

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

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

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

*Acta Cryst.* (1998). **C54**, 829–831

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

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

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

(Received 14 November 1997; accepted 18 December 1997)

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  $\omega$ -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*.

This work was supported by the Korea Science and Engineering Foundation through the Center for Molecular Catalysis at Seoul National University, Korea.

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.

### References

- Jalal, M. A. F., Hossain, M. B. & Helm, D. (1986). *Acta Cryst.* **C42**, 733–738.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Murthy, Y. K. S., Thiemann, J. E., Coronelli, C. & Sensi, P. (1966). *Nature (London)*, **211**, 1198–1199.
- Saavedra, J. E., Dunams, T. M., Flippen-Anderson, J. L. & Keefer, L. K. (1992). *J. Org. Chem.* **57**, 6134–6138.
- Scanlan, R. A. & Tannenbaum, S. R. (1981). In *N-Nitroso Compounds*. *Am. Chem. Soc. Symp. Ser.* No. 174. Washington, DC: American Chemical Society.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Yoon, T.-S., Kim, S. W. & Shin, W. (1994). *Proceedings of the American Crystallographic Association Meetings*, Atlanta, GA, USA. Abstract PM01.

### Abstract

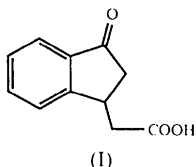
The crystal structure of (±)-2,3-dihydro-3-oxo-1H-indeneacetic acid, C<sub>11</sub>H<sub>10</sub>O<sub>3</sub>, involves carboxyl-to-ketone hydrogen-bonding catemers [O...O 2.691 (2) Å] of an unusual type. Hydrogen bonds progress from the carboxyl H atom of one molecule to the ketone O (O1) atom of a 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

pattern with screw-related components. Compound (I) belongs to the category of  $\delta$ -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)°, and the substituents attached to C1 and C8 are staggered [C7a—C1—C8—C9 179.6(2)°]. 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)°. A slight deviation of C2 from the general bicyclic plane produces a shallow dihedral angle of 13.0(1)° between that plane (omitting C2) and C1—C2—C3 [cf. 7.2(3)° for the lower homolog ( $\pm$ )-3-indanone-1-carboxylic acid].

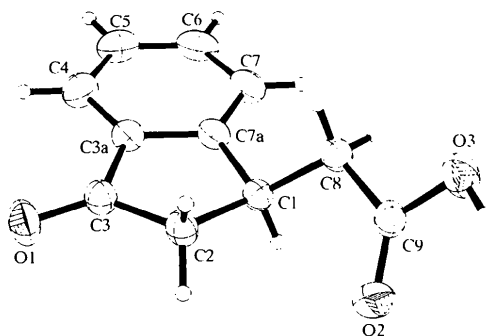


Fig. 1. The asymmetric unit of (I), with the atom numbering. Ellipsoids are set at the 30% probability level.

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)°. 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)° 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)°. The dihedral angle between the carboxyl and ketone planes in sequential hydrogen-bonded molecules is 51.2(1)° [cf. 7.1(2)° 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).

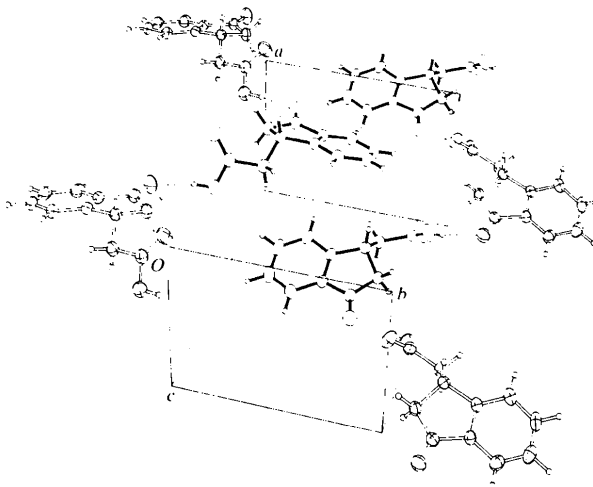


Fig. 2. A partial packing diagram for (I) with extracellular molecules. A chain of glide-related hydrogen-bonding molecules is shown along with a parallel counter-directional screw-related partner. The handedness of the molecules is differentiated by patterning of the bonds and atoms. The two close contacts 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<sup>-1</sup>, 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<sup>-1</sup> for ( $\pm$ )-3-indanone-1-carboxylic acid]. In CHCl<sub>3</sub> solution, where dimers predominate,

the absorptions coalesce to a single broader peak at  $1712\text{ cm}^{-1}$  [cf.  $1715\text{ cm}^{-1}$  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.  $426\text{ K}$ ) were obtained from ethyl acetate.

### Crystal data

$\text{C}_{11}\text{H}_{10}\text{O}_3$   
 $M_r = 190.19$   
 Orthorhombic  
*Pca*2<sub>1</sub>  
 $a = 14.140(2)\text{ \AA}$   
 $b = 9.167(1)\text{ \AA}$   
 $c = 7.263(1)\text{ \AA}$   
 $V = 941.4(2)\text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.342\text{ Mg m}^{-3}$   
 $D_m = 1.35(1)\text{ Mg m}^{-3}$   
 $D_m$  measured by flotation in  $\text{CCl}_4$ -toluene

### 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  
 $I > 2\sigma(I)$

### 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  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$

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

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

$\Delta\rho_{\max} = 0.27\text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.15\text{ e \AA}^{-3}$   
 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 ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{eq}}$
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 <sup>i</sup>	0.87 (2)	1.84 (3)	2.691 (2)	167 (2)
C2—H2B...O2 <sup>ii</sup>	0.97	2.49	3.431 (3)	164
C6—H6A...O2 <sup>iii</sup>	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.

## References

- Berkovitch-Yellin, Z. & Leiserowitz, L. (1982). *J. Am. Chem. Soc.* **104**, 4052–4064.  
 Borthwick, P. W. (1980). *Acta Cryst.* **B36**, 628–632.  
 Coté, M. L., Thompson, H. W. & Lalancette, R. A. (1996). *Acta Cryst.* **C52**, 684–687.  
 Dobrzynska, D. & Turowska-Tyrk, I. (1997). *Acta Cryst.* **C53**, 238–239.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Jönsson, P.-G. (1972). *Acta Chem. Scand.* **26**, 1599–1619.  
 Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1997). *Acta Cryst.* **C53**, 1838–1842.  
 Lalancette, R. A., Thompson, H. W. & Brunskill, A. P. J. (1998). *Acta Cryst.* **C54**, 421–424.  
 Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.  
 Sheldrick, G. M. (1994). SHELXTL/PC. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Siemens (1991). XSCANS Users Manual. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Thompson, H. W., Lalancette, R. A. & Vanderhoff, P. A. (1992). *Acta Cryst.* **C48**, 66–70.  
 Watson, W. H., Nagl, A., Kashyap, R. P., Marchand, A. P. & Vidyasagar, V. (1990). *Acta Cryst.* **C46**, 1265–1268.