

Table 2. Bond lengths (Å) and bond angles (°), with estimated standard deviations in parentheses

S(1)–C(1)	1.749 (14)	C(4)–C(8)	1.527 (19)
S(1)–C(9)	1.791 (12)	C(5)–C(6)	1.395 (19)
S(2)–S(2)	2.044 (7)	C(9)–C(10)	1.342 (17)
S(2)–C(6)	1.813 (13)	C(9)–C(16)	1.486 (17)
C(1)–C(2)	1.347 (20)	C(10)–C(11)	1.482 (20)
C(1)–C(6)	1.407 (20)	C(11)–C(12)	1.306 (23)
C(2)–C(3)	1.419 (20)	C(12)–C(13)	1.486 (24)
C(3)–C(4)	1.421 (20)	C(13)–C(14)	1.337 (22)
C(3)–C(7)	1.510 (20)	C(14)–C(15)	1.473 (21)
C(4)–C(5)	1.391 (19)	C(15)–C(16)	1.328 (19)
C(1)–S(1)–C(9)	102.2 (6)	S(2)–C(6)–C(1)	116.8 (10)
S(2)–S(2)–C(6)	105.4 (6)	S(2)–C(6)–C(5)	121.6 (11)
S(1)–C(1)–C(2)	119.3 (10)	C(1)–C(6)–C(5)	121.3 (12)
S(1)–C(1)–C(6)	121.9 (10)	S(1)–C(9)–C(10)	117.3 (9)
C(2)–C(1)–C(6)	117.1 (12)	S(1)–C(9)–C(16)	116.7 (9)
C(1)–C(2)–C(3)	124.7 (13)	C(10)–C(9)–C(16)	125.0 (11)
C(2)–C(3)–C(4)	116.2 (12)	C(9)–C(10)–C(11)	130.2 (11)
C(2)–C(3)–C(7)	120.1 (13)	C(10)–C(11)–C(12)	125.0 (14)
C(1)–C(3)–C(7)	123.6 (12)	C(11)–C(12)–C(13)	126.1 (15)
C(3)–C(4)–C(5)	120.4 (12)	C(12)–C(13)–C(14)	126.7 (13)
C(3)–C(4)–C(8)	121.4 (12)	C(13)–C(14)–C(15)	127.5 (13)
C(5)–C(4)–C(8)	118.2 (12)	C(14)–C(15)–C(16)	126.2 (13)
C(4)–C(5)–C(6)	119.6 (12)	C(9)–C(16)–C(15)	124.6 (12)

monosubstituted derivative (Bordner, Parker & Stanford, 1972). The average values may be compared with those for cyclooctatetraenecarboxylic acid (Shoemaker, Kindler, Sly & Srivastava, 1965) given in parentheses: C–C 1.482 (1.470), C=C 1.319 Å (1.322 Å), C=C=C 126.4° (126.4°). The torsion angles C=C–C=C lie between 55.6 (15) and 59.3 (13)°, averaging 57.1° (57.1°). The angle between the normals to the planes defined by the double bonds [C(9), (10), (13), (14)] and [C(11), (12), (15), (16)] is 0.8 (7)°. The only significant deviation from an idealized tub structure occurs at C(10) where the angle C(9)–C(10)–C(11) is opened out to 130.2° by the close contact C(10)⋯S(1) 2.686 Å, compared with C(16)⋯S(1) 2.795 Å. The conformation requires the protons on C(10) and C(16) to be remote from S(1).

The three C–S bonds are barely significantly different [average 1.784 (13) Å, with a range of 5σ]. S(1) and S(2) both lie on the same side of the benzene ring, 0.165 (6) and 0.060 (6) Å respectively above the plane, whereas in (I) the S atoms are on opposite sides of the benzene plane and 0.175 Å from it.

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### α-Methyl-trans-cinnamic Acid (m.p. 355 K)

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**Abstract.** C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>, monoclinic, *P*2<sub>1</sub>/*c*, *a* = 7.633 (2), *b* = 11.454 (3), *c* = 11.514 (3) Å, β = 120.91 (2)°, *U* = 863.7 Å<sup>3</sup>, *M<sub>r</sub>* = 162.2, *D<sub>x</sub>* = 1.247 Mg m<sup>-3</sup>, *Z* = 4,

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The dimer is completed by S(2)–S(2)', 2.044 Å, lying across the twofold crystallographic axis. The torsion angle C(6)–S(2)–S(2)'–C(6)' is 90.8 (8)°. The normals to the two benzene-ring planes intersect at 82 (2)°.

This structure could be compared to that of the precursor (II), a cyclooctatriene derivative. However, the structure given by Kaiser, Richter, Moegel & Schroth (1979) shows some surprising features. C(9)–C(16), which is formally a single bond, is only 1.38 Å. These two atoms have by far the largest thermal parameters (apart from the methyl groups): *B*<sub>iso</sub> values are 8.18, 8.27 Å<sup>2</sup> compared with an average for the other ring atoms of 5.00 Å<sup>2</sup>. Also, the anisotropic thermal parameters of these bridgehead atoms suggest that the major axes of the ellipsoids are perpendicular to the molecular plane. These observations seem very improbable for an ordered structure. It seems likely that there is disorder at C(9), C(16) so that the crystals of (II) contain either two conformers of the cyclooctatriene or possibly include some molecules of the bridged cyclooctatetraene.

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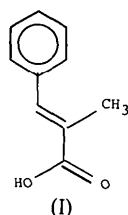
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*D<sub>m</sub>* (flotation in aqueous KI) = 1.24 Mg m<sup>-3</sup>, *F*(000) = 344, μ(Cu Kα) = 0.71 mm<sup>-1</sup>. The structure was solved by the multiresolution tangent-formula method. Least-

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squares refinement gave  $R = 0.041$  for 812 independent reflections measured by diffractometer. The molecules are present in the crystal as centrosymmetric hydrogen-bonded dimers (O—H...O 2.625 Å). The plane of the phenyl ring is inclined at 3.4° to that of the double bond which, in turn, is inclined by a further 4.3° to the plane of the carboxy group. Though the crystal packing is formally of the  $\alpha$  type, the closest approaches of atoms of the double bonds of nearest-neighbor molecules are 4.28 Å — longer than the 4.1 Å held to be the upper limit of such a separation in this normally photochemically active type.

**Introduction.** In their original report of the preparation of this acid (I), Stoermer & Voht (1915) noted that the granular prismatic crystals obtained on recrystallization from ethanol, and having a m.p. of 354–355 K, were converted on repeated recrystallization from petroleum ether to shiny ductile needles of m.p. 346–347 K. Such solvent-dependent polymorphs are of interest, and we planned to examine the differences in molecular packing between these two forms. However, repeated efforts to obtain the lower-melting form from solvents from which it is stated to recrystallize (benzene, carbon disulfide, petroleum ether) consistently yielded only the form of higher melting point. We report here the crystal structure of that form.



The crystal used was obtained by recrystallization of a commercial sample (Aldrich Chemical Co.) from a 75% ethanol–water mixture. Systematic absences in  $h0l$  with  $l$  odd and in  $0k0$  with  $k$  odd uniquely define the space group as  $P2_1/c$ . Intensity measurements were made from a crystal  $0.75 \times 0.30 \times 0.15$  mm, mounted with  $a^*$  parallel to the  $\phi$  axis of a Picker diffractometer. Cu  $K\alpha$  radiation (graphite monochromator) was used with the  $\theta/2\theta$  scan method, scan widths of 4° in  $2\theta$ , and a scan speed of 2° min<sup>-1</sup>. The reflections in a single quadrant of reciprocal space were measured by scintillation counting with pulse-height analysis. Intensity significantly above background [ $I > 3\sigma(I)$ ] was found at 812 of the 1282 (63.3%) locations examined. No absorption corrections were made.

The structure was solved by routine application of the program *MULTAN* in its 1974 version (Germain, Main & Woolfson, 1971). Block-diagonal least-squares refinement, minimizing the function  $\sum w(|F_o| - |F_c|)^2$ , gave  $R = 0.041$  and  $R_w = 0.044$ , at convergence, for

the 812 reflections used.\* The maximum shift-to-error ratio in the final cycle of refinement was 0.17 and the average ratio was 0.02. A final electron density map was structurally featureless. Anisotropic thermal parameters were used for O and C, and individual isotropic  $B$  values were refined for H. The scattering functions used were those of Cromer & Waber (1974) for O and C, and of Stewart, Davidson & Simpson (1965) for H.

**Discussion.** Final atomic coordinates and equivalent  $B$  values are given in Table 1. A projection of the molecule onto the dimer plane, with bond lengths and angles and showing the numbering scheme adopted, is shown in Fig. 1. The presence of the  $\alpha$ -methyl group leads to intramolecular crowding and angular deformations in the vicinity of the double bond. The intramolecular contact C(6)...C(10) is 3.17 Å and the contact C(6)...C(8) is 3.16 Å. The angular strain may be seen in a comparison of the relevant bond angles with those found in  $\alpha$ -*trans*-cinnamic acid (Bryan & Freyberg, 1975) where the exocyclic angles at C(1) are 120.1 and 122.6°, C(1)–C(9)–C(8) is 126.2°, C(7)–C(8)–C(9) is 122.3°, and the O–C–C angles are 118.6 and 122.7°.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36511 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ , for H  $\times 10^3$ ) and isotropic  $B$  values (Å<sup>2</sup>)

Hydrogen atoms have been numbered to correspond to the atom of attachment. For non-hydrogen atoms  $B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} a_i \cdot a_j$ .

	$x$	$y$	$z$	$B_{eq}/B$
O(1)	701 (3)	–1139 (1)	1091 (2)	6.82 (8)
O(2)	380 (3)	728 (1)	1434 (2)	6.96 (9)
C(1)	2575 (4)	427 (2)	5545 (2)	4.61 (10)
C(2)	2396 (4)	1509 (2)	6014 (2)	5.24 (11)
C(3)	3187 (4)	1698 (2)	7399 (2)	6.52 (15)
C(4)	4108 (5)	807 (2)	8296 (3)	6.80 (15)
C(5)	4268 (5)	–262 (2)	7846 (3)	7.57 (15)
C(6)	3492 (4)	–461 (2)	6475 (3)	6.76 (13)
C(7)	875 (4)	–321 (2)	1860 (3)	5.17 (10)
C(8)	1730 (4)	–560 (2)	3324 (2)	4.66 (10)
C(9)	1776 (4)	335 (2)	4085 (3)	4.82 (8)
C(10)	2445 (5)	–1779 (2)	3768 (3)	7.10 (15)
H(O)	–6 (5)	88 (3)	24 (4)	18.5 (12)
H(2)	167 (3)	219 (2)	535 (2)	5.2 (5)
H(3)	266 (3)	254 (2)	753 (2)	10.3 (8)
H(4)	486 (4)	93 (2)	938 (2)	10.2 (7)
H(5)	483 (3)	–92 (2)	841 (2)	8.1 (6)
H(6)	355 (3)	–126 (2)	623 (2)	7.6 (6)
H(9)	116 (3)	111 (1)	361 (2)	4.3 (4)
H(10a)	205 (4)	–214 (2)	436 (3)	10.4 (7)
H(10b)	230 (4)	–226 (2)	305 (3)	12.6 (8)
H(10c)	364 (2)	–176 (2)	437 (2)	10.7 (8)

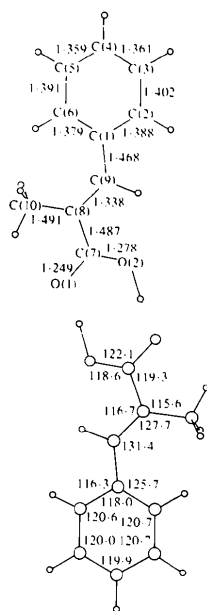


Fig. 1. Projection onto the dimer plane showing bond lengths (Å) and bond angles ( $^{\circ}$ ). E.s.d.'s are: O—C 0.002, C—C 0.003 Å; and for bond angles 0.2 $^{\circ}$ .

Table 2. Selected least-squares mean planes

Planes: (1) phenyl ring; (2) C(1)—C(9)—C(8)—C(7); (3) O(1), O(2), C(7), C(8); (4) all atoms.

Coefficients are given for the equations in the form:  $aX + bY + cZ + d = 0$ , where  $X$ ,  $Y$ , and  $Z$  are in Å with respect to an orthogonal set of axes.

Plane	$a$	$b$	$c$	$d$	$A_{\max}^*$ (Å)	$A_{\text{ave}}$ (Å)
(1)	0.95789	0.26261	0.11610	0.50457	0.010	0.005
(2)	0.95321	0.24764	0.07342	0.19661	0.020	0.014
(3)	0.96781	0.17382	0.18204	0.14027	0.007	0.004
(4)	0.95797	0.23823	0.15981	0.22192	0.11	0.04

\* E.s.d.'s for  $A_{\max}$  are  $\sim 0.002$  Å.

The molecule is closely planar overall, the maximum deviation of an atom from the least-squares mean plane being 0.11 Å, with the average deviation being 0.04 Å. The molecular conformation is more accurately defined, however, in terms of the angles between the planes (1), (2) and (3), as defined in Table 2. These angles are: (1)—(2) 3.4, (1)—(3) 6.4, and (2)—(3) 4.3 $^{\circ}$ .

A view of the molecular packing, seen in  $b$ -axis projection, is shown in Fig. 2. In his classification of packing modes in substituted *trans*-cinnamic acids, Schmidt (1964) distinguished three different types,

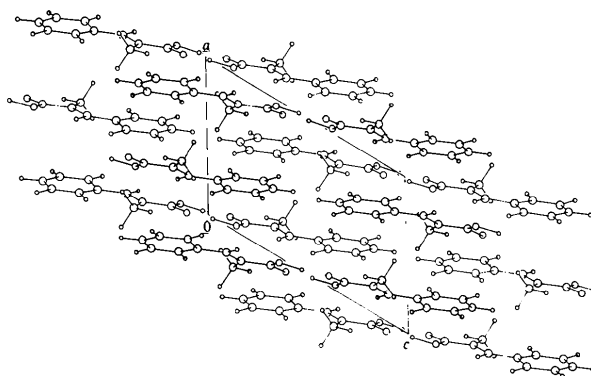


Fig. 2. View of the molecular packing in  $b$ -axis projection.

based on the length of the shortest unit-cell axis. Two of these, the  $\alpha$  and  $\beta$  types, with shortest axes, respectively,  $>5.1$  and  $3.9 \pm 0.2$  Å, were photochemically active with dimerization taking place through reactions of the double bonds in nearest-neighbor molecules. The third,  $\gamma$  type, with shortest axes in the range  $4.9 \pm 0.2$  Å, is photochemically inert. Schmidt suggested that for reaction to occur in the active  $\alpha$  and  $\beta$  types, the atoms of the double bonds should be no more than 4.1 Å apart. In this crystal, which is formally of the  $\alpha$  type, the closest approaches between such atoms are 4.28 Å, between the reference molecule and the double bond of a centrosymmetrically related neighbor at  $1-x, -y, 1-z$ . Such a separation is somewhat larger than Schmidt's suggested upper limit. We have not carried out any experiments to establish the photoreactivity, or otherwise, of this acid so that it is not clear whether it is a member of a new class of photochemically inert  $\alpha$  type or whether Schmidt's criterion is set too conservatively.

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