by more than 2·0°. Although the C—C bonds of (5) and (1a) are almost similar, the C4—C5 bonds vary (by about 0·04 Å). The N—C bond lengths of N^+—CH_3 and N^+—CH_2—N^+ are very close.

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Structure of 3-(4-Hydroxy-3-methoxyphenyl)-2-propenoic Acid (Ferulic Acid)

BY M. NETHAJI AND VASANTHA PATTABHI*

Department of Crystallography and Biophysics,† University of Madras, Guindy Campus, Madras 600 025, India

AND GAUTAM R. DESIRAJU*

School of Chemistry, University of Hyderabad, PO Central University, Hyderabad 500 134, India

Abstract. $C_{10}H_{10}O_4$, $M_r = 194·19$, monoclinic, $P2_1/n$, $a = 4·6405$ (4), $b = 16·824$ (5), $c = 12·019$ (4) Å, $\beta = 90·15$ (1)°, $V = 938·4$ (1) Å^3, $Z = 4$, D_m (by flotation) = 1·38, $D_x = 1·38$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 0·808 mm^{-1}, $T = 295$ K, $F(000) = 408$, final $R = 0·036$ for 1219 significant reflections where $I_o > 2·5\sigma(I_o)$. The structure was solved by direct methods. The carbonyl oxygen is in the *syn* conformation with respect to the olefinic linkage. The phenyl ring makes an angle of 4·0 (1)° with the carboxyl group. Molecules are strongly O—H⋯O hydrogen bonded across inversion centres [O⋯O 2·629 (2) Å]. Additionally, there are unusual O—H⋯O—H bonds [O⋯O 2·889 (2) Å] between phenolic and carboxylic O—H groups of glide-related neighbours. The molecules are stabilized by an infinite zigzag chain of these intermolecular O—H⋯O and also C—H⋯O bonds. Molecules related by the short-axis translation are too far apart for solid-state photodimerization and the solid is thus photostable.

Introduction. Substituted *trans*-cinnamic acids are excellent choices for the study of organic solid-state photochemical processes (Schmidt, 1964; Desiraju, Kamala, Kumari & Sarma, 1984; Nakanishi & Hasegawa, 1985) and as model compounds for 'crystal engineering', that is the deliberate design and prediction of organic crystal structures (Sarma & Desiraju, 1986). These acids crystallize in one of three forms, the photoactive α and β modifications and the photostable γ modification. The distinguishing criterion for these forms is the value of the crystallographic short axis which is greater than 5·1 Å for the α, between 3·8 and 4·2 Å for the β and between 4·6 and 5·1 Å for the γ form. The title compound is part of a series of 3,4-dioxygenated cinnamic acids whose crystal structures and solid-state photochemistry have been studied systematically. Earlier reports have dealt with the 3,4-methylenedioxy and 3,4-dimethoxy acids (Desiraju,

* To whom correspondence should be addressed.
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Kamala, Kumari & Sarma, 1984) and with the 3,4-dihydroxy derivative (Garcia-Granda, Beurskens, Beurskens, Krishna & Desiraju, 1987). The particular crystal structure adopted in these and other 3- and 4-oxygenated cinnamic acids seems to depend on the type of O—H···O and C—H···O bonding that is possible (Sarma & Desiraju, 1986). Additionally, it has been noted that while cis-cinnamic acids possess a good auxin activity, the trans-isomers do not. For all these reasons, a crystal structure determination of the title compound was undertaken.

HO—⟨benzene⟩—CH=CH—CO$_2$H
CH$_3$O
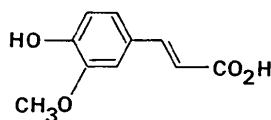
Experimental. The compound was prepared from vanillin using literature procedures. Pale pink crystals from ethanol, $0.275 \times 0.175 \times 0.125$ mm, $\omega/2\theta$ scan with $2\theta_{max} = 130°$, Cu $K\alpha$ ($\lambda = 1.5418$ Å), Enraf–Nonius CAD-4 diffractometer, no absorption correction, data corrected for Lorentz and polarization effects, unit-cell parameters from 25 reflections with $28 < 2\theta < 74°$, 1590 independent reflections, $0 \le h \le 5$; $0 \le k \le 18$; $-13 \le l \le 13$, 1219 non-zero with $I_o > 2.5\sigma(I_o)$, two standard reflections (131, 141) measured after every 100 reflections showed 1% variations, structure solution by direct methods using the program MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980), full-matrix least-squares refinement on F_o, isotropic refinement for non-hydrogens converged at $R(F) = 0.124$, $wR = 0.132$, hydrogen positions from ΔF synthesis, isotropic refinement for hydrogens with anisotropic refinement for non-hydrogens converged at $R(F) = 0.036$, $wR(F) = 0.036$ for weighting scheme based on counting statistics, $w = 1/[\sigma^2(F) + 0.0067F_o^2]$, $S = 3.58$ for 166 parameters, $\Delta/\sigma(max.) = 0.47$, $\Delta/\sigma(mean) = 0.0153$, final difference Fourier map had no peaks >0.12 e Å^{-3}, refinements using SHELX76 (Sheldrick, 1976), atomic scattering factors as in SHELX, atomic positions and equivalent isotropic temperature factors are listed in Table 1.*

Discussion. Fig. 1 shows the intramolecular bond lengths and angles and the atom-numbering scheme. A stereoview of the crystal structure looking down the short axis is shown in Fig. 2. The C(8)—C(9) and C(7)—C(1) distances exhibit partial double-bond

* Lists of structure factors, anisotropic thermal parameters, torsion angles, H-atom parameters, least-squares-planes data and a geometric comparison with related structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44379 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$) *and equivalent isotropic temperature factors of non-hydrogen atoms with e.s.d.'s in parentheses*

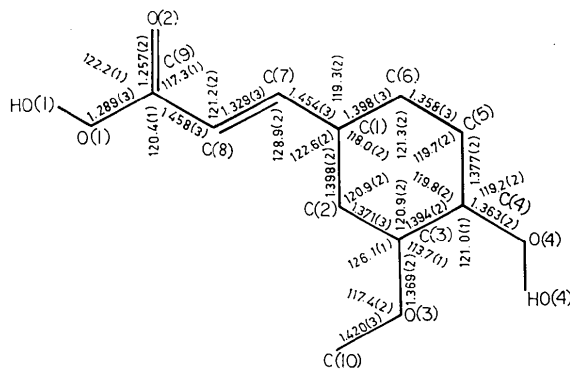|	x	y	z	B_{eq}(Å^2)
O(1)	8501 (3)	978 (1)	−128 (1)	3.79 (4)
O(2)	7627 (3)	−34 (1)	1020 (1)	4.07 (4)
O(3)	−2601 (3)	3175 (1)	3110 (1)	4.19 (4)
O(4)	−4549 (3)	2391 (1)	4865 (1)	4.01 (4)
C(1)	1514 (4)	1300 (1)	2841 (2)	3.08 (5)
C(2)	566 (4)	2072 (1)	2602 (2)	3.12 (5)
C(3)	−1459 (4)	2433 (1)	3269 (1)	3.07 (5)
C(4)	−2565 (4)	2038 (1)	4194 (1)	3.15 (5)
C(5)	−1655 (5)	1278 (1)	4435 (2)	3.93 (6)
C(6)	377 (5)	915 (1)	3762 (2)	3.85 (6)
C(7)	3627 (4)	892 (1)	2156 (2)	3.32 (5)
C(8)	5017 (4)	1156 (1)	1264 (2)	3.19 (5)
C(9)	7152 (4)	665 (1)	700 (2)	3.05 (5)
C(10)	−1622 (9)	3615 (2)	2176 (2)	5.80 (9)

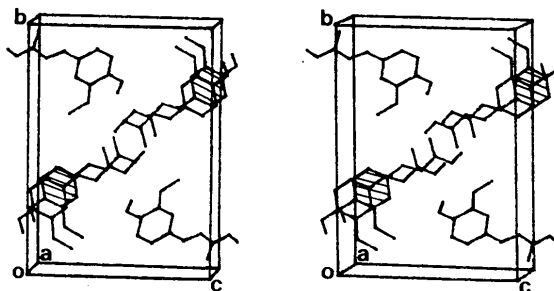Fig. 1. Bond lengths (Å) and angles (°), and atom-numbering scheme for the title compound.

Fig. 2. Stereoview of the crystal structure of the title compound viewed down [100]. The shaded molecules are short-axis translated but are too far apart for a solid-state photoreaction.

character and the values are comparable with those found in 2- and 3-coumaric acids (Raghunathan & Pattabhi, 1979, 1981). The near equality of the bonds O(1)—C(9) and O(2)—C(9) and of the angles C(8)—C(9)—O(1) and C(8)—C(9)—O(2) indicates partial disorder of the carboxyl group by carboxyl–hydroxyl exchange. Widening of the angles C(8)—C(7)—C(1) and C(2)—C(3)—O(3) may minimize steric interaction between hydrogen atoms bonded to C(2), C(8) and C(10). The former widening is normal for trans-cinnamic acids. The carbonyl O is again, as expected,

syn with respect to the C=C bond (Leiserowitz, 1976). In this respect, it resembles the 3,4-methylenedioxy and 3,4-dimethoxy acids but not the 3,4-dihydroxy derivative which adopts the *anti* conformation (García-Granda, Beurskens, Beurskens, Krishna & Desiraju, 1987). The phenyl ring is almost planar ($\chi^2 = 20\cdot4$) and makes an angle of $4\cdot0$ (1)° with the carboxyl group, in agreement with related structures. Salient geometrical details of these structures may be found in the deposited material.

The crystal structure is typical of the γ family. Centrosymmetrically-related molecules are strongly hydrogen bonded [$O\cdots O$ $2\cdot629$ (2) Å], forming dimers. These dimers are stacked in the short axis separation ($4\cdot64$ Å). The crystal therefore belongs to the γ domain and is predictably stable to solid-state UV irradiation ($\lambda > 300$ nm) (Desiraju, Kamala, Kumari & Sarma, 1984). Such behaviour is normal. It might be noted, in this connection, that 4-formylcinnamic acid, which has a similar γ structure (short axis $4\cdot825$ Å), exhibits anomalous solid-state photoreactivity (Nakanishi & Hasegawa, 1985).

The carboxyl oxygen O(1) is hydrogen-bonded ($2\cdot869$ Å) to the phenolic oxygen O(4) of the *n*-glide related molecule ($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$). This scheme of hydrogen bonding has been observed in 3-coumaric acid (Raghunathan & Pattabhi, 1981). Further, the molecules are stabilized by infinite zigzag chains of O—H$\cdots$O and C—H$\cdots$O hydrogen bonds. The relevant

$C\cdots O$ distances for the latter are: O(4)$\cdots$C(10) ($1\frac{1}{2}-x$, $\frac{1}{2}+y$, $\frac{1}{2}-z$) $3\cdot394$ (3) Å; O(2)$\cdots$C(10) ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$) $3\cdot177$ (3) Å. The angular approaches of the atoms are favourable for C—H$\cdots$O bonding (Taylor & Kennard, 1984).

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X-ray Structure of 1,4-Bis(diphenylphosphino)butane

By A. Valentina Rivera, Dora Gómez C., Eldrys Rodulfo de Gil* and Trino Suárez

Departamento de Química, Facultad de Ciencias, Universidad de los Andes, Mérida, Venezuela

Abstract. $C_{28}H_{28}P_2$, $M_r = 426\cdot48$, monoclinic, $P2_1/c$, $a = 6\cdot134$ (2), $b = 8\cdot166$ (3), $c = 24\cdot634$ (5) Å, $\beta = 106\cdot4$ (2)°, $V = 1184$ Å^3, $Z = 2$, $D_m = 1\cdot20$, $D_x = 1\cdot196$ g cm^{-3}, λ(Mo $K\alpha$) = $0\cdot71069$ Å, $\mu = 1\cdot55$ cm^{-1}, $F(000) = 452$, $T = 295$ K, $R = 0\cdot051$ for 924 unique reflections with $I > 3\sigma(I)$. The structure found for the free ligand is very similar to that reported for the one coordinated to Rh atoms in [Rh$_2${Ph$_2$P(CH$_2$)$_4$PPh$_2$}-(η-C$_5$H$_5$)$_2$(CO)$_2$], the only known X-ray determination of this ligand. The —(CH$_2$)$_4$— moiety is planar within $0\cdot004$ (5) Å with the P atoms $+0\cdot105$ (2) and $-0\cdot105$ (2) Å from its calculated mean plane. The P atoms have the usual distorted tetrahedral configuration.

Introduction. Metal complexes with polydentate phosphines are becoming increasingly important due to their implication in catalytic reactions. Our current interest in the synthesis and catalytic properties of Ru complexes with polydentate phosphines led us to the study of the Ph$_2$P(CH$_2$)$_4$PPh$_2$ ligand and its Ru complexes. Here we report the X-ray determination of the free ligand.

Experimental. Density determined by flotation in nitrobenzene. Greenish transparent parallelepiped

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* To whom correspondence should be addressed.