position, and is *cis* to the equatorially-substituted acetyl group at C(7) (Fig. 2).

One of us (MRS) is grateful to the SERC and Roche Products Ltd for a CASE Research Studentship (1977–1980). We thank Drs M. J. Broadhurst, C. H. Hassall and W. A. Thomas for discussions and the provision of material.

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Structure of 3,4-Dihydroxy-*trans*-cinnamic Acid (Caffeic Acid) and its Lack of Solid-State Topochemical Reactivity

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(*Received 2 September 1986; accepted 24 October 1986*)

Abstract. $C_9H_8O_4$, $M_r = 180{\cdot}16$, monoclinic, $P2_1/n$, $a = 6{\cdot}6953$ (7), $b = 5{\cdot}7960$ (5), $c = 21{\cdot}193$ (2) Å, $\beta = 93{\cdot}83$ (1)°, $V = 820{\cdot}6$ (1) Å^3, $Z = 4$, $D_x = 1{\cdot}46$ Mg m^{-3}, Cu $K\alpha$ radiation (graphite crystal monochromator, $\lambda = 1{\cdot}54184$ Å), $\mu(\text{Cu } K\alpha) = 0{\cdot}943$ mm^{-1}, $T = 290$ K, $F(000) = 376$, final $R = 0{\cdot}044$ for 884 'observed' reflections and 150 variables. The geometry about the double bond is *trans*, torsion angle $-178{\cdot}9$ (3)°. The interplanar angle between the phenyl ring and the carboxyl group is $4{\cdot}33$ (8)°. O—H···O hydrogen bonds link the molecules to form dimers. Even though the crystal structure predicts that inversion-related molecules should undergo solid-state topochemical dimerization, the material is in fact photostable and a reason for this is presented.

Introduction. According to Schmidt (1964), the crystallographic short axis (SA) may be used to classify *trans*-cinnamic acids into three structural types, the photoactive α (SA > 5·1 Å) and β (SA < 4·1 Å) and the photostable γ (4·7 < *SA* < 5·1 Å) forms. The reactivity of the α and β forms is ascribed to the fact that parallel double bonds are at a centre-to-centre separation of < 4·2 Å. Many simple acids conform to these topochemical rules (Schmidt, 1964). However, the crystal chemistry of more complicated structures such as 3,4-dimethoxycinnamic acid (Desiraju, Kamala, Kumari & Sarma, 1984) and its 1:1 complex with 2,4-dinitrocinnamic acid (Desiraju & Sarma, 1983; Sarma & Desiraju, 1985) cannot be readily described in terms of such geometrical criteria.

Further, there has been much discussion as to what exactly constitutes a deviation from topochemical 2+2 photoreactivity, since there are cases like 2-benzylidenecyclopentanone (Kearsley & Desiraju, 1985) which is photostable even though parallel double bonds

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are aligned at 4·14 Å separation, or the photoreactive 2,5-dibenzylidenecyclopentanone (Theocharis, Jones, Thomas, Motevalli & Hursthouse, 1984) where the double bonds are not parallel, or 4-formylcinnamic acid (Nakanishi, Hasegawa & Mori, 1985) which reacts even though the parallel double bonds are more than 4·8 Å apart in the crystal. The packing of 3,4-dihydroxycinnamic acid (caffeic acid) was considered to be of interest in this context, because while it is expected to have the photoreactive α structure on the basis of its 5·8 Å SA, the material is unaffected by UV irradiation.

Experimental. The acid was prepared from vanillin by literature procedures (Lange, 1962) and a yellow crystal of approximately 0·30 × 0·12 × 0·06 mm, obtained from 1:1 methanol–water, was used during the measurements. Throughout the experiment Cu *Kα* radiation was used with a graphite-crystal monochromator on a Nonius CAD-4 diffractometer. The unit-cell dimensions were determined from the angular settings of 25 reflections. The intensity data of 3092 reflections, with $0 < \theta < 70°$ and *hkl* range (–8, –6, 0) to (8, 6, 25), were measured using the ω–2θ scan technique with a scan angle of 1·50° and a variable scan rate, with a maximum scan time of 60 s per reflection. The intensity of the primary beam was checked throughout the data collection by monitoring three standard reflections every 30 min. The final drift correction factors were between 0·98 and 1·01. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Symmetry-equivalent reflections were averaged, $R_{\rm int} = 0{\cdot}023$, resulting in 1390 unique reflections of which 884 were observed with $I > 3\sigma(I)$. Lorentz and polarization corrections were applied and the data were reduced to $|F_o|$ values.

The structure was solved using *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); in space group $P2_1/n$ no solution was obtained; we reduced the symmetry to $P2_1$ and the resulting *E* map showed two molecules related by a centre of symmetry (0·25, 0·29, 0·25). The origin was shifted accordingly, and the refinement was continued in $P2_1/n$. Isotropic least-squares refinement with *SHELX* (Sheldrick, 1976), converged to $R = 0{\cdot}010$. At this stage an empirical absorption correction was applied (Walker & Stuart, 1983); maximum and minimum correction factors were 1·400 and 0·598 respectively. All H atoms were located by difference Fourier synthesis. During the final stages of the refinement the positional parameters of all atoms and the anisotropic thermal parameters of the non-hydrogen atoms were refined. The H atoms were refined with isotropic temperature factors. The final $R = 0{\cdot}044$ and $wR = 0{\cdot}046$ for the 884 'observed' reflections and 150 variables. The function minimized was $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}00020F_o{}^2]$ with $\sigma(F_o)$ from counting statistics. The maximum shift-over-e.s.d. ratio in the last full-matrix least-squares cycle was less than 0·06. In the final difference Fourier map the residual electron density was within $\pm 0{\cdot}20$ e Å^{-3}. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Final positional and thermal parameters are given in Table 1.* Molecular geometry data calculated with *PARST* (Nardelli, 1983) are in Table 2. The figures were drawn with *PLUTO* (Motherwell, 1976). The crystallographic numbering scheme is given in Fig. 1. C(4) is *trans* to C(1), the torsion angle C(1)—C(2)—C(3)—C(4) being –178·9 (3)°. The angle between the least-squares planes of the phenyl ring and the carboxyl group is 4·33 (8)°, which is in the range expected for the *trans*-acid (Raghunathan & Pattabhi, 1981). Fig. 2 shows the molecular packing. Pairs of acid molecules are strongly associated through their

Table 1. *Fractional positional and equivalent isotropic thermal parameters* (Å^2 × 10^2) *with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	$U_{\rm eq}$
O(1)	–0·2894 (3)	–0·1877 (4)	–0·01378 (9)	5·58 (8)
O(2)	–0·3923 (3)	0·1515 (4)	–0·05268 (9)	5·93 (8)
O(3)	0·64547 (28)	–0·5455 (4)	–0·15139 (9)	5·51 (8)
O(4)	0·6985 (3)	–0·2359 (4)	–0·23751 (9)	5·38 (8)
C(1)	–0·2734 (4)	–0·0104 (6)	–0·05046 (13)	4·56 (11)
C(2)	–0·1037 (4)	–0·0114 (6)	–0·09117 (14)	5·24 (12)
C(3)	0·0317 (4)	–0·1744 (5)	–0·09116 (12)	4·36 (11)
C(4)	0·2048 (4)	–0·1800 (5)	–0·13014 (11)	3·98 (10)
C(5)	0·3401 (4)	–0·3616 (5)	–0·12209 (13)	4·26 (10)
C(6)	0·5056 (4)	–0·3743 (5)	–0·15740 (12)	4·08 (10)
C(7)	0·5353 (4)	–0·2061 (5)	–0·20257 (11)	3·92 (10)
C(8)	0·4024 (4)	–0·0255 (5)	–0·21110 (13)	4·61 (11)
C(9)	0·2391 (4)	–0·0127 (6)	–0·17487 (13)	4·57 (11)

Table 2. *Bond lengths* (Å) *and hydrogen-bond*, O···O, *lengths* (Å)

O(1)–C(1)	1·297 (3)	C(5)–C(6)	1·380 (3)
O(2)–C(1)	1·229 (3)	C(6)–C(7)	1·390 (3)
O(3)–C(6)	1·364 (3)	C(7)–C(8)	1·378 (4)
O(4)–C(7)	1·371 (3)	C(8)–C(9)	1·379 (4)
C(4)–C(5)	1·392 (4)	C(3)–C(2)	1·309 (4)
C(4)–C(9)	1·386 (4)	C(2)–C(1)	1·472 (4)
C(4)–C(3)	1·467 (3)		

O(1)–H(O1)···O(2)	$(-x-1, -y, -z)$	2·640 (3)
O(3)–H(O3)···O(2)	$(x+1, y-1, z)$	2·756 (3)
O(4)–H(O4)···O(3)	$(-x+\frac{3}{2}, y+\frac{1}{2}, -z-\frac{1}{2})$	2·860 (3)
O(4)–H(O4)···O(4)	$(-x+\frac{3}{2}, y+\frac{1}{2}, -z-\frac{1}{2})$	3·034 (3)

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* Lists of structure amplitudes, anisotropic thermal parameters, H-atom parameters, bond angles, details of the hydrogen bonding, selected torsion angles and angles between least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43520 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

carboxylic groups by hydrogen bonds. Additional hydrogen bonding occurs between screw-axis-related 4-hydroxy groups. This bonding is similar to that found in 4-hydroxycinnamic acid (Bryan & Forcier, 1980). Curiously the packing does not show any obvious similarity to the polymorphs of 3,4-dihydroxybenzoic acid (Agmon & Herbstein, 1983). Further, the 3-hydroxy group does not seem to participate in the hydrogen-bonding scheme. This fact is confirmed by the IR spectrum which shows distinct frequencies corresponding to both free (3425 cm^{-1}) and hydrogen-bonded (3250 cm^{-1}) hydroxyl groups.

The 'potentially reactive' olefinic double bonds [for instance in molecules x, y, z and $-x, -y, -z$ (see Fig. 2)] are inversion-related and the centre-to-centre separation of such parallel bonds is 4·01 Å with orbital overlap favourable for photoreaction. The title compound therefore has the α structure, but it is completely stable to UV irradiation ($\lambda > 300$ nm, 303 K), while both 2- and 4-hydroxycinnamic acid with α structures are photoreactive. The inertness of the title compound may perhaps be ascribed to the strong hydrogen bonding which does not permit the molecular flexibility essential for these reactions. Such flexibility is required since atoms which are around 4·0 Å apart in the reactant must come to within 1·6 Å or so in the product. Accordingly, it has been stated (Hasegawa & Shiba, 1982) that while the efficiency of 2+2 topochemical processes varies with temperature, the optimal temperature may be rather high for hydrogen-bonded systems. Carboxyl hydrogen bonding is perhaps not the discriminating factor since it is found in all cinnamic acids, but the extra anchoring by hydrogen bonding between phenolic groups may render the material sluggish towards photoreaction. Another explanation for the photostability of the title compound is the existence of polymorphs, but more detailed work is required to substantiate such suggestions.

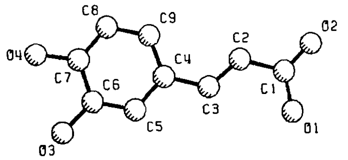

Fig. 1. View of the molecule, showing the crystallographic atomic numbering scheme.

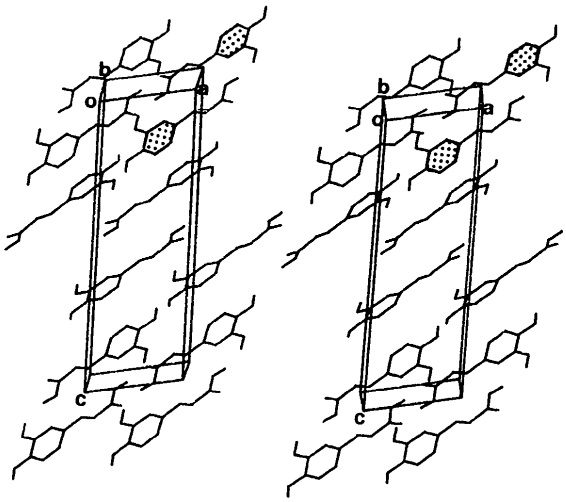

Fig. 2. Stereoview of the structure along **b**. The pair of inversion-related molecules (shaded) are 'potentially photoreactive'. The phenolic hydrogen bonding, involving the 4-hydroxy groups, is along **b**.

SG-G, on leave from the Physical Chemistry Department, University of Oviedo (Spain), gratefully acknowledges the Spanish Ministerio de Educacion y Ciencia (MEC) for a postdoctoral grant and the University of Oviedo for granting him leave. The award of a Junior Research Fellowship (to TSRK) by the Council of Scientific and Industrial Research, New Delhi, is acknowledged. We thank J.A.R.P. Sarma for the preparation of the title compound.

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