

$$w = 1/[\sigma^2(F_o^2) + (0.0828P)^2 + 1.1606P]$$

where $P = (F_o^2 + 2F_c^2)/3$

Scattering factors from
*International Tables for
Crystallography* (Vol. C)

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(±)-3-Indanone-1-acetic Acid: Heterochiral Catemeric Hydrogen Bonding in a δ-Keto Acid

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Abstract

The crystal structure of (±)-2,3-dihydro-3-oxo-1*H*-indeneacetic acid, C₁₁H₁₀O₃, involves carboxyl-to-ketone hydrogen-bonding catemers [O...O 2.691 (2) Å] of an unusual type. Hydrogen bonds progress from the carboxyl H atom of one molecule to the ketone O (O1) atom of a glide-related enantiomer, resulting in heterochiral chains. Parallel screw-related hydrogen-bonding chains proceed in counter-directional pairs through the cell. Two different close contacts (2.49 and 2.58 Å) are found between the carboxyl C=O group and H atoms on neighboring molecules.

Comment

Keto carboxylic acids offer options for varying the standard pattern of dimeric hydrogen bonding that dominates functionally unadorned acids. Usually the ketone fails to participate, resulting in typical carboxyl dimers, but less commonly intermolecular carboxyl-to-ketone hydrogen bonds occur, yielding a catemer. A third, rare arrangement has an internal hydrogen bond and two instances are known of acid-to-ketone dimerization, plus one of carboxyl catemerization (see below). Several cases also exist of hydrates with more complex hydrogen-bonding patterns. We have referenced and discussed numerous examples of these hydrogen-bonding modes (Thompson *et al.*, 1992; Coté *et al.*, 1996). Part of our continuing interest in this behavior lies in the discovery of new hydrogen-bonding patterns. We have recently reported an instance of carboxyl-to-carboxyl catemerization, a pattern not previously observed in keto acids (Lalancette *et al.*, 1998), and we now report a hydrogen-bonding pattern of a heretofore rarely observed type.

The title compound, (I), was of particular interest to us as a one-carbon homolog of (±)-3-indanone-1-carboxylic acid (Lalancette *et al.*, 1997). We have recently reported crystal structures for both the anhydrous and monohydrate forms of that compound, the former of which displays a catemeric hydrogen-bonding

Table 1. Selected geometric parameters (Å, °)

C1—C2	1.507 (7)	C5—O1	1.245 (4)
C2—C3	1.511 (5)	C5—N1	1.322 (5)
C2—C13	1.531 (6)	C5—C6	1.498 (6)
C3—N2	1.498 (4)	N2—N3	1.271 (4)
C3—C4	1.518 (5)	N2—O2	1.265 (3)
C4—N1	1.449 (5)	N3—O3	1.369 (4)
C1—C2—C3	112.6 (4)	O1—C5—C6	120.6 (4)
C1—C2—C13	110.4 (5)	N1—C5—C6	117.0 (4)
C3—C2—C13	110.5 (4)	C5—C6—C7	110.9 (4)
N2—C3—C2	109.7 (3)	C5—N1—C4	124.3 (4)
N2—C3—C4	107.4 (3)	N3—N2—O2	126.8 (3)
C2—C3—C4	114.5 (3)	N3—N2—C3	114.5 (3)
N1—C4—C3	113.0 (3)	O2—N2—C3	118.6 (3)
O1—C5—N1	122.3 (4)	N2—N3—O3	108.4 (3)

Diffraction peaks were very broad and the intensity data were collected with the ω -scan mode. H atoms of atoms C7–C12 in the *n*-alkyl chain were generated geometrically and refined using the AFIX 23 or 137 option of *SHELXL93* (Sheldrick, 1993), with the isotropic displacement parameters fixed at 1.3 times the isotropic equivalents of their bonded atoms. All other H atoms were found from a difference Fourier map and refined isotropically.

Data collection: local program (Yoon *et al.*, 1994). Cell refinement: local program. Data reduction: local program. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

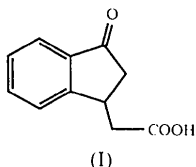
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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1075). Services for accessing these data are described at the back of the journal.

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pattern with screw-related components. Compound (I) belongs to the category of δ -keto acids, which embraces examples of dimeric and internal hydrogen bonds, as well as both anhydrous and hydrated catemers. We further categorize catemers as either homo- or heterochiral to denote the handedness of the intrachain units. With two exceptions (Watson *et al.*, 1990; Dobrzynska & Turowska-Tyrk, 1997), previously reported keto-acid catemers have been of either the screw-related or translational type, and hence homochiral. We report here a rare instance of a heterochiral carboxyl-to-ketone catemer, involving hydrogen bonding between alternating glide-related chain components.



The asymmetric unit for (I) with its numbering is shown in Fig. 1. The molecule is skeletally rigid except for possible rotation about the C1—C8 and C8—C9 bonds. The C8—C1—C7a—C7 torsion angle is $48.7(3)^\circ$, and the substituents attached to C1 and C8 are staggered [C7a—C1—C8—C9 $179.6(2)^\circ$]. The carboxyl is turned, with its C=O group toward the ketone, so that the carboxyl group and the aromatic ring have a dihedral angle of $54.4(1)^\circ$. A slight deviation of C2 from the general bicyclic plane produces a shallow dihedral angle of $13.0(1)^\circ$ between that plane (omitting C2) and C1—C2—C3 [cf. $7.2(3)^\circ$ for the lower homolog ($\pm$)-3-indanone-1-carboxylic acid].

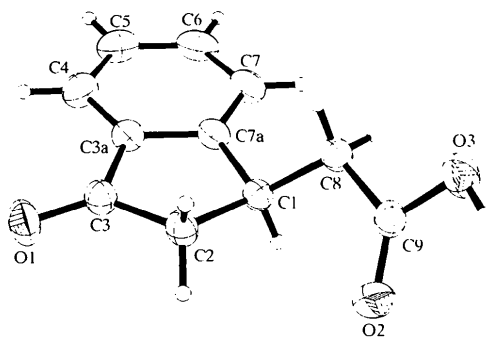


Fig. 1. The asymmetric unit of (I), with the atom numbering. Ellipsoids are set at the 30% probability level.

Averaging of C—O bond lengths and C—C—O angles by disorder is common in carboxyl dimers (Leiserowitz, 1976) but is not observed in catemers, whose geometry cannot support the mechanisms responsible for the averaging. In (I), these C—O bond lengths are 1.200(3) and 1.326(3) Å, with angles of $125.2(2)$ and $111.3(2)^\circ$. Our survey of 28 catemeric keto-acid structures gives average values of 1.20(1) and 1.32(1) Å,

and $124.5(10)$ and $112.8(14)^\circ$ for these lengths and angles, respectively, in accord with typical values of 1.21 and 1.31 Å, and 123 and 112° cited for highly ordered dimeric carboxyls (Borthwick, 1980).

The packing arrangement for (I) is shown in Fig. 2. Almost all previously observed carboxyl-to-ketone catemers involve intrachain units of a single handedness. In (I), the hydrogen bonding [O...O 2.691(2) Å] progresses between molecules with a glide relationship, so that chain members are of alternating chirality. The dihedral angle between the general molecular planes of successive hydrogen-bonded molecules is $14.8(1)^\circ$. The dihedral angle between the carboxyl and ketone planes in sequential hydrogen-bonded molecules is $51.2(1)^\circ$ [cf. $7.1(2)^\circ$ for the lower homolog ($\pm$)-3-indanone-1-carboxylic acid]. The resulting parallel screw-related hydrogen-bonding chains proceed in counter-directional pairs along the *ac* face of the cell, following the *a* cell axis. A 2.49 Å close contact is found between the carboxyl C=O O2 atom and the H2B atom of a neighbor screw-related along *c*. A second close contact of 2.58 Å exists between O2 and the H6A atom on a neighbor translationally related in *b*. These probably represent polar attractions contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982).

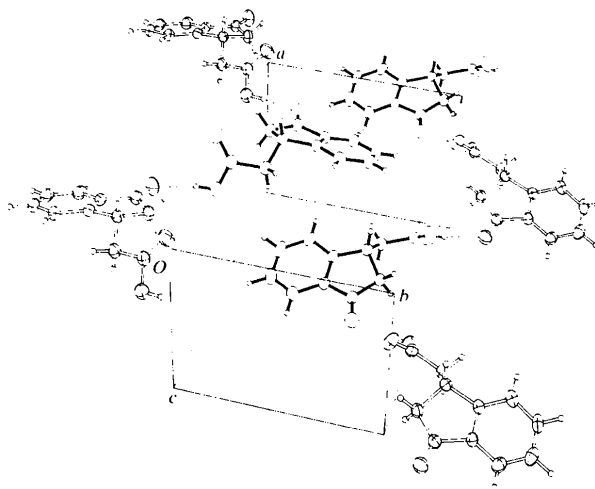


Fig. 2. A partial packing diagram for (I) with extracellular molecules. A chain of glide-related hydrogen-bonding molecules is shown along with a parallel counter-directional screw-related partner. The handedness of the molecules is differentiated by patterning of the bonds and atoms. The two close contacts have been omitted for clarity. Ellipsoids are set at the 30% probability level.

The solid-state (KBr) IR spectrum of (I) has C=O absorptions at 1728 and 1673 cm^{-1} , consistent with the shifts typically seen in catemers, and due, respectively, to removal of hydrogen bonding from carboxyl C=O and addition of hydrogen bonding to an indanone [cf. 1736 and 1679 cm^{-1} for ($\pm$)-3-indanone-1-carboxylic acid]. In CHCl_3 solution, where dimers predominate,

the absorptions coalesce to a single broader peak at 1712 cm^{-1} [cf. 1715 cm^{-1} for ($\pm$)-3-indanone-1-carboxylic acid].

Experimental

Compound (I) was synthesized by polyphosphoric acid cyclization of 3-phenylglutaric acid, purchased from Acros Organics, Pittsburgh, PA, USA. Crystals of (I) (m.p. 426 K) were obtained from ethyl acetate.

Crystal data

$\text{C}_{11}\text{H}_{10}\text{O}_3$
 $M_r = 190.19$
 Orthorhombic
 $Pca2_1$
 $a = 14.140(2)\text{ \AA}$
 $b = 9.167(1)\text{ \AA}$
 $c = 7.263(1)\text{ \AA}$
 $V = 941.4(2)\text{ \AA}^3$
 $Z = 4$
 $D_x = 1.342\text{ Mg m}^{-3}$
 $D_m = 1.35(1)\text{ Mg m}^{-3}$
 D_m measured by flotation in CCl_4 -toluene

Mo $K\alpha$ radiation
 $\lambda = 0.71073\text{ \AA}$
 Cell parameters from 37 reflections
 $\theta = 5.30\text{--}17.76^\circ$
 $\mu = 0.098\text{ mm}^{-1}$
 $T = 293(2)\text{ K}$
 Rectangular prism singly capped with a rectangular prismoid
 $0.70 \times 0.60 \times 0.32\text{ mm}$
 Colorless

Data collection

Siemens P4 diffractometer
 $2\theta/\theta$ scans
 Absorption correction: face-indexed numerical (Sheldrick, 1994)
 $T_{\min} = 0.943$, $T_{\max} = 0.971$
 2688 measured reflections
 2493 independent reflections
 1900 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$
 $\theta_{\max} = 29.00^\circ$
 $h = -19 \rightarrow 19$
 $k = -12 \rightarrow 12$
 $l = -9 \rightarrow 9$
 3 standard reflections every 97 reflections
 intensity decay: -0.63%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.129$
 $S = 1.05$
 2493 reflections
 140 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F_o^2) + (0.0598P)^2 + 0.1029P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.27\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.15\text{ e \AA}^{-3}$
 Extinction correction: none (refined to zero)
 Scattering factors from *International Tables for Crystallography* (Vol. C)
 Absolute structure: Flack (1983)
 Flack parameter = 0.5 (16)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ($\text{\AA}^2$)

	x	y	z	U_{eq}
O1	0.69784 (10)	0.2412 (2)	0.5696 (3)	0.0719 (6)
O2	1.03289 (13)	-0.0079 (2)	0.3813 (3)	0.0724 (5)
O3	1.14967 (10)	0.0427 (2)	0.5768 (3)	0.0656 (5)
C1	0.94389 (13)	0.2652 (2)	0.4420 (3)	0.0417 (4)

C2	0.86081 (13)	0.1704 (2)	0.5095 (3)	0.0477 (5)
C3	0.78086 (14)	0.2736 (2)	0.5457 (3)	0.0480 (5)
C3a	0.81876 (13)	0.4226 (2)	0.5479 (3)	0.0442 (4)
C4	0.7736 (2)	0.5520 (2)	0.5958 (3)	0.0588 (6)
C5	0.8234 (2)	0.6794 (2)	0.5833 (4)	0.0658 (7)
C6	0.9166 (2)	0.6776 (2)	0.5225 (4)	0.0626 (6)
C7	0.9627 (2)	0.5499 (2)	0.4758 (3)	0.0558 (6)
C7a	0.91256 (14)	0.4192 (2)	0.4886 (3)	0.0433 (4)
C8	1.03914 (14)	0.2275 (2)	0.5256 (3)	0.0492 (5)
C9	1.07195 (14)	0.0756 (2)	0.4834 (3)	0.0480 (5)

Table 2. Selected geometric parameters ($\text{\AA}$, $^\circ$)

O1—C3	1.223 (2)	O3—C9	1.326 (3)
O2—C9	1.200 (3)		
O2—C9—C8	125.2 (2)	O3—C9—C8	111.3 (2)

Table 3. Hydrogen-bonding geometry ($\text{\AA}$, $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O1 ⁱ	0.87 (2)	1.84 (3)	2.691 (2)	167 (2)
C2—H2B...O2 ⁱⁱ	0.97	2.49	3.431 (3)	164
C6—H6A...O2 ⁱⁱⁱ	0.93	2.58	3.474 (3)	163

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

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 with their displacement parameters free to refine. The carboxyl H atom was found in an electron-density difference map and was allowed to refine with its displacement parameter also free to refine.

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1417). Services for accessing these data are described at the back of the journal.

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