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(±)-3-Benzoylbicyclo[2.2.1]heptane-2-carboxylic acid: structures and hydrogen-bonding patterns of the di-*endo* and the 2-*endo*-3-*exo* isomers

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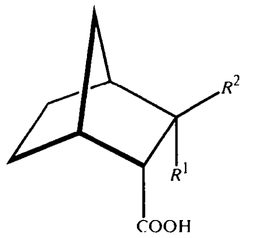
Abstract

Both the di-*endo*, (I), and the 2-*endo*-3-*exo*, (II), diastereomers of the title keto acid ($C_{15}H_{16}O_3$) crystallize as centrosymmetric carboxyl dimers, whose hydrogen bonding does not involve the ketone function [(I) $O\cdots O$ = 2.635 (3), (II) $O\cdots O$ = 2.675 (2) Å]. Conformational differences between (I) and (II) include significant rotations of the carboxyl group and of the benzoyl moiety relative to the bicycloheptane skeleton, plus a slight rotation of the phenyl ring relative to the ketone. Steric interactions involving the di-*endo* substituents in (I) produce significant twisting of the bridged bicyclic structure, which is essentially absent in (II). A C—$H\cdots O$ close contact at 2.58 Å was found for (I), involving the ketone, and at 2.49 Å for (II), also involving the ketone.

Comment

Compared with unelaborated carboxylic acids, the keto acids on which our crystallographic studies focus have an expanded repertoire of five solid-state hydrogen-bonding motifs. The commonest of these is acid dimerization without ketone involvement (Lalancette *et al.*, 1996), but carboxyl-to-ketone chains (catemers) constitute a sizable minority of cases (Brunskill *et al.*, 1997). The remaining modes, intramolecular hydrogen bonds (Thompson *et al.*, 1996), acid-to-acid catemers (Lalancette *et al.*, 1998) and carboxyl-to-ketone dimers (Kosela *et al.*, 1995), are all comparatively rare. We have previously referenced numerous examples and discussed factors that appear to govern the choice of hydrogen-bonding mode (Brunskill *et al.*, 1999; Lalancette *et al.*, 1999).

We report here the structure and hydrogen-bonding behavior of the title γ-keto acid, in both its di-*endo* (I) and 2-*endo*-3-*exo* (II) forms. The category of γ-keto acids is particularly diverse in hydrogen-bonding types, embracing internal hydrogen bonds, hydrated and anhydrous dimers, and catemers of both the heterochiral (glide-related) and homochiral types (screw-related or translational), plus other more complex hydrated patterns.



(I) : R^1 = CO-C_6H_5, R^2 = H
(II) : R^1 = H, R^2 = CO-C_6H_5

Fig. 1 shows the asymmetric unit for (I) with its atom numbering scheme. Full rotation of skeletal bonds is possible only for C2—C8, C3—C9 and C9—C10. The benzoyl group, whose component parts are only approximately coplanar [torsion angle O1—C9—C10—C15 = 11.2 (4)°], is oriented so that the ketone C═O is aimed toward C2 [torsion angle O1—C9—C3—C2 = −20.9 (4)°]. The carboxyl group is turned, with its carbonyl toward C1, so that the O2—C8—C2—C1 torsion angle is −1.2 (4)°. The dihedral angle between the ketone and carboxyl groups is 59.7 (1)°.

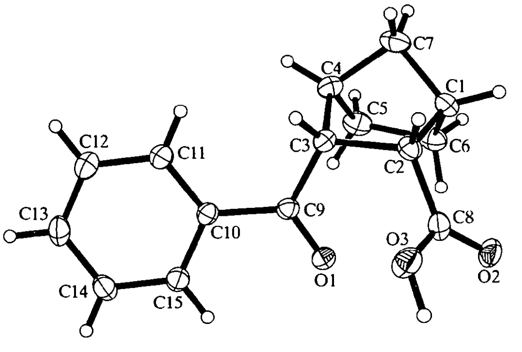


Fig. 1. The asymmetric unit of (I) with the atom numbering scheme. Ellipsoids are set at the 20% probability level.

Although nominally quite rigid, many bicyclo[2.2.1]-heptane systems adopt some degree of twist to relieve eclipsing strain in their ethylene bridges. In (I), that strain entails both serious eclipsing and 1,3-diaxial interactions of the di-*endo* substituents. The resulting twist is visible in Fig. 1 in the extent to which the ethylene bridges are not parallel. The torsion angles involving these bridges, C1—C2—C3—C4 and C1—C6—C5—C4, which would be 0° in an untwisted system, here have values of −6.6 (3) and −4.3 (3)°, respectively, illustrating the twist and showing that the bridge bearing the substituents is, indeed, twisted somewhat more than the other. The torsion angle C8—C2—C3—C9, involving the two *endo* substituents, which would also be 0° in the absence of twist, is −16.0 (4)°.

Although it is not seen in catemers, carboxyl dimers frequently display complete or partial averaging of C—O bond lengths and C—C—O angles due to disorder (Leiserowitz, 1976). However, no significant averaging is observed in (I), where the bond lengths are 1.229 (3) and 1.317 (3) Å, with angles of 123.8 (3) and 113.0 (3)° 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° (Borthwick, 1980).

Fig. 2 shows the packing for (I), which is fairly typical for racemic keto acids adopting the dimeric arrangement. Centrosymmetric dimers are found centered on the *ab* faces of the chosen cell, with a second glide-related set of dimers centered on the *ac* faces. The O· · ·O distance is 2.635 (3) Å and the O—H· · ·O angle is 174 (3)°. A 2.58 Å attractive C—H· · ·O close contact was found for (I) involving the ketone (O1) and H7*A* of a neighboring molecule translationally related in **b**. This presumably represents a polar attraction contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

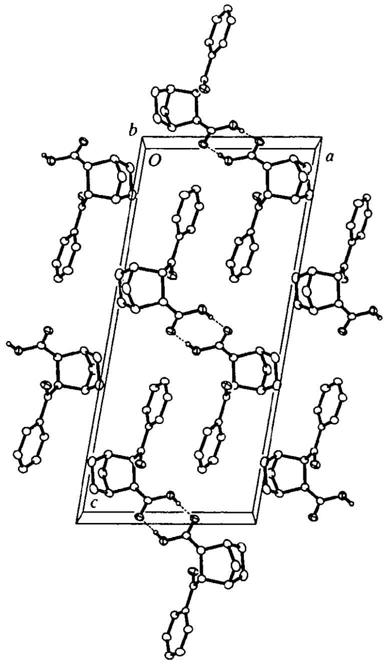


Fig. 2. A packing diagram (with extracellular molecules included), showing the glide-related dimers centered across the *ab* and *ac* faces of the chosen cell. For clarity, all H(—C) atoms have been removed. Ellipsoids are set at the 20% probability level.

Fig. 3 shows the asymmetric unit for (II) with the atom numbering scheme. The benzoyl group has 4.6 (5)° less ketone coplanarity than in (I) [torsion angle (II) O1—C9—C10—C11 = 15.8 (3)°], and is oriented so that the O1—C9—C3—C2 torsion angle is 12.6 (2)°. The carboxyl group in (II) is only about two-thirds as ordered as in (I), with bond lengths 1.238 (2) and 1.301 (2) Å, and angles 121.6 (2) and 115.5 (2)° (Borthwick, 1980). It is also rotated approximately 145° from its conformation in (I), with its C=O turned away from C1, so that the O2—C8—C2—C1 torsion angle is −144.8 (2)°, in this case. The dihedral angle between the ketone and carboxyl groups is 73.8 (1)°.

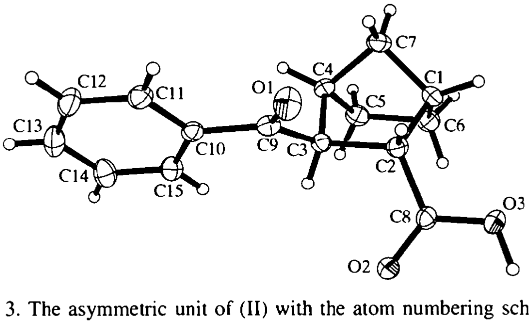


Fig. 3. The asymmetric unit of (II) with the atom numbering scheme. Ellipsoids are set at the 20% probability level.

Much of the eclipsing strain and many of the 1,3-diaxial interactions associated with the di-*endo* configuration in (I) are absent in (II), with the result that its ethylene bridges are much more nearly parallel. These bridges have torsion angles C1—C2—C3—C4 = −2.8 (2) and C1—C6—C5—C4 = 0.9 (2)°, and the C8—C2—C3—C9 torsion angle involving the two substituents (ideally 120°) is 108.6 (2)°.

Fig. 4 shows the packing for (II), also typical for racemic keto acids that are dimerized. One set of centrosymmetric dimers is found centered at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ in the chosen cell, with a second glide-related set centered on the *a* edge. The O···O distance is 2.675 (2) Å and the O—H···O angle is 178 (2)°. A 2.49 Å C—H···O close contact was found for (II), involving the ketone (O1) and H5*B* of a molecule screw-related in **b**.

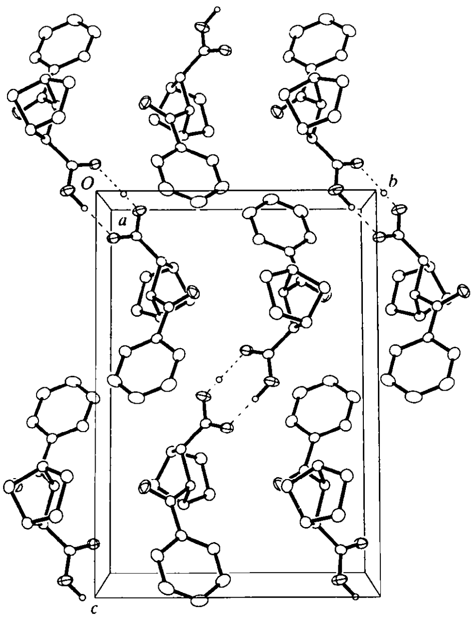


Fig. 4. A packing diagram (with extracellular molecules included), showing the glide-related dimers centered on $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and the *a* edge of the chosen cell. For clarity, all H(—C) atoms have been removed. Ellipsoids are set at the 20% probability level.

The solid-state IR spectrum (KBr) of (I) has C=O absorptions at 1705 and 1674 cm^{-1}, positions normal for, respectively, dimerized COOH and a benzoyl group without hydrogen bonding but with significant benzoyl conjugation (Lalancette *et al.*, 1996). In KBr, (II) has these absorptions at 1696 and 1675 cm^{-1}, respectively. In CHCl$_3$ solution, these absorptions appear at 1711 and 1682 cm^{-1} (I) and at 1703 and 1679 cm^{-1} (II), with typical carboxyl-dilution shoulders at 1735–1740 cm^{-1} in each case.

Experimental

The di-*endo* keto acid (I) (Morgan *et al.*, 1944) was purchased from Acros Organics/Fisher Scientific, Pittsburgh, PA 15205, USA, and recrystallized from MeCN/acetone (m.p. 451 K). Epimerization of (I) by refluxing in excess aqueous KOH (Scribner & Miller, 1965) provided (II), which was crystallized from Et$_2$O [m.p. 445 K; literature m.p. 427 K (Winternitz *et al.*, 1955)]. The crystal used for the determination of (II), although large, was well within the size permitted by a normal-focus X-ray tube.

Compound (I)

Crystal data

$C_{15}H_{16}O_3$
M_r = 244.28
Monoclinic
$P2_1/c$
a = 9.866 (2) Å
b = 6.010 (3) Å
c = 21.697 (5) Å
β = 99.58 (1)°
V = 1268.6 (7) Å^3
Z = 4
D_x = 1.279 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 3.07–14.83°
μ = 0.088 mm^{-1}
T = 293 (2) K
Tablet
0.50 × 0.40 × 0.22 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: none
3188 measured reflections
2232 independent reflections
1315 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.035

$\theta_{\rm max}$ = 25°
$h = -1 \rightarrow 11$
$k = -1 \rightarrow 7$
$l = -25 \rightarrow 25$
3 standard reflections every 97 reflections intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.122
S = 1.06
2228 reflections
170 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0264P)^2 + 0.4905P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.16 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.14 e Å^{-3}
Extinction correction: *SHELXL* (Sheldrick, 1997)
Extinction coefficient: 0.0049 (10)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C9	1.223 (3)	O3—C8	1.317 (3)
O2—C8	1.229 (3)		
O2—C8—C2	123.8 (3)	O3—C8—C2	113.0 (3)

Table 2. *Hydrogen-bonding and close contact geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2$^{\rm i}$	0.93 (3)	1.70 (3)	2.635 (3)	174 (3)
C7—H7*A*···O1$^{\rm ii}$	0.97	2.58	3.486 (4)	156

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

Compound (II)

Crystal data

$C_{15}H_{16}O_3$
$M_r = 244.28$
Monoclinic
$P2_1/c$
$a = 7.646$ (2) Å
$b = 10.799$ (4) Å
$c = 15.446$ (5) Å
$\beta = 93.02$ (2)°
$V = 1273.5$ (7) Å^3
$Z = 4$
$D_x = 1.274$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 36 reflections
$\theta = 6.07$–15.01°
$\mu = 0.088$ mm^{-1}
$T = 293$ (2) K
Hexagonal column
0.65 × 0.50 × 0.30 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: none
3106 measured reflections
2245 independent reflections
1659 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$

$\theta_{\rm max} = 25°$
$h = -1 \rightarrow 9$
$k = -1 \rightarrow 12$
$l = -18 \rightarrow 18$
3 standard reflections every 97 reflections intensity variation: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.101$
$S = 1.02$
2244 reflections
169 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.399P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.11$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.13$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

O1—C9	1.224 (2)	O3—C8	1.301 (2)
O2—C8	1.238 (2)		
O2—C8—C2	121.56 (16)	O3—C8—C2	115.55 (17)

Table 4. *Hydrogen-bonding and close contact geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2$^{\rm i}$	0.98 (3)	1.69 (3)	2.675 (2)	178 (2)
C5—H5*B*···O1$^{\rm ii}$	0.97	2.49	3.423 (3)	161

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

For both (I) and (II), all H(—C) atoms were found in electron-density difference maps but were replaced in calculated positions and allowed to refine in riding models. Displacement parameters for the methylene, methine and aromatic protons were refined as individual groups. Carboxyl protons were found in electron density difference maps and their positional parameters were allowed to refine with their displacement parameters fixed at 0.08 Å^2.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1565). Services for accessing these data are described at the back of the journal.

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(+)-*cis*-Pinonic acid: catemeric hydrogen bonding in a non-racemic ε-keto acid

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Abstract

The title compound, (1*S*,3*S*)-(+)-*cis*-3-acetyl-2,2-dimethylcyclobutaneacetic acid, $C_{10}H_{16}O_3$, forms carboxyl-to-ketone hydrogen-bonding catemers, with a chain of screw-related molecules passing through the cell in the *b* direction [O···O = 2.713 (3) Å]. Two intermolecu-