

The hydrogen-bond lengths are longer for O20'—H1 (Table 2), which indicates a somewhat weaker bond for the primed nitrobenzyl group allowing a larger degree of freedom of movement for this group. In general the primed benzyl group has higher thermal motion (Table 1), supporting this assumption. Furthermore O19 and O19' form a short intramolecular contact with H11A and H11A', the distances being 2.36 (1) and 2.47 (1) Å, respectively.

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Structure of 4'-Acetoxy-3'-methoxycinnamic Acid

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Abstract. C₁₂H₁₂O₃, *M_r* = 236.23, triclinic, *P* $\bar{1}$, *a* = 9.021 (3), *b* = 7.987 (3), *c* = 9.498 (2) Å, α = 94.24 (2), β = 106.80 (2), γ = 114.25 (3)°, *V* = 582.5 (4) Å³, *Z* = 2, *D_m* = 1.34, *D_x* = 1.347 Mg m⁻³, $\lambda(\text{Mo } K\alpha)$ = 0.71073 Å, $\mu(\text{Mo } K\alpha)$ = 0.0989 mm⁻¹, *F*(000) = 248, *T* = 293 (1) K, *R* = 0.037 for 1541 unique reflections. Hydrogen bonds are formed between terminal O and H atoms of adjacent molecules. The results prove that the dimer produced by mechanochemical reaction of 3,4-dimethoxycinnamyl alcohol is an *anti* head–tail cyclobutane dimer.

Introduction. Mechanochemical reaction products from crystalline 3,4-dimethoxycinnamyl alcohol have been found to contain a cyclobutane dimer (Lee, Tachibana & Sumimoto, 1988). To identify the stereochemical structure, crystalline 4'-acetoxy-3'-methoxycinnamic acid was submitted to a solid photodimerization. Reduction of the methyl ester of the acid with lithium

aluminium hydride followed by methylation with dimethyl sulfate afforded the cyclobutane dimer, which was identical in all respects to the dimer obtained from the mechanochemical reaction products. According to Schmidt (1964), upon UV irradiation of cinnamic acid the α -form crystals give the *anti* head–tail cyclobutane dimer; by contrast the β -form crystals afford the *syn* head–head cyclobutane dimer. The stereochemical structure of the mechanochemically produced dimer should therefore be defined by the crystal structure of the title compound.

Experimental. The acid was prepared from vanillin by literature procedures (Adams & Bockstahler, 1952; Lee, Tachibana & Sumimoto, 1987). Colourless transparent crystal from methanol–water (2:1) solution. *D_m* by flotation in a mixture of *n*-hexane and carbon tetrachloride. Specimen (0.2 mm)³ mounted on Enraf–Nonius CAD-4 diffractometer, graphite-monochro-

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters (\AA^2) with e.s.d.'s in parentheses

	x	y	z	B_{eq}^*
O(1)	0.2957 (2)	0.9636 (2)	-0.0032 (2)	4.04 (4)
O(2)	0.4656 (2)	0.8401 (2)	0.1136 (2)	4.65 (4)
O(3)	-0.2021 (2)	0.2305 (2)	0.3715 (2)	4.14 (4)
O(4)	-0.4892 (2)	0.2768 (2)	0.3118 (2)	3.73 (4)
O(5)	-0.3475 (2)	0.4323 (2)	0.5544 (2)	4.13 (4)
C(1)	-0.0890 (2)	0.6230 (3)	0.1758 (2)	3.20 (5)
C(2)	-0.0720 (2)	0.4847 (3)	0.2523 (2)	3.22 (5)
C(3)	-0.2031 (2)	0.3710 (3)	0.2995 (2)	3.11 (5)
C(4)	-0.3509 (2)	0.3995 (3)	0.2721 (2)	3.26 (5)
C(5)	-0.3689 (2)	0.5345 (3)	0.1991 (2)	3.73 (5)
C(6)	-0.2375 (3)	0.6465 (3)	0.1500 (2)	3.86 (5)
C(7)	0.0469 (2)	0.7405 (3)	0.1205 (2)	3.51 (5)
C(8)	0.1972 (2)	0.7388 (3)	0.1412 (2)	3.60 (5)
C(9)	0.3252 (2)	0.8567 (3)	0.0786 (2)	3.44 (5)
C(10)	-0.0599 (3)	0.1882 (3)	0.3905 (3)	4.39 (6)
C(11)	-0.4701 (2)	0.3047 (3)	0.4601 (2)	3.38 (5)
C(12)	-0.6218 (3)	0.1587 (3)	0.4849 (3)	4.65 (6)

$$* B_{eq} = \frac{4}{3}(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}abc\cos\gamma + \beta_{13}acc\cos\beta + \beta_{23}bcc\cos\alpha).$$

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

O(1)-C(9)	1.252 (3)	C(1)-C(7)	1.469 (3)
O(2)-C(9)	1.278 (3)	C(2)-C(3)	1.382 (3)
O(3)-C(3)	1.358 (3)	C(3)-C(4)	1.398 (3)
O(3)-C(10)	1.422 (3)	C(4)-C(5)	1.363 (3)
O(4)-C(4)	1.407 (2)	C(5)-C(6)	1.390 (3)
O(4)-C(11)	1.359 (3)	C(7)-C(8)	1.318 (3)
O(5)-C(11)	1.196 (2)	C(8)-C(9)	1.470 (3)
C(1)-C(2)	1.401 (3)	C(11)-C(12)	1.485 (3)
C(1)-C(6)	1.384 (3)		
C(3)-O(3)-C(10)	117.3 (2)	C(3)-C(4)-C(5)	121.6 (2)
C(4)-O(4)-C(11)	116.9 (1)	C(4)-C(5)-C(6)	119.4 (2)
C(2)-C(1)-C(6)	119.3 (2)	C(1)-C(6)-C(5)	120.6 (2)
C(2)-C(1)-C(7)	121.0 (2)	C(1)-C(7)-C(8)	126.5 (2)
C(6)-C(1)-C(7)	119.7 (2)	C(7)-C(8)-C(9)	123.6 (2)
C(1)-C(2)-C(3)	120.5 (2)	O(1)-C(9)-O(2)	123.6 (2)
O(3)-C(3)-C(2)	125.4 (2)	O(1)-C(9)-C(8)	121.5 (2)
O(3)-C(3)-C(4)	115.9 (2)	O(2)-C(9)-C(8)	114.9 (2)
C(2)-C(3)-C(4)	118.6 (2)	O(4)-C(11)-O(5)	123.2 (2)
O(4)-C(4)-C(3)	118.8 (2)	O(4)-C(11)-C(12)	110.5 (1)
O(4)-C(4)-C(5)	119.4 (2)	O(5)-C(11)-C(12)	126.2 (2)

matized Mo $K\alpha$ radiation. Lattice parameters determined from the setting angles of 17 reflections. 2610 unique reflections with $2\theta \leq 28^\circ$ in the hkl range $(-11, 0, -12) \rightarrow (11, 10, 12)$ measured with $\omega-2\theta$ scan technique. Three standard reflections monitored every 3600 s, no significant intensity variation. Data corrected for Lorentz and polarization effects but not for absorption. 1544 reflections considered observed [$I \geq 1\sigma(I)$] and used in subsequent calculations. Structure solved by direct methods; H positions determined by difference Fourier synthesis. Refinement by full-matrix least squares using F^2 s. C and O anisotropic, H isotropic with B fixed at 4.0\AA^2 . Final $R = 0.037$, $wR = 0.059$ [$w = 4F_o^2 / \{\sigma(F_o)^2\}^2$], $S = 2.38$; $(\Delta/\sigma)_{\max}$ in final least-squares cycle 0.34; final difference Fourier height maximum (absolute value) 0.21 e \AA^{-3} ; refined secondary-extinction value $g = 4.33 \times 10^{-6}$. Atomic

scattering factors and f' , f'' values from *International Tables for X-ray Crystallography* (1974). Computation on PDP 11/23 computer using Enraf-Nonius (1985) *SDP-Plus* and *ORTEPII* (Johnson, 1976) programs.

Discussion. Final atomic coordinates, and bond lengths and angles are given in Tables 1 and 2.* The numbering

* Lists of structure factors, atomic coordinates of H atoms, bond lengths and angles related to H atoms, and anisotropic thermal parameters of C and O atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44825 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

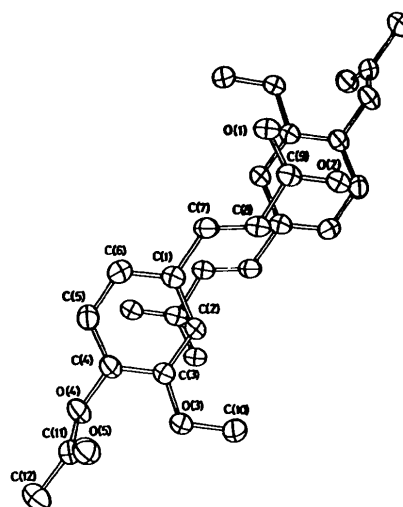


Fig. 1. Structure of dimer with atomic labeling (with H atoms omitted).

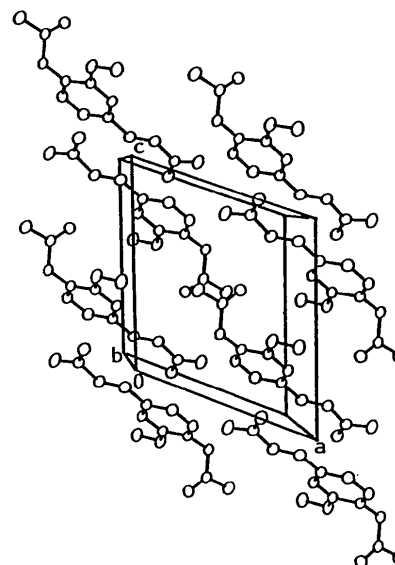


Fig. 2. A view of the packing in the unit cell.

system used here is shown in Fig. 1. The benzene ring, ethylene, carboxy and methoxy groups are planar. Dihedral angles are $2.2 (3)^\circ$ between benzene ring and carboxy planes, $3.4 (3)^\circ$ between benzene ring and ethylene planes, and $4.8 (3)^\circ$ between benzene ring and methoxy planes. However, the dihedral angle between benzene and acetoxy planes is $77.7 (3)^\circ$.

Fig. 2 shows the molecular packing. A pair of acid molecules are associated through their carboxy groups by hydrogen bonds with distances of 1.80 \AA in $O(1)\cdots H$ and 0.84 \AA in $O(2)-H$. The reactive olefinic double bonds are inversion-related and stacked parallel and the centre-to-centre separation of such parallel bonds is 3.77 \AA . The title compound therefore, has the α -structure and gives *anti* head-tail cyclobutane dimers on photoreaction as reported by Schmidt (1964). This indicates that the cyclobutane dimer obtained by the

mechanochemical reaction of 3,4-dimethoxycinnamyl alcohol has an *anti* head-tail structure.

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1-Phenyl-3-carbethoxy-4-hydroxypyrroline

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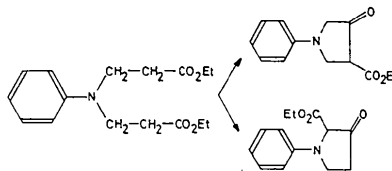
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(Received 13 August 1987; accepted 2 March 1988)

Abstract. Ethyl 4-hydroxy-1-phenyl-2,5-dihydro-pyrrole-3-carboxylate, $C_{13}H_{15}NO_3$, $M_r = 233.27$, monoclinic, $C2/c$, $a = 23.000 (8)$, $b = 4.993 (4)$, $c = 21.14 (1) \text{ \AA}$, $\beta = 93.61 (5)^\circ$, $V = 2422.4 \text{ \AA}^3$, $Z = 8$, $F(000) = 992$, $D_m = 1.27$ (floatation in aqueous K_2HgI_4 solution), $D_x = 1.279 \text{ Mg m}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $\mu = 0.084 \text{ mm}^{-1}$, $T = 295 \text{ K}$, $R = 0.087$, $wR = 0.048$ for 2314 unique diffractometer data [$F^2 > 1\sigma(F^2)$]. The five-membered ring has the enol form. The angle between the planes of the pyrroline and the phenyl ring is 2.5° , the angle between the carbethoxy (ethoxy-carbonyl) group and the pyrroline ring 33.7° . The pyrroline ring is planar; the deviation of the N atom is $0.020 (3) \text{ \AA}$. There exists an intramolecular hydrogen bond between the hydroxyl and the carbonyl group. The same H atom is involved in an intermolecular bifurcated hydrogen bond (2.805 \AA) to build a dimer. The intermolecular distance of the oxygens of the carbonyls is 2.838 \AA . They are twice bonded by bifurcated hydrogen bonds.

Introduction. The Dieckmann condensation (see Scheme) may result in one of two different products. De

Mouilpied (1905) could not decide which of these two products is formed. IR and NMR spectroscopic investigations were unable definitely to prove which formula is correct, in terms of either the given keto or the enol tautomers (Southwick, Madhav & Fitzgerald, 1969; Bauer & Safir, 1971, 1972). Our own spectroscopic investigations were equally unsuccessful. We decided to perform an X-ray structure analysis.



Experimental. Suitable crystals were obtained by recrystallization from a 2:1 mixture of ethanol and acetone. A crystal of dimensions $0.7 \times 0.3 \times 0.3 \text{ mm}$ was sealed in a Lindemann-glass capillary; 25 reflections with $2\theta > 18^\circ$ were used for the cell refinement; one standard reflection (512); 3829 measured reflections ($h: -30$ to 6 ; $k: 0$ to 6 ; $l: -27$ to 27 ; $R_{\text{int}} = 0.035$) resulted in 2314 of a total of 2949 unique reflections with an intensity $I > \sigma(I)$ which were used for the

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