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(±)-*cis*-2-Methyl-4-oxocyclohexanecarboxylic acid: catemeric hydrogen bonding in a *δ*-keto acid derived from Hagemann's ester

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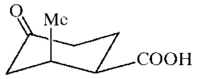
The title compound, $C_8H_{12}O_3$, crystallizes as acid-to-ketone hydrogen-bonding catemers, in which hydrogen bonds progress from the carboxyl group of each molecule to the ketone group of a translationally related neighbor [O···O = 2.738 (3) Å and O—H···O = 153 (4)°]. Four separate hydrogen-bonding chains proceed through the cell in centrosymmetrically related pairs along axes lying in the *ab* plane. Three intermolecular C—H···O close contacts exist involving both carboxyl O atoms. Factors contributing to the choice of hydrogen-bonding mode are discussed.

Comment

Our study of the crystallography of keto-carboxylic acids explores the molecular characteristics that control their five known hydrogen-bonding modes. Beyond the dimeric and catemeric (chain) modes seen in simple acids, the presence of an additional receptor in the system leads to another three observed hydrogen-bonding modes involving the ketone group. The title compound, (I), crystallizes with acid-to-ketone catemeric hydrogen bonding. We have previously shown that this pattern, overall the second most commonly encountered, becomes predominant wherever centrosymmetry is precluded (Thompson & Lalancette, 2003) or rendered difficult. Among the latter cases are those like (I) where molecular flexibility is severely restricted (Barcon *et al.*, 2002). When this occurs, the acid is often unable to find a dimeric crystallization mode of suitably low potential energy *vis-à-vis* alternative packing modes, and catemeric hydrogen-bonding results. We have studied several examples of simple cyclohexane and cyclopentane keto acids in which such low degrees of conformational flexibility are found to lead to acid-to-ketone catemers.

Fig. 1 shows the asymmetric unit for compound (I). In either chair conformation for (I), one of the two *cis*-related substituents must be axial. The steric requirements of the sp^3 methyl group are normally significantly greater than for the sp^2 carboxyl group (Hirsch, 1967). However, in the present case, an axial methyl group encounters only a single 1,3-diaxial interaction (at C6) because of the presence of the C4 ketone, while an axial carboxyl has interactions at both C3 and C5. The result is that, in (I), the methyl group is the less sterically demanding, and therefore the preferred, axial substituent. Once these demands (and the need to stagger the methyl H atoms) have been met, the resulting conformer is quite rigid, in contrast to the dynamic situation in solution. The only remaining conformational option is rotation of the carboxyl unit about C1—C7. In (I), this group is turned so that the C1—C6 bond coincides with the carboxyl plane [torsion angle O2—C7—C1—C6 = −0.5 (4)°]. The dihedral angle for the ketone (O1/C3/C4/C5) *versus* the carboxyl (O2/O3/C7/C1) groups is 46.7 (2)°.



(I)

The partial averaging of C—O bond lengths and C—C—O angles by disorder often seen in acids is unique to the carboxyl-pairing hydrogen-bonding mode, whose geometry permits transposition of the two carboxyl O atoms. With catemers and other non-dimeric acid modes, no significant averaging is observed. For (I), the C—O bond lengths are 1.194 (3) and 1.332 (4) Å, with C—C—O angles of 126.1 (3) and 111.9 (3)°. Our own survey of 56 keto acid structures which are not acid dimers gives average values of 1.200 (10) and 1.32 (2) Å, and 124.5 (14) and 112.7 (17)° for these lengths and angles, in accord with typical values of 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. There are no hydrogen-bonding connections among any of the four molecules within the chosen cell. Rather, each is part of one of four separate translational hydrogen-bonding chains proceeding through the cell along axes lying in the *ab* plane [O···O = 2.738 (3) Å and O—H···O = 153 (4)°]. Because of the centrosymmetry of the cell, the chains are counterdirectionally paired. Those at the ends of the chosen cell advance by one cell each, either positively or negatively, in both *a* and *b*. The remaining mol-

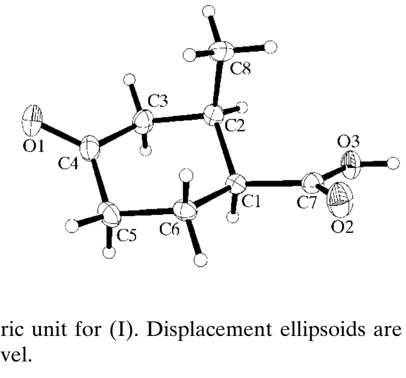


Figure 1
The asymmetric unit for (I). Displacement ellipsoids are set at the 20% probability level.

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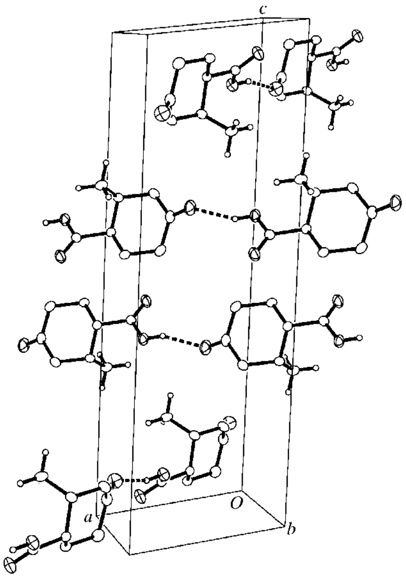

Figure 2
A packing diagram, with extracellular molecules included to illustrate the four hydrogen-bonding catemers. For clarity, all carbon-bound H atoms, except for the methyl H atoms, have been removed. Displacement ellipsoids are set at the 20% probability level.

ecules are glide-related to those at the cell ends, and their chains proceed either by one cell positively in *a* and one negatively in *b* or *vice versa*.

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 describe the approach of the H atom to the O atom in terms of its deviation from, respectively, C═O axiality (ideal = 120°) and planarity with the carbonyl group (ideal = 0°). In (I), these angles are H···O═C = 138.0 (11)° and H···O═C—C = −52.2 (2)°. The latter angle represents hydrogen bonding markedly out of the plane of the ketone carbonyl and would appear to be far from 'ideal'.

Three intermolecular C—H···O close contacts were found for the carboxylic acid O atoms [O2···H5*A* (2.58 Å) to a molecule translationally related in *a*, and O3···H6*B* (2.65 Å) and O3···H8*B* (2.6 Å), both to the same neighbor translationally related in *b*]. These distances all lie within the 2.7 Å range we employ for non-bonded C—H···O packing interactions (Steiner, 1997). Using compiled data for a large number of such 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 1732 (COOH) and 1693 cm^{-1} (ketone). This peak separation conforms to the shifts seen typically in catemers, due, respectively, to removal of hydrogen bonding from the acid C═O group and addition of hydrogen bonding to the ketone group. In $CHCl_3$ solution, these absorptions are seen, probably reversed, at 1710 and 1705 cm^{-1}, consistent with a dimerically hydrogen-bonded carboxyl and a normal ketone group.

Experimental

A commercially available technical (90% pure) grade of Hagemann's ester (4-carbethoxy-3-methyl-2-cyclohexen-1-one) was hydrogenated in 95% ethanol with a 5% Pd/C catalyst, and the concentrated liquid product was directly saponified without purification. After passage through a short column of Al_2O_3 and distillation in a short-path cold-finger apparatus, the product crystallized upon refrigeration. Crystals suitable for X-ray analysis (m.p. 333 K) were obtained from hexane/diethyl ether. An attempt to produce the *trans*-epimer by base-catalyzed equilibration of the ketal ester led to an approximately 4:1 epimer mixture, which showed no inclination to crystallize.

Crystal data

$C_8H_{12}O_3$
$M_r = 156.18$
Monoclinic, $P2_1/n$
$a = 6.7540$ (10) Å
$b = 5.7250$ (10) Å
$c = 21.078$ (4) Å
$\beta = 97.46$ (2)°
$V = 808.1$ (2) Å^3
$Z = 4$
$D_x = 1.284$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 37 reflections
$\theta = 3.3$–11.4°
$\mu = 0.10$ mm^{-1}
$T = 296$ (2) K
Parallelepiped, colourless
0.50 × 0.20 × 0.04 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{\min} = 0.976$, $T_{\max} = 0.996$
2174 measured reflections
1415 independent reflections
910 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 6$
$l = -25 \rightarrow 25$
3 standard reflections every 97 reflections intensity variation: <1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.172$
$S = 1.05$
1415 reflections
104 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.076P)^2 + 0.2612P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.24$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—C7	1.194 (3)	O3—C7	1.332 (4)
O2—C7—C1	126.1 (3)	O3—C7—C1	111.9 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1$^{\rm i}$	0.84 (4)	1.96 (4)	2.738 (3)	153 (4)

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

All H atoms were found in electron-density difference maps. The carbon-bound H atoms were placed in calculated positions (0.97 Å for methylene, 0.98 Å for methine, and 0.96 Å for methyl H atoms) and allowed to refine as riding models on their parent atoms; their isotropic displacement parameters were fixed at 120% of the anisotropic displacement parameters of their parent atoms for methine and methylene H atoms, and 150% for methyl H atoms. The hydroxyl H atom was allowed to vary positionally, and its displacement parameter was fixed at 0.08 Å^2.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 in *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 in *SHELXTL*; molecular graphics: *SHELXP*97 in *SHELXTL*; software used to prepare material for publication: *SHELXL*97 in *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1436). Services for accessing these data are described at the back of the journal.

References

Barcon, A., Brunskill, A. P. J., Lalancette, R. A. & Thompson, H. W. (2002). *Acta Cryst.* C**58**, o154–o156.

Borthwick, P. W. (1980). *Acta Cryst.* B**36**, 628–632.

Hirsch, J. A. (1967). *Topics in Stereochemistry*, Vol. 1, edited by N. L. Allinger & E. L. Eliel, pp. 204–208. New York: Wiley Interscience.

Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.

Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Steiner, T. (1997). *Chem. Commun.* pp. 727–734.

Steiner, T. & Desiraju, G. R. (1998). *Chem. Commun.* pp. 891–892.

Thompson, H. W. & Lalancette, R. A. (2003). *Acta Cryst.* C**59**, o580–o582.