8566 measured reflections
7766 independent reflections
3 standard reflections every 100 reflections
intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0415$
$wR(F^2) = 0.1092$
$S = 1.032$
7766 reflections
768 parameters
H atoms not refined
$w = 1/[\sigma^2(F_o^2) + (0.0564P)^2 + 0.9086P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0014 (1)
Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)
Flack parameter for absolute configuration determination = −0.003 (15)

Table 1. *Selected torsion angles (°)*

C6—C5—O8—C9	−17.8 (6)	C55—O58—C59—C60	173.8 (4)
C5—O8—C9—C10	−170.2 (4)	O58—C59—C60—C61	67.9 (4)
O8—C9—C10—C11	−60.1 (5)	C59—C60—C61—N62	165.1 (3)
C9—C10—C11—N12	−169.2 (3)	C64—C65—N70—C71	−84.8 (4)
C14—C15—N20—C21	74.7 (4)	C64—C65—C66—O68	−64.4 (4)
N20—C15—C16—O18	−53.8 (4)	N70—C65—C66—O68	59.2 (4)
N20—C15—C16—C17	−177.2 (3)	N70—C65—C66—C67	−179.5 (3)
C15—C16—O18—C19	163.0 (3)	C65—C66—O68—C69	−159.7 (4)
N20—C21—C23—C28	−1.7 (6)	N70—C71—C73—C78	8.0 (6)
C23—C28—O29—C30	−178.3 (3)	C73—C78—O79—C80	178.2 (3)
C35—C36—C38—O39	52.1 (4)	C85—C86—C88—O89	68.4 (4)
C35—C36—C38—C40	173.3 (3)	C85—C86—C88—C90	−170.0 (3)
O37—C36—C38—O39	−71.3 (4)	O87—C86—C88—O89	−55.7 (4)
C54—C55—O58—C59	28.7 (6)		

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

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
N20—H20···O29	1.98	2.647 (4)	134
N31—H31*A*···O87	2.21	3.041 (5)	162
N31—H31*B*···O41	2.37	3.195 (5)	160
N70—H70···O79	1.96	2.646 (4)	136
N81—H81*B*···O42	2.29	3.109 (5)	158
O91—H91···O42	1.81	2.624 (4)	171
O33—H33···O72^{i}	1.89	2.628 (5)	149
N12—H12···O83^{ii}	1.82	2.726 (5)	172
N81—H81*A*···O83^{iii}	2.66	3.435 (5)	151
N81—H81*A*···O84^{iii}	2.50	3.106 (5)	128
O37—H37···O84^{iii}	2.08	2.846 (4)	157
N62—H62···O41^{iv}	1.87	2.749 (4)	163
O89—H89···O22^{v}	1.95	2.757 (4)	166

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

The data were collected using a variable scan speed with a scan range of 0.4° below $K\alpha_1$ to 0.4° above $K\alpha_2$. The ratio of total background time to scan time was 0.5. The structure was solved by direct methods and refined by anisotropic full-matrix least squares on F^2. All H atoms were found from difference Fourier syntheses but placed at geometrical positions and allowed to ride on their parent atom. The absolute configuration was determined according to Flack (1983).

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *DIAMOND* (Bergerhoff, 1996). Software used to prepare material for publication: *PARST* (Nardelli, 1983).

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Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: NA1275). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Catemeric Hydrogen Bonding in a γ-Keto Acid: (±)-2a,3,4,5-Tetrahydro-1(2*H*)-oxoacenaphthylene-2a-carboxylic Acid

ANDREW P. J. BRUNSKILL, HUGH W. THOMPSON AND ROGER A. LALANCETTE*

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA.
E-mail: lalancette@hades.rutgers.edu

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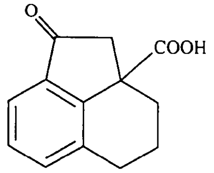
Abstract

The title keto-carboxylic acid, $C_{13}H_{12}O_3$, forms spiral carboxyl-to-ketone hydrogen-bonding catemers, whose helical axes are parallel to the *b* cell axis. Two single-strand hydrogen-bonding chains pass through the cell, each composed of molecules of a single chirality.

Comment

Keto-carboxylic acids offer opportunities for variation on the standard pattern of dimeric hydrogen bonding observed in functionally unelaborated acids. In most cases, however, the ketone does not participate and typical hydrogen-bonded dimers result. Less frequently, intermolecular carboxyl-to-ketone hydrogen bonds are seen, usually repeating helically along a cell axis to give a catemer. A third rare arrangement has an internal hydrogen bond and one instance is known of acid-to-ketone dimerization. We have previously referenced and discussed numerous examples of these keto acid hydrogen-bonding modes (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

We report here the structure and hydrogen-bonding behavior of (±)-2a,3,4,5-tetrahydro-1(2*H*)-oxoacenaphthylene-2a-carboxylic acid, (I), a γ-keto acid. The category of γ-keto acids is especially rich in hydrogen-bonding types, embracing internal hydrogen bonds and both hydrated and anhydrous dimers, as well as catemers of both the helical and translational type.



(I)

The asymmetric unit of (I) with its numbering is shown in Fig. 1. The tricyclic portion of the molecule has conformational flexibility only in the non-aromatic six-membered ring and the expected half-chair conformation is the one observed [C2*A*—C3—C4—C5 −60.5 (4)°]. Only the carboxyl group is fully rotatable; it is turned, with its carbonyl group towards the ketone, so that the carboxyl plane coincides roughly with the C2*A*—C8*B* bond [O2—C9—C2*A*—C8*B* 12.6 (4)°]. The dihedral angle formed between the ketone and carboxyl planes is 86.4 (1)°.

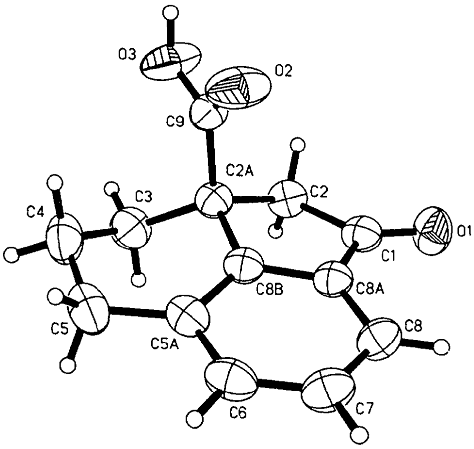


Fig. 1. The asymmetric unit of (I), with the atomic numbering. Ellipsoids are set at the 40% probability level.

Complete or partial averaging of the C—O bond lengths and C—C—O angles by disorder is frequent in carboxyl dimers (Leiserowitz, 1976). This may be due to static positional disorder in the crystal, to rotation of the entire dimer subunit or to tautomeric H-atom exchange (Meier, Graf & Ernst, 1982; Nagaoka, Terao, Imashiro, Hirota & Hayashi, 1983) permitted by the local symmetry at the dimer site. Acids involved in catemeric hydrogen bonding lack the geometry that allows any of these disorder mechanisms and typically are highly ordered. In (I), no significant averaging is observed and the bond lengths are 1.192 (3) and 1.311 (3) Å, with angles of 112.5 (3) and 125.2 (3)°. Our own survey of 28 catemeric keto acid structures gives average values of 1.197 (7) and 1.320 (10) Å, and 112.8 (14) and 124.5 (10)°. Values cited as typical for highly ordered dimeric carboxyls are 1.21 and 1.31 Å, and 112 and 123° (Borthwick, 1980).

The packing of the cell, with extracellular molecules included in order to illustrate the hydrogen-bonding catemers, whose helical axes are parallel to the *b* axis, is shown in Fig. 2. In an arrangement typical of catemeric racemates, two centrosymmetrically related single-strand helices pass through the cell, each composed of only one enantiomeric species (Vanderhoff, Thompson & Lalancette, 1986; Lalancette, Vanderhoff & Thompson, 1991; Lalancette, Thompson & Vanderhoff, 1991). The screw relationship seen here within the chains is more common than are translational catemers (Lalancette, Coté & Thompson, 1997; Brunskill, Lalancette & Thompson, 1997).

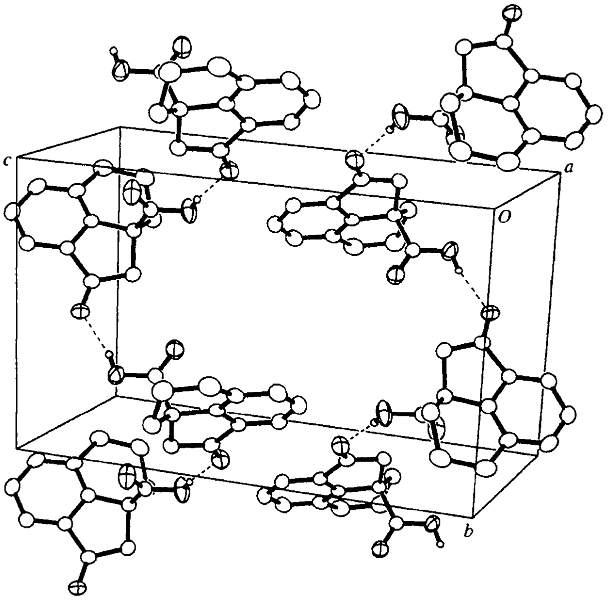


Fig. 2. A view of the packed cell with extracellular molecules. The two single-strand hydrogen-bonding helices passing through the cell are centrosymmetrically related. Each is composed of molecules of a single chirality. The non-carboxyl H atoms have been removed for clarity. Ellipsoids are set at the 30% probability level.

The solid-state (KBr) IR spectrum of (I) displays a double C═O peak at 1729 and 1724 cm^{-1} assigned to the carboxyl, plus a peak assigned to the ketone at 1678 cm^{-1}. These absorption positions are consistent with the known shifts due to removal of hydrogen bonding from carboxylic acid C═O and addition of hydrogen bonding to an indanone (Lalancette, Vanderhoff & Thompson, 1991). In $CHCl_3$ solution, where dimers predominate, all these peaks coalesce to a single broader absorption centered at 1714 cm^{-1}.

Experimental

7,8-Dihydro-2-oxoacenaphthylene-1,8a(6*H*)-dicarboximide (Aldrich Chemical Company) was subjected to acid-catalyzed decarboxylative hydrolysis (Campaigne, Roelofs & Weddleton, 1966, 1968). The resulting product, (I), after recrystallization from absolute ethanol, had a melting point of 448 K. Crystals of (I) suitable for analysis were obtained from acetone.

Crystal data

$C_{13}H_{12}O_3$
$M_r = 216.23$
Monoclinic
$P2_1/n$
$a = 6.780\,(1)$ Å
$b = 10.229\,(3)$ Å
$c = 15.991\,(2)$ Å
$\beta = 98.83\,(2)°$
$V = 1095.9\,(4)$ Å^3
$Z = 4$
$D_x = 1.311$ Mg m^{-3}
$D_m = 1.30\,(1)$ Mg m^{-3}
D_m measured by flotation in cyclohexane/CCl_4

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 21 reflections
$\theta = 6.5–18.2°$
$\mu = 0.093$ mm^{-1}
$T = 293\,(2)$ K
Hexagonal prism
0.48 × 0.28 × 0.12 mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: face-indexed numerical
$T_{\min} = 0.974$, $T_{\max} = 0.990$
2729 measured reflections
1917 independent reflections
1135 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.0333$
$\theta_{\max} = 25°$
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 12$
$l = -19 \rightarrow 19$
3 standard reflections every 97 reflections intensity decay: 1.55%

Refinement

Refinement on F^2
$R(F) = 0.0565$
$wR(F^2) = 0.1481$
$S = 1.037$
1916 reflections
152 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2 + 0.195P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.027$

$\Delta\rho_{\max} = 0.268$ e Å^{-3}
$\Delta\rho_{\min} = -0.182$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.015 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) and hydrogen-bonding geometry (Å, °)*

O1—C1	1.225 (3)	C1—C8*A*	1.470 (4)
O2—C9	1.192 (3)	C1—C2	1.514 (4)
O3—C9	1.311 (3)	C2*A*—C9	1.520 (4)
O1—C1—C8*A*	126.1 (3)	O2—C9—O3	122.3 (3)
O1—C1—C2	125.9 (3)	O2—C9—C2*A*	125.2 (3)
C8*A*—C1—C2	108.0 (2)	O3—C9—C2*A*	112.5 (3)
C2*A*—C3—C4—C5	−60.5 (4)	O2—C9—C2*A*—C8*B*	12.6 (4)
H3*B*—C3—C4—H4*A*	−178.6		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O1$^{\rm i}$	0.82 (4)	1.87 (4)	2.667 (3)	163 (4)

Symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

All non-carboxyl H atoms were found in electron-density difference maps but replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms. The carboxyl H3 atom was found in an electron-density difference map and was allowed to refine with its displacement parameter held at 0.08. The aromatic, six-membered-ring secondary (CH_2 type) and five-membered-ring secondary (CH_2 type) H-atom displacement parameters were allowed to refine as three separate groups.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1238). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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