$C_{26}H_{31}NO_4$

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Solution. Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft University Press.

George, R., Clark, G. & Stewart, M. (1986). *Acta Cryst.* C42, 628–630.

Hempel, A., Hull, S. E., Ledochowska, M. B. & Dauter, Z. (1979). *Acta Cryst.* B35, 474–476.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. University of Cambridge, England.

Nardelli, M. (1983). *Comput. Chem.* 7, 95–98.

Neidle, S. (1979). *Prog. Med. Chem.* 16, 151–221.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A24, 351–359.

Orgel, L. E. (1965). *Adv. Enzymol.* 27, 289–293.

Selladurai, S., Subramanian, K. & Ramakrishnan, V. T. (1990). *J. Crystallogr. Spectrosc. Res.* 20, 227–232.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Sivaraman, J. (1994). PhD thesis, Anna University, Madras, India.

Talacki, R., Carrell, H. L. & Glusker, J. P. (1974). *Acta Cryst.* B30, 1044–1047.

served in functionally unelaborated acids. In most cases, however, the ketone does not participate and typical mutually hydrogen-bonded carboxylic acid dimers result. Less frequently, intermolecular carboxyl-to-ketone hydrogen bonds repeat along one cell axis to yield a catemer. A third, rare, arrangement has an internal hydrogen bond and one instance is known of acid-to-ketone dimerization (Abell, Trent & Morris, 1991). We have previously referenced and discussed numerous examples of these various hydrogen-bonding patterns (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

Previous reports of internal hydrogen bonding in solid β-oxo acids have involved the oxo functions of vinylogous esters or amides rather than of genuine ketones. We recently reported the first instance of an intramolecularly hydrogen-bonded true β-keto acid, 2-carboxy-4,5-benzotropone (Thompson, Lalancette & Coté, 1996). In that case, the coplanarity of ketone and carboxyl required for internal hydrogen bonding was favored by unsaturation α,β to both the ketone and acid, plus a cyclic system holding the ketone and vinyl groups coplanar. We now report a closely analogous case which has the α,β-unsaturation without the coplanarity constraints of the ring.

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(E)-2-Acetylcinnamic Acid: Hydrogen-Bonding Pattern of an α,β-Unsaturated β'-Keto Acid

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Abstract

The title compound, (E)-2-acetyl-3-phenylpropenoic acid, $C_{11}H_{10}O_3$, adopts a conformation incorporating a planar *trans*-cinnamic acid, with the α-acetyl group rotated orthogonal to it. Pairs of molecules of identical conformational chirality form carboxyl dimers across C_2 axes, and the acid group displays disorder. There is a 2.64 Å ketone-O···methyl-H close contact between centrosymmetrically related dimer units.

Comment

Keto carboxylic acids offer opportunities for variation on the standard pattern of dimeric hydrogen bonding ob-
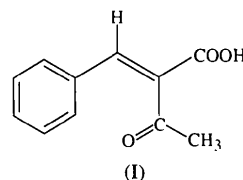

(I)

Fig. 1 shows the title compound, (I), in the chiral conformation it adopts and with its atom-numbering scheme. The cinnamic acid portion of (I) is very nearly planar, as is the case in cinnamic acid itself (Bryan & Freyberg, 1975; Wierda, Feng & Barron, 1989), with a dihedral angle between the aromatic ring and the carboxyl group of 7.5 (2)°. The acetyl group is
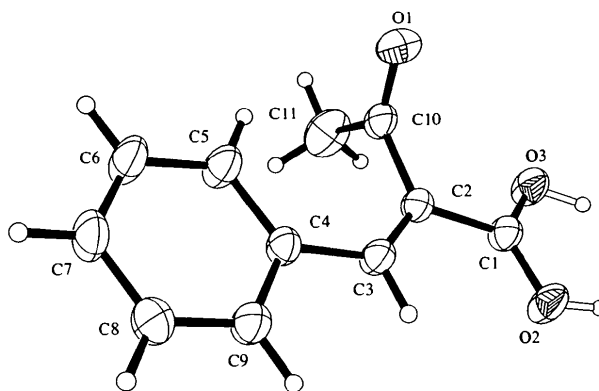

Fig. 1. Compound (I) with its numbering scheme. Ellipsoids are at the 40% probability level. The half-occupancy carboxyl-H atoms are shown with clear bonds.

turned nearly orthogonal to this; its dihedral angle with C1—C2—C3 is 88.1 (1)°. Models indicate that total coplanarity, prevented in (I) by steric hindrance involving the hydrogen at C5, is impossible in the Z isomer as well; however that material has been made only as an E/Z mixture (Kato, Chiba & Sato, 1978). As indicated by electron-density difference maps used to find the methyl group H atoms, the methyl group is rotated so that one H is nearly eclipsed with the ketone O (torsion angle H11C—C11—C10—O1 of −6.2°). This conformation presumably minimizes steric repulsions between the other two methyl H atoms (H11A and H11B) and C2, to which the remainder of the molecule is attached.

In (I), the shape of the carboxyl group is substantially averaged by disorder, as is frequent in carboxylic acids (Leiserowitz, 1976), with a C2—C1—O2 angle of 120.2 (1) and a C2—C1—O3 angle of 115.8 (1)°, a C1—O2 length of 1.257 (2) and C1—O3 length of 1.268 (2) Å. Typical values for highly ordered cases are 112 and 123°, and 1.21 and 1.31 Å (Borthwick, 1980). The carboxyl H atoms, shown with open bonds in Fig. 1, were both found in electron-density difference maps, whose occupancies were initially refined (to approximately 50%) and then fixed at 0.5 for the final cycles of refinement.

Fig. 2 is a partial packing diagram of the cell, showing the hydrogen-bonding association of pairs of chirally and conformationally identical molecules into carboxyl dimers. Each dimer has internal symmetry around a C_2 axis parallel to **b** and lying either in the *bc* cell face or in the *bc* plane at $a = 1/2$. The C1—C2 bond is not collinear with C1′—C2′, resulting in different intermolecular O···O′ distances, 2.671 (2) Å for O2···O2′ and 2.610 (2) Å for O3···O3′. The two carboxyl groups in the dimer do not lie in the same plane; there is a dihedral angle of 1.8 (3)° between the carboxylic acid groups C1—O2—O3 and C1′—O2′—O3′. There are 2.64 Å ketone-O···methyl-H close contacts between centrosymmetrically related dimer units. These probably represent polar attractions contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982). The layering is such that each carboxyl dimer is sandwiched flat between two benzene rings in the **c** direction in a repeating *abbabba* pattern. Similar arrangements are common in aromatic acids (Leiserowitz, 1976).

The solid-state (KBr) infrared spectrum of the title compound displays two separate carbonyl absorptions. Because the ketone function is orthogonal to the plane of the cinnamic acid system, it is decoupled from conjugation and its absorption appears, unshifted, amid multishouldered complex absorption, at 1707 cm⁻¹. The carboxyl group absorbs at 1679 cm⁻¹ (*cf.* 1672 cm⁻¹ for *trans*-cinnamic acid). In CHCl₃ solution, the C=O absorptions appear in a single broad peak centered at 1704 cm⁻¹.
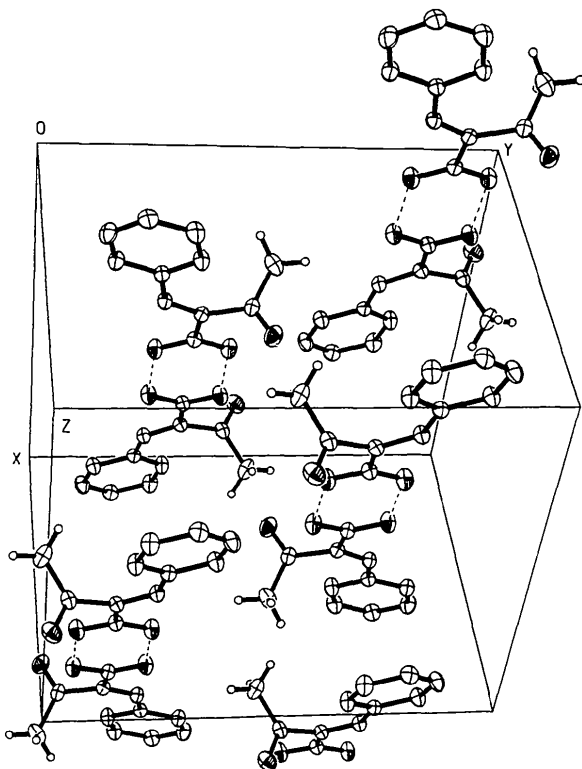

Fig. 2. A partial packing diagram, with extracellular molecules and all non-methyl H atoms removed for clarity. One complete centrosymmetric pair of dimers, centered at 1/2, 1/2, 1/2, is shown with its ketone···methyl close contacts. Ellipsoids are at the 20% probability level.

Experimental

Compound (I), m.p. 393 K, was synthesized by formic acid-catalyzed ester cleavage (Chandrasekaran, Kluge & Edwards, 1977) of the product obtained by Knoevenagel condensation of benzaldehyde with *tert*-butyl acetoacetate (Knoevenagel, 1896, 1898; Cope & Hofmann, 1941); it was recrystallized from cyclohexane. It has been previously obtained only as an E/Z mixture (Kato, Chiba & Sato, 1978).

Crystal data

$C_{11}H_{10}O_3$	Mo $K\alpha$ radiation
$M_r = 190.19$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 35
$C2/c$	reflections
$a = 12.846 (2)$ Å	$\theta = 7.19–21.45°$
$b = 13.608 (2)$ Å	$\mu = 0.095$ mm⁻¹
$c = 11.146 (1)$ Å	$T = 296 (2)$ K
$\beta = 91.89 (1)°$	Prism
$V = 1947.4 (5)$ Å³	$0.64 \times 0.44 \times 0.26$ mm
$Z = 8$	Clear
$D_x = 1.297$ Mg m⁻³	
$D_m = 1.28 (1)$ Mg m⁻³	
D_m measured by flotation in cyclohexane/CCl₃Br	

Data collection

Siemens *P*4 diffractometer	$R_{int} = 0.0463$
$2\theta/\theta$ scans	$\theta_{max} = 27.5°$
Absorption correction:	$h = -16 \rightarrow 16$
face-indexed numerical	$k = -1 \rightarrow 17$
$T_{min} = 0.968$, $T_{max} =$	$l = 0 \rightarrow 14$
0.980	3 standard reflections
2738 measured reflections	monitored every 97
2230 independent reflections	reflections
1256 observed reflections	intensity decay: 1.09%
$[F > 4\sigma(F)]$	

Refinement

Refinement on F^2	Extinction correction:
$R[F^2 > 2\sigma(F^2)] = 0.0436$	*SHELXL*93 (Sheldrick,
$wR(F^2) = 0.1081$	1993)
$S = 1.055$	Extinction coefficient:
2230 reflections	0.006 (2)
132 parameters	Atomic scattering factors
$w = 1/[\sigma^2(F_o^2) + (0.0765P)^2]$	from *International Tables*
where $P = (F_o^2 + 2F_c^2)/3$	*for Crystallography* (1992,
$(\Delta/\sigma)_{max} = -0.001$	Vol. C, Tables 4.2.6.8 and
$\Delta\rho_{max} = 0.137$ e Å^{-3}	6.1.1.4)
$\Delta\rho_{min} = -0.141$ e Å^{-3}	

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
O1	0.77548 (11)	0.48311 (10)	0.04186 (13)	0.0785 (4)
O2	0.59941 (8)	0.25431 (8)	0.21848 (11)	0.0621 (4)
O3	0.59795 (8)	0.41814 (8)	0.22245 (11)	0.0635 (4)
C1	0.64153 (12)	0.33645 (12)	0.20240 (14)	0.0469 (4)
C2	0.74986 (11)	0.34201 (11)	0.15971 (13)	0.0447 (4)
C3	0.80322 (12)	0.25924 (12)	0.14194 (14)	0.0478 (4)
C4	0.90959 (11)	0.24345 (11)	0.10204 (13)	0.0460 (4)
C5	0.97595 (13)	0.31758 (13)	0.0642 (2)	0.0607 (5)
C6	1.07523 (13)	0.29581 (15)	0.0293 (2)	0.0676 (5)
C7	1.10960 (13)	0.20057 (15)	0.0299 (2)	0.0637 (5)
C8	1.04581 (13)	0.12661 (14)	0.0653 (2)	0.0673 (5)
C9	0.94611 (13)	0.14826 (13)	0.1013 (2)	0.0586 (5)
C10	0.78714 (12)	0.44530 (12)	0.1396 (2)	0.0517 (4)
C11	0.8367 (2)	0.49717 (15)	0.2432 (2)	0.0839 (7)

Table 2. *Selected geometric parameters (Å, °)*

O1—C10	1.209 (2)	C2—C10	1.504 (2)
O2—C1	1.257 (2)	C3—C4	1.467 (2)
O3—C1	1.268 (2)	C10—C11	1.480 (3)
C1—C2	1.487 (2)	O1—H11B^i	2.64
C2—C3	1.337 (2)		
O2—C1—O3	124.0 (1)	C2—C3—C4	131.0 (1)
O2—C1—C2	120.2 (1)	O1—C10—C11	122.5 (2)
O3—C1—C2	115.8 (1)	O1—C10—C2	120.1 (2)
C3—C2—C1	119.6 (1)	C11—C10—C2	117.4 (2)
C3—C2—C10	126.7 (1)	C1—O2—O2^{ii}	117.2 (1)
C1—C2—C10	113.6 (1)	C1—O3—O3^{ii}	118.4 (1)
O2—C1—C2—C3	−2.0 (2)	C1—C2—C3—C4	−179.3 (2)
O3—C1—C2—C3	176.8 (1)	C3—C2—C10—O1	87.9 (2)
O2—C1—C2—C10	177.3 (1)	C1—C2—C10—O1	−91.4 (2)
O3—C1—C2—C10	−3.9 (2)	C3—C2—C10—C11	−92.7 (2)

Symmetry codes: (i) $x, 1 - y, z - \frac{1}{2}$; (ii) $1 - x, y, \frac{1}{2} - z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2$'\cdots$O2^i	0.90	1.78	2.671 (2)	168
O3—H3$'\cdots$O3^i	0.90	1.73	2.610 (2)	166

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

All non-carboxyl H atoms were placed in calculated positions and allowed to refine as riding models; their temperature factors were allowed to refine, with the vinylic H3 having $U_{iso} = 0.049$ and all the other ring H atoms, H5–H9, having the group $U_{iso} = 0.069$. The methyl group H atoms had a group displacement parameter $U_{iso} = 0.141$. Carboxyl H atoms H2$'$ and H3$'$ were found in disordered positions in an electron-density difference map. The occupancies of these two H atoms were initially refined (to approximately 50%), and then held at 50% for the last cycles of refinement. Their positional parameters were refined as riding models on their respective O atoms; their isotropic displacement parameters U_{iso} were refined to 0.092.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1990*b*). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

References

Abell, A. D., Trent, J. O. & Morris, K. B. (1991). *J. Chem. Soc. Perkin Trans. 2*, pp. 1077–1083.

Berkovitch-Yellin, Z. & Leiserowitz, L. (1982). *J. Am. Chem. Soc.* **104**, 4052–4064.

Borthwick, P. W. (1980). *Acta Cryst.* B**36**, 628–632.

Bryan, R. F. & Freyberg, D. P. (1975). *J. Chem. Soc. Perkin Trans. 2*, pp. 1835–1840.

Chandrasekaran, S., Kluge, A. F. & Edwards, J. A. (1977). *J. Org. Chem.* **42**, 3972–3974.

Cope, A. C. & Hofmann, C. M. (1941). *J. Am. Chem. Soc.* **63**, 3456–3459.

Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1996). *Acta Cryst.* C**52**, 684–687.

Fait, J. (1991). *XSCANS Users Manual.* Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Jönsson, P.-G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.

Kato, T., Chiba, T. & Sato, M. (1978). *Chem. Pharm. Bull.* **26**, 3877–3879.

Knoevenagel, E. (1896). *Ber.* **29**, 172–174.

Knoevenagel, E. (1898). *Ber.* **31**, 730–737, footnote 4.

Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.

Sheldrick, G. M. (1990*a*). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1990*b*). *SHELXTL/PC Users Manual.* Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Thompson, H. W., Lalancette, R. A. & Coté, M. L. (1996). *Acta Cryst.* C**52**, 2372–2376.

Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* C**48**, 66–70.

Wierda, D. A., Feng, T. L. & Barron, A. R. (1989). *Acta Cryst.* C**45**, 338–339.