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(1*SR*,8a*RS*)-1,2,3,5,6,7,8,8a-Octahydro-3-oxonaphthalene-1-carboxylic acid: catemeric hydrogen bonding in a bicyclic unsaturated γ-keto acid

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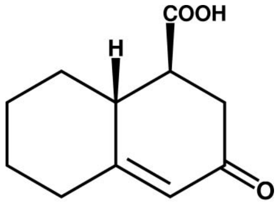
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.036; wR factor = 0.095; data-to-parameter ratio = 13.0.

The title racemate ($C_{11}H_{14}O_3$) aggregates in the solid as acid-to-ketone hydrogen-bonding catemers [$\mathrm{O}\cdots\mathrm{O}$ = 2.6557 (13) Å and $\mathrm{O}-\mathrm{H}\cdots\mathrm{O}$ = 170°], whose components are glide-related. The stereochemistry of the carboxyl group arises spontaneously during the synthesis. One intermolecular $\mathrm{C}-\mathrm{H}\cdots\mathrm{O}{=}\mathrm{C}$ close contact was found.

Related literature

For related literature, see: Barcon *et al.* (1998, 2002); Borthwick (1980); Dufort *et al.* (2007); House *et al.* (1965); Steiner (1997); Stork *et al.* (1963).



Experimental

Crystal data

$C_{11}H_{14}O_3$
M_r = 194.22
Monoclinic, $P2_1/c$
a = 5.2691 (3) Å
b = 16.1279 (11) Å
c = 11.9181 (7) Å
β = 98.252 (3)°

V = 1002.31 (11) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.76 mm^{-1}
T = 100 (2) K
0.38 × 0.36 × 0.16 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min}$ = 0.78, $T_{\max}$ = 0.86

5164 measured reflections
1662 independent reflections
1600 reflections with $I > 2\sigma(I)$
R_{int} = 0.018

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.095
S = 1.08
1662 reflections

128 parameters
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bond and close-contact geometry (Å, °).

$D-\mathrm{H}\cdots A$	$D-\mathrm{H}$	$\mathrm{H}\cdots A$	$D\cdots A$	$D-\mathrm{H}\cdots A$
$\mathrm{O3}-\mathrm{H3}A\cdots\mathrm{O1}^{\mathrm{i}}$	0.84	1.82	2.6557 (13)	170
$\mathrm{C1}-\mathrm{H1}A\cdots\mathrm{O2}^{\mathrm{ii}}$	1.00	2.45	3.2230 (15)	134

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *APEX2*; data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXTL* (Sheldrick, 2004); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors gratefully acknowledge support in the form of NSF–CRIF grant No. 0443538. MD and HWT also thank the Rutgers University Undergraduate Research Fellows Program for support and Professor G. L. Spoog for helpful discussions.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LW2029).

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supplementary materials

Acta Cryst. (2007). E**63**, o4014 [**doi:10.1107/S1600536807043425**]

(1*SR*,8a*RS*)-1,2,3,5,6,7,8,8a-Octahydro-3-oxonaphthalene-1-carboxylic acid: catemeric hydrogen bonding in a bicyclic unsaturated γ-keto acid

M. Davison, M. H. Malak, R. A. Lalancette and H. W. Thompson

Comment

Among ketocarboxylic acids, we have shown that the normally dominant dimerization is disfavored by lowering molecular flexibility, as measured by the number of fully rotatable bonds present. Typically this results in an increased frequency of acid-to-ketone catemers, as in the title compound, (I), whose structure and H-bonding pattern we report here.

Fig. 1 shows the asymmetric unit, whose only conformational options lie in the carboxyl side-chain, which is turned [8a-C1—C9—O2 torsion angle = 20.11 (18)°] so as to avoid interaction with the equatorial H at C8.

The disordering of C—O bond lengths and C—C—O angles often seen in carboxyl dimers is not possible in H-bonding modes that preclude the averaging mechanisms involved. Because (I) is not dimeric the distances and angles here (Table 1) are typical of those in highly ordered dimeric carboxyls (Borthwick, 1980).

Fig. 2 shows the the acid-to-ketone H-bonding scheme. Each carboxylic acid is linked to the ketone in a molecule glide related in the c direction, creating H-bonding chains that advance at an angle to the cell axes. In all, four separate parallel chains pass through the cell in counterdirectional pairs related centrosymmetrically about 1/2, 1/2, 1/2. The intra-chain glide relationship found is considerably rarer than either screw or translational schemes generally, and is shared with three other γ-keto acids of our experience (Barcon *et al.*, 1998, 2002; Dufort *et al.*, 2007).

We characterize the geometry of H bonding to carbonyls using a combination of the H···O=C angle and the H···O=C—C torsional angle. These describe the approach of the H atom to the receptor O in terms of its deviation from, respectively, C=O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). In (I) these angles are 122 & −7°. Within the 2.6 Å range we standardly survey for C—H···O packing interactions (Steiner, 1997), one intermolecular close contact was found, involving C1 & O2 (Table 2).

Experimental

Compound (I) is previously unreported, although its ethyl ester has been described by Stork *et al.* (1963), whose procedure we used to prepare the analogous methyl ester, mp 330 K. Saponification, sublimation and crystallization from Et_2O/hexane yielded crystals suitable for X-ray, mp 352 K. The C1/C8a stereochemistry clearly represents the stabler of the two epimers possible and probably arises from equilibrations during the alkylation or saponification steps (House *et al.*, 1965).

The solid-state (KBr) infrared spectrum of (I) has C=O absorptions at 1723 & 1636 cm^{-1}, with a peak separation typical of the shifts seen in catemers, due, respectively, to removal of H bonding from the acid C=O and addition of H bonding to the ketone; an alkene peak appears at 1616 cm^{-1}. In $CHCl_3$ solution, where dimers predominate, these bands appear, respectively, at 1713, 1667 and 1622 cm^{-1}.

Refinement

All H atoms for (I) were found in electron-density difference maps. The O—H was constrained to an idealized position with distance fixed at 0.84 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The methylene, methine, and vinyl Hs were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C—H distances of 0.99, 1.00, and 0.95 Å, respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

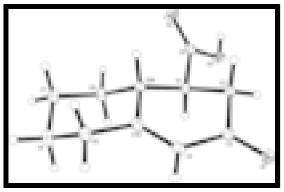

Fig. 1. The asymmetric unit of (I), with its numbering. Displacement ellipsoids are shown at the 30% probability level.

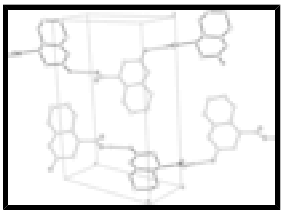

Fig. 2. A partial packing diagram with extracellular molecules, illustrating two of the four acid-to-ketone H-bonding chains passing through the cell. The remaining two chains are related by centrosymmetry about 1/2, 1/2, 1/2 to the ones shown and are therefore counterdirectional to them. All carbon-bound H atoms are removed for clarity, and the handedness of the molecules is differentiated by shading of the bonds. Displacement ellipsoids are shown at the 30% probability level.

'(1SR,8aRS)-1,2,3,5,6,7,8,8a-Octahydro-3-oxonaphthalene-1-carboxylic acid'

Crystal data

$C_{11}H_{14}O_3$

$M_r = 194.22$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 5.2691 (3)$ Å

$b = 16.1279 (11)$ Å

$c = 11.9181 (7)$ Å

$\beta = 98.252 (3)$°

$V = 1002.31 (11)$ Å^3

$Z = 4$

$F_{000} = 416$

$D_x = 1.287$ Mg m^{-3}

Melting point: 352 K

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å

Cell parameters from 5164 reflections

$\theta = 4.6$–67.0°

$\mu = 0.76$ mm^{-1}

$T = 100 (2)$ K

Parallelepiped, colourless

0.38 × 0.36 × 0.16 mm

Data collection

Bruker APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100(2)$ K

φ and ω scans

1662 independent reflections

1600 reflections with $I > 2\sigma(I)$

$R_{int} = 0.018$

$\theta_{max} = 67.0$°

$\theta_{min} = 4.6$°

Absorption correction: multi-scan (SADABS; Sheldrick, 2001)	$h = -5\rightarrow6$
$T_{\text{min}} = 0.78$, $T_{\text{max}} = 0.86$	$k = -18\rightarrow18$
5164 measured reflections	$l = -13\rightarrow13$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.036$	$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2 + 0.4766P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.095$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.21$ e Å^{-3}
1662 reflections	$\Delta\rho_{\text{min}} = -0.21$ e Å^{-3}
128 parameters	Extinction correction: SHELXTL (Sheldrick, 2004), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods	Extinction coefficient: 0.0030 (7)
Secondary atom site location: difference Fourier map	

Special details

Experimental. 'crystal mounted on cryoloop using Paratone-N'

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	$U_{\text{iso}}*/U_{\text{eq}}$
C1	0.4880 (2)	0.16063 (8)	0.05233 (11)	0.0183 (3)
H1A	0.6262	0.1271	0.0248	0.022*
O1	0.98255 (17)	0.29981 (6)	0.18075 (8)	0.0224 (3)
C2	0.5929 (2)	0.24841 (8)	0.07921 (11)	0.0199 (3)
H2A	0.6534	0.2720	0.0111	0.024*
H2B	0.4536	0.2843	0.0991	0.024*
O2	0.04242 (18)	0.16180 (7)	−0.03204 (9)	0.0297 (3)
C3	0.8103 (2)	0.24758 (8)	0.17578 (11)	0.0189 (3)
O3	0.34570 (18)	0.18208 (6)	−0.14192 (8)	0.0254 (3)
H3A	0.2185	0.1869	−0.1928	0.038*
C4	0.7986 (3)	0.18636 (8)	0.26462 (12)	0.0210 (3)

H4A	0.9289	0.1866	0.3286	0.025*
C4A	0.6117 (3)	0.12961 (8)	0.25999 (11)	0.0206 (3)
C5	0.5812 (3)	0.07688 (9)	0.36134 (12)	0.0264 (3)
H5A	0.4392	0.0995	0.3982	0.032*
H5B	0.7401	0.0806	0.4166	0.032*
C6	0.5259 (3)	−0.01464 (9)	0.33257 (12)	0.0287 (4)
H6A	0.6802	−0.0408	0.3094	0.034*
H6B	0.4843	−0.0440	0.4006	0.034*
C7	0.3024 (3)	−0.02239 (9)	0.23702 (13)	0.0285 (4)
H7A	0.2720	−0.0816	0.2175	0.034*
H7B	0.1450	0.0003	0.2619	0.034*
C8A	0.4120 (2)	0.11763 (8)	0.15658 (11)	0.0194 (3)
H8AA	0.2484	0.1433	0.1730	0.023*
C8	0.3614 (3)	0.02474 (9)	0.13348 (12)	0.0239 (3)
H8A	0.2152	0.0187	0.0719	0.029*
H8B	0.5140	−0.0002	0.1071	0.029*
C9	0.2656 (2)	0.16697 (8)	−0.04338 (12)	0.0192 (3)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0169 (6)	0.0171 (7)	0.0206 (7)	0.0001 (5)	0.0023 (5)	−0.0003 (5)
O1	0.0222 (5)	0.0197 (5)	0.0244 (5)	−0.0035 (4)	0.0005 (4)	−0.0018 (4)
C2	0.0201 (7)	0.0171 (7)	0.0220 (7)	0.0001 (5)	0.0015 (5)	0.0020 (5)
O2	0.0170 (5)	0.0446 (7)	0.0273 (6)	−0.0026 (4)	0.0021 (4)	0.0028 (5)
C3	0.0194 (7)	0.0163 (6)	0.0212 (7)	0.0024 (5)	0.0037 (5)	−0.0039 (5)
O3	0.0191 (5)	0.0369 (6)	0.0196 (5)	0.0013 (4)	0.0004 (4)	0.0053 (4)
C4	0.0225 (7)	0.0202 (7)	0.0192 (7)	0.0023 (5)	−0.0009 (5)	−0.0019 (5)
C4A	0.0254 (7)	0.0175 (7)	0.0192 (7)	0.0039 (5)	0.0050 (5)	−0.0019 (5)
C5	0.0368 (8)	0.0226 (7)	0.0200 (7)	−0.0022 (6)	0.0047 (6)	0.0004 (6)
C6	0.0427 (9)	0.0201 (7)	0.0245 (8)	−0.0021 (6)	0.0089 (7)	0.0037 (6)
C7	0.0355 (8)	0.0218 (7)	0.0297 (8)	−0.0067 (6)	0.0099 (6)	0.0006 (6)
C8A	0.0183 (6)	0.0181 (7)	0.0220 (7)	−0.0001 (5)	0.0037 (5)	−0.0002 (5)
C8	0.0277 (7)	0.0195 (7)	0.0242 (7)	−0.0049 (5)	0.0025 (6)	−0.0012 (6)
C9	0.0199 (7)	0.0143 (6)	0.0233 (7)	−0.0001 (5)	0.0027 (5)	−0.0011 (5)

Geometric parameters (Å, °)

C1—C9	1.5171 (18)	C4A—C8A	1.5138 (19)
C1—C8A	1.5258 (18)	C5—C6	1.5337 (19)
C1—C2	1.5367 (18)	C5—H5A	0.9900
C1—H1A	1.0000	C5—H5B	0.9900
O1—C3	1.2335 (16)	C6—C7	1.521 (2)
C2—C3	1.5028 (18)	C6—H6A	0.9900
C2—H2A	0.9900	C6—H6B	0.9900
C2—H2B	0.9900	C7—C8	1.519 (2)
O2—C9	1.2056 (16)	C7—H7A	0.9900
C3—C4	1.4555 (19)	C7—H7B	0.9900
O3—C9	1.3263 (17)	C8A—C8	1.5395 (18)

O3—H3A	0.8400	C8A—H8AA	1.0000
C4—C4A	1.340 (2)	C8—H8A	0.9900
C4—H4A	0.9500	C8—H8B	0.9900
C4A—C5	1.5046 (19)		

C9—C1—C8A	112.21 (10)	C7—C6—C5	110.39 (12)
C9—C1—C2	108.09 (10)	C7—C6—H6A	109.6
C8A—C1—C2	112.19 (11)	C5—C6—H6A	109.6
C9—C1—H1A	108.1	C7—C6—H6B	109.6
C8A—C1—H1A	108.1	C5—C6—H6B	109.6
C2—C1—H1A	108.1	H6A—C6—H6B	108.1
C3—C2—C1	111.30 (10)	C8—C7—C6	109.89 (11)
C3—C2—H2A	109.4	C8—C7—H7A	109.7
C1—C2—H2A	109.4	C6—C7—H7A	109.7
C3—C2—H2B	109.4	C8—C7—H7B	109.7
C1—C2—H2B	109.4	C6—C7—H7B	109.7
H2A—C2—H2B	108.0	H7A—C7—H7B	108.2
O1—C3—C4	122.42 (12)	C4A—C8A—C1	111.82 (11)
O1—C3—C2	120.36 (12)	C4A—C8A—C8	110.61 (11)
C4—C3—C2	117.12 (11)	C1—C8A—C8	110.83 (11)
C9—O3—H3A	109.5	C4A—C8A—H8AA	107.8
C4A—C4—C3	122.76 (12)	C1—C8A—H8AA	107.8
C4A—C4—H4A	118.6	C8—C8A—H8AA	107.8
C3—C4—H4A	118.6	C7—C8—C8A	113.08 (12)
C4—C4A—C5	121.04 (13)	C7—C8—H8A	109.0
C4—C4A—C8A	122.81 (12)	C8A—C8—H8A	109.0
C5—C4A—C8A	116.08 (12)	C7—C8—H8B	109.0
C4A—C5—C6	113.78 (12)	C8A—C8—H8B	109.0
C4A—C5—H5A	108.8	H8A—C8—H8B	107.8
C6—C5—H5A	108.8	O2—C9—O3	123.47 (12)
C4A—C5—H5B	108.8	O2—C9—C1	124.87 (12)
C6—C5—H5B	108.8	O3—C9—C1	111.62 (11)
H5A—C5—H5B	107.7		

C9—C1—C2—C3	178.46 (10)	C4—C4A—C8A—C8	138.44 (13)
C8A—C1—C2—C3	54.22 (14)	C5—C4A—C8A—C8	−44.76 (16)
C1—C2—C3—O1	149.92 (12)	C9—C1—C8A—C4A	−166.25 (10)
C1—C2—C3—C4	−33.63 (15)	C2—C1—C8A—C4A	−44.33 (14)
O1—C3—C4—C4A	179.79 (12)	C9—C1—C8A—C8	69.82 (14)
C2—C3—C4—C4A	3.41 (19)	C2—C1—C8A—C8	−168.25 (11)
C3—C4—C4A—C5	−169.72 (12)	C6—C7—C8—C8A	−59.22 (16)
C3—C4—C4A—C8A	6.9 (2)	C4A—C8A—C8—C7	51.49 (15)
C4—C4A—C5—C6	−137.03 (14)	C1—C8A—C8—C7	176.11 (11)
C8A—C4A—C5—C6	46.11 (17)	C8A—C1—C9—O2	20.11 (18)
C4A—C5—C6—C7	−51.45 (17)	C2—C1—C9—O2	−104.11 (15)
C5—C6—C7—C8	57.55 (16)	C8A—C1—C9—O3	−162.19 (11)
C4—C4A—C8A—C1	14.39 (18)	C2—C1—C9—O3	73.59 (13)
C5—C4A—C8A—C1	−168.81 (11)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3A···O1[i]	0.84	1.82	2.6557 (13)	170
C1—H1A···O2[ii]	1.00	2.45	3.2230 (15)	134

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

Fig. 1

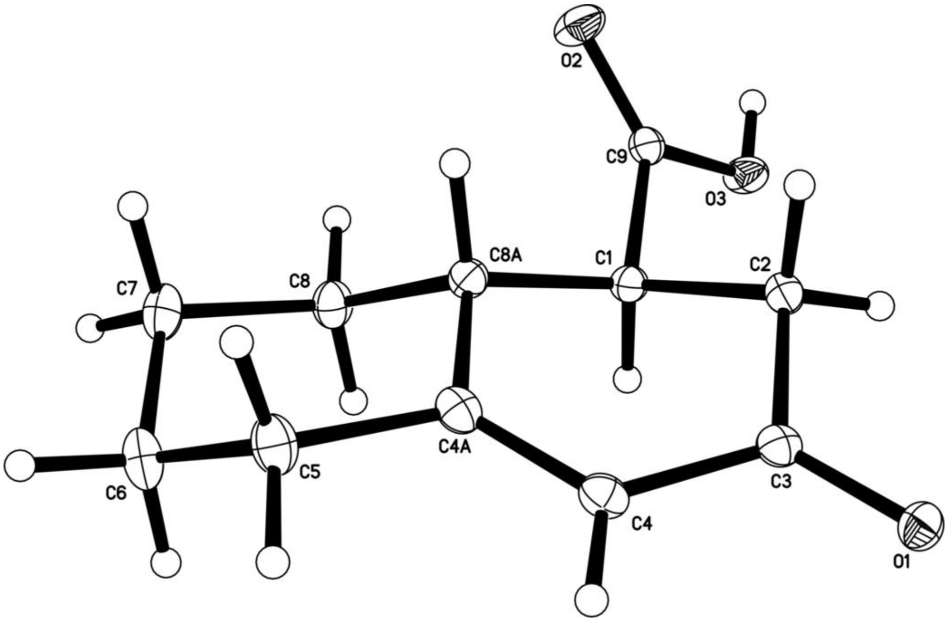

Fig. 2