4221 independent reflections
2095 reflections with
  $I > 2\sigma_I$

6 standard reflections
every 150 reflections
intensity decay: 4.0%

Refinement

Refinement on F^2
$R(F) = 0.057$
$wR(F^2) = 0.070$
$S = 1.71$
4221 reflections
225 parameters
H atoms: see below
$w = 1/\sigma^2(F^2)$

$(\Delta/\sigma)_{max} < 0.01$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: none
Scattering factors from
Stewart *et al.* (1965) (H)
and Creagh & McAuley
(1992) (C, O)

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

O1—C13	1.447 (3)	O3—C16	1.419 (3)
O2—C17	1.439 (3)	O4—C12	1.400 (3)
O3—C6	1.394 (2)	O4—C20	1.396 (3)
C6—O3—C16	115.5 (2)	O4—C12—C7	118.5 (2)
C12—O4—C20	115.4 (2)	O4—C12—C11	118.9 (2)
O3—C6—C1	118.6 (2)	O1—C13—C2	110.1 (2)
O3—C6—C5	119.6 (2)	O2—C17—C8	113.5 (2)

Table 2. *Hydrogen-bonding geometry (Å, °) and significant C—H···O interactions in (I) at 296 K*

Note that no uncertainties are given for quantities involving H19C, H20A and H20B since these H atoms are fixed.

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^i	0.93 (3)	1.91 (3)	2.807 (2)	163 (3)
O2—H2···O1	0.83 (3)	1.97 (3)	2.805 (2)	175 (3)
C20—H20B···O3	0.98	2.52	3.400 (3)	150
C19—H19C···O4	0.98	2.57	2.866 (3)	97
C20—H20A···O3^{ii}	0.98	2.68	3.630 (3)	165

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

Scan widths were $(1.40 + 0.35\tan\theta)°$ in ω, with a background/scan time-ratio of 0.5. The data (with h 0 to 10, k 0 to 17, and l −20 to 20) were corrected for Lorentz and polarization effects. A linear decay correction was applied. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated space group $P2_1/a$ (No. 14); the cell was then transformed to the standard $P2_1/c$ setting, and since refinement proceeded well this space group was adopted. Difference Fourier methods were used to locate the initial H-atom positions. All H atoms were then refined isotropically. Subsequently, all H atoms except the hydroxyl-H atoms, H1 and H2, were made canonical, with C—H = 0.98 Å and U_{iso} = $1.2U_{eq}$ of the attached C atom. The hydroxyl-H atoms were refined isotropically; the refined O—H distances are given in Table 2. An extinction coefficient, predicted to be negative in the later stages of refinement, was not included in the model. The maximum positive residual peak is located between C3 and C14, ~0.6 Å from C3, and the maximum negative peak is located ~0.3 Å from C12.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Hydrogen bonding in [(1R*,7aS*)-hexahydro-5-oxo-1H-pyrrolizinyl-1-yl]acetic acid

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Abstract

The title acid, [(1R*,7aS*)-2,3,5,6,7,7a-hexahydro-5-oxo-1H-pyrrolizinyl-1-yl]acetic acid ($C_9H_{13}NO_3$), crystallized in the centrosymmetric space group $P\bar{1}$, with one molecule in the asymmetric unit. The single hydrogen bond, which involves the carboxyl group and the

keto-O atom, has an ordered carboxyl-H atom and an $O_D \cdots O_A$ distance of 2.640(1) Å. The structure comprises two sets of hydrogen-bonded chains cross-linked by C—H$\cdots$O interactions.

Comment

This report on the title compound, (I), is one of a series on hydrogen bonding in carboxylic acids, which includes another keto-acid, ortho-(1-naphthoyl)benzoic acid (Gerkin, 1998). Molecule (I) crystallized in the

(I)
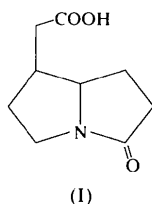
centrosymmetric space group $P\bar{1}$, with one molecule in the asymmetric unit. The refined molecule is shown in Fig. 1, together with the numbering scheme. A single hydrogen bond occurs in this structure, and in it the H atom is ordered. Geometric details of the hydrogen bond are given in Table 2. Hydrogen bond graph-set analysis (Bernstein et al., 1995) gives the first-level descriptor as $C(9)$, a chain propagating along [1$\bar{1}$0]; there are, of course, no higher-level graphs. There are two sets of such chains, one consisting of molecules of space group symmetry type 1 and the other of molecules of symmetry type 2. In addition, there are two significant intermolecular C—H$\cdots$O interactions whose H$\cdots$O distances are less than the corresponding sum of the van der Waals radii (Bondi, 1964); geometric details of these are also given in Table 2. These latter interactions cross-link the two types of hydrogen-

bonded chains described above, forming rings (at first-level) with descriptors $R_2^2(12)$ and $R_2^2(14)$, each about a center of symmetry. These features are illustrated in Fig. 2, which shows a central molecule and the four molecules with which it is linked by the interactions described. It may be noted that N1 does not act as an acceptor in this structure. Further, the catenation of the carboxyl group and the keto-O atom occurring here is the second most common pattern of hydrogen bonding seen in simple keto-carboxylic acids (Cote et al., 1996), the most common being that involving carboxyl–carboxyl interaction [as seen, for example, in ortho-(1-naphthoyl)benzoic acid].
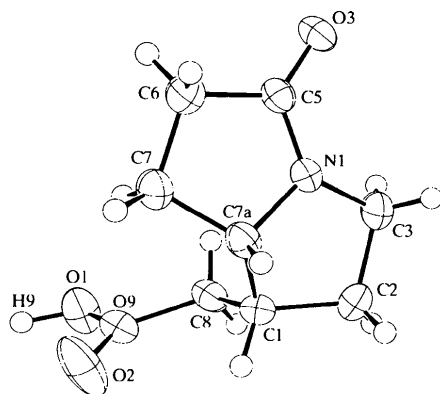
Comparisons of the geometry of the ketone core of (I) (O3, N1, C1–C3, C5–C7 and C7a) with the geometries of the same core in $C_{11}H_{17}NO_3$ (core with a substituent at C2), as reported by Hart & Yang (1985; hereafter HY), and in $C_{15}H_{15}Cl_2NO_3$ (core with a substituent at C3), as reported by Ferguson et al. (1990; hereafter FLM), show good agreement. Thus, for the ten interatomic distances in the core, the mean difference within pairs of corresponding distances is 0.015 Å for (I) and HY, and 0.019 Å for (I) and FLM. Similar agreement is shown by the angular geometry at N1,
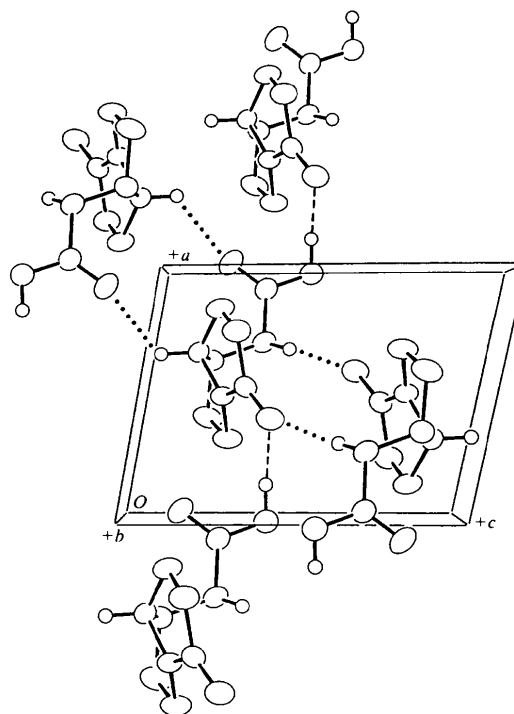

Fig. 2. ORTEPII (Johnson, 1976) diagram of a central molecule of (I) and the four neighboring molecules with which it interacts by hydrogen bonding or C—H$\cdots$O interactions. Displacement ellipsoids are drawn at 50% probability for non-H atoms; circles of arbitrary small radius depict H atoms. For clarity, H atoms not involved in these interactions are omitted. Hydrogen bonds are depicted by dashed lines and C—H$\cdots$O interactions by dotted lines.

Fig. 1. ORTEPII (Johnson, 1976) drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability for non-H atoms; circles of arbitrary small radius depict H atoms.

a matter of particular interest in these molecules: the external angle at N1 (C3—N1—C5) and the angular sum at N1 are, respectively, 129.9 (1) and 357.9 (2)° for (I), 125.2 (2) and 350.6 (3)° for HY, and 131.6 (2) and 359.8 (3)° for FLM. In agreement with FLM and three additional cases cited therein from Flippen-Anderson *et al.* (1984) and Winkler (1979), both five-membered rings in (I) have envelope conformations, and the same atoms form the flaps in all these cases. For (I), N1/C5/C6/C7a form one plane (from which their average deviation is 0.015 Å), with flap atom C7 0.370 (2) Å out of the plane, while N1/C2/C3/C7a form the other plane [from which their average deviation is 0.011 (2) Å], with flap atom C1 0.600 (2) Å out of the plane. Further, in FLM the out-of-plane distances for the same flap atoms are 0.466 (3) and 0.563 (3) Å, respectively, so that the ring geometries of (I) and FLM are in quite good agreement. Finally, the dihedral angle between the two ring planes just described is 14.1 (1) in (I) and 8.0° in FLM.

Bond lengths and angles of special interest are given in Table 2; all fall within normal ranges. The closest intermolecular approaches in this structure, excluding pairs of atoms in groups hydrogen-bonded to each other or involved in the tabulated C—H···O interactions, occur between C5 and H9^{iv} [symmetry code: (iv) $-1 + x$, $1 + y$, z] and are 0.24 Å less than the corresponding van der Waals radius sum (Bondi, 1964). It may be noted, however, that C5 is bonded to O3, which participates in a hydrogen bond with H9^{iv}.

Experimental

The title acid, whose synthesis is described by Hart & Tsai (1984), was obtained as a colorless chunk from a crystalline sample in Dr D. J. Hart's chemical collection. This was cut to provide the experimental sample.

Crystal data

C₉H₁₃NO₃	Mo $K\alpha$ radiation
$M_r = 183.21$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 7.1459 (10)$ Å	$\theta = 14.7–17.5°$
$b = 7.5905 (9)$ Å	$\mu = 0.105$ mm⁻¹
$c = 8.8515 (8)$ Å	$T = 296$ K
$\alpha = 82.682 (9)°$	Cut chunk
$\beta = 77.437 (9)°$	$0.38 \times 0.38 \times 0.31$ mm
$\gamma = 68.864 (10)°$	Colorless
$V = 436.47 (9)$ Å³	
$Z = 2$	
$D_x = 1.394$ Mg m⁻³	
D_m not measured	

Data collection

Rigaku AFC-5S diffractom-	$R_{int} = 0.009$
eter	$\theta_{max} = 27.56°$
$\omega/2\theta$ scans	$h = 0 \rightarrow 9$
Absorption correction: none	$k = -8 \rightarrow 9$
2181 measured reflections	$l = -11 \rightarrow 11$
2017 independent reflections	6 standard reflections
1658 reflections with	every 150 reflections
$I > 2\sigma(I)$	intensity decay: 1.53%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.01$
$R(F) = 0.040$	$\Delta\rho_{max} = 0.25$ e Å⁻³
$wR(F^2) = 0.095$	$\Delta\rho_{min} = -0.17$ e Å⁻³
$S = 1.97$	Extinction correction: none
2017 reflections	Scattering factors from
170 parameters	Stewart *et al.* (1965) (H)
All H atoms refined	and Creagh & McAuley
$w = 1/\sigma^2(F^2)$	(1992) (C, O, N)

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

O1—C9	1.320 (2)	N1—C3	1.459 (2)
O2—C9	1.195 (2)	N1—C5	1.325 (2)
O3—C5	1.242 (2)	N1—C7a	1.469 (2)
C3—N1—C5	129.9 (1)	O1—C9—O2	122.3 (1)
C3—N1—C7a	112.84 (10)	O1—C9—C8	113.3 (1)
C5—N1—C7a	115.2 (1)	O2—C9—C8	124.5 (1)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H9···O3^i	0.94 (2)	1.70 (2)	2.640 (1)	175 (2)
C7a—H7a···O2^{ii}	0.98 (1)	2.54 (1)	3.139 (2)	120 (1)
C8—H8A···O3^{iii}	0.95 (2)	2.60 (2)	3.544 (2)	176 (1)

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

Fourier difference methods were used to locate initial H-atom positions, and the H atoms were then refined isotropically. Refined C—H distances ranged from 0.95 (2) to 1.02 (2) Å, with a mean value of 0.98 (2) Å. The refined O—H distance is given in Table 2.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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