

4221 independent reflections 6 standard reflections
 2095 reflections with every 150 reflections
 $I > 2\sigma_I$ intensity decay: 4.0%

Refinement

Refinement on F^2 $(\Delta/\sigma)_{\max} < 0.01$
 $R(F) = 0.057$ $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$
 $wR(F^2) = 0.070$ $\Delta\rho_{\min} = -0.43 \text{ e } \text{\AA}^{-3}$
 $S = 1.71$ Extinction correction: none
 4221 reflections Scattering factors from
 225 parameters Stewart *et al.* (1965) (H)
 H atoms; see below and Creagh & McAuley
 $w = 1/\sigma^2(F^2)$ (1992) (C, O)

Table 1. Selected geometric parameters (\AA , $^\circ$)

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 (\AA , $^\circ$) 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'	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 $(1.40 + 0.35\tan\theta)^\circ$ 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 \AA and $U_{\text{iso}} = 1.2U_{\text{eq}}$ 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, $\sim 0.6 \text{ \AA}$ from C3, and the maximum negative peak is located $\sim 0.3 \text{ \AA}$ from C12.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC 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).

We acknowledge with pleasure our use of the departmental X-ray crystallographic facility, which is supervised by staff crystallographer Dr J. C. Gallucci. The diffractometer system was purchased with funds provided, in part, by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1410). Services for accessing these data are described at the back of the journal.

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

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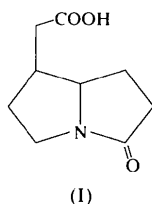
Abstract

The title acid, [(1R*,7aS*)-2,3,5,6,7,7a-hexahydro-5-oxo-1H-pyrroliziny-1-yl]acetic acid (C₉H₁₃NO₃), 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



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-

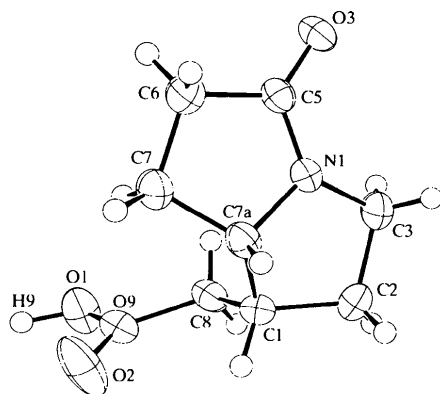


Fig. 1. ORTEPII (Johnson, 1976) drawing of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability for non-H atoms; circles of arbitrary small radius depict H atoms.

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,

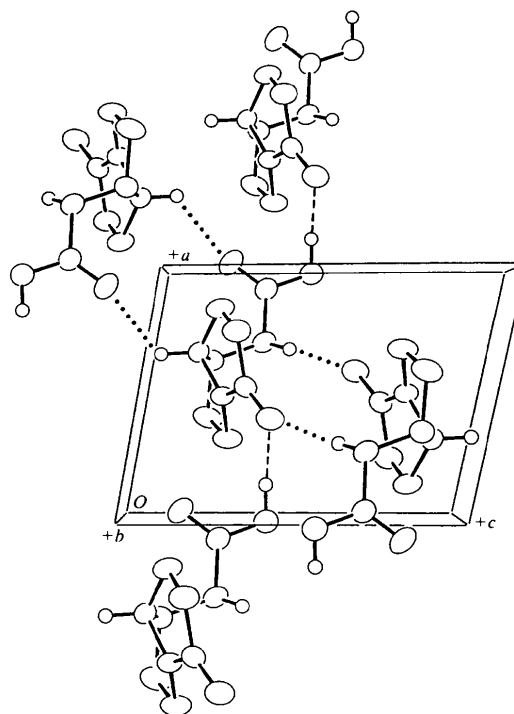


Fig. 2. ORTEPII (Johnson, 1976) diagram of a central molecule of (I) and the four neighboring molecules with which it interacts by hydrogen bonding or C—H \cdots O interactions. Displacement ellipsoids are drawn at 50% probability for non-H atoms; circles of arbitrary small radius depict H atoms. For 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.

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

C ₉ H ₁₃ NO ₃	Mo K α radiation
$M_r = 183.21$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 14.7\text{--}17.5^\circ$
$a = 7.1459$ (10) Å	$\mu = 0.105$ mm ⁻¹
$b = 7.5905$ (9) Å	$T = 296$ K
$c = 8.8515$ (8) Å	Cut chunk
$\alpha = 82.682$ (9)°	0.38 × 0.38 × 0.31 mm
$\beta = 77.437$ (9)°	Colorless
$\gamma = 68.864$ (10)°	
$V = 436.47$ (9) Å ³	
$Z = 2$	
$D_x = 1.394$ Mg m ⁻³	
D_m not measured	

Data collection

Rigaku AFC-5S diffractometer	$R_{\text{int}} = 0.009$
	$\theta_{\text{max}} = 27.56^\circ$

$\omega/2\theta$ scans

Absorption correction: none

2181 measured reflections

2017 independent reflections

1658 reflections with

$I > 2\sigma(I)$

Refinement

Refinement on F^2

$R(F) = 0.040$

$wR(F^2) = 0.095$

$S = 1.97$

2017 reflections

170 parameters

All H atoms refined

$w = 1/\sigma^2(F^2)$

$h = 0 \rightarrow 9$

$k = -8 \rightarrow 9$

$l = -11 \rightarrow 11$

6 standard reflections

every 150 reflections

intensity decay: 1.53%

$(\Delta/\sigma)_{\text{max}} < 0.01$

$\Delta\rho_{\text{max}} = 0.25$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.17$ e Å⁻³

Extinction correction: none

Scattering factors from

Stewart *et al.* (1965) (H)

and Creagh & McAuley

(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, °)

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
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: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC 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).

I thank Dr David Hart for providing the sample and Dr Kurt Loening for assistance with nomenclature. I acknowledge with pleasure my use of the departmental X-ray crystallographic facility, which is supervised by staff crystallographer Dr J. C. Gallucci. The diffractometer system was purchased with funds provided, in part, by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1513). Services for accessing these data are described at the back of the journal.

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2-Aminopyrimidine–terephthalic acid (1:1) complex

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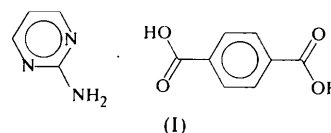
Abstract

Mutual recognition of 2-aminopyrimidine, C₄H₅N₃, and terephthalic acid, C₈H₆O₄, is possible through the formation of cyclic eight-membered hydrogen-bonded rings in the co-crystal. Each molecule can participate in two such hydrogen-bonded ring patterns, and these result in infinite hydrogen-bonded zigzag chains.

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Comment

Hydrogen bonding plays a key role in molecular recognition (Goswami & Ghosh, 1997) and crystal engineering research (Goswami *et al.*, 1998). The design of highly specific solid-state structures is of considerable significance in organic chemistry due to their important applications in the development of new optical, magnetic and electronic systems (Lehn, 1990). The crystal structure of 2-aminopyrimidine itself has been reported (Scheinbeim & Schempp, 1976) where the pyrimidine ring nitrogen and amine groups are both involved to make an eight-membered hydrogen-bonded pattern. This self-assembling pattern can be replaced by a hetero-assembling pattern on co-crystallization of 2-aminopyrimidine with carboxylic acids (Etter & Admond, 1990; Etter *et al.*, 1990) where the best donors (acid OH) are paired with the best acceptors (ring N). This communication reports the hydrogen-bonded heterodimer of 2-aminopyrimidine with terephthalic acid, (I), where the two molecules are associated through a typical eight-membered hydrogen-bonded ring pattern.



The asymmetric unit contains a half molecule each of 2-aminopyrimidine and terephthalic acid. The 2-aminopyrimidine molecules have crystallographic *m* symmetry, with N2, C1 and C3 in the mirror plane. The terephthalic acid molecule lies on an inversion centre. The bond lengths and bond angles observed in the molecules of the co-crystal agree with those observed in their independent crystal structures (Scheinbeim & Schempp, 1976; Bailey & Brown, 1967). The acid molecule is planar within ± 0.028 (1) Å and it forms a dihedral angle of 22.34 (6)° with the planar pyrimidine ring. In the co-crystal the 2-aminopyrimidine molecules are linked to the terephthalic acid molecules by N—H···O and O—H···N hydrogen bonds through the formation of eight-

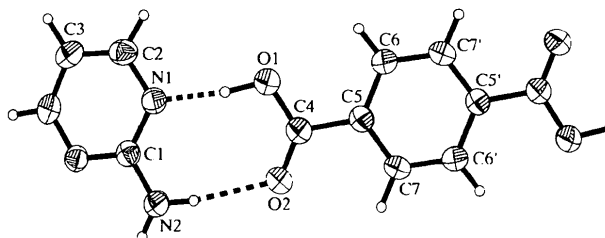


Fig. 1. The structure of the title complex showing 50% probability displacement ellipsoids and the atom-numbering scheme, where ' signifies the symmetry operation $2-x, 1-y, -z$. Also note that the pyrimidine molecule lies across a mirror plane and the terephthalic acid molecule on an inversion centre.