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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1170). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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(±)-3-Oxo-*trans*-2-phenylcyclohexaneacetic Acid: Structure and Hydrogen-Bonding Pattern of a Partially Hydrated δ -Keto Acid

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Abstract

In the title compound, $C_{14}H_{16}O_3 \cdot 0.25H_2O$, enantiomeric pairs of molecules form centrosymmetric dimers by mutual hydrogen bonding of carboxyl groups; the dimers are centered on the *b* and *c* edges of the chosen unit cell. The ketone has a close contact of 2.738 (7) Å to the O atom of a water molecule (which has an occupancy of approximately 25%).

Comment

Of the four hydrogen-bonding motifs known to occur in simple crystalline keto carboxylic acids, the commonest, in which the ketone does not participate, is the dimer pattern typical of almost all functionally unsubstituted acids. 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 numerous examples (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1995).

The title compound, (I), is a δ -keto acid which crystallizes as a partial hydrate (25%) from 60:40 water-ethanol. The δ -keto acids include catemers of both the helical and translational type, as well as dimers. However, hydrates are remarkably rare among the simple keto acids for which X-ray structures have been determined. Those known include a carboxyl-to-water-to-ketone catemer (Winkler, Hong, Hey & Williard, 1991) and a dimer containing two inserted hydrogen-bonded water molecules (Lalancette, Vanderhoff & Thompson, 1990). The latter is apparently the only one with crystal structures known for both hydrated and anhydrous forms.

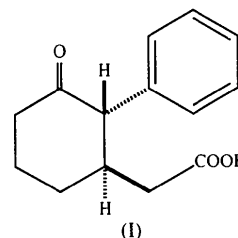


Fig. 1 presents a view of the title compound, with its numbering scheme. As expected, the cyclohexanone has a chair conformation with both substituents equatorial. The aromatic ring adopts a conformation that is nearly orthogonal [$86.32(8)^\circ$] to the plane through C(1), C(3), C(4) and C(6) of the cyclohexanone. The aromatic ring is thus nearly coplanar [$3.3(2)^\circ$] with the plane defined by C(9)—C(2)—H(2). The substituent methylene C atom adopts a staggered conformation relative to the adjacent ring C atom [torsion angles H(1)—C(1)—C(7)—H(7B) $64.9(3)^\circ$ and H(1)—C(1)—C(7)—H(7A) $-176.3(3)^\circ$] with the carboxyl directed away from the aromatic ring. The dihedral angle between the planes described by C(7)—C(8)—O(2) and H(1)—C(1)—C(2) is $17.1(3)^\circ$.

Although disorder of carboxyl C=O bond lengths and C—C=O angles is common in dimeric acids (Dieterich, Paul & Curtin, 1974), it is not substantial here. The lengths are 1.224(4) and 1.287(4) Å, with angles of $115.7(3)^\circ$ and $123.0(3)^\circ$; typical values for

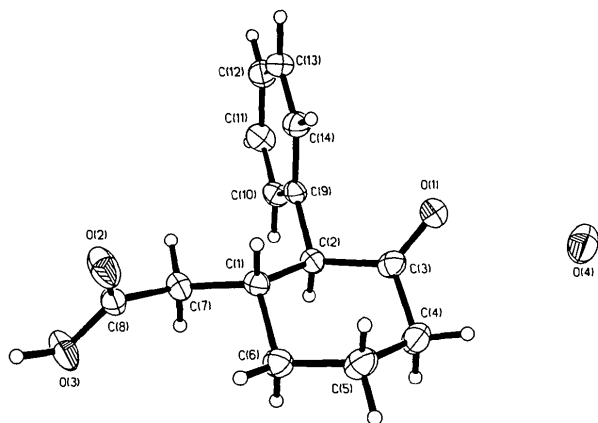


Fig. 1. A view of the title compound with its numbering scheme. All of the O atoms in the structure including that of the water of hydration [26.7 (8)% partial occupancy] are shown as shaded ellipsoids. The ellipsoids are drawn at the 25% probability level.

highly ordered carboxyl dimers are 1.21 and 1.31 Å, and 112 and 123° for the corresponding distances and angles (Borthwick, 1980).

A water molecule of hydration is partially present. Its O atom was found in an electron-density difference map at a height equivalent to 25% of a known oxygen electron density; its occupancy was refined to 26.7 (8)%. Although the low occupancy prevented our finding the attached H atoms, there is a close contact of 2.738 (7) Å between this water O atom, O(4), and the ketone O atom, O(1), which probably indicates the presence of a hydrogen bond between these two O atoms (see Fig. 1).

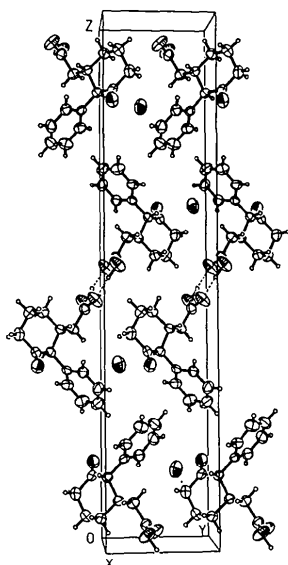


Fig. 2. A partial packing diagram for the title compound. Extracellular molecules illustrate the dimers arranged centrosymmetrically across the *b* and *c* edges of the cell. The ellipsoids are drawn at the 40% probability level.

Fig. 2 shows the screw-related centrosymmetric dimers formed by the pairing of enantiomers across the *b* and *c* edges in the cell. All O atoms in the structure are shown as shaded ellipsoids.

The compound's solid-state (KBr) IR spectrum displays a single, somewhat broadened C=O stretching absorption centered at 1703 cm⁻¹ for both the carboxyl and ketone, which is normal for such compounds showing the dimeric hydrogen-bonding motif (Vanderhoff, Lalancette & Thompson, 1990; Coté, Lalancette & Thompson, 1995).

Experimental

Compound (I) was prepared *via* addition of diethyl malonate to 2-phenylcyclohexenone (Thompson & Long, 1988) and crystallized from 60:40 water-ethanol at room temperature. The density D_m was measured by flotation in cyclohexane/CCl₄.

Crystal data

C₁₄H₁₆O₃·0.25H₂O

$M_r = 236.8$

Monoclinic

$P2_1/c$

$a = 5.7473$ (6) Å

$b = 6.8421$ (8) Å

$c = 32.155$ (4) Å

$\beta = 90.634$ (8)°

$V = 1264.4$ (3) Å³

$Z = 4$

$D_x = 1.245$ Mg m⁻³

$D_m = 1.24$ (1) Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 20 reflections

$\theta = 5.3$ – 12.3 °

$\mu = 0.090$ mm⁻¹

$T = 297$ K

Prism

$0.60 \times 0.50 \times 0.35$ mm

Colorless

Data collection

Siemens P4 diffractometer

$2\theta/\omega$ scans

Absorption correction:

16 ψ scans

$T_{\min} = 0.792$, $T_{\max} =$

0.859

5385 measured reflections

3678 independent reflections

1275 observed reflections

$[F > 4\sigma(F)]$

$R_{\text{int}} = 0.035$

$\theta_{\text{max}} = 30$ °

$h = -8 \rightarrow 8$

$k = 0 \rightarrow 9$

$l = 0 \rightarrow 44$

3 standard reflections

monitored every 97

reflections

intensity decay: 1.27%

Refinement

Refinement on F

$R = 0.056$

$wR = 0.060$

$S = 1.32$

1274 reflections

172 parameters

Weighting scheme based

on measured e.s.d.'s

$(\Delta/\sigma)_{\text{max}} = 0.045$

$\Delta\rho_{\text{max}} = 0.24$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.23$ e Å⁻³

Extinction correction:

$F^* = F/[1.0 + (0.002\chi$

$\times F^2/\sin 2\theta)]^{1/4}$

Extinction coefficient:

$\chi = 0.0023$ (7)

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

	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.

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

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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.