

(±)-3-Oxocyclopentanecarboxylic acid: the smallest keto acid known to aggregate by catemeric hydrogen bonding

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The title compound, $C_6H_8O_3$, is the smallest keto acid yet found to aggregate in the solid as acid-to-ketone hydrogen-bonded catemers. Four translational chains pass through the cell in the a direction [$O \cdots O = 2.6915(14)$ Å and $O-H \cdots O = 166^\circ$]. Two intermolecular $C-H \cdots O$ close contacts exist, involving both carbonyl functions.

Comment

Our study of crystalline ketocarboxylic acids explores their five known hydrogen-bonding modes. Acid-to-ketone catemers constitute a sizable minority of cases, appearing among a wide variety of keto acids, from polycyclic C_{30} non-racemates to far smaller racemic compounds. Of interest are the minimum requirements for catemeric aggregation, but the smallest molecules offer experimental problems (*e.g.* low crystallinity and little structural variability), and among C_3 – C_6 keto acids, only the crystal structure of pyruvic acid has been reported to date, as a carboxyl dimer (Harata *et al.*, 1977). We now report the structure of the title six-carbon γ -keto acid, (I). To date, this is the smallest crystalline keto acid found to aggregate as a catemer.

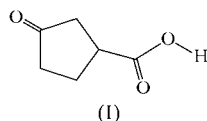


Fig. 1 shows the molecule of (I). The ring conformation is not a typical 'folded-envelope' cyclopentane. Rather, it is a twist conformation, in which only atom C3 lies in the average ring-plane [deviation for C3 = $-0.0083(9)$ Å]. The adjoining atoms (C2 and C4) lie nearly equidistant from the average plane on alternate faces [$-0.1235(8)$ and $0.1381(9)$ Å, respectively], as do the remaining two atoms (C1 and C5), but in the opposite sense [$0.2147(9)$ and $-0.2211(9)$ Å, respec-

tively]. This arrangement avoids eclipsing among all the ring substituents. The carboxyl group projects outward, with a $C6-C1-C2-C3$ torsion angle of $-153.28(11)^\circ$, and its rotation about $C1-C6$ places its carbonyl group on the same face of the average plane as atom C5 and nearly eclipsed with it, so that the $C5-C1-C6-O2$ torsion angle is $6.8(2)^\circ$.

The averaging of C–O bond lengths and C–C–O angles by disorder often observed in dimeric carboxyls typically results from tautomerism within the symmetrical eight-membered dimer structure. This is not observed in catemers, whose geometry cannot support this averaging mechanism. Hence in (I), which is catemeric, these values (Table 1) are typical of those in highly ordered dimeric carboxyls (Borthwick, 1980).

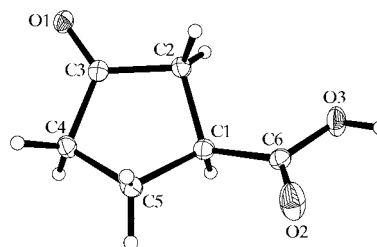


Figure 1

A view of the asymmetric unit of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

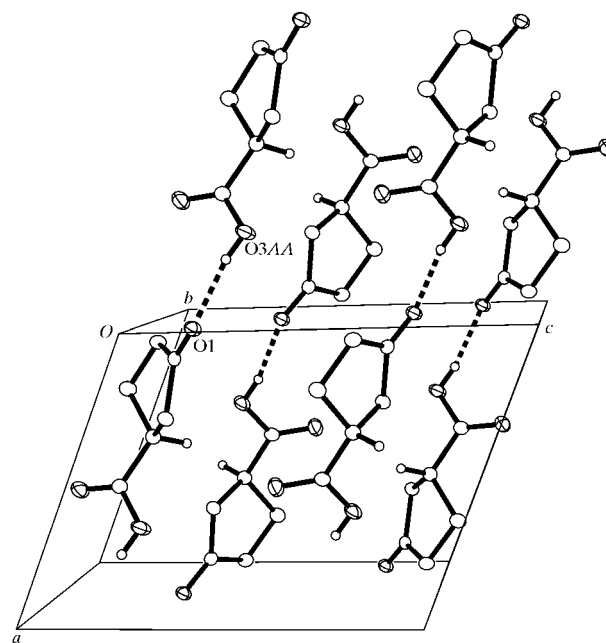


Figure 2

A packing diagram for (I), showing the four catemeric connections created by acid-to-ketone hydrogen bonds (dashed lines) proceeding along chains of molecules translationally related in a . All methylene H atoms have been omitted for clarity. The O atoms involved in the hydrogen bonding are labelled in one of the chains; atom O3AA is at the symmetry position ($x - 1, y, z$). Displacement ellipsoids are drawn at the 40% probability level.

Fig. 2 illustrates the packing of (I) ($Z = 4$), in which the centrosymmetric array about $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, combined with the formation of translational catemers, yields four separate hydrogen-bonded chains, all passing through the cell in the a and $-a$ directions. These chains display the four permutations of molecular chirality plus chain direction; proceeding along c from the origin, these combinations are encountered in the order $S + a$, $S - a$, $R + a$ and $R - a$.

A combination of the $\text{C}=\text{O} \cdots \text{H}$ angle and the $\text{C}=\text{O} \cdots \text{H}$ torsion angle characterizes the geometry of hydrogen bonding to carbonyl groups. These describe the approach of the acid H atom to the O-atom receptor in terms of its deviation from, respectively, $\text{C}=\text{O}$ axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). In (I), these two angles are 128 and -21° , respectively. Two close $\text{C}-\text{H} \cdots \text{O}$ non-bonded intermolecular contacts exist (Table 2), whose $\text{H} \cdots \text{O}$ distances fall within the range we survey as standard for such polar packing interactions.

As previously seen (Thompson *et al.*, 1999), among the minimum molecular requirements for the formation of translational catemers, a 'linear-anti' arrangement of ketone and carboxyl, as found in (I), is clearly important. When such arrangements are not forced by inflexible molecular geometry (Lalancette *et al.*, 1997), they may be facilitated when alternative conformations are precluded sterically or discouraged energetically (Lalancette & Thompson, 2003), as also occurs in (I).

Experimental

Compound (I) was prepared by conjugate addition of malonic ester to diethyl itaconate (Hope, 1912; Kay & Perkin, 1906). After hydrolysis and decarboxylation, the sublimed material gave crystals suitable for X-ray analysis from EtOAc-hexane (m.p. 335 K). Because of the similar but opposite shifts produced by ketone ring-strain and by hydrogen bonding, solid-state *versus* liquid IR spectra of carboxycyclopentanones are typically ambiguous regarding hydrogen bonding in the crystal. The solid-state (KBr) spectrum of (I) has $\text{C}=\text{O}$ stretching absorptions at 1734 (acid) and 1713 cm^{-1} (ketone), consistent with known shifts produced when hydrogen bonding is, respectively, removed from a carboxyl $\text{C}=\text{O}$ and added to a ketone. These bands appear in CHCl_3 solution, but presumably reversed, at 1743 and 1712 cm^{-1} .

Crystal data

$\text{C}_6\text{H}_8\text{O}_3$	$Z = 4$
$M_r = 128.12$	$D_x = 1.443\text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	$\text{Cu K}\alpha$ radiation
$a = 7.8564(8)\text{ \AA}$	$\mu = 0.99\text{ mm}^{-1}$
$b = 7.9812(8)\text{ \AA}$	$T = 100(2)\text{ K}$
$c = 10.1367(10)\text{ \AA}$	Block, colourless
$\beta = 111.862(5)^\circ$	$0.32 \times 0.19 \times 0.13\text{ mm}$
$V = 589.90(10)\text{ \AA}^3$	

Data collection

Bruker SMART APEXII CCD	4895 measured reflections
area-detector diffractometer	1027 independent reflections
φ and ω scans	985 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{\text{int}} = 0.019$
(SADABS; Sheldrick, 2001)	$\theta_{\text{max}} = 67.9^\circ$
$T_{\text{min}} = 0.871$, $T_{\text{max}} = 0.926$	
(expected range = $0.827\text{--}0.879$)	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2 + 0.3094P]$
$R[F^2 > 2\sigma(F^2)] = 0.037$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.093$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.12$	$\Delta\rho_{\text{max}} = 0.23\text{ e \AA}^{-3}$
1027 reflections	$\Delta\rho_{\text{min}} = -0.22\text{ e \AA}^{-3}$
83 parameters	
H-atom parameters constrained	

Table 1

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

O2—C6	1.1983 (18)	O3—C6	1.3330 (17)
O2—C6—C1	125.30 (13)	O3—C6—C1	111.98 (11)

Table 2

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

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O3—H3 \cdots O1 ⁱ	0.84	1.87	2.6915 (14)	166
C4—H4A \cdots O1 ⁱⁱ	0.99	2.57	3.5239 (17)	162
C2—H2A \cdots O2 ⁱⁱⁱ	0.99	2.52	3.4800 (18)	164

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

All H atoms were located in electron-density difference maps. The O-bound H atom was constrained to its idealized position, with the O—H distance fixed at 0.84 \AA and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$. The methylene and methine H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C—H distances of 0.99 and 1.00 \AA , respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3038). Services for accessing these data are described at the back of the journal.

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