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(2*SR*,8a*SR*)-1,2,3,4,6,7,8,8a-Octahydro-6-oxonaphthalene-2-acetic acid: hydrogen bonding in an unsaturated bicyclic keto acid

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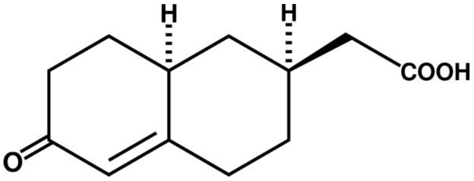
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.038; wR factor = 0.104; data-to-parameter ratio = 13.6.

The title racemate, $C_{12}H_{16}O_3$, aggregates in the solid state as translational acid-to-ketone hydrogen-bonded catemers. The stereochemistry of the side chain relative to the ring junction arises spontaneously during the synthesis. The four hydrogen-bonding chains passing through the unit cell are of alternating handedness, and are aligned along the [101] direction. Starting at the origin, the order of the directional alignment of these four chains with respect to the a axis is ++−−. One intermolecular C—H⋯O═C close contact exists to the carboxyl O atom.

Related literature

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



Experimental

Crystal data

$C_{12}H_{16}O_3$
M_r = 208.26
Monoclinic, $P2_1/c$
a = 7.5832 (2) Å
b = 16.9532 (4) Å
c = 8.3785 (2) Å
β = 96.323 (1)°
V = 1070.58 (5) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 0.75 mm^{-1}
T = 100 (2) K
0.33 × 0.28 × 0.22 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.790, T_{max} = 0.853
5950 measured reflections
1879 independent reflections
1818 reflections with $I > 2\sigma(I)$
R_{int} = 0.017

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.104
S = 1.05
1879 reflections
138 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O3—H3⋯O1^{i}	0.84	1.86	2.6793 (14)	163
C7—H7B⋯O2^{ii}	0.99	2.53	3.4758 (17)	161

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

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 are grateful to Professor Jonathan L. Vennerstrom of the University of Nebraska Medical Center for a generous gift of methyl cyclohexanone-4-acetate. JD and HWT also thank the Rutgers University Undergraduate Research Fellows Program for support, and we thank Professor G. L. Spoog for helpful discussions. The authors acknowledge support by the NSF–CRIF (grant No. 0443538) and the Rutgers Academic Excellence Fund.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FL2147).

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supplementary materials

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(2*SR*,8a*SR*)-1,2,3,4,6,7,8,8a-Octahydro-6-oxonaphthalene-2-acetic acid: hydrogen bonding in an unsaturated bicyclic keto acid

M. H. Malak, J. Desai, R. A. Lalancette and H. W. Thompson

Comment

Among the five hydrogen-bonding modes known for ketocarboxylic acids, the commonest involves centrosymmetric dimerization. However, we have shown that when centrosymmetry is thwarted or disfavored, the frequency of acid-to-ketone catemers increases. Thus, among chiral non-racemates this chain-mode actually predominates, and its occurrence also rises markedly among conformationally constrained molecules. The latter is the case for compound (I), whose structure and hydrogen-bonding pattern we report here.

Fig. 1 shows the asymmetric unit, whose only conformational options lie in the side-chain. The C2—C9 staggering requires that C10 be involved in a *gauche* interaction with an equatorial proton either at C1 or at C3. Compared to alkane systems in which all centers are tetrahedral, such *gauche* arrangements are less serious here because the sp^2 hybridization at the carboxyl diminishes the steric repulsions involved. Within the asymmetric unit, any energy advantage to the arrangement actually found [torsion angle C3—C2—C9—C10 = 64.16 (15)°] appears negligible and the observed choice is probably dictated by packing considerations. The remaining available rotation yields a C2—C9—C10—O2 torsion angle of 38.58 (19)° for the carboxyl group.

The disordering of bond lengths and angles often seen in carboxyl dimers is not possible in (I), which is not dimeric. Thus its C—O bond lengths [O2—C10 = 1.2054 (18) and O3—C10 = 1.3213 (17) Å] and C—C—O angles [O2—C10—C9 = 124.23 (12) and O3—C10—C9 = 112.41 (12) °] are typical of those in highly ordered dimeric carboxyls (Borthwick, 1980).

Fig. 2 shows the centrosymmetric packing of the cell, with extra molecules included to illustrate the acid-to-ketone hydrogen-bonding scheme. Each carboxylic acid is linked to the ketone in a molecule translationally related in both the a and c directions, so that the chains advance at an angle to the cell axes, along the [101] direction. The four hydrogen-bonding chains passing through the cell are of alternating handedness. Starting at the origin, the order of the directional alignment of these four chains with respect to the *a* axis is + + - -. The racemate aggregates in the solid as translational acid-to-ketone hydrogen-bonding catemers [O···O = 2.6793 (14)Å and O—H···O = 163°].

We characterize the geometry of H 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 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 124.8 & 0.1°.

One intermolecular C—H···O close contact was found involving the carboxyl oxygen [H7B—O2 = 2.53; C7—O2 = 3.4758 (17) Å; C7—H7B—O2 = 161 °]. This distance lies within the 2.6-Å range we standardly survey for such packing interactions (Steiner, 1997).

Experimental

Compound (I) has not previously been reported. The methyl ester of cyclohexanone-4-acetic acid (see Acknowledgments) was converted to its pyrrolidine enamine and then treated with methyl vinyl ketone as described by Stork *et al.* (1963). The usual workup and isolation yielded directly the crystalline methyl ester of (I), which was then saponified. Crystals of (I) suitable for X-ray were obtained from ether/CH_2Cl_2, mp 423 K. The stereochemistry obtained for C4a *versus* C6 arises during the synthesis, probably as the result of equilibrations occurring during saponification or earlier (House *et al.*, 1965), as (I) is clearly the stabler of the two epimers possible.

The solid-state (KBr) infrared spectrum of (I) has C=O absorptions at 1724 & 1633 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 shoulder appears at *ca* 1618 cm^{-1}. In $CHCl_3$ solution, where dimers predominate, these bands appear, respectively, at 1710, 1662 and 1621 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 and methine Hs were placed in geometrically idealized positions and constrained to ride on their parent C atoms with C—H distances of 0.99 and 1.00 Å, respectively, and $U_{iso}(H) = 1.2U_{eq}(C)$.

Figures

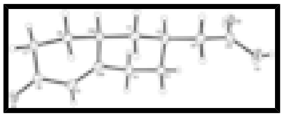

Fig. 1. The asymmetric unit of (I), with its numbering. Displacement ellipsoids are shown at the 40% probability level.

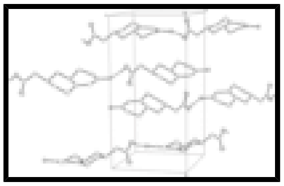

Fig. 2. A packing diagram with extracellular molecules, illustrating the four translational acid-to-ketone hydrogen-bonding chains of alternating handedness. The molecules are aligned along the [101] direction in the cell. All carbon-bound H atoms are removed for clarity. Displacement ellipsoids are shown at the 40% probability level.

(2SR,8aSR)-1,2,3,4,6,7,8,8a-Octahydro-6-oxonaphthalene-2-acetic acid

Crystal data

$C_{12}H_{16}O_3$	$F_{000} = 448$
$M_r = 208.26$	$D_x = 1.292$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 423 K
Hall symbol: -P 2ybc	Cu $K\alpha$ radiation $\lambda = 1.54178$ Å
$a = 7.5832$ (2) Å	Cell parameters from 5950 reflections
$b = 16.9532$ (4) Å	$\theta = 5.9$–68.1°

$c = 8.3785$ (2) Å

$\beta = 96.3230$ (10)°

$V = 1070.58$ (5) Å^3

$Z = 4$

$\mu = 0.75$ mm^{-1}

$T = 100$ (2) K

Block, colourless

0.33 × 0.28 × 0.22 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 100(2)$ K

φ and ω scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2001)

$T_{\min} = 0.790$, $T_{\max} = 0.853$

5950 measured reflections

1879 independent reflections

1818 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.017$

$\theta_{\max} = 68.1$°

$\theta_{\min} = 5.9$°

$h = -9 \rightarrow 9$

$k = -18 \rightarrow 19$

$l = -10 \rightarrow 9$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.104$

$S = 1.05$

1879 reflections

138 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.5351P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.24$ e Å^{-3}

$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Extinction correction: SHELXTL (Sheldrick, 2004), $Fc^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0015 (4)

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 $F^2 > 2\text{sigma}(F^2)$ 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*	$U_{\rm iso}$*/$U_{\rm eq}$
O1	0.33270 (13)	0.62327 (6)	1.12458 (11)	0.0253 (3)
C1	0.51750 (16)	0.66286 (8)	0.51501 (15)	0.0199 (3)
H1A	0.4298	0.6718	0.4202	0.024*
H1B	0.5558	0.7151	0.5586	0.024*
O2	0.90901 (13)	0.56090 (6)	0.22963 (14)	0.0340 (3)
C2	0.67798 (17)	0.62052 (8)	0.46056 (15)	0.0197 (3)
H2A	0.6371	0.5698	0.4079	0.024*
O3	1.04100 (14)	0.67826 (6)	0.24051 (14)	0.0346 (3)
H3	1.1187	0.6536	0.1965	0.052*
C3	0.81062 (17)	0.60176 (8)	0.60609 (16)	0.0224 (3)
H3A	0.8576	0.6517	0.6553	0.027*
H3B	0.9115	0.5718	0.5707	0.027*
C4A	0.55889 (17)	0.59049 (8)	0.77883 (16)	0.0199 (3)
C4	0.72564 (17)	0.55353 (9)	0.73159 (16)	0.0237 (3)
H4A	0.6977	0.5001	0.6882	0.028*
H4B	0.8120	0.5477	0.8284	0.028*
C5	0.52730 (17)	0.59475 (8)	0.93349 (16)	0.0212 (3)
H5A	0.6199	0.5814	1.0147	0.025*
C6	0.35638 (18)	0.61914 (8)	0.98126 (16)	0.0205 (3)
C7	0.20938 (17)	0.63442 (8)	0.84973 (16)	0.0230 (3)
H7A	0.1229	0.6715	0.8888	0.028*
H7B	0.1467	0.5844	0.8203	0.028*
C8A	0.42640 (16)	0.61828 (8)	0.64259 (15)	0.0194 (3)
H8AA	0.3684	0.5705	0.5902	0.023*
C8	0.28119 (17)	0.66910 (8)	0.70197 (16)	0.0216 (3)
H8A	0.1826	0.6747	0.6149	0.026*
H8B	0.3292	0.7224	0.7282	0.026*
C9	0.76216 (18)	0.67094 (8)	0.33847 (17)	0.0231 (3)
H9A	0.6693	0.6862	0.2515	0.028*
H9B	0.8092	0.7199	0.3918	0.028*
C10	0.91038 (17)	0.62978 (8)	0.26540 (15)	0.0205 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0254 (5)	0.0284 (6)	0.0232 (5)	−0.0011 (4)	0.0073 (4)	−0.0009 (4)
C1	0.0182 (6)	0.0209 (7)	0.0206 (6)	0.0022 (5)	0.0016 (5)	0.0008 (5)
O2	0.0282 (6)	0.0243 (6)	0.0520 (7)	−0.0004 (4)	0.0152 (5)	−0.0066 (5)
C2	0.0183 (6)	0.0192 (7)	0.0221 (7)	0.0009 (5)	0.0037 (5)	0.0004 (5)
O3	0.0302 (6)	0.0287 (6)	0.0489 (7)	−0.0064 (4)	0.0218 (5)	−0.0073 (5)
C3	0.0166 (6)	0.0264 (7)	0.0248 (7)	0.0032 (5)	0.0040 (5)	0.0008 (5)
C4A	0.0181 (6)	0.0167 (7)	0.0248 (7)	−0.0002 (5)	0.0027 (5)	0.0019 (5)
C4	0.0200 (7)	0.0275 (8)	0.0238 (7)	0.0062 (5)	0.0031 (5)	0.0040 (6)
C5	0.0187 (6)	0.0207 (7)	0.0238 (7)	0.0008 (5)	0.0011 (5)	0.0024 (5)

C6	0.0221 (7)	0.0155 (7)	0.0244 (7)	−0.0028 (5)	0.0053 (5)	−0.0003 (5)
C7	0.0166 (6)	0.0259 (7)	0.0272 (7)	0.0010 (5)	0.0053 (5)	−0.0007 (5)
C8A	0.0167 (6)	0.0196 (7)	0.0220 (7)	0.0003 (5)	0.0022 (5)	−0.0014 (5)
C8	0.0156 (6)	0.0245 (7)	0.0247 (7)	0.0027 (5)	0.0017 (5)	0.0007 (5)
C9	0.0224 (7)	0.0217 (7)	0.0260 (7)	0.0018 (5)	0.0061 (5)	0.0009 (5)
C10	0.0197 (7)	0.0221 (8)	0.0195 (6)	0.0004 (5)	0.0016 (5)	0.0023 (5)

Geometric parameters (Å, °)

O1—C6	1.2356 (17)	C4A—C8A	1.5105 (18)
C1—C2	1.5253 (17)	C4—H4A	0.9900
C1—C8A	1.5341 (18)	C4—H4B	0.9900
C1—H1A	0.9900	C5—C6	1.4578 (18)
C1—H1B	0.9900	C5—H5A	0.9500
O2—C10	1.2054 (18)	C6—C7	1.5012 (19)
C2—C9	1.5260 (18)	C7—C8	1.5243 (18)
C2—C3	1.5263 (18)	C7—H7A	0.9900
C2—H2A	1.0000	C7—H7B	0.9900
O3—C10	1.3213 (17)	C8A—C8	1.5241 (17)
O3—H3	0.8400	C8A—H8AA	1.0000
C3—C4	1.5293 (18)	C8—H8A	0.9900
C3—H3A	0.9900	C8—H8B	0.9900
C3—H3B	0.9900	C9—C10	1.5088 (18)
C4A—C5	1.3454 (19)	C9—H9A	0.9900
C4A—C4	1.5029 (18)	C9—H9B	0.9900
C2—C1—C8A	114.33 (11)	O1—C6—C5	120.78 (12)
C2—C1—H1A	108.7	O1—C6—C7	121.87 (12)
C8A—C1—H1A	108.7	C5—C6—C7	117.27 (11)
C2—C1—H1B	108.7	C6—C7—C8	111.10 (11)
C8A—C1—H1B	108.7	C6—C7—H7A	109.4
H1A—C1—H1B	107.6	C8—C7—H7A	109.4
C1—C2—C9	110.08 (11)	C6—C7—H7B	109.4
C1—C2—C3	109.66 (11)	C8—C7—H7B	109.4
C9—C2—C3	111.39 (11)	H7A—C7—H7B	108.0
C1—C2—H2A	108.5	C4A—C8A—C8	111.96 (11)
C9—C2—H2A	108.5	C4A—C8A—C1	111.54 (10)
C3—C2—H2A	108.5	C8—C8A—C1	110.24 (11)
C10—O3—H3	109.5	C4A—C8A—H8AA	107.6
C2—C3—C4	111.73 (11)	C8—C8A—H8AA	107.6
C2—C3—H3A	109.3	C1—C8A—H8AA	107.6
C4—C3—H3A	109.3	C8A—C8—C7	112.50 (11)
C2—C3—H3B	109.3	C8A—C8—H8A	109.1
C4—C3—H3B	109.3	C7—C8—H8A	109.1
H3A—C3—H3B	107.9	C8A—C8—H8B	109.1
C5—C4A—C4	121.35 (12)	C7—C8—H8B	109.1
C5—C4A—C8A	122.47 (12)	H8A—C8—H8B	107.8
C4—C4A—C8A	116.10 (11)	C10—C9—C2	113.47 (11)
C4A—C4—C3	112.87 (11)	C10—C9—H9A	108.9
C4A—C4—H4A	109.0	C2—C9—H9A	108.9

C3—C4—H4A	109.0	C10—C9—H9B	108.9
C4A—C4—H4B	109.0	C2—C9—H9B	108.9
C3—C4—H4B	109.0	H9A—C9—H9B	107.7
H4A—C4—H4B	107.8	O2—C10—O3	123.33 (12)
C4A—C5—C6	122.52 (12)	O2—C10—C9	124.23 (12)
C4A—C5—H5A	118.7	O3—C10—C9	112.41 (12)
C6—C5—H5A	118.7		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1^{i}	0.84	1.86	2.6793 (14)	163
C7—H7B···O2^{ii}	0.99	2.53	3.4758 (17)	161

Symmetry codes: (i) *x*+1, *y*, *z*−1; (ii) −*x*+1, −*y*+1, −*z*+1.

Fig. 1

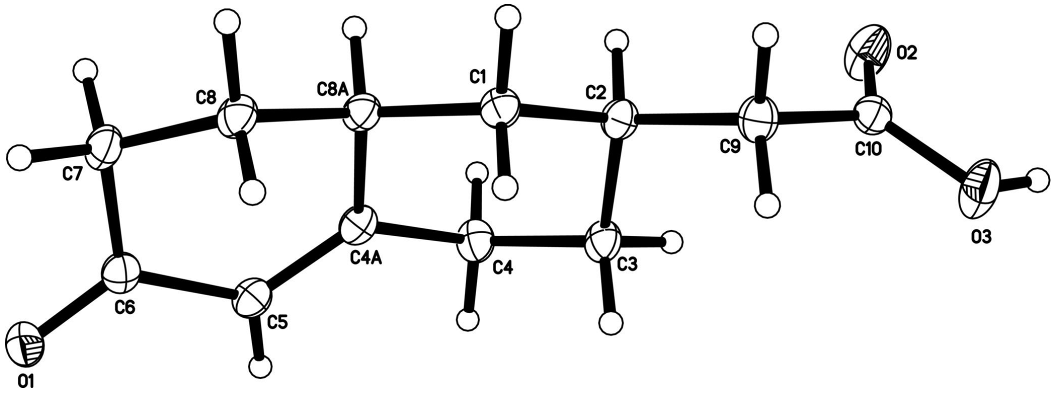

Fig. 2