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(2*RS*,4a*RS*,8a*RS*)-6-Oxoperhydronaphthalene-2-acetic acid: catemeric hydrogen bonding in a bicyclic keto acid

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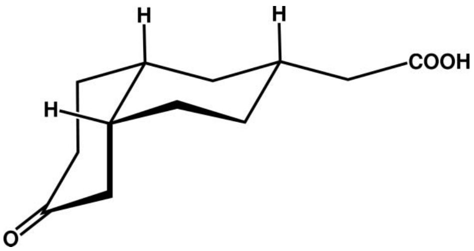
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.037; wR factor = 0.102; data-to-parameter ratio = 13.5.

The title racemate, $C_{12}H_{18}O_3$, aggregates in the solid as translational acid-to-ketone hydrogen-bonding catemers [O···O = 2.6816 (17) Å and O—H···O = 169°]. The stereochemistry obtained for the side chain arises spontaneously during the synthesis, prior to the hydrogenation that produces the *cis* ring juncture. Three intermolecular C—H···O close contacts were found.

Related literature

For related literature, see: House *et al.* (1965); Malak *et al.* (2007).



Experimental

Crystal data

$C_{12}H_{18}O_3$
M_r = 210.26
Monoclinic, $C2/c$
a = 21.1804 (4) Å
b = 10.1644 (2) Å
c = 11.3208 (3) Å
β = 113.841 (2)°
V = 2229.24 (8) Å^3
Z = 8
Cu $K\alpha$ radiation
μ = 0.72 mm^{-1}
T = 100 (2) K
0.39 × 0.25 × 0.25 mm

Data collection

Bruker SMART CCD APEX II area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.767, T_{max} = 0.841
11737 measured reflections
1848 independent reflections
1516 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.102
S = 1.04
1848 reflections
137 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1^{i}	0.84	1.85	2.6816 (17)	169
C1—H1A···O2^{ii}	0.99	2.53	3.4997 (18)	167
C5—H5A···O2^{ii}	0.99	2.51	3.368 (2)	145
C8—H8A···O3^{iii}	0.99	2.52	3.4559 (19)	158

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

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; 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 Gree Loober Spoog for helpful discussions. The authors acknowledge support by NSF–CRIF grant No. 0443538.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2498).

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supplementary materials

Acta Cryst. (2007). E**63**, o4009 [**doi:10.1107/S1600536807043206**]

(2*RS*,4a*RS*,8a*RS*)-6-Oxoperhydronaphthalene-2-acetic acid: catemeric hydrogen bonding in a bicyclic keto acid

J. Desai, **R. A. Lalancette** and **H. W. Thompson**

Comment

Among the five H-bonding modes known for ketocarboxylic acids, dimers are found most often. However, we have shown that acid-to-ketone catemers occur more frequently when centrosymmetry is thwarted or disfavored, as well as among conformationally constrained molecules. The latter is the case for the title compound.

Fig. 1 shows the asymmetric unit with its numbering. In principle, the flexibility of the *cis*-decalin system permits either of two double-chair conformations. However, the disfavored arrangement would place the side-chain on an axial bond on the inside of the system's curvature, resulting in serious steric interference with an axial H at C8. The C2—C9 staggering requires that C10 have a *gauche* interaction with an equatorial hydrogen either at C1 or C3. Such *gauche* arrangements are less serious here than in systems where all centers are tetrahedral, because the carboxyl's sp^2 hybridization diminishes the steric repulsions involved. The observed C2—C9 conformation has torsion angle C3—C2—C9—C10 = −174.51 (13)°). Within the asymmetric unit, any energy advantage for this arrangement appears so slight that the choice is likely dictated by packing considerations. The remaining available rotation yields a C2—C9—C10—O3 torsion angle of 41.98 (19)° for the carboxyl group.

The averaging of C—O bond lengths and C—C—O angles by disorder often found in carboxyl dimers it is not seen in H-bonding modes whose geometries exclude the averaging mechanisms responsible. Because the title compound's aggregation is not dimeric, these bond lengths and angles are typical of those in highly ordered dimeric carboxyls.

Fig. 2 shows the packing of the cell, with extra molecules included to illustrate the acid-to-ketone H-bonding scheme. Each carboxylic acid is linked to the ketone in a molecule translationally related in the b direction [O···O = 2.6816 (17) Å; O—H···O = 169°], with each of the cell's eight molecules participating in a separate H-bonding chain. These eight parallel chains appear as four counterdirectional pairs arrayed centrosymmetrically about 1/2,1/2,1/2.

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 O in terms of its deviation from, respectively, C=O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). Here, these angles are 125 & −7.5°.

Three intermolecular close contacts were found within the 2.6 Å range we standardly survey for non-bonded C—H···O packing interactions (Table 1).

Experimental

The title compound has not previously been reported. The corresponding $\Delta^{4a,5}$ keto acid, prepared as described by Malak *et al.* (2007), was hydrogenated over Pd/C in absolute ethanol solution and yielded material mp 405 when recrystallized from Et_2O/hexane. The stereochemistry obtained for C2 *versus* C8a arises prior to the hydrogenation, probably as a result of equilibrations during saponification or earlier (House *et al.*, 1965), while the *cis* ring-juncture stereochemistry obtained in the reduction is typical of results in a variety of octalones.

The solid-state (KBr) infrared spectrum of (I) has C=O absorptions at 1721 & 1678 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. In $CHCl_3$ solution, where dimers predominate, these bands coalesce and appear at 1706 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

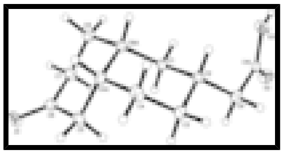

Fig. 1. The asymmetric unit with its numbering. Displacement ellipsoids are set at the 30% probability level.

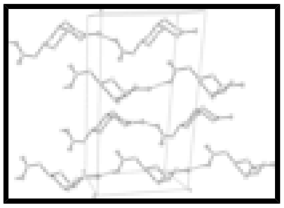

Fig. 2. A partial packing diagram with extracellular molecules, illustrating four of the eight translational acid-to-ketone H-bonding chains passing through the cell; the remaining four chains are related by centrosymmetry (about 1/2,1/2,1/2) to the ones shown and are therefore counterdirectional to them. All carbon-bound H atoms are removed for clarity. Displacement ellipsoids are set at the 30% probability level. Hydrogen bonds are shown as dashed lines.

'(2RS,4aRS,8aRS)-6-Oxoperhydronaphthalene-2-acetic acid'

Crystal data

$C_{12}H_{18}O_3$

$M_r = 210.26$

Monoclinic, *C*2/*c*

Hall symbol: -C 2yc

$a = 21.1804 (4)$ Å

$b = 10.1644 (2)$ Å

$c = 11.3208 (3)$ Å

$\beta = 113.841 (2)°$

$V = 2229.24 (8)$ Å^3

$Z = 8$

$F_{000} = 912$

$D_x = 1.253$ Mg m^{-3}

Melting point: 405 K

Cu *K*α radiation

$\lambda = 1.54178$ Å

Cell parameters from 11741 reflections

$\theta = 4.6–64.8°$

$\mu = 0.72$ mm^{-1}

$T = 100 (2)$ K

Parallelepiped, colourless

0.39 × 0.25 × 0.25 mm

Data collection

Bruker SMART CCD APEX II 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)

$T_{\min} = 0.767$, $T_{\max} = 0.841$

11737 measured reflections

1848 independent reflections

1516 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

$\theta_{\max} = 64.8°$

$\theta_{\min} = 4.6°$

$h = -24\rightarrow24$

$k = -11\rightarrow11$

$l = -11\rightarrow12$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.102$

$S = 1.04$

1848 reflections

137 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

$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 1.3738P]$
where $P = (F_o^2 + 2F_c^2)/3$

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

$\Delta\rho_{\max} = 0.31$ e Å^{-3}

$\Delta\rho_{\min} = -0.15$ e Å^{-3}

Extinction correction: *SHELXTL* (Sheldrick, 2004)

Extinction coefficient: none

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_{iso}*/U_{eq}
C1	0.12293 (7)	0.55256 (15)	0.08048 (14)	0.0208 (3)
H1A	0.1606	0.6001	0.1498	0.025*
H1B	0.1081	0.4792	0.1208	0.025*

O1	0.10016 (6)	1.02711 (11)	0.15128 (12)	0.0359 (3)
C2	0.15039 (7)	0.49638 (14)	−0.01477 (14)	0.0213 (3)
H2A	0.1128	0.4436	−0.0809	0.026*
O2	0.23668 (6)	0.24042 (12)	0.21637 (11)	0.0348 (3)
C3	0.16989 (8)	0.60852 (15)	−0.08379 (16)	0.0260 (4)
H3A	0.2084	0.6596	−0.0201	0.031*
H3B	0.1858	0.5714	−0.1479	0.031*
O3	0.13891 (6)	0.22685 (11)	0.04077 (11)	0.0324 (3)
H3	0.1322	0.1624	0.0807	0.049*
C4	0.10842 (9)	0.69988 (16)	−0.15210 (15)	0.0285 (4)
H4A	0.1232	0.7730	−0.1928	0.034*
H4B	0.0718	0.6503	−0.2216	0.034*
C4A	0.07856 (8)	0.75706 (15)	−0.06068 (14)	0.0237 (4)
H4AA	0.0343	0.8022	−0.1145	0.028*
C5	0.12764 (8)	0.86090 (16)	0.02976 (15)	0.0254 (4)
H5A	0.1742	0.8220	0.0735	0.030*
H5B	0.1313	0.9363	−0.0226	0.030*
C6	0.10384 (8)	0.90974 (16)	0.12963 (16)	0.0262 (4)
C7	0.08506 (9)	0.80542 (16)	0.20388 (16)	0.0282 (4)
H7A	0.0631	0.8470	0.2569	0.034*
H7B	0.1275	0.7601	0.2629	0.034*
C8	0.03537 (8)	0.70459 (16)	0.11229 (16)	0.0275 (4)
H8A	−0.0098	0.7474	0.0640	0.033*
H8B	0.0281	0.6322	0.1639	0.033*
C8A	0.06196 (7)	0.64682 (15)	0.01577 (14)	0.0222 (3)
H8AA	0.0234	0.5938	−0.0479	0.027*
C9	0.21235 (8)	0.40612 (16)	0.05273 (16)	0.0262 (4)
H9A	0.2308	0.3787	−0.0111	0.031*
H9B	0.2489	0.4574	0.1206	0.031*
C10	0.19796 (7)	0.28470 (15)	0.11360 (15)	0.0229 (3)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0221 (7)	0.0191 (8)	0.0203 (7)	−0.0016 (6)	0.0075 (6)	0.0014 (6)
O1	0.0488 (7)	0.0217 (6)	0.0414 (7)	−0.0043 (5)	0.0228 (6)	−0.0076 (5)
C2	0.0211 (7)	0.0202 (8)	0.0215 (8)	−0.0015 (6)	0.0072 (6)	−0.0014 (6)
O2	0.0273 (6)	0.0412 (8)	0.0292 (7)	0.0041 (5)	0.0043 (5)	0.0073 (5)
C3	0.0324 (8)	0.0242 (8)	0.0264 (9)	−0.0012 (7)	0.0171 (7)	−0.0012 (6)
O3	0.0322 (6)	0.0251 (6)	0.0297 (6)	−0.0043 (5)	0.0020 (5)	0.0036 (5)
C4	0.0396 (9)	0.0248 (8)	0.0230 (8)	0.0010 (7)	0.0146 (7)	0.0030 (6)
C4A	0.0261 (8)	0.0206 (8)	0.0213 (8)	0.0018 (6)	0.0062 (6)	0.0020 (6)
C5	0.0293 (8)	0.0212 (8)	0.0280 (8)	−0.0013 (6)	0.0139 (6)	0.0025 (6)
C6	0.0246 (8)	0.0245 (9)	0.0265 (8)	−0.0019 (6)	0.0072 (6)	−0.0033 (6)
C7	0.0337 (8)	0.0269 (9)	0.0282 (9)	−0.0008 (7)	0.0168 (7)	−0.0032 (7)
C8	0.0260 (8)	0.0249 (9)	0.0342 (9)	−0.0002 (6)	0.0148 (7)	0.0003 (7)
C8A	0.0219 (7)	0.0206 (8)	0.0228 (8)	−0.0010 (6)	0.0076 (6)	0.0001 (6)
C9	0.0208 (7)	0.0258 (8)	0.0314 (9)	0.0023 (6)	0.0098 (6)	0.0007 (7)

C10	0.0209 (7)	0.0229 (8)	0.0246 (8)	0.0065 (6)	0.0090 (6)	−0.0032 (6)

Geometric parameters (Å, °)

C1—C2	1.528 (2)	C4A—C8A	1.541 (2)
C1—C8A	1.536 (2)	C4A—C5	1.544 (2)
C1—H1A	0.9900	C4A—H4AA	1.0000
C1—H1B	0.9900	C5—C6	1.496 (2)
O1—C6	1.227 (2)	C5—H5A	0.9900
C2—C9	1.529 (2)	C5—H5B	0.9900
C2—C3	1.530 (2)	C6—C7	1.503 (2)
C2—H2A	1.0000	C7—C8	1.533 (2)
O2—C10	1.207 (2)	C7—H7A	0.9900
C3—C4	1.530 (2)	C7—H7B	0.9900
C3—H3A	0.9900	C8—C8A	1.534 (2)
C3—H3B	0.9900	C8—H8A	0.9900
O3—C10	1.3252 (19)	C8—H8B	0.9900
O3—H3	0.8400	C8A—H8AA	1.0000
C4—C4A	1.529 (2)	C9—C10	1.504 (2)
C4—H4A	0.9900	C9—H9A	0.9900
C4—H4B	0.9900	C9—H9B	0.9900

C2—C1—C8A	112.53 (12)	C6—C5—H5B	109.1
C2—C1—H1A	109.1	C4A—C5—H5B	109.1
C8A—C1—H1A	109.1	H5A—C5—H5B	107.8
C2—C1—H1B	109.1	O1—C6—C5	122.79 (15)
C8A—C1—H1B	109.1	O1—C6—C7	121.45 (15)
H1A—C1—H1B	107.8	C5—C6—C7	115.76 (14)
C1—C2—C9	111.49 (12)	C6—C7—C8	110.96 (13)
C1—C2—C3	109.89 (12)	C6—C7—H7A	109.4
C9—C2—C3	110.36 (12)	C8—C7—H7A	109.4
C1—C2—H2A	108.3	C6—C7—H7B	109.4
C9—C2—H2A	108.3	C8—C7—H7B	109.4
C3—C2—H2A	108.3	H7A—C7—H7B	108.0
C4—C3—C2	111.11 (12)	C7—C8—C8A	112.85 (12)
C4—C3—H3A	109.4	C7—C8—H8A	109.0
C2—C3—H3A	109.4	C8A—C8—H8A	109.0
C4—C3—H3B	109.4	C7—C8—H8B	109.0
C2—C3—H3B	109.4	C8A—C8—H8B	109.0
H3A—C3—H3B	108.0	H8A—C8—H8B	107.8
C10—O3—H3	109.5	C8—C8A—C1	112.28 (12)
C4A—C4—C3	112.88 (13)	C8—C8A—C4A	110.76 (13)
C4A—C4—H4A	109.0	C1—C8A—C4A	112.51 (12)
C3—C4—H4A	109.0	C8—C8A—H8AA	107.0
C4A—C4—H4B	109.0	C1—C8A—H8AA	107.0
C3—C4—H4B	109.0	C4A—C8A—H8AA	107.0
H4A—C4—H4B	107.8	C10—C9—C2	115.43 (12)
C4—C4A—C8A	110.76 (13)	C10—C9—H9A	108.4
C4—C4A—C5	110.91 (13)	C2—C9—H9A	108.4
C8A—C4A—C5	111.72 (12)	C10—C9—H9B	108.4

C4—C4A—H4AA	107.8	C2—C9—H9B	108.4
C8A—C4A—H4AA	107.8	H9A—C9—H9B	107.5
C5—C4A—H4AA	107.8	O2—C10—O3	122.47 (15)
C6—C5—C4A	112.69 (13)	O2—C10—C9	124.27 (14)
C6—C5—H5A	109.1	O3—C10—C9	113.22 (13)
C4A—C5—H5A	109.1		

C8A—C1—C2—C9	178.32 (12)	C6—C7—C8—C8A	52.53 (18)
C8A—C1—C2—C3	55.63 (16)	C7—C8—C8A—C1	71.69 (17)
C1—C2—C3—C4	−56.71 (16)	C7—C8—C8A—C4A	−55.02 (17)
C9—C2—C3—C4	179.93 (13)	C2—C1—C8A—C8	−179.09 (12)
C2—C3—C4—C4A	56.59 (17)	C2—C1—C8A—C4A	−53.33 (16)
C3—C4—C4A—C8A	−52.68 (17)	C4—C4A—C8A—C8	177.19 (12)
C3—C4—C4A—C5	71.97 (17)	C5—C4A—C8A—C8	53.01 (16)
C4—C4A—C5—C6	−174.28 (13)	C4—C4A—C8A—C1	50.61 (16)
C8A—C4A—C5—C6	−50.18 (17)	C5—C4A—C8A—C1	−73.58 (16)
C4A—C5—C6—O1	−130.97 (16)	C1—C2—C9—C10	63.15 (17)
C4A—C5—C6—C7	49.60 (19)	C3—C2—C9—C10	−174.43 (13)
O1—C6—C7—C8	130.45 (16)	C2—C9—C10—O2	−140.42 (16)
C5—C6—C7—C8	−50.12 (18)	C2—C9—C10—O3	41.91 (19)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1^{i}	0.84	1.85	2.6816 (17)	169
C1—H1A···O2^{ii}	0.99	2.53	3.4997 (18)	167
C5—H5A···O2^{ii}	0.99	2.51	3.368 (2)	145
C8—H8A···O3^{iii}	0.99	2.52	3.4559 (19)	158

Symmetry codes: (i) *x*, *y*−1, *z*; (ii) −*x*+1/2, *y*+1/2, −*z*+1/2; (iii) −*x*, −*y*+1, −*z*.

Fig. 1

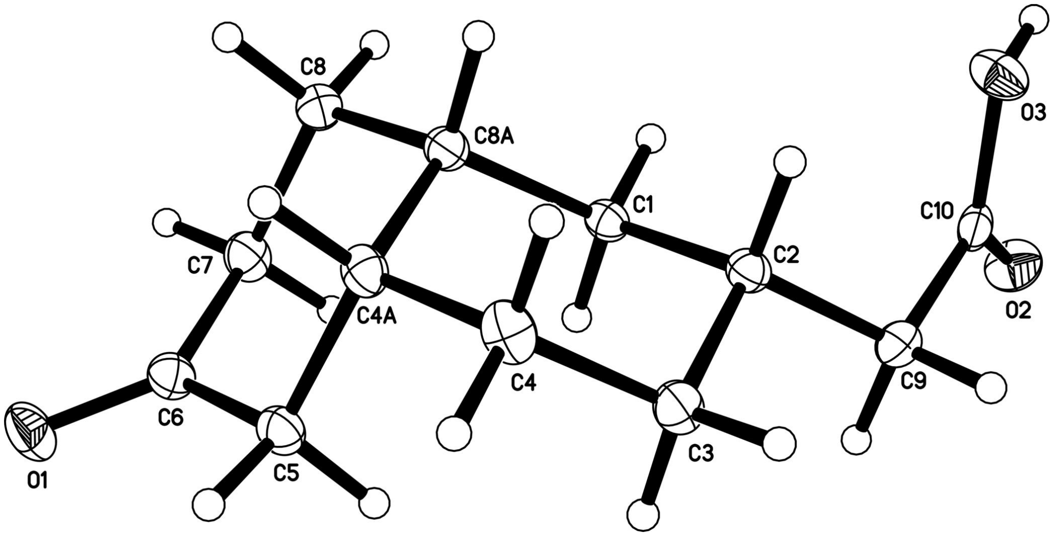

Fig. 2