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7-Oxobicyclo[2.2.1]heptane-1-carboxylic acid and (±)-7-oxobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid: hydrogen bonding in two norbornyl keto acids

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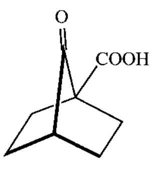
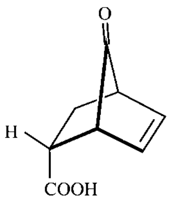
Molecules of the title β-keto acid, 7-oxobicyclo[2.2.1]heptane-1-carboxylic acid, $C_8H_{10}O_3$, exhibit chirality due to the bridgehead carboxyl group, which is partially ordered and has a slightly asymmetric conformation. The molecules form centrosymmetric hydrogen-bonded carboxyl dimers [O$\cdots$O 2.639 (2) Å]. The title alkenoic γ-keto acid, (±)-7-oxobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid, $C_8H_8O_3$, also forms typical centrosymmetric hydrogen-bonded carboxyl dimers [O$\cdots$O 2.660 (3) Å]. There is partial disorder of the carboxyl group in each compound.

Comment

Our continuing interest in the crystallography of keto acids lies in mapping the molecular characteristics that control their five known hydrogen-bonding modes. Among several small cyclic systems we have investigated, carboxy bicyclo[2.2.1]-heptanones stand out as producing significant proportions of catemeric acid-to-ketone hydrogen bonding (Lalancette *et al.*, 1997). We present here the crystal structures of two further compounds in this series, a β-keto acid, 7-oxobicyclo[2.2.1]-heptane-1-carboxylic acid, (I), and a γ-keto acid,(±)-7-oxobicyclo[2.2.1]hept-5-ene-2-*endo*-carboxylic acid, (II).



(I)



(II)

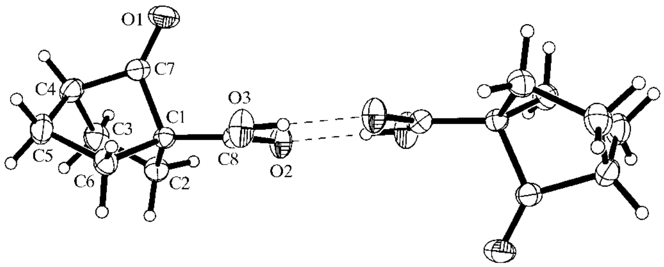


Figure 1
A centrosymmetric hydrogen-bonded dimer composed of two asymmetric units of (I), shown with the atom-numbering scheme. Only the major (68%) contributor to the disordered carboxyl group is shown. Ellipsoids are set at the 20% probability level and H atoms are shown as spheres of arbitrary radii.

Although their geometry appears favorable for internal hydrogen bonding, the few β-keto acids whose X-ray structures have been determined display scant tendency toward that hydrogen-bonding mode (Thompson *et al.*, 1996), opting instead for catemeric (Lalancette *et al.*, 1991) or dimeric aggregation (Lalancette *et al.*, 1999). Among simple keto acids, internal hydrogen bonding is better served by seven-membered geometry, and, indeed, occurs most often among γ-keto acids. Fig. 1, showing a pair of molecules of (I) hydrogen-bonded together as a centrosymmetric dimer, reveals that (I) is not internally but dimerically hydrogen bonded. Although the homologous 9-oxobicyclo[3.3.1]nonane-1-carboxylic acid (Thompson *et al.*, 1992) possesses a plane of symmetry, (I) is found to have conformational chirality, even though the molecule is not inherently chiral. A major source of this asymmetry in (I) is the partial order in the carboxyl group. Some averaging of carboxyl bond lengths and angles by disorder is common in acid dimers (Leiserowitz, 1976), and the C═O and C—O bond lengths in (I) are 1.233 (2) and 1.284 (2) Å, respectively, with angles of 121.0 (2) and 116.4 (2)° for C—C═O and C—C—O, respectively. Values cited as typical for highly ordered dimeric carboxyls are 1.21 and 1.31 Å, and 123 and 112°, respectively (Borthwick, 1980). Consistent with this, partial carboxyl H atoms were found in electron density difference maps and were refined to an occupancy ratio of 0.68 (4):0.32(4) for H atoms bonded to O3 and O2, respectively. The carboxyl group is also rotated very slightly from orthogonality relative to the ketone plane. This departure of the carboxyl group from the 'symmetric' arrangement is indicated by the C1—C7—C4 *versus* O2—C8—O3 dihedral angle of 87.2 (2)° and by a C7—C1—C8—O2 torsion angle of −91.8 (2)°. Additional chirality is imparted by a very slight twist of the bicycloheptane system: torsion angle C1—C2—C3—C4 is −1.3 (2)°, while angle C1—C6—C5—C4 is −1.1 (2)°. The packing for (I) involves typical centrosymmetric dimers centered at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), with a second screw-related set centered on the *a* edge of the chosen cell; the O$\cdots$O distance is 2.639 (2) Å.

Fig. 2 shows a pair of molecules for (II), hydrogen-bonded together as a centrosymmetric dimer. Despite the rigidity of the system, eclipsing strains around C2—C3 are relieved by a significant twist of that bridge, producing a C8—C2—C3—C4 torsion angle of 128.3 (2)° (ideal value 120°). The carboxyl

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group is rotated as shown [O2—C8—C2—C3 46.1 (3)°] and displays significant disorder. The C═O and C—O bond lengths in (II) are 1.245 (3) and 1.273 (3) Å, respectively, with angles of 119.1 (2) and 117.8 (2)° for C—C═O and C—C—O, respectively. The partial H atoms found for (II) in difference maps were refined to an occupancy ratio of 0.65 (5):0.35(5) for H atoms bonded to O3 and O2, respectively.

Compound (II) belongs to the category of γ-keto acids which is especially rich in hydrogen-bonding types, embracing dimers, internal hydrogen bonds and carboxyl-to-ketone catemers. The 'linearly aligned *anti*' arrangement seen here for the ketone and acid groups is one which often leads to translational catemers in other systems (Barcon *et al.*, 1998; Zewge *et al.*, 1998). Nevertheless, in (II) the result is again a packing typical for centrosymmetric dimerization, with an O···O distance of 2.660 (3) Å. Parallel screw-related sets of dimers are centered at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and the *a* edge of the chosen cell, while a second parallel screw-related set, oriented at an angle and screw-related to the first, is centered on the *c* cell edge.

For both (I) and (II) several close intermolecular C—H···O contacts (2.65–2.71 Å; Tables 2 and 4) were found within the range often used as the 'van der Waals limit' (Steiner, 1997) for non-bonded H···O packing interactions. Steiner & Desiraju (1998) have compiled data for a large number of C—H···O contacts and found significant statistical directionality even at cutoff distances as great as 3.0 Å, leading to the conclusion that these may be legitimately viewed as 'weak hydrogen bonds', presumably contributing significantly more to packing forces than simple van der Waals attractions. Comparison of our distances and angles (Tables 2 and 4) with such data for other Csp^3—H···O═C cases suggests that these interactions are important in the packing of (I) and (II).

Part of the reluctance of (I) and (II) to adopt hydrogen-bonding modes involving the ketone may be attributable to lowered ketone basicity due to angle strain. Carbonyl basicity has been shown to correlate positively with ring size for the seven-, six-, five- and four-membered simple cycloalkanones, whose pK_a values (for the protonated species) are −6.6, −6.8, −7.5 and −9.5, respectively (Campbell & Edwards, 1960; Butler, 1976). The ketone angles for these cycloalkanones are cited as 121, 116, 101 and 82°, respectively (Avram & Mateescu, 1972), and the observed bridge angles in (I) and (II) are 98.3 (2) and 97.1 (2)°, respectively. The above trend in basicity also appears generally consistent with hydrogen-bonding solvent shifts for the $n \rightarrow \pi^*$ absorptions of these same cycloalkanones (Wheeler, 1957; Lambert *et al.*, 1998), which are related to charge distribution in the ground *versus* excited states (Pimentel, 1957; Jaffé & Orchin, 1962). Since ring strain directly affects IR C═O stretching frequencies (see below), these are also correlatable with pK_a, as has been shown for an homologous series of lactams (Huisgen *et al.*, 1954), and basicity has been directly related to $\nu_{C=O}$ even for non-cyclic cases (Stewart & Yates, 1958).

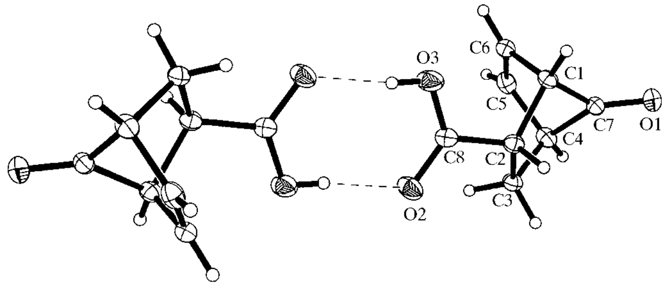

Figure 2
A centrosymmetric hydrogen-bonded dimer composed of two asymmetric units of (II), shown with the atom-numbering scheme. Only the major (65%) contributor to the disordered carboxyl group is shown. Ellipsoids are set at the 20% probability level and H atoms are shown as spheres of arbitrary radii.

The solid-state (KBr) IR spectrum of (I) has C═O absorption peaks at 1772 and 1693 cm^{-1}, for free ketone and hydrogen-bonded carboxyl, respectively. In $CHCl_3$ solution the same absorptions are seen at 1776 and 1704 cm^{-1}, with the usual carboxyl-dilution shoulder around 1735–1740 cm^{-1}. Compound (II) gives similar data, the values being 1771 and 1691 cm^{-1} for KBr, and 1781 and 1710 cm^{-1} for $CHCl_3$.

Experimental

Compound (I) was synthesized according to the method of Hatchard & Schneider (1957) and purified by sublimation. Recrystallization from either benzene or EtOAc/cyclohexane gave crystals suitable for X-ray analysis (m.p. 433 K). Compound (II) was prepared by hydrolysis of the corresponding dimethyl ketal, synthesized as described by Thompson *et al.* (1985). The crystals used in this work (m.p. 376 K) were obtained from Et_2O/hexane.

Compound (I)

Crystal data

$C_8H_{10}O_3$
$M_r = 154.16$
Monoclinic, $P2_1/c$
$a = 6.3714$ (9) Å
$b = 10.560$ (2) Å
$c = 11.610$ (3) Å
$\beta = 98.616$ (14)°
$V = 772.3$ (3) Å^3
$Z = 4$

$D_x = 1.326$ Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 22 reflections
$\theta = 2.60$–17.46°
$\mu = 0.101$ mm^{-1}
$T = 293$ (2) K
Block, colorless
0.64 × 0.48 × 0.28 mm

Table 1
Selected geometric parameters (Å, °) for (I).

O2—C8	1.233 (2)	O3—C8	1.284 (2)
O2—C8—C1	121.0 (2)	O3—C8—C1	116.4 (2)

Table 2
Close-contact and hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6B···O1^{i}	0.97	2.65	3.362 (3)	130
C4—H4A···O2^{ii}	0.98	2.65	3.369 (3)	131
O3—H3···O2^{iii}	0.82	1.82	2.639 (2)	173

Symmetry codes: (i) $x, \frac{3}{2}-y, \frac{1}{2}+z$; (ii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $1-x, 1-y, 1-z$.

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{\min} = 0.96$, $T_{\max} = 0.97$
1957 measured reflections
1362 independent reflections
960 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\max} = 25°$
$h = -7 \rightarrow 1$
$k = -1 \rightarrow 12$
$l = -13 \rightarrow 13$
3 standard reflections every 97 reflections intensity variation: <1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.117$
$S = 1.05$
1362 reflections
103 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 0.2509P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.14$ e Å^{-3}

Compound (II)

Crystal data

$C_8H_8O_3$
$M_r = 152.14$
Orthorhombic, *Pbca*
$a = 6.0039$ (9) Å
$b = 10.5565$ (14) Å
$c = 22.151$ (2) Å
$V = 1403.9$ (3) Å^3
$Z = 8$
$D_x = 1.440$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 11.36$–$14.91°$
$\mu = 0.111$ mm^{-1}
$T = 293$ (2) K
Parallelepiped, colorless
0.50 × 0.50 × 0.35 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
1719 measured reflections
1231 independent reflections
827 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$
$\theta_{\max} = 25°$
$h = -7 \rightarrow 1$
$k = -1 \rightarrow 12$
$l = -1 \rightarrow 26$
3 standard reflections every 97 reflections intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.136$
$S = 1.03$
1231 reflections
104 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0578P)^2 + 0.5877P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.20$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.006 (2)

For both (I) and (II), all non-carboxyl H atoms were found in electron density difference maps but replaced in calculated positions and allowed to refine as riding models with isotropic displacement parameters set at 120% of their respective C atoms. For both (I) and (II), the disordered pair of carboxyl H atoms was also found in electron-density difference maps and allowed to refine in idealized positions, with isotropic displacement parameters set at 150% of their respective O atoms; their occupancies were allowed to refine [values 0.68 (4)/0.32 (4) for (I), 0.65 (5)/0.35 (5) for (II)].

For both compounds, data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Table 3
Selected geometric parameters (Å, °) for (II).

O2—C8	1.245 (3)	O3—C8	1.273 (3)
O2—C8—C2	119.1 (2)	O3—C8—C2	117.8 (2)

Table 4
Close-contact and hydrogen-bonding geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O2$^{\rm i}$	0.98	2.68	3.339 (3)	125
C3—H3B···O1$^{\rm ii}$	0.97	2.71	3.580 (4)	149
O3—H3···O2$^{\rm iii}$	0.82	1.84	2.660 (3)	173

Symmetry codes: (i) $1 + x, y, z$; (ii) $\frac{3}{2} - x, \frac{1}{2} + y, z$; (iii) $1 - x, 1 - y, 1 - z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1572). Services for accessing these data are described at the back of the journal.

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