

(±)-3-Ethyl-2-methyl-4-oxocyclohexanecarboxylic acid: catemeric hydrogen bonding in a cyclic δ -keto acid

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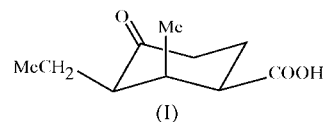
In the title compound, $C_{10}H_{16}O_3$, the two molecules of the asymmetric unit form acid-to-ketone hydrogen-bonded chains. The two species differ only very slightly and are related by a pseudo-center, so that the apparent translational relationship among the units of the hydrogen-bonded chain is actually a pseudo-translation, with the molecules alternating in type. Two counterdirectional pairs of chains proceed through each cell [$O \cdots O = 2.743$ (2) and 2.683 (2) Å, and $O-H \cdots O = 171$ (3) and 157 (3)°]. Three intermolecular $C-H \cdots O$ close contacts were found, involving all three O atoms of one of the molecules.

Comment

Our study of the crystallography of solid ketocarboxylic acids explores the molecular characteristics that control their five known hydrogen-bonding modes. The generality of carboxyl dimerization frequently declines when other functional groups are present, and we have extensively documented this case for keto acids. Specifically, we find that the acid-to-ketone catemer mode becomes dominant whenever centrosymmetry is precluded (chiral non-racemates) and when low conformational flexibility restricts the ability of the acid to find centrosymmetric crystallization modes of suitably low energy. Among the many acid-to-ketone catemers that we have observed, several exist for simple cyclohexanone and cyclopentanone acids (Barcon *et al.*, 1998, 2002; Lalancette & Thompson, 2003). The strong occurrence of catemers in such systems may at first seem surprising because of the perceived conformational flexibility of their rings. However, this flexibility is entirely a solution phenomenon, absent in the solid, and even in solution the set of available conformations is typically quite restricted.

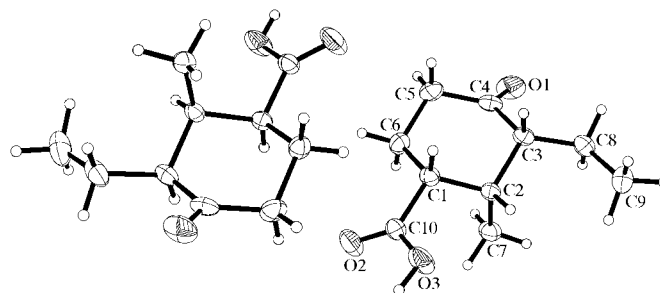
Fig. 1 shows the two molecules of the asymmetric unit of the title compound, (I), designated (IA) and (IB), which differ

only very slightly. The substituents all lie on the same molecular face, so that at least one substituent must be axial in any chair arrangement. The observed conformation for both species, that expected in terms of cyclohexane-based equatorial/axial ΔG° preferences for these groups (Hirsch, 1967), actually has even less strain than those values suggest, since the ketone site lacks an axial H atom. Once the requirement of staggering the substituents on the exocyclic bonds at atoms C2 and C3 is met, just two significant options remain for bond rotation. Of the three staggered conformations about the C3—C8 bond, only two are feasible, since the conformation positioning the C8—C9 bond parallel to C2—C7 is equivalent to a 1,3-diaxial interaction. The conformation actually chosen for both species places atom C9 in an *anti* rather than a *syn* relationship to the ketone C=O bond. The remaining conformational option, carboxyl rotation, has the carboxyl plane coinciding closely with the C1—C6 bond [$O2-C10-C1-C6 = 1.7$ (3)° for (IA) and 0.5 (3)° for (IB)]. The dihedral angle between the ketone (O1/C3—C5) and carboxyl (O2/O3/C10/C1) planes is 47.98 (11) for (IA) and 48.70 (11)° for (IB).



These slight angular variations are typical of the differences between molecules (IA) and (IB); the molecules are superimposable (with an inversion of one of them), with no paired atoms deviating from one another by more than 0.063 Å. The largest variation in torsion angle between (IA) and (IB) is 4.0 (3)° for C4—C3—C8—C9. Because the apparent pseudo-center relating (IA) and (IB) lies at what might be a special position, *viz.* $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$, we attempted solutions with half the *c* cell dimension and $Z = 2$. However, all such trials either resisted solution or led to dramatically worse refinements.

The partial averaging of carboxyl C—O bond lengths and C—C—O angles by disorder, often seen in acids, is unique to the paired hydrogen-bonding mode, whose geometry permits transposition of the two carboxyl O atoms. In non-dimeric acid modes, no significant averaging occurs. For (IA), the C—O bond lengths are 1.198 (2) and 1.327 (2) Å, with C—C—O angles of 125.03 (19) and 112.00 (18)°; for (IB), the lengths are

**Figure 1**

The asymmetric unit for (I), with numbering shown only for the (IA) species. The apparent centrosymmetry is due to a pseudo-center at $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$. Displacement ellipsoids are shown at the 30% probability level.

1.193 (2) and 1.318 (2) Å, with C—C—O angles of 125.39 (18) and 112.01 (16)° (Table 1). Our own survey of 56 keto acid structures that are not acid dimers gives average values of 1.20 (1) and 1.32 (2) Å, and 124.5 (14) and 112.7 (17)°, for these lengths and angles, in accordance with the typical values (1.21 and 1.31 Å, and 123 and 112°) cited for highly ordered dimeric carboxyls (Borthwick, 1980).

Fig. 2 illustrates the packing of the cell and the hydrogen-bonding arrangement, which involves aggregation in the acid-to-ketone catemeric hydrogen-bonding mode. The combination of the true center at $(0, \frac{1}{2}, \frac{1}{2})$ and the pseudo-center presents each molecule with a partner of the opposite type for hydrogen bonding. The result is chains in which (IA) and (IB) alternate, and in which the O...O distances and O—H...O angles differ depending on type (Table 2). Because of the tilt of (IA) and (IB) within the chosen cell, every hydrogen bond involves a partner either one cell away in the (positive) *c* direction and one away (negative) in *a*, or *vice versa*, and thus the chains are also tilted with respect to the chosen cell. Each asymmetric unit generates a counterdirectional pair of hydrogen-bonded chains, and by centrosymmetry about $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, two such pairs of hydrogen-bonded chains proceed through each cell.

The variations in intermolecular connections cited above for (IA) and (IB) are significantly larger than any of their internal differences, and emphasize that the two molecules are significantly different and that no *Z* = 2 solution is possible. Another assessment of the notion of a pseudo-center at $(\frac{1}{2}, \frac{1}{2}, \frac{3}{4})$

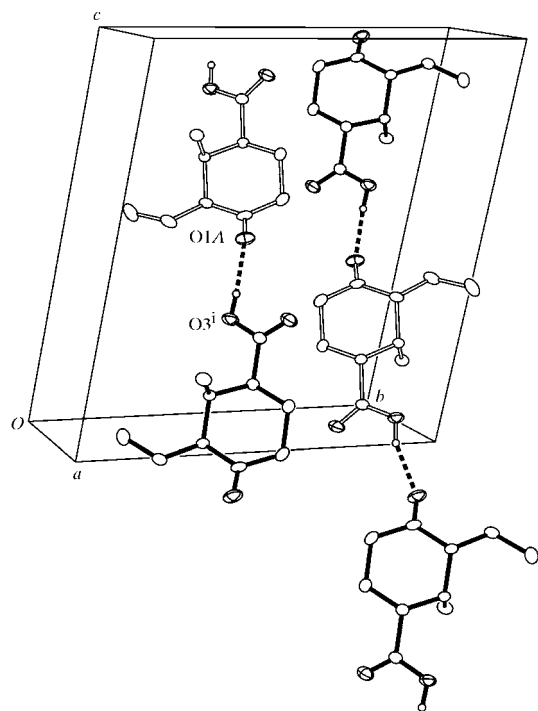


Figure 2
A partial packing diagram with extra molecules, illustrating the two hydrogen-bonded catemers. For clarity, all C-bound H atoms have been omitted and molecules of type (IB) are represented by open bonds. Displacement ellipsoids are shown at the 20% probability level. [Symmetry code: (i) $2 - x, 1 - y, 1 - z$.]

can be achieved by a symmetry-based superposition of the two halves of the asymmetric unit, which shows that the distances for correlated atom pairs range from 0.117 (3) (for O3) to 1.132 (3) Å (for O1). An additional demonstration lies in the measurably different orientations of (IA) and (IB) within the cell; the dihedral angle for the average (non-H atom) plane of (IA) relative to the average plane for all the non-H atoms shown in Fig. 2 is 26.98 (5)°, but this angle is 28.09 (5)° for (IB). This differential tilt of the two species generates markedly different angles for the hydrogen bonding beyond the O...O distances and O—H...O angles noted above.

We characterize the geometry of hydrogen bonding to carbonyls using a combination of the H...O=C angle and the H...O=C—C torsion angle. These parameters describe the approach of the H atom to the O atom in terms of its deviation from, respectively, C=O axuality (ideal = 120°) and planarity with the carbonyl group (ideal = 0°). For hydrogen bonds from (IA) to (IB), the H...O=C and H...O=C—C angles are 142.8 (9) and -70.1 (14)°; for the alternative type, from (IB) to (IA), they are, respectively, 138.0 (9) and -42.4 (14)°.

Three intermolecular C—H...O close contacts exist for the system (see Table 2), involving all three O atoms in (IB) and lying within the 2.7 Å range we normally employ for non-bonded H...O packing interactions (Steiner, 1997). Using compiled data for a large number of C—H...O contacts, Steiner & Desiraju (1998) find significant statistical directionality even as far out as 3.0 Å and conclude that these are legitimately viewed as 'weak hydrogen bonds', with a greater contribution to packing forces than simple van der Waals attractions.

The solid-state (KBr) IR spectrum of (I) has C=O absorptions at 1730 (COOH) and 1691 cm^{-1} (ketone). This peak separation conforms to the shifts seen typically in catemers where hydrogen bonding is absent from the acid C=O but present in the ketone. In CHCl_3 solution, these absorptions converge to a single peak at 1709 cm^{-1} , consistent with a dimerically hydrogen-bonded carboxyl and a normal ketone.

Experimental

A technical grade (described as >60% pure) of 4-carbethoxy-2-ethyl-3-methyl-2-cyclohexen-1-one (2-ethyl-Hagemann's ester) was purchased from Acros Organics/Fisher Scientific, Springfield, NJ, USA. Hydrogenation in 95% ethanol with a 5% Pd/C catalyst led to a concentrated liquid product that was directly saponified without purification. After distillation in a short-path apparatus, the product crystallized on refrigeration. Crystals of (I) suitable for X-ray analysis (m.p. 376 K) were obtained from ethyl acetate.

Crystal data

$\text{C}_{10}\text{H}_{16}\text{O}_3$
 $M_r = 184.23$
 Triclinic, *P*1
 $a = 5.5739$ (12) Å
 $b = 12.814$ (3) Å
 $c = 14.396$ (3) Å
 $\alpha = 80.425$ (14)°
 $\beta = 85.53$ (2)°
 $\gamma = 82.67$ (2)°
 $V = 1003.9$ (4) Å³

$Z = 4$
 $D_x = 1.219$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 36 reflections
 $\theta = 1.7$ – 8.9 °
 $\mu = 0.09$ mm^{-1}
 $T = 296$ (2) K
 Trapezoidal block, colorless
 0.50 × 0.36 × 0.20 mm

Data collection

Siemens P4 diffractometer	$R_{\text{int}} = 0.025$
2 θ/θ scans	$\theta_{\text{max}} = 25.1^\circ$
Absorption correction: numerical (SHELXTL; Sheldrick, 1997b)	$h = -1 \rightarrow 6$
$T_{\text{min}} = 0.962$, $T_{\text{max}} = 0.982$	$k = -15 \rightarrow 15$
4736 measured reflections	$l = -17 \rightarrow 17$
3556 independent reflections	3 standard reflections
2587 reflections with $I > 2\sigma(I)$	every 97 reflections intensity variation: <2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0519P)^2 + 0.3545P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.133$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.20 \text{ e } \text{\AA}^{-3}$
3556 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e } \text{\AA}^{-3}$
244 parameters	Extinction correction: SHELXL97
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.024 (3)

Table 1

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

O2A—C10A	1.198 (2)	O2B—C10B	1.193 (2)
O3A—C10A	1.327 (2)	O3B—C10B	1.318 (2)
O2A—C10A—C1A	125.03 (19)	O2B—C10B—C1B	125.39 (18)
O3A—C10A—C1A	112.00 (18)	O3B—C10B—C1B	112.01 (16)

Table 2

Hydrogen-bonding and close-contact geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O3—H3C \cdots O1A ⁱ	0.87 (3)	1.88 (3)	2.743 (2)	171 (3)
O3A—H3D \cdots O1 ⁱⁱ	0.86 (3)	1.87 (3)	2.683 (2)	157 (3)
C3A—H3A \cdots O1A ⁱⁱⁱ	0.98	2.68	3.567 (3)	151
C5—H5B \cdots O2A ^{iv}	0.97	2.66	3.355 (3)	129
C7A—H73A \cdots O3A ^v	0.96	2.60	3.432 (3)	145

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $-x, 1-y, 2-z$; (iii) $x-1, y, z$; (iv) $1-x, 1-y, 2-z$; (v) $x+1, y, z$.

All H atoms for (I) were found in electron-density difference maps and were refinable ($R = 0.048$ and $wR = 0.136$ for 332 parameters), but C-bound H atoms were placed in calculated positions (0.97 \AA for methylene H atoms, 0.98 \AA for methine H atoms and 0.96 \AA for methyl H atoms) and allowed to refine as riding on their respective C atoms. The $U_{\text{iso}}(\text{H})$ values were fixed at $1.2U_{\text{eq}}(\text{C})$ [$1.5U_{\text{eq}}(\text{C})$ for methyl H atoms]. The hydroxyl H atoms were allowed to refine completely (Table 2).

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: XSCANS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXP97 (Sheldrick, 1997); software used to prepare material for publication: SHELXL97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1484). Services for accessing these data are described at the back of the journal.

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