

Monoclinic  
 $P2_1/c$   
 $a = 5.561 (2) \text{ \AA}$   
 $b = 8.159 (3) \text{ \AA}$   
 $c = 11.353 (4) \text{ \AA}$   
 $\beta = 100.73 (4)^\circ$   
 $V = 506.1 (3) \text{ \AA}^3$   
 $Z = 2$   
 $D_x = 1.209 \text{ Mg m}^{-3}$

#### Data collection

Enraf–Nonius CAD-4  
 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  
 none  
 796 measured reflections  
 754 independent reflections  
 391 observed reflections  
 $[F > 3\sigma(F)]$

#### Refinement

Refinement on  $F^2$   
 $R = 0.035$   
 $wR = 0.038$   
 $S = 1.20$   
 391 reflections  
 88 parameters  
 Unit weights applied  
 $(\Delta/\sigma)_{\max} = 0.0002$

Cell parameters from 16  
 reflections  
 $\theta = 17\text{--}19^\circ$   
 $\mu = 0.0730 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Prism  
 $0.40 \times 0.24 \times 0.16 \text{ mm}$   
 White

$R_{\text{int}} = 0.035$   
 $\theta_{\text{max}} = 34^\circ$   
 $h = -6 \rightarrow 6$   
 $k = -9 \rightarrow 0$   
 $l = -12 \rightarrow 0$   
 3 standard reflections  
 monitored every 200  
 reflections  
 intensity decay: none

$\Delta\rho_{\text{max}} = 0.10 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.14 \text{ e \AA}^{-3}$   
 Extinction correction: none  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV) and  
 Cromer & Mann (1968)

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances, angles and torsion angles involving H atoms have been deposited with the IUCr (Reference: NA1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

	$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	$B_{\text{eq}}$
C4	0.6678 (4)	0.1880 (4)	0.8366 (2)	4.18 (7)
C2	0.9312 (5)	0.0328 (4)	0.7416 (2)	4.56 (7)
C3	0.8810 (4)	0.0980 (3)	0.8459 (2)	3.79 (7)
C5	0.5236 (5)	0.2098 (4)	0.7266 (2)	4.68 (7)
N1	0.5683 (4)	0.1479 (3)	0.6252 (2)	5.07 (6)
C1	0.7714 (5)	0.0618 (4)	0.6349 (2)	5.23 (8)
C6	1.0472 (5)	0.0663 (4)	0.9647 (2)	5.14 (8)

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

C4—C3	1.382 (4)	C3—C6	1.509 (3)
C4—C5	1.364 (3)	C5—N1	1.323 (4)
C2—C3	1.373 (4)	N1—C1	1.317 (4)
C2—C1	1.383 (3)		
C3—C4—C5	119.3 (3)	C2—C3—C6	121.0 (2)
C3—C2—C1	119.2 (3)	C4—C5—N1	125.0 (3)
C4—C3—C2	116.7 (2)	C5—N1—C1	115.3 (2)
C4—C3—C6	122.2 (2)	C2—C1—N1	124.5 (3)

The structure was solved by direct methods and refined by full-matrix least squares. H atoms were found by a difference Fourier synthesis and refined isotropically.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *MULTAN80* (Main *et al.*, 1980). Program(s) used to refine structure: *MolEN LSPM*. Molecular graphics: *ORTEPII* (Johnson, 1976).

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### (±)-2-Oxocyclohexaneacetic Acid: Structure and Hydrogen-Bonding Pattern of a $\gamma$ -Keto Acid

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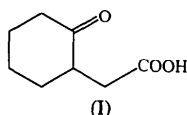
#### Abstract

In the title compound,  $\text{C}_8\text{H}_{12}\text{O}_3$ , enantiomeric pairs of molecules form centrosymmetric dimers by mutual hydrogen bonding of carboxyl groups, with the ketone not involved in the hydrogen bonding. The dimers are of four types, centered on the three edges and the center of the cell. The carboxyl C—O bond lengths and angles are substantially disordered. There is a  $2.551 (3) \text{ \AA}$  intermolecular contact between methine H and ketone O atoms.

## Comment

Simple crystalline keto-carboxylic acids have four known hydrogen-bonding motifs. The most common retains 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 is 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).

The category of  $\gamma$ -keto acids is especially rich in hydrogen-bonding types, containing examples of dimers, internal hydrogen bonds, and catemers of both the helical and translational type. The title  $\gamma$ -keto acid, (I), was prepared *via* enamine alkylation of cyclohexanone with ethyl bromoacetate.



The cell's eight molecules are all crystallographically related; Fig. 1 presents a view of (I) with its numbering scheme. As expected, the side chain is equatorial to a chair cyclohexanone. The substituent methylene C atom adopts a staggered conformation relative to its ring C atom [torsion angle H(7A)—C(7)—C(1)—H(1) = 178.6(2)°]. The carboxyl group is aimed toward the ketone and rotated such that the plane [O(2)—C(8)—O(3)] makes an angle of 79.5(4)° with the plane containing the ketone [C(1)—C(2)—O(1)—C(3)].

The carboxyl C—O bond lengths and C—C—O angles are found to be partially disordered; this is common in dimeric acids (Dieterich, Paul & Curtin, 1974) and we have previously discussed some of its implications (Thompson, Lalancette & Vanderhoff, 1992). The lengths here are 1.243(6) and 1.289(6) Å,

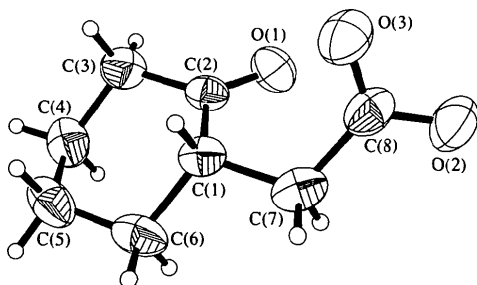


Fig. 1. A view of the title compound with its atomic numbering scheme. The carboxyl group is shown as found, with C—O bond lengths and C—C—O angles partially averaged by disordering and without the carboxyl H atom. The ellipsoids are drawn at the 30% probability level.

with angles 116.9(4) and 120.3(4)°, in contrast to typical lengths of 1.21 and 1.31 Å and angles of 112 and 123° in highly ordered carboxyl dimers (Borthwick, 1980). This may be described roughly as *ca* 65–80% disordered. The carboxyl H atom was not found.

Fig. 2 includes extracellular molecules to illustrate the four types of centrosymmetric dimers formed through carboxyl pairing of enantiomers across the center and the three edges of the cell. Also shown is the 2.551(3) Å intermolecular contact between the methine H atom of one molecule and the ketone O atom of an adjacent molecule of identical chirality; the C(2)—O(1)—H(1A<sup>i</sup>) angle is 134.8(1)° [ $(i) -x, y - \frac{1}{2}, \frac{3}{2} - z$ ]. This probably represents a significant polar attraction contributing to the packing forces (Leiserowitz, 1976; Jönsson, 1972; Berkovitch-Yellin & Leiserowitz, 1982).

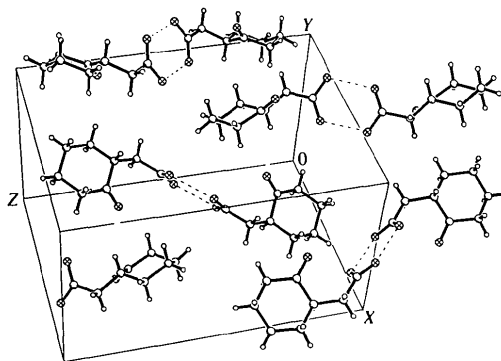


Fig. 2. A partial packing diagram for the title compound. Extracellular molecules illustrate the four types of hydrogen-bonded carboxyl dimers (in the partially disordered state and without carboxyl H atoms), arranged centrosymmetrically across the edges and the center of the cell. Also shown is the 2.551(3) Å intermolecular contact between the methine H of one molecule and the ketone O atom of an adjacent molecule.

The solid-state (KBr) IR spectrum of the compound displays a single relatively sharp C=O stretching absorption centered at *ca* 1707 cm<sup>-1</sup> for both ketone and carboxyl, which is normal for such compounds showing the dimeric hydrogen-bonding motif (Vanderhoff, Lalancette & Thompson, 1990).

## Experimental

Crystals of the title compound were grown from absolute ethanol.

### Crystal data

C<sub>8</sub>H<sub>12</sub>O<sub>3</sub>  
*M<sub>r</sub>* = 156.19  
 Orthorhombic  
*Pbca*  
*a* = 11.742(3) Å  
*b* = 9.100(2) Å  
*c* = 15.705(3) Å

Mo K $\alpha$  radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 31 reflections  
 $\theta$  = 7.8–13.5°  
 $\mu$  = 0.094 mm<sup>-1</sup>  
*T* = 297 K

$V = 1678.2 (7) \text{ \AA}^3$   
 $Z = 8$   
 $D_x = 1.236 \text{ Mg m}^{-3}$

Parallelepiped  
 $0.30 \times 0.20 \times 0.15 \text{ mm}$   
 Colorless

#### Data collection

Siemens P4 diffractometer  
 $\theta/2\theta$  scans  
 Absorption correction:  
 none  
 1304 measured reflections  
 1100 independent reflections  
 582 observed reflections  
 $[F > 4.0\sigma(F)]$

$\theta_{\max} = 22.5^\circ$   
 $h = 0 \rightarrow 12$   
 $k = 0 \rightarrow 9$   
 $l = -16 \rightarrow 0$   
 3 standard reflections  
 monitored every 47  
 reflections  
 intensity decay: 1.3%

#### Refinement

Refinement on  $F^2$   
 $R = 0.0446$   
 $wR = 0.0529$   
 $S = 1.10$   
 582 reflections  
 103 parameters  
 H atoms riding on associated  
 C atoms except for the  
 carboxyl H atom which  
 was not located  
 $w = 1/[\sigma^2(F) + 0.00070F^2]$

$(\Delta/\sigma)_{\max} = 0.006$   
 $\Delta\rho_{\max} = 0.17 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = 0.00 \text{ e \AA}^{-3}$   
 Extinction correction:  
 empirical isotropic  
 Extinction coefficient:  
 0.0059  
 Atomic scattering factors  
 from *International Tables*  
 for *X-ray Crystallography*  
 (1974, Vol. IV)

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

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

	x	y	z	$U_{\text{eq}}$
O(1)	0.0314 (3)	-0.0761 (3)	0.7415 (2)	0.088 (1)
O(2)	0.0253 (3)	0.1223 (3)	0.5785 (2)	0.097 (1)
O(3)	0.1234 (3)	-0.0767 (4)	0.5416 (2)	0.107 (1)
C(1)	0.1504 (3)	0.1337 (4)	0.7372 (2)	0.066 (2)
C(2)	0.0636 (3)	0.0341 (5)	0.7765 (3)	0.063 (2)
C(3)	0.0213 (4)	0.0778 (5)	0.8634 (3)	0.084 (2)
C(4)	0.1181 (4)	0.1118 (5)	0.9246 (3)	0.095 (2)
C(5)	0.1984 (4)	0.2225 (5)	0.8846 (3)	0.099 (2)
C(6)	0.2447 (4)	0.1688 (5)	0.8000 (3)	0.089 (2)
C(7)	0.1958 (4)	0.0700 (5)	0.6549 (3)	0.088 (2)
C(8)	0.1075 (4)	0.0380 (6)	0.5884 (3)	0.084 (2)

Table 2. Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

O(1)—C(2)	1.204 (5)	O(2)—C(8)	1.243 (6)
O(3)—C(8)	1.289 (6)	C(1)—C(2)	1.496 (5)
C(1)—C(6)	1.518 (6)	C(1)—C(7)	1.513 (6)
C(2)—C(3)	1.507 (6)	C(3)—C(4)	1.519 (6)
C(4)—C(5)	1.516 (7)	C(5)—C(6)	1.517 (7)
C(7)—C(8)	1.501 (6)	O(3)···O(2 <sup>i</sup> )	2.604 (3)
C(2)—C(1)—C(6)	110.9 (3)	C(2)—C(1)—C(7)	111.1 (3)
C(6)—C(1)—C(7)	112.3 (3)	O(1)—C(2)—C(1)	122.0 (3)
O(1)—C(2)—C(3)	122.0 (4)	C(1)—C(2)—C(3)	116.0 (3)
C(2)—C(3)—C(4)	112.3 (3)	C(3)—C(4)—C(5)	109.8 (3)
C(4)—C(5)—C(6)	111.8 (4)	C(1)—C(6)—C(5)	112.1 (4)
C(1)—C(7)—C(8)	115.2 (3)	O(2)—C(8)—O(3)	122.7 (4)
O(2)—C(8)—C(7)	120.3 (4)	O(3)—C(8)—C(7)	116.9 (4)
C(8)—O(2)···O(3 <sup>i</sup> )	120.9 (2)	C(8)—O(3)···O(2 <sup>i</sup> )	116.4 (2)

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

The structure was solved by direct methods. Integrated intensities were corrected for Lorentz and polarization effects. Full-matrix least-squares refinement was performed using *SHELXTL/PC* (Sheldrick, 1990). All non-H atoms were refined anisotropically. Although all non-carboxyl H atoms were found in difference maps, they were nonetheless replaced by H

atoms in calculated positions and refined with a riding model, which gave a slightly better goodness of fit.

Data collection, cell refinement, data reduction, structure solution, structure refinement, molecular graphics and preparation of material for publication: *SHELXTL/PC*.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: PT1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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### *cis*-(±)-1,2,3,6,11,11a-Hexahydro-6-methyl-4*H*-benzo[*b*]quinolizin-4-one

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#### Abstract

In the title compound,  $C_{14}H_{17}NO$ , the methyl substituent and the H atom at the ring junction are *cis* and both occupy pseudo-axial positions. The angles at the N atom sum to  $360^\circ$  indicating that there is no pyramidalization of this atom. Both rings of the quinolizidine moiety are in half-chair conformations.

#### Comment

During our studies on the diastereoselective synthesis of alkaloids containing the benzo[*b*]quinolizidine nucleus, it was found that dihydroisoquinolines of the general