

(*E*)-2-Methyl-5-(1-naphthylmethyl)-cinnamic acid

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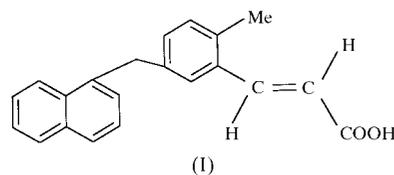
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The title compound, C₂₁H₁₈O₂, crystallized in the centrosymmetric space group *P*2₁/*n* with one molecule in the asymmetric unit. There is a single hydrogen bond, with an O_{donor}...O_{acceptor} distance of 2.624 (2) Å, which forms a cyclic dimer about a center of symmetry. The carboxyl group O atoms are ordered, while the carboxyl-H atom is disordered. A single leading intermolecular C—H...O interaction has an H...O distance of 2.68 Å and a C—H...O angle of 178°; this interaction forms chains. Taken together with the hydrogen bond, it generates chains and rings. Structural comparisons are made with *trans*-cinnamic acid and with 4-methyl-*trans*-cinnamic acid.

Comment

This report is one of a series on hydrogen bonding and C—H...O interactions in carboxylic acids. The title compound, (I), crystallized in the centrosymmetric space group *P*2₁/*n* with one molecule as the asymmetric unit. The refined molecule and the labeling scheme are given in Fig. 1. The carboxyl-O atoms are ordered, as evidenced by the orientation of their substantially largest principal displacement axes almost normal to the plane of the carboxyl group (see, *e.g.*, Fitzgerald & Gerkin, 1993). The carboxyl-H atom, however, is found to be disordered (see *Experimental*). A cyclic dimer hydrogen bond is formed about a center of symmetry. The donor...acceptor distance, *e.g.* O1...O2ⁱ, in these *R*₂²(8) cyclic dimers is 2.624 (2) Å [symmetry code: (i) 2 - *x*, -1 - *y*, 1 - *z*]. A single leading intermolecular C—H...O interaction (Taylor & Kennard, 1982; Steiner & Desiraju, 1998), C16—H16...O2ⁱⁱ is present in this structure [symmetry code: (ii) $\frac{3}{2} - x, \frac{3}{2} + y, \frac{3}{2} - z$]. The geometric parameters of this interaction are: H...O = 2.68, C...O = 3.658 (4) Å and C—H...O = 178°. Each molecule is linked by these two interactions directly to three other molecules. Basic first- and second-level graph-set analysis (Bernstein *et al.*, 1995) involving these interactions gives at the first level, the *R*₂²(8) ring formed by carboxyl groups and a *C*(13) chain involving C—H...O interactions, which propagates along **b**, and at the second level a *C*₂²(15) chain propagating along [10 $\bar{1}$]. Twisted *R*₂²(50) rings are prominent complex second-level features in this structure.

For the benzene ring of (I), the maximum deviation of any of its atoms from the best-fit plane describing them is 0.010 (2) Å, while the average deviation is 0.006 (3) Å. These deviations are in good agreement with the respective corresponding values, 0.008 (2) and 0.004 (3) Å, calculated for



4-methyl-*trans*-cinnamic acid, (II) (Kashino *et al.*, 1989), and 0.007 (4) and 0.003 (3) Å, calculated for unsubstituted *trans*-cinnamic acid, (III) (Bryan & Freyberg, 1975), two molecules which appear to be particularly suitable for comparison. In contrast, the maximum and average deviations from the best-fit plane through the C1/C7/C8/C9 string are 0.023 (3) and 0.020 (3) Å for (I), but only 0.004 (2) and 0.003 (1) Å for (II), and 0.005 (4) and 0.004 (1) Å for (III). The dihedral angles between the best-fit planes of the strings and the carboxyl planes are 3.4 (4), 4.8 (4) and 2.3 (6)° for (I), (II) and (III), respectively. Thus, the propenoic acid moiety is nearly planar in all three molecules. The dihedral angles between the ring plane and the string plane are 27.0 (3), 0.6 (3) and 4.6 (4)°, respectively. Thus, the cinnamic acid cores of (II) and (III) are nearly planar, while that of (I) is not, as is apparent in the packing diagram of (I), Fig. 2. For the naphthalene core in (I), the maximum and average deviations of the atoms from the best-fit plane describing them are 0.034 (3) and 0.021 (9) Å, respectively. The intramolecular dihedral angle between the benzene ring plane and the naphthalene ring plane is 80.5 (1)°. The dihedral angle between benzene ring planes not required by symmetry to be parallel is 89.6 (1)°, while the corresponding angle between naphthalene ring planes is 71.1 (1)°. Thus, the best-fit planes of benzene and naphthalene rings of all the molecules are either strictly or almost parallel or roughly perpendicular to each other. The packing diagram, Fig. 2, displays these features.

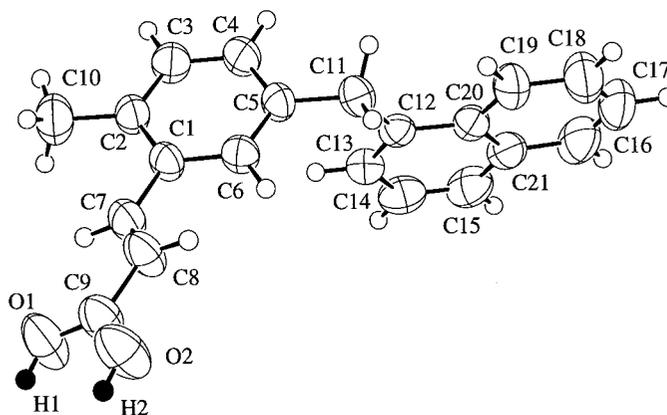


Figure 1
Displacement ellipsoids at the 50% probability level with half-occupied H atoms shaded.

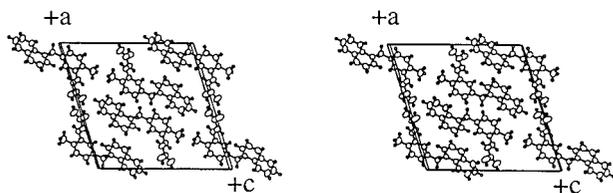


Figure 2

Stereoview of the packing viewed down the b axis. The origin is at the lower left in the background.

Selected distances and angles of (I) are given in Tables 1 and 2. In (I), all distances and angles fall within normal limits. Bond distances and angles for the propenoic acid moiety of (I) are given in Table 1 together with the corresponding quantities for (II) and (III). As shown in Table 1, the agreement among these three studies is very good. It may be noted further that, as in (I), cyclic hydrogen-bond dimers about centers of symmetry are formed in (II) and (III). The values of distances and angles involving the carboxyl groups of (II) and (III), given in Table 1, strongly support disordering of the carboxyl group H atom in these cases, also as in (I); indeed, Bryan & Freyberg's Fig. 3 presents a difference electron-density map demonstrating such disorder. In (I), the closest intermolecular approaches, excluding pairs of atoms involved in the hydrogen bonding or $C-H \cdots O$ interactions described above, are between C19 and H3ⁱⁱⁱ [symmetry code: (iii) $1 - x, 1 - y, 1 - z$] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.08 Å. This closest approach is a consequence of a single noteworthy $C-H \cdots \pi$ interaction: $C3-H3 \cdots (C16-C21)^{iii}$. The (non-normalized) H3 to ring-midpoint distance is 2.66 Å, while the H3 to ring-atom distances range from 2.82 to 3.2 Å, and the $C3-H3 \cdots$ ring-midpoint angle is 153°. These values are consistent with those cited, e.g., by Steiner *et al.* (1995) for significant $C-H \cdots \pi$ interactions. The favorable approach of H3 to the C16–C21 ring is apparent in Fig. 2.

Experimental

Compound (I) was obtained as an ecru crystalline powder from a sample in Dr M. S. Newman's chemical collection. A solution of this material in an acetone/ethanol solvent produced suitable colorless crystals upon slow evaporation at room temperature. One of these was cut to provide the experimental sample. No reference for a demonstrated method of synthesis is apparently available.

Crystal data

$C_{21}H_{18}O_2$
 $M_r = 302.37$
 Monoclinic, $P2_1/n$
 $a = 16.942$ (1) Å
 $b = 5.932$ (2) Å
 $c = 17.265$ (1) Å
 $\beta = 108.122$ (5)°
 $V = 1649.2$ (5) Å³
 $Z = 4$

$D_x = 1.218$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 13.2$ – 17.4 °
 $\mu = 0.077$ mm⁻¹
 $T = 296$ K
 Cut column, colorless
 $0.38 \times 0.19 \times 0.15$ mm

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 3942 measured reflections
 3816 independent reflections
 1452 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.043$
 $\theta_{max} = 27.56$ °
 $h = 0 \rightarrow 22$

$k = 0 \rightarrow 7$
 $l = -22 \rightarrow 21$
 6 standard reflections
 every 150 reflections
 intensity variation: $\pm 1.6\%$
 (average maximum relative intensity)

Refinement

Refinement on F^2
 $R(F) = 0.057$
 $wR(F^2) = 0.073$
 $S = 1.36$
 3816 reflections
 216 parameters

H atoms: see below
 $w = 1/[\sigma_{cs}^2 + (0.004I)^2]$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.54$ e Å⁻³
 $\Delta\rho_{min} = -0.49$ e Å⁻³

Table 1

Selected geometric parameters (Å, °) [using atom labeling as for (I)] for the propenoic acid moiety in three *trans*-cinnamic acids: (I), the title compound; (II), 4-methyl-*trans*-cinnamic acid (Kashino *et al.*, 1989); (III), *trans*-cinnamic acid (Bryan & Freyberg, 1975).

Parameter	(I)	(II)	(III)
C1–C7	1.468 (3)	1.458 (4)	1.467 (4)
C7–C8	1.311 (3)	1.315 (4)	1.322 (4)
C8–C9	1.459 (3)	1.458 (4)	1.470 (4)
C9–O1	1.263 (3)	1.274 (4)	1.279 (4)
C9–O2	1.267 (3)	1.255 (4)	1.259 (4)
C1–C7–C8	127.0 (3)	127.4 (3)	126.2 (3)
C7–C8–C9	121.8 (3)	123.1 (3)	122.3 (3)
C8–C9–O1	119.9 (3)	118.8 (3)	122.7 (3)
C8–C9–O2	117.9 (3)	118.8 (3)	118.6 (3)
O1–C9–O2	122.2 (3)	122.4 (3)	122.7 (3)

Table 2

Selected torsion angles (°).

O1–C9–C8–C7	0.8 (5)	C2–C1–C7–C8	–155.1 (3)
O2–C9–C8–C7	178.9 (3)	C4–C5–C11–C12	–80.7 (3)
C1–C7–C8–C9	–176.2 (3)	C6–C5–C11–C12	98.9 (3)

Difference Fourier maps gave initial locations of the H atoms except for the carboxyl group. Since the C9–O1 and C9–O2 distances are very nearly equal, and intermediate to C–O single and double-bond distances, a model involving a disordered carboxyl-H atom was adopted. Moreover, the O atoms of an inversion-related carboxyl group lie 2.624 (2) Å from O1 and O2, indicating a cyclic dimer hydrogen-bonding arrangement. Accordingly, half-occupancy H atoms were fixed 0.77 Å from the carboxyl-O atoms along the line of centers to the two hydrogen-bonded carboxyl-O atoms, and with $B = 1.2B_{eq}$ of the respective carboxyl-O atoms. The distance, 0.77 Å, was chosen on the basis that it is the mean of two refined values for similarly disordered half-occupancy H atoms in the hydrogen bonds of naphthalene-1,8-dicarboxylic acid (Fitzgerald *et al.*, 1991).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992–1997); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN*; molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1261). Services for accessing these data are described at the back of the journal.

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