

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)
$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
O(1)	0.7222 (4)	0.4127 (4)	0.3435 (1)	0.068 (1)
O(2)	0.2068 (4)	0.9421 (4)	0.4674 (1)	0.078 (1)
O(3)	-0.1560 (4)	0.8459 (4)	0.4639 (1)	0.078 (1)
O(4)†	1.0453 (16)	0.1186 (14)	0.3473 (3)	0.083 (5)
C(1)	0.3146 (5)	0.6222 (5)	0.4103 (1)	0.042 (1)
C(2)	0.3502 (5)	0.5315 (5)	0.3666 (1)	0.040 (1)
C(3)	0.5646 (6)	0.3976 (5)	0.3678 (1)	0.048 (1)
C(4)	0.5673 (7)	0.2470 (6)	0.4016 (1)	0.062 (1)
C(5)	0.5312 (7)	0.3420 (5)	0.4439 (1)	0.062 (1)
C(6)	0.3097 (6)	0.4647 (5)	0.4437 (1)	0.054 (1)
C(7)	0.0890 (5)	0.7419 (5)	0.4105 (1)	0.049 (1)
C(8)	0.0520 (6)	0.8510 (5)	0.4496 (1)	0.048 (1)
C(9)	0.3542 (5)	0.6787 (5)	0.3321 (1)	0.039 (1)
C(10)	0.1780 (6)	0.6843 (6)	0.3025 (1)	0.051 (1)
C(11)	0.1774 (7)	0.8188 (6)	0.2710 (1)	0.065 (1)
C(12)	0.3528 (7)	0.9562 (6)	0.2682 (1)	0.066 (2)
C(13)	0.5282 (7)	0.9557 (6)	0.2977 (1)	0.059 (1)
C(14)	0.5293 (6)	0.8196 (5)	0.3292 (1)	0.050 (1)
H(3)	-0.168 (7)	0.930 (6)	0.4898 (14)	

† Occupancy = 0.0267 (8).

Table 2. Selected geometric parameters (\AA , $^\circ$)

O(1)—C(3)	1.208 (4)	C(5)—C(6)	1.525 (5)
O(2)—C(8)	1.224 (4)	C(7)—C(8)	1.479 (5)
O(3)—C(8)	1.287 (4)	C(9)—C(10)	1.382 (4)
C(1)—C(2)	1.551 (4)	C(9)—C(14)	1.397 (5)
C(1)—C(6)	1.523 (5)	C(10)—C(11)	1.370 (5)
C(1)—C(7)	1.534 (5)	C(11)—C(12)	1.382 (6)
C(2)—C(3)	1.536 (5)	C(12)—C(13)	1.376 (6)
C(2)—C(9)	1.498 (4)	C(13)—C(14)	1.376 (5)
C(3)—C(4)	1.498 (5)	O(1)···O(4)	2.738 (7)
C(4)—C(5)	1.523 (5)	O(3)···O(2')	2.662 (2)
C(2)—C(1)—C(6)	111.1 (3)	O(2)—C(8)—O(3)	121.2 (3)
C(2)—C(1)—C(7)	109.7 (2)	O(2)—C(8)—C(7)	123.0 (3)
C(6)—C(1)—C(7)	110.6 (3)	O(3)—C(8)—C(7)	115.7 (3)
C(1)—C(2)—C(3)	109.2 (2)	C(2)—C(9)—C(10)	120.7 (3)
C(1)—C(2)—C(9)	113.8 (3)	C(2)—C(9)—C(14)	122.0 (3)
C(3)—C(2)—C(9)	113.7 (3)	C(10)—C(9)—C(14)	117.3 (3)
O(1)—C(3)—C(2)	122.7 (3)	C(9)—C(10)—C(11)	121.6 (3)
O(1)—C(3)—C(4)	121.8 (3)	C(10)—C(11)—C(12)	120.6 (3)
C(2)—C(3)—C(4)	115.6 (3)	C(11)—C(12)—C(13)	118.9 (4)
C(3)—C(4)—C(5)	110.7 (3)	C(12)—C(13)—C(14)	120.4 (4)
C(4)—C(5)—C(6)	110.7 (3)	C(9)—C(14)—C(13)	121.2 (3)
C(1)—C(6)—C(5)	111.8 (3)	C(3)—O(1)···O(4)	115.1 (2)
C(1)—C(7)—C(8)	113.8 (3)	C(8)—O(3)—H(3)	111 (2)
D—H···A	D—H	D···A	D—H···A
O(3)—H(3)···O(2')	1.01 (4)	2.662 (2)	176 (2)

Symmetry code: (i) $-x, 2 - y, 1 - z$.

Integrated intensities were corrected for Lorentz and polarization effects and 16 ψ -scan reflections were used to correct for absorption. Full-matrix least-squares refinement was performed. All non-H atoms were refined anisotropically. All H atoms, except those associated with the water O atom, were located in difference maps. The carboxyl H atom was refined isotropically; the remaining H atoms were placed in calculated optimum geometric positions and then refined using a riding model.

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

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1110). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Borthwick, P. W. (1980). *Acta Cryst.* **B36**, 628–632.
 Coté, M. L., Lalancette, R. A. & Thompson, H. W. (1995). *Acta Cryst.* **C51**, 2305–2307.
 Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1995). *Acta Cryst.* In the press.
 Dieterich, D. A., Paul, I. C. & Curtin, D. Y. (1974). *J. Am. Chem. Soc.* **96**, 6372–6380.
 Lalancette, R. A., Vanderhoff, P. A. & Thompson, H. W. (1990). *Acta Cryst.* **C46**, 1682–1686.
 Sheldrick, G. M. (1990). *SHELXTL/PC Users Manual*. Release 4.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* **C48**, 66–70.
 Thompson, H. W. & Long, D. J. (1988). *J. Org. Chem.* **53**, 4201–4209.
 Vanderhoff, P. A., Lalancette, R. A. & Thompson, H. W. (1990). *J. Org. Chem.* **55**, 1696–1698.
 Winkler, J. D., Hong, B.-C., Hey, J. P. & Williard, P. G. (1991). *J. Am. Chem. Soc.* **113**, 8839–8846.

Acta Cryst. (1995). **C51**, 2617–2619

cis-2-Oxo-1,3-cyclohexanedipropionic Acid: Structure and Hydrogen-Bonding Pattern of a δ -Keto 1,9-Diacid

ROGER A. LALANCETTE, HUGH W. THOMPSON AND MARIE L. COTÉ

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA

(Received 5 October 1994; accepted 23 June 1995)

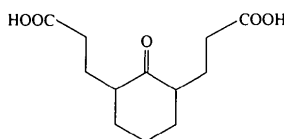
Abstract

The title compound, $C_{12}H_{18}O_5$, adopts a conformation that retains the plane of symmetry of its *meso* structure. Intermolecular chains are formed by reciprocal centrosymmetric hydrogen bonding of carboxyl groups from adjacent molecules, with the ketone not involved in the hydrogen bonding. There is a 2.523 (4) \AA intermolecular contact between a ring H atom and the ketone O atom.

Comment

Simple crystalline keto carboxylic acids have four known hydrogen-bonding motifs. The commonest displays the dimer pattern characteristic of almost all functionally unsubstituted acids, in which the ketone is not involved. Less commonly, intermolecular carboxyl-to-ketone hydrogen bonds repeat infinitely along one cell axis to yield a chain, or catemer. A third, rare arrangement has an internal hydrogen bond, and one instance is known of acid-to-ketone dimerization. We have previously referenced and discussed many examples (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1995).

As part of our investigation of these patterns, we have examined the crystal structure of the title compound, (I) (m.p. 416 K), prepared *via* enamine dialkylation of cyclohexanone with ethyl acrylate (Stork, Brizzolara, Landesman, Szmuszkovic & Terrell, 1963; Thompson, 1967). Fig. 1 presents a view of the molecule with its numbering scheme. The cyclohexanone has a chair conformation with both side-chains equatorial and symmetrically disposed, giving this *meso* molecule a crystallographic mirror plane of symmetry [atoms O(1), C(1) and C(4) are on the mirror plane]. The side-chain methylene groups adopt typical staggered conformations relative to each other and to their ring methines, and lie in the general plane of the ring so that the entire molecule is relatively shallow. The plane of the carboxyl group [O(2)=C(7)—O(3)] is at a dihedral angle of 79.4 (3)° to that of the ketone {C(2)—C(1)[=O(1)]—C(2A)}.



Each carboxyl group displays C—O lengths of 1.216 (5) and 1.306 (5) Å, with C—C—O angles of 113.6 (3) and 123.3 (3)°, typical of highly ordered carboxyl dimers (Borthwick, 1980). The carboxyl H atom was found and its positional parameters were refined; its displacement parameter was held constant. The angle O(3)—H(3)···O(2ⁱⁱ) [symmetry code: (ii) 1 - x, -y, 1 - z] is 177 (4)°, and is fairly typical for carboxyl dimers.

Fig. 2 is a packing diagram which includes extracellular molecules to show the zigzag intermolecular chains which form through centrosymmetric pairing of carboxyl groups with those of neighboring molecules across the *ab* and *ac* faces, the *a* edge, and the cell center. The ketone is not involved in the hydrogen bonding, which displays a pattern resembling those found in β -ketoglutaric acid (Martuscelli & Avitabile, 1967) and tetramethyl- β -ketoglutaric acid (Avitabile, Ganis & Martuscelli, 1969; Avitabile, Ganis & Lepore, 1971). Since all the hydrogen bonds involve laterally adjacent

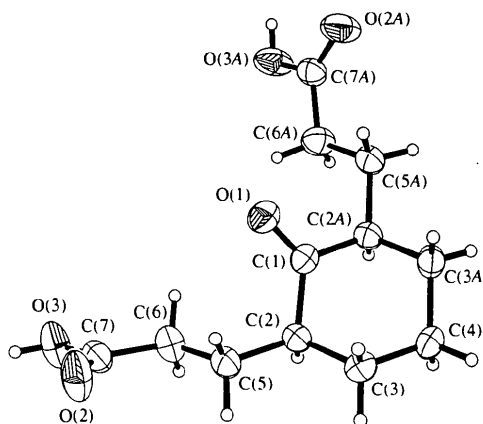


Fig. 1. A view of the title compound with its numbering scheme. Owing to the mirror plane through O(1), C(1) and C(4), the asymmetric unit consists of one-half of the molecule. Ellipsoids are drawn at the 40% probability level.

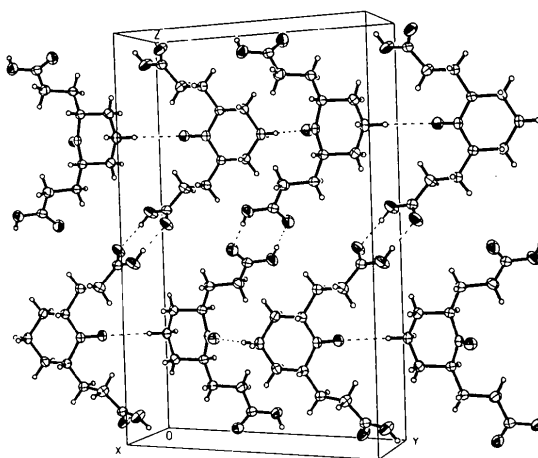


Fig. 2. A packing diagram for the title compound. Extracellular molecules illustrate the zigzag intermolecular chains formed by centrosymmetric hydrogen-bonded carboxyl pairing across the *ac* face and the cell center. Additional dimers form across the *ab* face and the *a* edge. Also shown is the 2.523 (4) Å intermolecular contact between the ketone O(1) atom and the equatorial H atom H(4A¹) from a symmetry-related molecule. Ellipsoids are drawn at the 30% probability level.

molecules and the hydrogen-bonding chains are glide-related, a shallow dimpled sheet arrangement is formed, which repeats at the frequency of the *a* cell dimension [4.663 (1) Å].

Apart from the carboxyl pairing, with an intermolecular O···Oⁱⁱ distance of 2.660 (2) Å, the closest intermolecular contact occurs between the ketone O atom O(1) and a ring H atom, H(4A¹), of an adjacent molecule, glide-related in the *b* direction [2.523 (4) Å; symmetry code: (i) 1 - x, y - 1/2, z], also shown in Fig. 2. This probably represents a significant polar attraction contributing to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

The solid-state (KBr) IR spectrum displays a single, somewhat broadened stretching absorption at 1700 cm^{-1} for all carbonyls, which is normal for keto acids when the ketone is not involved in the hydrogen bonding (Coté, Lalancette & Thompson, 1995; Vanderhoff, Lalancette & Thompson, 1990).

Experimental

The title compound was prepared by enamine dialkylation of cyclohexanone with ethyl acrylate (Stork, 1963; Thompson, 1967) and crystallized from 4:1 toluene–2-propanol at room temperature. The density D_m was measured by flotation in cyclohexane/ CCl_4 .

Crystal data

$\text{C}_{12}\text{H}_{18}\text{O}_5$
 $M_r = 242.3$
 Orthorhombic
Pbcm
 $a = 4.663(1)\text{ \AA}$
 $b = 13.275(2)\text{ \AA}$
 $c = 20.551(3)\text{ \AA}$
 $V = 1272.2(4)\text{ \AA}^3$
 $Z = 4$
 $D_x = 1.265\text{ Mg m}^{-3}$
 $D_m = 1.256(6)\text{ Mg m}^{-3}$

Data collection

Siemens P4 diffractometer
 $2\theta/\omega$ scans
 Absorption correction:
 face-indexed numerical
 $T_{\min} = 0.932$, $T_{\max} = 0.990$
 1745 measured reflections
 1489 independent reflections
 606 observed reflections
 $[F > 4\sigma(F)]$

Refinement

Refinement on F^2
 $R = 0.049$
 $wR = 0.053$
 $S = 1.11$
 606 reflections
 88 parameters
 Weighting scheme based on measured e.s.d.'s
 $(\Delta/\sigma)_{\max} = 0.170$
 $\Delta\rho_{\max} = 0.18\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.17\text{ e \AA}^{-3}$

Mo $K\alpha$ radiation
 $\lambda = 0.71073\text{ \AA}$
 Cell parameters from 28 reflections
 $\theta = 5.5\text{--}17.7^\circ$
 $\mu = 0.098\text{ mm}^{-1}$
 $T = 296\text{ K}$
 Parallelepiped
 $0.44 \times 0.40 \times 0.12\text{ mm}$
 Colorless

$\theta_{\max} = 25^\circ$
 $h = 0 \rightarrow 6$
 $k = 0 \rightarrow 17$
 $l = 0 \rightarrow 26$
 3 standard reflections monitored every 97 reflections
 intensity decay: 1.86%

Extinction correction:
 $F^* = F/[1.0 + (0.002)\chi \times F^2/\sin 2\theta]^{1/4}$
 Extinction coefficient:
 $\chi = 0.0025(6)$
 Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O(1)	0.5248 (8)	0.2013 (2)	3/4	0.057 (1)
O(2)	0.5250 (6)	0.1132 (2)	0.5329 (1)	0.076 (1)
O(3)	0.2236 (6)	-0.0083 (2)	0.5615 (1)	0.074 (1)

C(1)	0.3219 (11)	0.2589 (3)	3/4	0.038 (2)
C(2)	0.2001 (7)	0.3015 (2)	0.6879 (1)	0.041 (1)
C(3)	0.2655 (8)	0.4148 (2)	0.6888 (2)	0.048 (1)
C(4)	0.1542 (11)	0.4664 (3)	3/4	0.051 (2)
C(5)	0.3070 (9)	0.2493 (2)	0.6265 (1)	0.050 (1)
C(6)	0.2034 (9)	0.1416 (3)	0.6209 (2)	0.057 (1)
C(7)	0.3317 (9)	0.0820 (3)	0.5672 (2)	0.052 (1)

Table 2. Selected geometric parameters (\AA , $^\circ$)

O(1)—C(1)	1.216 (6)	C(3)—C(4)	1.524 (4)
O(2)—C(7)	1.216 (5)	C(5)—C(6)	1.515 (5)
O(3)—C(7)	1.306 (5)	C(6)—C(7)	1.483 (5)
C(1)—C(2)	1.508 (4)	O(1)···H(4A ⁱ)	2.523 (4)
C(2)—C(3)	1.535 (4)	O(2)···O(3 ⁱⁱ)	2.660 (2)
C(2)—C(5)	1.523 (4)		
O(1)—C(1)—C(2)	121.9 (2)	C(2)—C(5)—C(6)	112.8 (3)
C(2)—C(1)—C(2 ⁱⁱⁱ)	115.7 (4)	C(5)—C(6)—C(7)	115.5 (3)
C(1)—C(2)—C(3)	106.5 (3)	O(2)—C(7)—O(3)	123.1 (3)
C(1)—C(2)—C(5)	114.0 (3)	O(2)—C(7)—C(6)	123.3 (3)
C(3)—C(2)—C(5)	113.0 (3)	O(3)—C(7)—C(6)	113.6 (3)
C(2)—C(3)—C(4)	112.5 (3)	O(3)—H(3)···O(2 ⁱⁱ)	177 (4)
C(3)—C(4)—C(3 ⁱⁱⁱ)	111.4 (4)		

Symmetry codes: (i) $1-x, y-\frac{1}{2}, z$; (ii) $1-x, -y, 1-z$; (iii) $x, y, \frac{3}{2}-z$.

All H atoms were placed in calculated positions and were refined using a riding model. The positional parameters of the carboxyl H atom, H(3), were refined, but its displacement parameter was held constant.

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

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1105). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Avitabile, G., Ganis, P. & Lepore, U. (1971). *Macromolecules*, **4**, 239–241.
 Avitabile, G., Ganis, P. & Martuscelli, E. (1969). *Acta Cryst.* **B25**, 2378–2385.
 Berkovitch-Yellin, Z. & Leiserowitz, L. (1982). *J. Am. Chem. Soc.* **104**, 4052–4064.
 Borthwick, P. W. (1980). *Acta Cryst.* **B36**, 628–632.
 Coté, M. L., Lalancette, R. A. & Thompson, H. W. (1995). *Acta Cryst.* **C51**, 2305–2307.
 Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1995). *Acta Cryst.* In the press.
 Jönsson, P.-G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.
 Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.
 Martuscelli, E. & Avitabile, G. (1967). *Ric. Sci.* **37**, 102–110.
 Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Siemens (1991). *XSCANS User's Manual*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Stork, G., Brizzolara, A., Landesman, H., Szmuszkovicz, J. & Terrell, R. (1963). *J. Am. Chem. Soc.* **85**, 207–222.
 Thompson, H. W. (1967). *J. Org. Chem.* **32**, 1222–1224.
 Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* **C48**, 66–70.
 Vanderhoff, P. A., Lalancette, R. A. & Thompson, H. W. (1990). *J. Org. Chem.* **55**, 1696–1698.