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# 5-Oxocyclooctanecarboxylic acid: hydrogen-bonding pattern and conformational disorder in a medium-ring $\varepsilon$-keto acid

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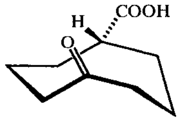
Molecules of the title compound, $C_9H_{14}O_3$, adopt a chiral 'boat–chair' conformation, in which the carboxyl group avoids potential cross-ring ketone interactions by an outward 'equatorial' orientation. The asymmetric unit contains two such molecules, one conformationally fixed without disorder, (I), and the other, (I′), extensively disordered, both in the bond lengths and angles of the carboxyl and by a coupled 'up-down' conformational disordering [ratio of 60:40 (1)] of the remote ends of the boat–chair system. Each molecule in the asymmetric unit forms a centrosymmetric hydrogen-bonded carboxyl dimer with a second molecule of its own type. For (I), $O\cdots O = 2.658$ (3) Å and $O-H\cdots O = 174°$. For (I′), $O\cdots O = 2.653$ (3) Å and $O-H\cdots O = 165°$. A number of intermolecular $C{=}O\cdots H-C$ close contacts are found.

## Comment

Because ketone and acid carbonyls have similar basicities and may compete as hydrogen-bond acceptors, the keto acids on which our X-ray crystallographic studies focus have an expanded repertoire of solid state hydrogen-bonding motifs compared with monofunctional carboxylic acids. The commonest hydrogen-bonding mode is acid dimerization without ketone involvement, but carboxyl-to-ketone chains (catemers) constitute a sizeable minority of cases. The remaining motifs are all relatively rare: intramolecular hydrogen bonds, acid-to-acid catemers and carboxyl-to-ketone dimers. We have previously referenced numerous examples and discussed factors that appear to govern the choice of hydrogen-bonding mode (Brunskill *et al.*, 1999; Thompson *et al.*, 1999). The title compound, (I), belongs to the category of $\varepsilon$-keto acids, which, besides dimers, includes at least five instances of carboxyl-to-ketone catemers and one of an internal hydrogen bond.

Fig. 1 shows the asymmetric unit with its numbering. Both molecules, (I) and (I′), adopt *transoid* 'boat–chair' conformations, in which, excluding attached atoms, the $C_8$ ring skeleton has symmetry visualizable as a mirror plane passing through C3 and C7. The boat–chair conformation is the one generally found to be of lowest energy in a variety of studies (Eliel *et al.*, 1994). The carboxyl group in both (I) and (I′) is aimed outward from the ring, 'equatorially', so that its potential cross-ring interaction with the ketone function is avoided and that juxtaposition involves not the carboxyl group but rather H1*A*. Because the ketone and carboxyl groups are arranged unsymmetrically on the ring, the resulting conformations are chiral, although the compound has no inherent chirality. Also contributing to the conformational chirality is the twist of the carboxyl group about C1—C9, described by the O2—C9—C1—C2 and O2—C9—C1—C8 torsion angles, which in (I) are 30.3 (4) and −95.7 (4)°, respectively; the corresponding angles in (I′) are 89.5 (4) and −37.0 (4)°, respectively. Although the carboxyl group in (I) is highly ordered, (I′) displays significant partial averaging of carboxyl C—O bond lengths and C—C—O angles, and, while adhering generally to the conformation adopted by (I), also displays a conformational disordering of the ring.



(I)

The conformational disorder in (I′) is produced by an 'up-down' disordering of the remote ends of the boat–chair system, C3′ and C7′. The overall ratio found in difference maps for the conformational contributors to (I′) is 60:40 (1), indicated in Fig. 1 by dark bonds for the major and 'ghost' bonds for the minor component. Separate iterative single-atom refinement of C3′ *versus* its disorder counterpart C3″ gave an occupancy ratio of 68:32 (1), while the same treatment for C7′ and C7″ produced a ratio of 51:49 (2). These data suggest that the similarity of these two ratios, almost within experimental error, strongly implies that the conformations involved in (I′) are coupled, *i.e.* entirely of the 'boat–chair' type, such that when C3′ is up, C7′ is down and *vice versa*, and not *cisoid* ones, in which these atoms might sometimes be 'both up' (chair–chair) or 'both down' (boat–boat) simultaneously. Significantly higher enthalpies have been estimated for the latter two species than for the boat–chair conformer (Eliel *et al.*, 1994). In addition, substantial estimated interconversion barriers make it very probable that the observed disorder is static. Because some additional disorder in C3″ is detectable as high anisotropy in its displacement ellipsoid, the displacement parameter for C3″ was refined isotropically. With respect to the carbon skeleton alone the two species inhabiting the (I′) site would be antipodal, but because of the twist of the carboxyl group the two are not symmetrically related.

Although not observed in catemers, disordering of carboxyl bond lengths and angles is common in carboxyl dimers (Leiserowitz, 1976). Significant partial averaging is found in (I′), where these C—O bond lengths are 1.247 (4) and 1.280 (4) Å, with angles of 120.5 (3) and 116.3 (3)°. Consistent with this disorder, partial carboxyl H atoms found in difference maps were refined to an occupancy ratio of 66:34 (6). In contrast, (I) is highly ordered, with values of 1.216 (4) and 1.314 (4) Å, and 123.8 (3)° and 113.1 (3)°, consistent with typical values of 1.21 and 1.31 Å, and 123 and 112°, cited for highly ordered dimeric carboxyls (Borthwick, 1980).

Fig. 2 shows the packing arrangement, which involves carboxyl dimers. Molecules of types (I) and (I′) are not paired together; rather, each pairs centrosymmetrically with a second molecule of its own type, yielding dimers of two kinds at different crystallographic sites in the chosen cell. Molecule (I) forms highly ordered dimers centered on the *bc* cell face [O···O 2.658 (3) Å and O—H···O = 174°], while the dimers formed by (I′) at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ are disordered as described above [O···O 2.653 (3) Å and O—H···O = 165°]. Because the two disorder components of species (I′) within the asymmetric unit are symmetrically unrelated, the resultant disorder in its dimers is not an enantiomeric transposition of D-L and L-D dimers, and it is even imaginable that individual dimers of (I′) might be non-centrosymmetric. We have no specific information concerning this possibility, but we are inclined against it because of the centrosymmetry of the space group and the strict centrosymmetry observed for dimers of type (I).

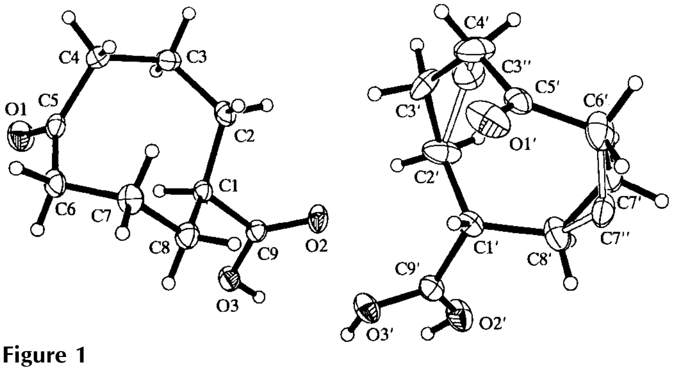


**Figure 1**
The asymmetric unit of (I), with its numbering. The enantiomeric ‘up-down’ disorder in (I′), involving C3′ and C7′, is shown using ghost bonds to represent the minor conformer [40 (1)%] found in difference maps. H atoms assigned only to the minor conformer are not shown. Displacement ellipsoids are set at the 20% probability level.

Two intermolecular C═O···H—C close contacts were found for the ketone (O1) in molecule (I), involving H7*A* of a molecule of (I) translated in **a** (2.67 Å) and H4′*D* of a molecule of (I′) (2.58 Å). There is a similar close contact for (I′) between O1′ and H6*B* in a molecule of (I) (2.65 Å). These contacts all lie within the 2.7 Å range often employed for non-bonded C—H···O packing interactions (Steiner, 1997). Using data compiled for a large number of such contacts, Steiner & Desiraju (1998) found significant statistical directionality even as far out as 3.0 Å, and concluded 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) infrared spectrum of (I) has discrete C═O absorptions at 1720, 1711 and 1692 cm$^{-1}$, all of which coalesce in $CHCl_3$ solution to a single broader asymmetric peak centered at 1704 cm$^{-1}$. Multiplicity of solid state C═O bands is often seen in structures with disorder in the carbonyl-bearing moieties (Lalancette *et al.*, 1997).

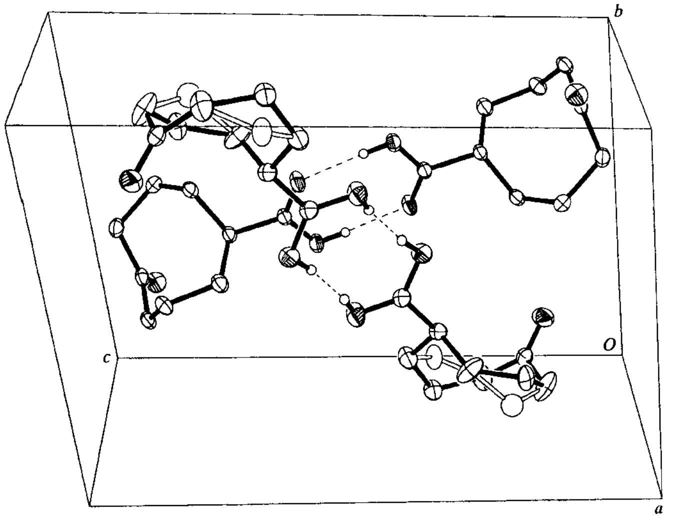


**Figure 2**
A partial packing diagram, illustrating the dimers formed by (I) centered on the *bc* cell face, and by (I′) centered at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; ghost bonds and unsegmented atoms represent the minor conformer. For clarity, carbon-bound H atoms have been omitted. Displacement ellipsoids are set at the 20% probability level.

## Experimental

Bicyclo[3.3.1]nonan-9-one, purchased from Aldrich Chemical Co., Milwaukee, Wisconsin, USA, was subjected to Baeyer–Villiger oxidation by the procedure of Zalikowski *et al.* (1980), and the resulting lactone (m.p. 416 K) was saponified. The hydroxy acid obtained showed a tendency to relactonize during the subsequent Jones oxidation, necessitating extractive separation of (I) from the lactone. Purification and crystallization from $Et_2O$–hexane gave (I) (m.p. 352 K).

### *Crystal data*

$C_9H_{14}O_3$
$M_r = 170.20$
Triclinic, $P\overline{1}$
$a = 6.7449 (8)$ Å
$b = 9.8755 (13)$ Å
$c = 13.878 (2)$ Å
$\alpha = 81.586 (10)°$
$\beta = 86.189 (10)°$
$\gamma = 88.519 (9)°$
$V = 912.3 (2)$ Å$^3$

$Z = 4$
$D_x = 1.239$ Mg m$^{-3}$
Mo *Kα* radiation
Cell parameters from 25 reflections
$\theta = 10.7–15.2°$
$\mu = 0.092$ mm$^{-1}$
$T = 293 (2)$ K
Block, colorless
0.54 × 0.38 × 0.20 mm

### *Data collection*

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: numerical (*SHELXTL*; Sheldrick, 1997)
$T_{min} = 0.97$, $T_{max} = 0.98$
4078 measured reflections
3190 independent reflections
2100 reflections with $I > 2\sigma(I)$

$R_{int} = 0.031$
$\theta_{max} = 25.02°$
$h = -7 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = 0 \rightarrow 16$
3 standard reflections every 97 reflections intensity variation: ±3.3%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.178$
$S = 1.02$
3190 reflections
234 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0611P)^2 + 0.8272P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.02$
$\Delta\rho_{\max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.28$ e Å$^{-3}$
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.041 (5)

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O2—C9 | 1.216 (4) | O2′—C9′ | 1.247 (4) |
| O3—C9 | 1.314 (4) | O3′—C9′ | 1.280 (4) |
| | | | |
| O2—C9—C1 | 123.8 (3) | O2′—C9′—C1′ | 120.5 (3) |
| O3—C9—C1 | 113.1 (3) | O3′—C9′—C1′ | 116.3 (3) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O3—H3···O2$^{i}$ | 0.82 | 1.84 | 2.658 (3) | 174 |
| O3′—H3′···O2′$^{ii}$ | 0.82 | 1.85 | 2.653 (3) | 165 |
| C7—H7*A*···O1$^{iii}$ | 0.97 | 2.67 | 3.621 (4) | 168 |
| C6—H6*B*···O1′$^{iv}$ | 0.97 | 2.65 | 3.437 (4) | 139 |
| C4′—H4′*D*···O1$^{v}$ | 0.97 | 2.58 | 3.285 (5) | 130 |

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

All H atoms were found in electron-density difference maps but were placed in calculated positions, with O—H 0.82 Å and C—H 0.97–0.98 Å, and allowed to refine as riding models with isotropic displacement parameters set at 120% of their respective C atoms for the ordered molecule; the isotropic displacement parameter for the carboxyl H was allowed to refine for the ordered molecule. For the disordered molecule, H atoms were generated for the disordered C3″ and C7″ positions, as well as for the geometric positions on C2′, C4′, C6′ and C8′; these H atoms were allowed to ride on their respective C atoms, with their isotropic displacement parameters fixed at 0.08 Å$^2$. The disordered pair of carboxyl-H atoms was also found in electron-density difference maps and refined in idealized positions to an occupancy ratio of 0.66:0.34 (6).

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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1293). Services for accessing these data are described at the back of the journal.

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