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4-Oxocyclohexanecarboxylic acid: hydrogen bonding in the monohydrate of a δ-keto acid

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The title monohydrate, $C_7H_{10}O_3 \cdot H_2O$, aggregates as a complex hydrogen-bonding network, in which the water molecule accepts a hydrogen bond from the carboxyl group of one molecule and donates hydrogen bonds to ketone and carboxyl C=O functions in two additional molecules, yielding a sheet-like structure of parallel ribbons. The keto acid adopts a chiral conformation through rotation of the carboxyl group by 62.50 (15)° relative to the plane defined by its point of attachment and the ketone C and O atoms. Two C—H⋯O close contacts exist in the structure.

Comment

Our studies of the crystallography of ketocarboxylic acids explore the molecular characteristics that control their hydrogen bonding. Beyond their five known hydrogen-bonding modes, keto acids sometimes occur as hydrates, with complex hydrogen-bonding patterns that typically involve both ketone and acid carbonyl groups. The title compound crystallizes as a monohydrate, (I), with such a pattern of hydrogen bonding. Although hydrate examples are known in which the ketone function is as far as 12 atoms away from the carboxyl group, most known hydrates are either γ- or, like the present case, δ-keto acids.

(I)

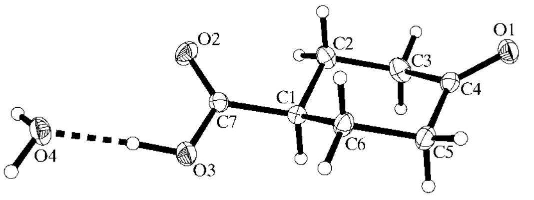

Figure 1
The asymmetric unit of (I); the water of hydration is shown, arbitrarily, in its relation to the carboxyl OH group. Displacement ellipsoids are shown at the 20% probability level.

Fig. 1 shows the asymmetric unit of (I). Although the organic portion lacks inherent chirality, it adopts a chiral conformation through rotation of its carboxyl unit about the C1—C7 bond, the only conformational option available. This group is turned so that the C1—C2 bond coincides with the carboxyl plane [O2—C7—C1—C2 = 2.0 (4)°]. The dihedral angle between the ketone (O1/C3–C5) and carboxyl (O2/O3/C7/C1) planes is 48.91 (13)°. The water molecule, which donates hydrogen bonds to atoms O1 and O2 in separate molecules, is shown here in its relationship to atom O3, from which it accepts a hydrogen bond.

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. As in other hydrates that involve the acid, no significant averaging is observed for (I), whose bond lengths are 1.206 (3) and 1.326 (3) Å, with angles of 124.5 (2) and 113.4 (2)° (Table 1). Our own survey of 56 keto acid structures that 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 accordance 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 in the cell and the hydrogen-bonding network (Table 2). The latter does not incorporate

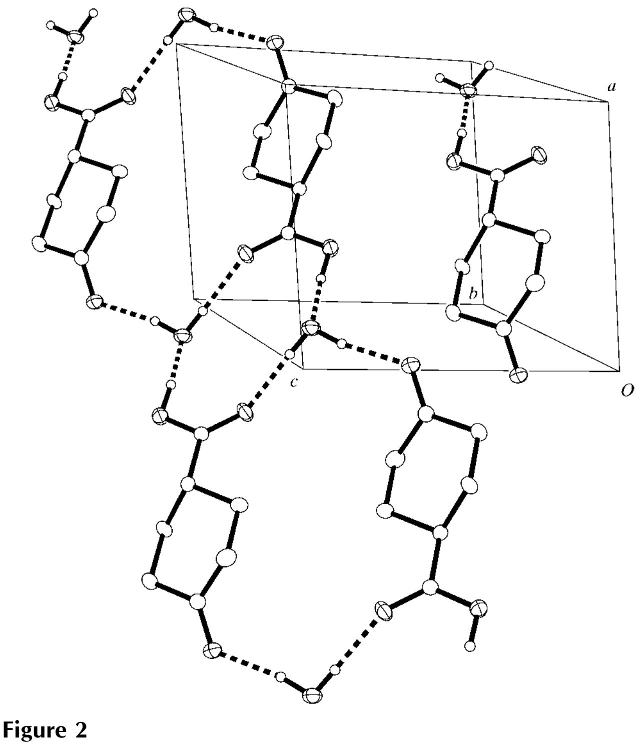

Figure 2
A packing diagram, with the cell contents and extra molecules; several water molecules have been included in order to clarify the hydrogen bonding. For clarity, all C-bound H atoms have been omitted. Displacement ellipsoids are shown at the 20% probability level.

any water-to-water hydrogen bonds (*cf.* Brunskill *et al.*, 2001); however, in an arrangement identical in its essentials to at least two previously reported cases (Lalancette *et al.*, 1990, 1997), the water molecule accepts a hydrogen bond from the carboxyl group of one molecule and donates hydrogen bonds to ketone and acid C═O functions in two separate molecules. This produces three-bond intermolecular connections of both the acid-to-water-to-acid and the acid-to-water-to-ketone type, plus a four-bond acid-to-water-to-ketone connection, all of which lie in a two-dimensional sheet of separate, parallel, ribbon-like structures. This structure may be contrasted with instances bearing exactly the same types of connections, which produce structures that are three-dimensional rather than lamellar (Thompson & Lalancette, 2001; Lalancette *et al.*, 2002).

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), the H···O═C and H···O═C—C angles are 145.2 (10) and 85.0 (16)° for the water-to-acid hydrogen bond, and 122.7 (9) and 8.5 (11)° for the water-to-ketone hydrogen bond. In particular, the 85.0° value departs dramatically from the supposed 'ideal' value of 0°. The O···O distances in this hydrogen-bonding network all lie within normal parameters, between 2.606 (3) and 2.797 (3) Å.

Intermolecular C—H···O close contacts were found for the acid carbonyl (2.56 Å to atom H6*B* in a centrosymmetrically related molecule) and for the water molecule (2.69 Å to atom H2*B* in a molecule translationally related along *b*). These distances lie within the 2.7 Å range that we employ as standard 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 away 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 the hydrate (I) displays a single broadened C═O absorption at 1702 cm^{-1} for both the acid and the ketone. In CHCl$_3$ solution, where dimers predominate, a single absorption is centered at 1711 cm^{-1}.

Experimental

Compound (I) was synthesized by catalytic hydrogenation of an ethanol solution of *p*-hydroxybenzoic acid over a rhodium catalyst; Jones oxidation of the resulting oil yielded crystalline material. Crystals of the monohydrate (I) suitable for X-ray diffraction (m.p. 336 K) were obtained from diethyl ether/hexane mixtures. The anhydrous form has also been reported (Perkin, 1904; Hardegger *et al.*, 1944; Applequist & Klieman, 1961), although its melting point (341 K) is so close to that of (I) that in some reports one cannot tell which form was present. Combustion analyses of the anhydrate seem always to err on the low-carbon side, suggesting, as we have found, that this material hydrates easily.

Crystal data

$C_7H_{10}O_3 \cdot H_2O$
$M_r = 160.17$
Triclinic, $P\overline{1}$
$a = 6.7298\ (8)$ Å
$b = 7.2091\ (11)$ Å
$c = 8.4367\ (12)$ Å
$\alpha = 85.928\ (13)^\circ$
$\beta = 83.075\ (17)^\circ$
$\gamma = 82.132\ (16)^\circ$
$V = 401.88\ (10)$ Å^3
$Z = 2$
$D_x = 1.324$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 reflections
$\theta = 3.8$–9.9°
$\mu = 0.11$ mm^{-1}
$T = 243\ (2)$ K
Flat plate, colorless
0.45 × 0.45 × 0.02 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
1798 measured reflections
1405 independent reflections
920 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 25.0^\circ$
$h = -7 \rightarrow 1$
$k = -8 \rightarrow 8$
$l = -10 \rightarrow 10$
3 standard reflections
every 97 reflections
intensity variation: <1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.105$
$S = 1.03$
1405 reflections
121 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2 + 0.0971P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.15$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.14$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—C7	1.206 (3)	O3—C7	1.326 (3)
O2—C7—C1	124.5 (2)	O3—C7—C1	113.4 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O4	0.97 (4)	1.64 (4)	2.606 (3)	172 (3)
O4—H41···O1$^{\rm i}$	0.91 (3)	1.90 (3)	2.797 (3)	171 (3)
O4—H42···O2$^{\rm ii}$	0.87 (4)	1.93 (4)	2.795 (3)	178 (3)

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

All H atoms were found in electron-density difference maps. C-bound H atoms were placed in calculated positions (C—H = 0.98 Å for methylene H atoms and 0.99 Å for methine H atoms) and allowed to refine as riding on their respective C atoms; their displacement parameters were allowed to refine. The hydroxy and water H atoms were not constrained positionally and their displacement parameters were allowed to refine.

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1456). Services for accessing these data are described at the back of the journal.

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