w), 1216, 1165 (w), 1140 (w), 1116 (w), (δ(C–H)), 1034 (s) (ring breathing), 883 (w), 844 (w) (δ(C–H) and ν(C–C)), 596 (vw), 545 (w) (ring deformation). **After photolysis, infrared:** 1721 (vs) (ν(C=O)), 1631 (vw), 1593 (w), 1572 (w) (ν(C=C) aromatic), 1478, 1426 (s), 1325, 1303 (s), 1269 (s), 1242 (s), 1205, 1171 (w), 1120, 1064 (w), 1051 (w), 1039 (w), 984 (w), 942 (w), 876 (w) (δ(C–H), ν(C–O) and ν(C–C)), 756 (br), 730 (w), 705 (w) (ring vibration). **Raman:** 3078, 2931 (v(C–H)), 1638 (w), 1591 (vs), 1574 (ν(C=C) aromatic), 1473 (vw), 1333 (vw), 1292, 1216, 1165 (w), 1129 (vw) (δ(C–H)), 1034 (s) (ring breathing), 679 (w), 575 (ring deformation).

β-3-Chloro-*trans*-cinnamic acid. Before photolysis, infrared: 1703 (vs) (ν(C=O)), 1629 (vs) (ν(C=C) aliphatic), 1573 (ν(C=C) aromatic), 1483, 1430, 1319, 1301, 1278, 1224, 1200, 1174, 1095, 1080, 981 (s), 905 (br, s), 859 (s), 782 (s) (δ(C–H), ν(C–C), ν(C–O)), 725, 678 (ring deformation). **Raman:** 3086, 3073, 3039 (w) (ν(C–H)), 1648 (vs) (ν(C=C) aliphatic), 1603 (ν(C=C) aromatic), 1488 (vw), 1447 (vw), 1425 (w), 1314 (w), 1286, 1265, 1207, 1180, 1085 (vw) (δ(C–H), ν(C–C), ν(C–O)), 1003 (ring breathing), 893 (vw), 866 (vw) (δ(C–H), ν(C–C), ν(C–O)), 676 (vw) (ring deformation). **After photolysis, infrared:** 1730 (br, s) (ν(C=O)), 1598, 1573, (ν(C=C) aliphatic), 1478, 1434, 1299, 1211, 1099, 1081, 998 (w), 931, 912, 880, 845, 789 (δ(C–H), ν(C–C), ν(C–O)), 747 (w), 690 (ring deformation). **Raman:** 3074, 3036 (ν(C–H)), 1653 (s) (ν(C=C) aliphatic), 1598 (ν(C=C) aromatic), 1480 (vw), 1439, 1315, 1287, 1254, 1209, 1175 (w), 1087 (w) (δ(C–H), ν(C–C), ν(C–O)), 1002 (ring breathing), 912, 880 (δ(C–H), ν(C–C), ν(C–O)), 695 (ring deformation).

β-4-Chloro-*trans*-cinnamic acid. Before photolysis, infrared: 1680 (vs) (ν(C=O)), 1627 (ν(C=C) aliphatic), 1593 (w), 1570 (w) (ν(C=C) aromatic), 1491, 1427, 1406 (w), 1341 (w), 1306, 1285, 1236 (w), 1207 (w), 1118 (w), 1088, 1012 (w), 984, 941 (br), 874 (w), 826 (δ(C–H), ν(C–C) and ν(C–C)), 719 (w), 708 (w) (ring deformation). **Raman:** 3064 (w) (ν(C–H)), 1645 (vs) (ν(C=C) aliphatic), 1635 (shoulder), 1593 (s) (ν(C=C) aromatic), 1492 (vw), 1449 (w), 1410, 1297, 1265 (w), 1217, 1210, 1178 (s) (δ(C–H)), 1091 (s) (ring breathing), 865 (w), 717, 642 (ring deformation). **After photolysis, infrared:** 1711 (vs) (ν(C=O)), 1635 (vw), 1593 (vw) (ν(C=C) aromatic), 1493, 1426 (br), 1293 (br), 1234 (br), 1094, 1014, 939 (vw), 824 (w) (δ(C–H), ν(C–O) and ν(C–C)), 720 (vw) (ring vibration). **Raman:** 3064, 2964 (ν(C–H)), 1635, 1598 (s) (ν(C=C) aromatic), 1490 (vw), 1450 (vw), 1213, 1184 (δ(C–H)), 1091 (vs) (ring breathing), 774, 639 (ring deformation).

α-2-Methoxy-*trans*-cinnamic acid. Before photolysis, infrared: 3077, 3011, 2974 (s), 2874 (s) (ν(C–H)), 1687 (vs) (ν(C=O)), 1620 (s) (ν(C=C) aliphatic), 1577 (ν(C=C) aromatic), 1489 (s), 1460 (s), 1431 (s), 1327 (s), 1243 (s), 1223 (s), 1199, 1157, 1103, 1045, 1025, 994, 973 (w), 938 (w), 878, 851 (w) (δ(C–H)), 781, 757 (ring deformation). **Raman:** 1628 (vs) (ν(C–H) aliphatic), 1598 (s) (ν(C–H) aromatic), 1491, 1443 (w), 1320, 1300, 1280, 1249, 1217 (s), 1201, 1161, 1106 (w), 1078 (vw), 1046, 1022 (w), 990 (vw), 978 (w), 871 (δ(C–H), ν(C–C), ν(C–O)), 776 (w), 760 (vw), 680 (vw), 593 (ring deformation). **After photolysis, infrared:** 3033 (w), 2996 (w), 2832 (w) (ν(C–H)), 1682 (vs) (ν(C=O)), 1585 (ν(C=C) aromatic), 1493 (s), 1461 (s), 1436 (s), 1372, 1324 (w), 1292 (s), 1240 (s), 1193 (w), 1174 (w), 1111 (s), 1050, 1028, 932 (w), 850 (vw) (δ(C–H)), 795, 748 (s) (ring deformation). **Raman:** 1596 (s) (ν(C=C) aromatic), 1286, 1243, 1191, 1159, 1143, 1048 (s), 1028 (w), 984 (w) (δ(C–H)), 776 (s), 726 (w) (ring deformation).

β-3-Nitro-*trans*-cinnamic acid. Before photolysis, infrared: 1696 (ν(C=O)), 1617 (ν(C=C) aliphatic), 1581 (ν(C=C) aromatic), 1524 ($\nu_{asym}(NO_2)$), 1491, 1460, 1419 (δ(C–H), ν(C–C), ν(C–O)), 1312 ($\nu_{sym}(NO_2)$), 1286, 1233, 1157 (w), 1049, 954, 927, 876, 784 (δ(C–H), ν(C–C), ν(C–O)), 698, 681 (ring deformation). **After photolysis, infrared:** 1703 (ν(C=O)), 1606, 1580 (w), 1530 (w) (ν(C=C) aromatic), 1491 ($\nu_{asym}(NO_2)$), 1455, 1436, 1350 (w) (δ(C–H), ν(C–C), ν(C–O)), *ca.* 1285 (br) ($\nu_{sym}(NO_2)$), 1230 (w), 1160, 1106 (w), 1092 (w), 1049, 983 (w), 946 (w), 877 (w), 787 (δ(C–H), ν(C–C), ν(C–O)), 728 (ring deformation). **Raman:** 1650 (ν(C=C) aliphatic), 1585, 1540 (w), (ν(C=C) aromatic), 1355, 1289, 1231, 1110 (δ(C–H), ν(C–C), ν(C–O)), 1002 (ring breathing), 794 (ring deformation).

Results and discussion

A comparison of 2-chloro, 3-chloro and 4-chloro-*trans*-cinnamic acid

Both 2- and 4-chloro-*trans*-cinnamic acid have been reported to crystallise only in the β-form whereas crystals are reported for both the β- and γ-forms of the 3-chloro derivative.[21] We have prepared samples of the three β-forms and the γ-form of the

3-chloro acid by the methods detailed previously. Excellent infrared and Raman spectra were obtained for single crystals of all of these samples. Each sample was then subjected to broad-band ultraviolet-visible photolysis for a period of four hours using a medium pressure mercury lamp and infrared and Raman spectra were recorded after photolysis. In Fig. 1 are shown infrared spectra of a single crystal of β-4-chloro-*trans*-cinnamic acid before and after photolysis, while in Fig. 2 are shown corresponding spectra of a single crystal of γ-3-chloro-*trans*-cinnamic acid. It is clear that the dimerisation of the β-derivative has proceeded to completion whereas no reaction is seen for the γ-derivative. In fact it was found that all three β-derivatives would undergo complete conversion to the dimer after *ca.* 30 min of photolysis under such conditions whereas the γ-derivative showed no conversion even when the photolysis time was extended to 4 hours. The most marked spectral changes seen upon dimerisation are a shift to high frequency of ν(C=O) of the carboxy group (caused by loss of conjugation) and disappearance of the bands at 1632 (2-chloro), 1629 (3-chloro) and 1627 (4-chloro) which arises from the aliphatic ν(C=C) vibration. The carboxy ν(C=O) band is noted to shift to high frequency by 29 cm^{-1} (2-chloro), 27 cm^{-1} (3-chloro) and 31 cm^{-1} (4-chloro).

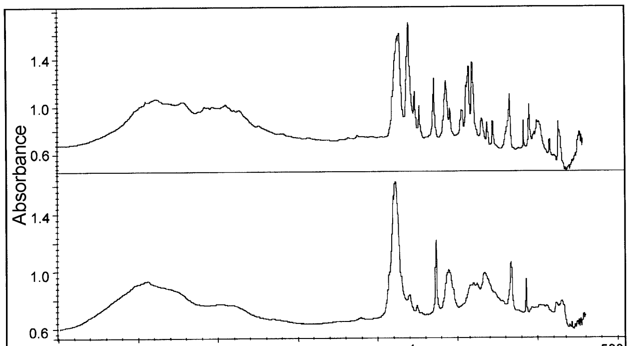


Fig. 1 Infrared spectra of a single crystal of β-4-chloro-*trans*-cinnamic acid before (top spectrum) and after (bottom spectrum) 4 h irradiation under a medium-pressure, water-cooled mercury lamp.

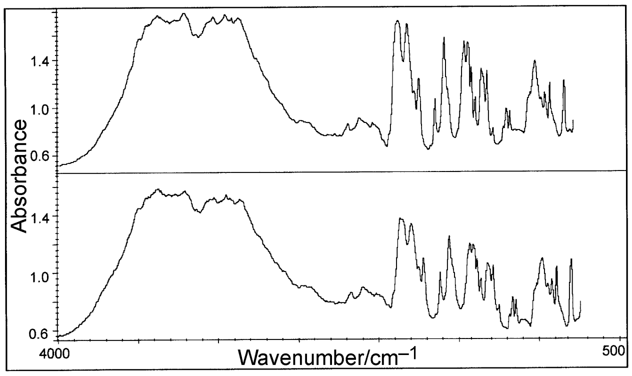
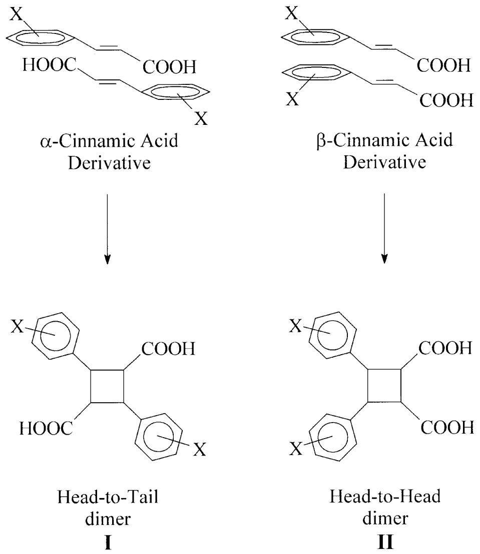


Fig. 2 Infrared spectra of a single crystal of γ-3-chloro-*trans*-cinnamic acid before (top spectrum) and after (bottom spectrum) 4 h irradiation under a medium-pressure, water-cooled mercury lamp.

It is of some interest to compare the positions of the infrared and Raman bands of the dimeric products. If the reaction proceeds *via* a topotactic route these products should be the β-truxinic acid derivatives (**II**) (Scheme 1) where the phenyl group is substituted by a chlorine atom in the 2, 3 or 4-position. These compounds are relatively poorly characterised. There is no structural data for 2,2′-dichloro- or 4,4′-dichlorotruxinic acid, while the only data for the 3,3′-compound is for the water–acetic acid solvate.[25] The β-truxinic acids (**II**) have C_s symmetry. By contrast, the head-to-tail isomers—the α-truxillic acids (**I**)—have C_i symmetry with planar four-membered cyclobutane rings.[25–29] Thus one may expect the *mutual exclusion principle* to apply and we would expect to see no coincidences between infrared and Raman bands for the α-truxillic acid derivatives (in C_i symmetry vibrations transform as either A_g—Raman active only—or A_u—infrared active only). For the β-truxinic acids, which have C_s symmetry, coincidences would be expected between infrared and Raman bands. The dimerisation product of β-4-chloro-*trans*-cinnamic acid shows infrared bands in the region 1000–2000 cm^{-1} at 1711, 1635, 1593, 1493, 1426, 1293, 1234, 1094 and 1014 cm^{-1}. These may be compared with Raman bands at 1635, 1598, 1490, 1450, 1213, 1184 and 1091 cm^{-1}. Given that the infrared bands at 1493, 1426 and 1293 cm^{-1} are all broad so that their exact positions cannot be measured very precisely there appears to be a good correspondence between the spectra. A similar situation is seen for the products of photodimerisation of β-2-chloro-*trans*-cinnamic acid and β-3-chloro-*trans*-cinnamic acid. For the 2-chloro product infrared bands at 1631, 1593, 1572, 1478, 1039 and a broad, complicated feature at *ca.* 1300 cm^{-1} are matched by Raman bands at 1638, 1591, 1574, 1473, 1034 and 1292 cm^{-1}. For the 3-chloro product infrared absorptions at 1478, 1434, 1211, 1081, 998, 912 and 880 cm^{-1} are matched by Raman scattering at 1480, 1439, 1209, 1087, 1002, 912 and *ca.* 880 cm^{-1}. The observation of coincidences between the infrared and Raman spectra which we have recorded in these experiments therefore allow us to identify the photodimerisation products as being the substituted β-truxinic acid derivatives and confirm that the reactions are topotactic. An X-ray diffraction study of a single crystal of β-3-chloro-*trans*-cinnamic acid used in this study showed the sample to be isostructural with previously studied crystals.[30]



Scheme 1 Diagram illustrating the conversion of the α- and β-forms of cinnamic acid derivatives to dimers *via* topotactic reactions. X indicates a substituent in the 2-, 3- or 4-position on the phenyl ring. It should be noted that the α- and β-forms of these derivatives are different crystalline forms not simply different orientations in space.

A comparison of 2-methoxy, 3-methoxy and 4-methoxy-*trans*-cinnamic acid

In previous studies crystals have been reported for 2-methoxy-*trans*-cinnamic acid in the α-form and for 3- and 4-methoxy-*trans*-cinnamic acids in the γ-form.[21] These crystals were prepared by recrystallisation from methanol, benzene and ethanol, respectively.[21] In the current work we have prepared samples of each of these crystalline derivatives. The aim of this part of the work was to monitor the photodimerisation of a *trans*-cinnamic acid derivative which crystallises in the α-form and to compare the structures of the α and γ forms in order to explore the reasons for the lack of reactivity of the γ derivatives.

Infrared and Raman spectra of a single crystal of α-2-methoxy-*trans*-cinnamic acid recorded before and after 3.75 h of broad band ultraviolet-visible photolysis with a medium pressure mercury lamp are shown in Figs. 3 and 4.

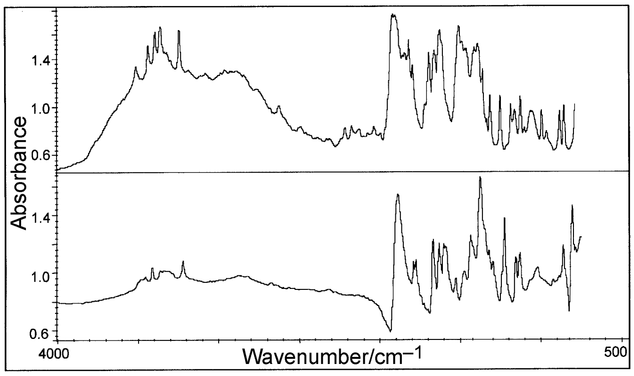


Fig. 3 Infrared spectra of a single crystal of α-2-methoxy-*trans*-cinnamic acid before (top spectrum) and after (bottom spectrum) 3.75 h irradiation under a medium-pressure, water-cooled mercury lamp.

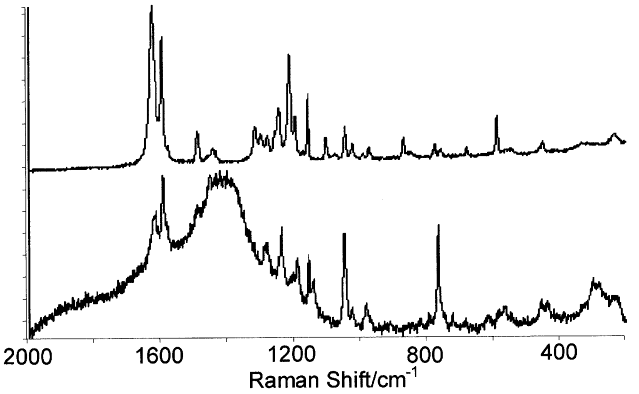


Fig. 4 Raman spectra of a single crystal of α-2-methoxy-*trans*-cinnamic acid before (top spectrum) and after (bottom spectrum) 3.75 h irradiation under a medium-pressure, water-cooled mercury lamp.

Once again it is apparent that photodimerisation has occurred as the band arising from ν(C=C) at 1620 cm^{-1} has decayed upon irradiation. Both sets of spectra suggest a conversion in excess of 80% on this timescale. Much longer photolysis times were not feasible because, under these conditions, extensive fragmentation of the crystals occurred and the quality of the spectra declined very markedly. It is, however, again of interest to compare the infrared and Raman spectra of the dimeric products. It is not totally straightforward to identify bands which arise from the dimer because 100% conversion was not achieved so spectra of the dimer necessarily contain some monomer bands. However, it is possible to identify features which must arise from the dimer because they occur at wavenumbers where there are no bands in the monomer spectra. These bands occur at: infrared 1372, 1292, 1174, 1111, 932 and 795 cm^{-1}; Raman 1191, 1143 and 726 cm^{-1}. There are no coincidences between these bands lending support to the suggestion that the reaction product is 2,2′-dimethoxy-α-truxillic acid. Once again this finding implies a topotactic reaction.

We have explored the reasons for the different reactivities of α-2-methoxy-*trans*-cinnamic acid and the γ-forms of 3-and 4-methoxy-*trans*-cinnamic acid by determining the orientations of the molecules within the single crystals by single crystal X-ray diffraction. Cell parameters, but no coordinates, have previously been reported for 2-methoxy-*trans*-cinnamic acid in the α-form and for the 3- and 4-methoxy compounds in the γ-form,[26] and while atomic coordinates have subsequently been published for the γ-form of 4-methoxy-*trans*-cinnamic acid,[31] there are no coordinates in the Cambridge Crystallographic database for the other two compounds. We have therefore determined and report here the structures of α-2-methoxy- and γ-4-methoxy-*trans*-cinnamic acid. Both structures show the usual form of planar dimers with two molecules connected *via* two hydrogen bonds between acid groups.

However, of major interest to this work is the relative alignment of the molecules and this is shown in Figs. 5 and 6. It may be seen that the monomers of α-2-methoxy-*trans*-cinnamic acid are aligned in a head-to-tail manner—the archetypal "α" structure. By contrast, γ-3-methoxy-*trans*-cinnamic acid shows a head-to-head arrangement of the monomers but with the molecules displaced significantly from one another. The structure of the γ-4-methoxy derivative, previously reported,[31] shows a similar head-to-head arrangement. The factors prohibiting reaction in single crystals of cinnamic acid derivatives have been examined previously in some detail.[32,33] In the first place the double bonds should not be more than about 4.3 Å apart (this implies that the molecules do not need to move more than *ca.* 2.75 Å to form C–C single bonds of about 1.56 Å). Second they should be parallel. Third they should be aligned so that a minimum translation of the adjacent molecules is required for them to line up.

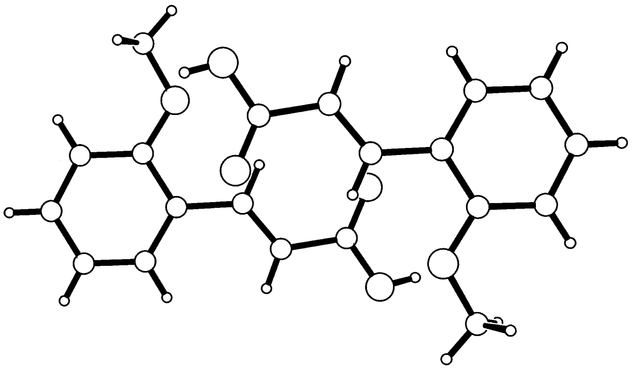


Fig. 5 The alignment of two adjacent parallel monomers within a single crystal of α-2-methoxy-*trans*-cinnamic acid, projected onto the plane of one molecule. Large circles, oxygen, medium, carbon, small, hydrogen.

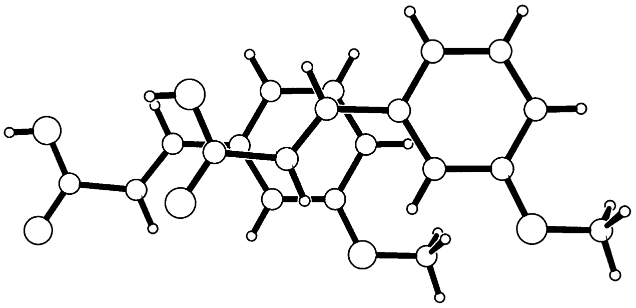


Fig. 6 The alignment of two adjacent monomers within a single crystal of γ-3-methoxy-*trans*-cinnamic acid, projected onto the plane of one molecule. Large circles, oxygen, medium, carbon, small, hydrogen.

In the γ-3 and γ-4-methoxy derivatives studied the vertical separation between successive molecules is about 3.5 Å, but, as is apparent from Fig. 6, there is a longitudinal displacement of *ca.* 3.2 Å and a lateral displacement of *ca.* 1.1 Å between the molecules in each layer. This separates the olefinic groups of each molecule making a dimerisation reaction impossible to achieve. By contrast in the α-2-methoxy derivative, while the vertical separation is also about 3.5 Å, now there is only minimal longitudinal displacement and a small lateral displacement, so dimerisation can occur.

A comparison of 2-nitro, 3-nitro and 4-nitro-*trans*-cinnamic acid

We have obtained samples of each of the three isomeric nitro derivatives in both the γ- and β-forms. The β-forms have previously been reported for all three isomers; the γ-form for the 3- and 4-nitro compounds only.[21] The only detailed report of the structure of any of these derivatives is of the 4-nitro compound in the photostable γ-form.[34] Infrared spectra have been recorded for single crystals of each of the three γ- and β-derivatives. As expected the γ-derivatives show no reaction upon photolysis. By contrast, the β form shows after 4 h of photolysis the disappearance of the band at 1627 cm^{-1} which arises from the stretching vibration of the aliphatic C=C bond. The spectra show a 100% conversion to dimer. We have succeeded in recording both infrared and Raman spectra for the dimeric product of 3-nitro-*trans*-cinnamic acid. These show coincidences between band positions in the two spectra: infrared absorption at 1580, 1530, 1350, 1285, 1230, 1106, and 787 cm^{-1} is matched by Raman scattering at 1585, 1540, 1355, 1289, 1231, 1110, 1002 and 794 cm^{-1}. This observation suggests that the product is that expected from a toptactic reaction, namely 3,3′-dinitro-β-truxinic acid.

Conclusions

The results presented in this paper show the usefulness of vibrational microspectroscopy as a tool to monitor the photodimerisation of solid *trans*-cinnamic acid derivatives and is of particular interest when used in conjunction with single crystal X-ray diffraction. This latter method is normally not suitable for monitoring such reactions because the crystals degrade during the course of the reaction making accurate diffraction data difficult to obtain. However, it provides information about the orientation of the monomers in the crystals of the starting compounds and gives an insight into the reasons for reactivity or a lack of it. It has already been noted that the reacting double bonds need to be between 3.6 and 4.1 Å apart for reaction to occur.[35] Our work demonstrates the importance of other geometric parameters in determining reactivity, namely the magnitude of the longitudinal and lateral displacements of adjacent molecules. Our studies suggest a wide applicability of this combination of techniques in solid-phase organic chemistry.

Acknowledgements

We thank the Engineering and Physical Sciences Research Council for the award of the grant through which the Reading microscopes were purchased (grant GR/R06908), and for studentships to SDMA and KSW. EJF is grateful to the Natural Environment Research Council and SLJ to University of Reading Research Endowment Trust Fund for the award of studentships. MJA thanks the Royal Society for the award of a travel grant to visit the group of GAB at the University of Auckland. We thank EPSRC and University of Reading for funds for the Image Plate system.

References

1 M. A. Garcia-Garibay, S. Shin and C. N. Sanrame, *Tetrahedron*, 2000, **56**, 6729.
2 G. Kaupp, H. Frey and G. Behmann, *Chem. Ber.*, 1988, **121**, 2135.
3 M. Sakamoto, N. Sekine, H. Miyoshi, T. Mino and T. Fujita, *J. Am. Chem. Soc.*, 2000, **122**, 10210.
4 M. Sakamoto, M. Takahashi, W. Arai, T. Mino, K. Yamaguchi, S. Watanabe and T. Fujita, *Tetrahedron*, 2000, **56**, 6795.
5 G. Kaupp and M. Haak, *Angew. Chem., Int. Ed.*, 1996, **35**, 2774.
6 K. Tanaka, E. Mochizuki, N. Yasui, Y. Kai, I. Miyahara, K. Hirotsu and F. Toda, *Tetrahedron*, 2000, **56**, 6853.
7 G. Kaupp, J. Schmeyers, A. Kuse and A. Atfeh, *Angew. Chem., Int. Ed.*, 1999, **38**, 2896.
8 H. Koshima, D. Matsushige, M. Miyauchi and J. Fujita, *Tetrahedron*, 2000, **56**, 6845.
9 Y. Ito, H. Hosomi and S. Ohba, *Tetrahedron*, 2000, **56**, 6833.
10 C. B. Aaakeroy, A. M. Beatty, M. Nieuwenhuyzen and M. Zou, *Tetrahedron*, 2000, **56**, 6693.
11 H. Ihmels, D. Leusser, M. Pfeiffer and D. Stalke, *Tetrahedron*, 2000, **56**, 6867.
12 H. Irngartinger and M. Skipinski, *Tetrahedron*, 2000, **56**, 6781.
13 V. Enklemann, G. Wegner, K. Novak and K. B. Wagener, *J. Am. Chem. Soc.*, 1993, **115**, 10390.
14 G. Kaupp, *Angew. Chem., Int. Ed.*, 1992, **31**, 592.
15 G. Kaupp, *Angew. Chem., Int. Ed.*, 1992, **31**, 595.
16 G. Kaupp and M. Haak, *J. Phys. Org. Chem.*, 1995, **8**, 545.
17 G. Kaupp, J. Schmeyers, F. Toda, H. Takumi and H. Koshima, *J. Phys. Org. Chem.*, 1996, **9**, 795.
18 S. D. M. Allen, M. J. Almond, J-L. Bruneel, A. Gilbert, P. Hollins and J. Mascetti, *Spectrochim. Acta, Part A*, 2000, **56**, 2423.
19 (*a*) A. W. K. de Jong, *Recueil*, 1912, **31**, 258; (*b*) A. W. K. de Jong, *Ber. Dtsch. Chem. Ges.*, 1922, **55**, 463; (*c*) A. W. K. de Jong, *Ber. Dtsch. Chem. Ges.*, 1923, **56**, 818.
20 (*a*) H. Stobbe and A. Lehfeldt, *Ber. Dtsch. Chem. Ges.*, 1925, **58**, 2415; (*b*) H. Stobbe and F. K. Steinberger, *Ber. Dtsch. Chem. Ges.*, 1922, **55**, 2225.
21 M. D. Cohen, G. M. J. Schmidt and F. I. Sonntag, *J. Chem. Soc.*, 1964, 2000.
22 W. Kabsch, *J. Appl. Crystallogr.*, 1988, **21**, 916.
23 G. M. Sheldrick, SHELXS86, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467.
24 G. M. Sheldrick, SHELXL, Program for Crystal Structure Refinement, University of Göttingen, 1993.
25 S. Kanao, S. Kashino and M. Haisa, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1990, **46**, 2439.
26 G. M. J. Schmidt, *J. Chem. Soc.*, 1964, 2014.
27 S. Kashino, H. Oka and M. Haisa, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1989, **45**, 154.
28 S. Kanao, S. Kashino and M. Haisa, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1990, **46**, 2436.
29 R. S. Gopalan and G. U. Kulkarni, *Proc. Ind. Acad. Sci. (Chem. Sci.)*, 2001, **113**, 307.
30 M. A. Fernandes, D. C. Levendis and C. B. de Koning, *Cryst. Eng.*, 2001, **4**, 215.
31 R. F. Bryan and D. P. Freyberg, *J. Chem. Soc., Perkin Trans 2*, 1975, 1835.
32 V. Ramamurthy and K. Venkatesan, *Chem. Rev.*, 1987, **87**, 433.
33 S. D. M. Atkinson, PhD Thesis, University of Reading, 2001.
34 Y. Kageyama, T. Iwamoto, M. Haisa and S. Kashino, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1993, **49**, 833.
35 M. A. Fernandes, C. B. de Konig and D. C. Levendis, presented at XVII Congress of the International Union of Crystallography, Seattle, Washington, USA, 1996.