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## Hydrogen-Bonding Pattern of a Bicyclic $\gamma$ -Keto Acid: (–)-*anti*-Isoketopinic Acid

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### Abstract

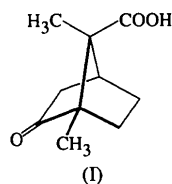
(–)-1,7-Dimethyl-2-oxobicyclo[2.2.1]heptane-7-*anti*-carboxylic acid, C<sub>10</sub>H<sub>14</sub>O<sub>3</sub>, crystallizes in space group *P*4<sub>1</sub> and forms intermolecular carboxyl-to-ketone hydrogen-bonded chains (catemers). The hydrogen-bonded chains are orthogonal to the 4<sub>1</sub> screw axis and involve translationally related molecules.

### Comment

Unlike the vast majority of functionally unelaborated carboxylic acids, acetic and formic acids in the solid state form intermolecular hydrogen-bonded chains (catemers) from the hydroxyl group of one molecule to the carbonyl group of the next (Jones & Templeton, 1958; Nahrungbauer, 1978). Crystalline keto-carboxylic acids offer even greater opportunity for variation on the standard pattern of dimeric hydrogen bonding. In most cases, however, the ketone does not participate and typical mutually hydrogen-bonded carboxylic acid dimers result. Less frequently, intermolecular carboxyl-to-ketone hydrogen bonds yield a catemer, which, in many instances, follows a cell axis (usually a 2<sub>1</sub> screw axis). A survey of X-ray structures of keto acids found that approximately 25% adopt the catemer motif. A third and 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 the above hydrogen-bonding modes (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

We report here the structure and hydrogen-bonding pattern of (–)-*anti*-isoketopinic acid, (I), a  $\gamma$ -keto acid related to camphor. The category of  $\gamma$ -keto acids is especially rich in hydrogen-bonding types, embracing dimers, internal hydrogen bonds and catemers of both the screw-related and translational types. Our X-ray studies of other carboxycamphor derivatives have included (+)- and (±)-camphorcarboxylic acid (Lalancette, Vanderhoff & Thompson, 1991) and (+)-camphoracetic acid (Coté, Thompson & Lalancette,

1997), all of which, like compound (I), display catemeric hydrogen bonding in the solid state.



Compound (I), with its atom-numbering scheme, is shown in Fig. 1. All H atoms, including the carboxyl H atom, were found in electron-density difference maps. Apart from the methyl groups, the only rotatable group is the carboxyl group, which is found to lie nearly parallel to the ketone group [dihedral angle C9, O2, O3 *versus* C3, C2, C1, O1 is 3.5(2)°], with the carboxyl C=O group aimed away from the ketone. The torsion angles C8—C7—C9—O2 [–83.1(4)°] and C8—C7—C9—O3 [93.2(3)°] illustrate the twist of the carboxyl group relative to the methyl group attached to C7. Averaging of the C—O bond lengths and C—C—O angles through disorder, frequently observed in dimeric carboxyl groups (Leiserowitz, 1976), is not found in catemers and is not seen here. The carboxyl C=O distance (C9=O2) is 1.197(4) Å and the C9—O3 distance is 1.304(4) Å. The C7—C9—O2 angle is 123.0(3)° and the C7—C9—O3 angle is 114.6(3)°. These values are comparable to those found in highly ordered cases, where typical distances are 1.21 and 1.31 Å, and typical angles are 123 and 112° (Borthwick, 1980).

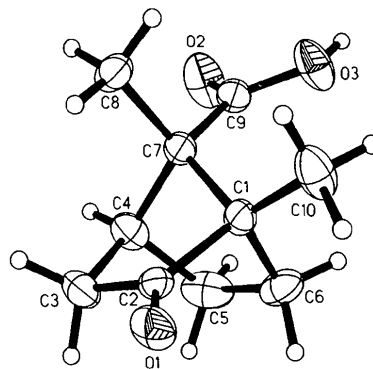


Fig. 1. Compound (I) with its numbering scheme. The predominant rotamer is shown for each methyl group. Ellipsoids are at the 30% probability level.

Difference electron-density maps in the late stages of refinement indicated some disorder in the H-atom positions on each of the two methyl groups. The occupancies of the H atoms were refined as a group,

using an idealized model consisting of three H atoms from each of two different conformations, defining a regular hexagon (see *Experimental*).

A partial packing diagram of the cell, showing the translational hydrogen-bonding chains of molecules (catemers) alternately parallel to the *a* and *b* axes, is shown in Fig. 2. These chains of molecules stack in layers which run alternately through the *ac* and *bc* faces of the unit cell. Chains in successive layers spiral up the  $4_1$  screw axis (*c*), such that chain 3 is directly above and parallel to chain 1, but  $180^\circ$  opposite in orientation. Chain 2 is similarly related to chain 4, but is turned  $90^\circ$  from chains 1 and 3.

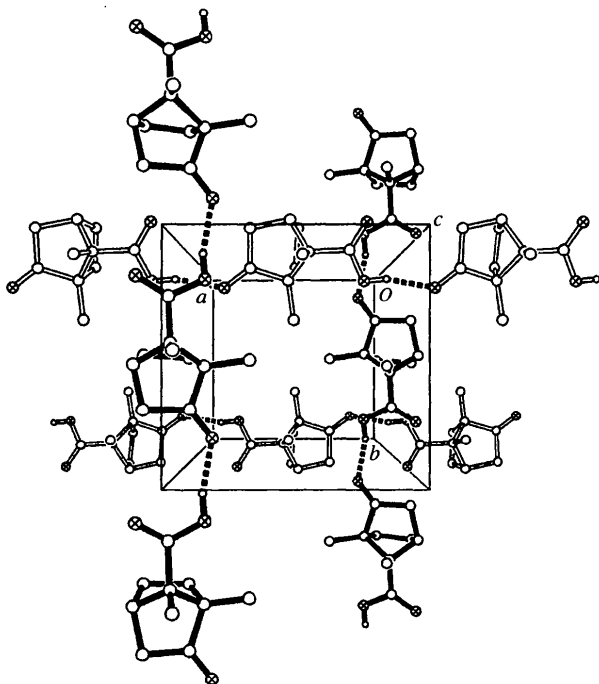


Fig. 2. A partial packing diagram, with extracellular molecules to illustrate the hydrogen-bonding catemers. Each molecule associated with the illustrated cell is bisected by a face and thus has a translational counterpart (omitted for clarity) lying in the opposite face. A separate translational chain is associated with each of the four screw-related molecules along the *c* axis. The alternating layers are distinguished by shading, with dark bonds corresponding to the 1st and 3rd layers, and open bonds denoting the 2nd and 4th layers. The chain closest to the observer is the vertical one at the left, with the  $4_1$  screw receding in a clockwise fashion. All non-carboxyl H atoms have been omitted for clarity.

The hydrogen bonding in compound (I) is unusual in that a substantial majority of observed keto-acid catemers are screw-related rather than translational (Coté, Thompson & Lalancette, 1996). The known instances of translational catemers include the single enantiomers with Refcodes BOTSAE (Bertolasi, Ferretti & Gilli, 1982) and DEFNOR (Preut, Kreiser, Muller & Jones,

1985), a racemate OTCHCX (Fortier, DeTitta, Fronkowiak, Smith & Hauptman, 1979) and TIENLC (Carpy, Goursole & Leger, 1980), racemic conformers of an achiral material. Compound (I) is the only keto-carboxylic acid we have observed to crystallize in a space group of symmetry higher than orthorhombic. It is also unusual that the hydrogen bonding in (I) is orthogonal to the  $4_1$  screw axis. In our experience with catemeric keto acids, when a screw axis is present, the intermolecular hydrogen bonding typically follows the screw axis.

The solid-state (KBr) IR spectrum of the title compound displays a major C=O peak at  $1731\text{ cm}^{-1}$ , with a minor one at  $1707\text{ cm}^{-1}$ . The positions of these peaks are consistent with the known shifts due to the removal of hydrogen bonding from carboxylic acid C=O and the addition of hydrogen bonding to a strained camphor-like ketone, respectively (Lalancette, Vanderhoff & Thompson, 1991). In  $\text{CHCl}_3$  solution, the absorptions appear, presumably reversed, at  $1743$  and  $1707\text{ cm}^{-1}$ .

## Experimental

Compound (I) (m.p. ca 518 K with sublimation) was synthesized from the  $\text{NH}_3$  salt of the corresponding (1*S*)-bromocamphorsulfonic acid (purchased from Acros Organics). Catalytic hydrogenolysis (Pd/C) was followed by chloride formation ( $\text{SOCl}_2$ ) and then basic aqueous  $\text{KMnO}_4$  oxidation (Bartlett & Knox, 1973) produced (I), also possessing the (1*S*) configuration; the (1*R*) enantiomer is known to be dextro-rotatory (Beilsteins Handbuch der Organischen Chemie, 1972). Sublimed material was crystallized from a 2:1 cyclohexane-ethyl ether solution.

### Crystal data

$\text{C}_{10}\text{H}_{14}\text{O}_3$

$M_r = 182.22$

Tetragonal

$P4_1$

$a = 7.908(1)\text{ \AA}$

$c = 15.150(2)\text{ \AA}$

$V = 947.4(2)\text{ \AA}^3$

$Z = 4$

$D_x = 1.277\text{ Mg m}^{-3}$

$D_m = 1.27(1)\text{ Mg m}^{-3}$

$D_m$  measured by flotation in cyclohexane/ $\text{CCl}_3\text{Br}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\text{ \AA}$

Cell parameters from 17 reflections

$\theta = 5.34\text{--}15.73^\circ$

$\mu = 0.093\text{ mm}^{-1}$

$T = 296(2)\text{ K}$

Prism

$0.64 \times 0.32 \times 0.16\text{ mm}$

Colorless

### Data collection

Siemens  $P4$  diffractometer

$2\theta/\theta$  scans

Absorption correction:

face-indexed numerical

$T_{\min} = 0.984$ ,  $T_{\max} = 0.988$

1994 measured reflections

1667 independent reflections

1203 reflections with

$F > 4\sigma(F)$

$R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 25.0^\circ$

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -18 \rightarrow 18$

3 standard reflections

every 97 reflections

intensity decay: 2.6%

## Refinement

Refinement on  $F^2$  $R(F) = 0.051$  $wR(F^2) = 0.122$  $S = 0.94$ 

1667 reflections

131 parameters

 $w = 1/[\sigma^2(F_o^2) + (0.0635P)^2]$ where  $P = (F_o^2 + 2F_c^2)/3$  $(\Delta/\sigma)_{\max} = -0.001$  $\Delta\rho_{\max} = 0.11 \text{ e } \text{\AA}^{-3}$  $\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$ 

Extinction correction:

*SHELXTL* (Sheldrick, 1994)

Extinction coefficient:

0.000 (7)

Scattering factors from

*International Tables for Crystallography* (Vol. C)Table 1. Selected geometric parameters and hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

O1—C2	1.204 (4)	C2—C3	1.497 (5)	
O2—C9	1.197 (4)	C3—C4	1.536 (4)	
O3—C9	1.304 (4)	C4—C5	1.527 (6)	
C1—C10	1.508 (4)	C4—C7	1.548 (4)	
C1—C2	1.521 (4)	C5—C6	1.548 (6)	
C1—C6	1.536 (5)	C7—C9	1.515 (4)	
C1—C7	1.560 (4)	C7—C8	1.530 (4)	
C9—O3—H3	113 (3)	C3—C4—C7	102.3 (2)	
C2—C1—C6	102.4 (2)	C4—C5—C6	102.8 (3)	
C2—C1—C7	99.9 (2)	C1—C6—C5	104.6 (3)	
C6—C1—C7	101.7 (2)	C9—C7—C4	110.6 (3)	
O1—C2—C3	126.9 (3)	O9—C7—C1	116.3 (2)	
O1—C2—C1	125.2 (3)	C4—C7—C1	94.2 (2)	
C3—C2—C1	107.9 (2)	O2—C9—O3	122.3 (3)	
C2—C3—C4	101.7 (2)	O2—C9—C7	123.0 (3)	
C5—C4—C3	107.0 (3)	O3—C9—C7	114.6 (3)	
C5—C4—C7	102.1 (3)			
O1—C2—C3—C4	-177.1 (3)	C8—C7—C9—O3	93.2 (3)	
C8—C7—C9—O2	-83.1 (4)	C4—C7—C9—O3	-141.3 (3)	
C4—C7—C9—O2	42.4 (4)	C1—C7—C9—O3	-35.5 (4)	
C1—C7—C9—O2	148.2 (3)			
D—H...A	D—H	H...A	D...A	D—H...A
O3—H3...O1 <sup>i</sup>	0.87 (4)	1.86 (4)	2.698 (3)	162 (4)

Symmetry code: (i)  $x, y - 1, z$ .

All non-carboxyl H atoms, although found in electron-density difference maps, were replaced in calculated positions and allowed to refine as riding models; their displacement parameters were allowed to refine, with the methine H4 atom having  $U_{\text{iso}} = 0.060$  and all the methylene H atoms (H3A–H6B) having a group  $U_{\text{iso}} = 0.077$ . The H atoms of both methyl groups were treated as disordered, with two different sets of three H atoms each; the C8 group H atoms (occupancy ratio 78/22) had a group  $U_{\text{iso}} = 0.053$  and the C10 group H atoms (occupancy ratio 73/27) had a group  $U_{\text{iso}} = 0.073$ . The carboxyl H3 atom was found in an electron-density difference map. Its positional parameters were refined and its isotropic displacement parameter  $U_{\text{iso}}$  was refined to 0.09 (1).

Data collection: *XSCANS* (Fait, 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: BK1292). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 2-(3-Methoxy-2-hydroxyphenyl)benzimidazole

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## Abstract

Molecules of the title compound, 2-(1,3-benzimidazol-2-yl)-6-methoxyphenol, C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>2</sub>, are nearly planar, the greatest deviations from the molecular least-squares plane being -0.145 (3) Å for C12 and -0.149 (3) Å for C14. An intramolecular O—H...N hydrogen bond [O1...N1 2.577 (6) Å] is observed.

## Comment

Schiff bases provide a large class of compounds of both stereochemical and magnetochemical interest (Garnovski, Nivorozhkin & Minkin, 1993; Maggio, Pizzino & Romano, 1974; Morassi, Bertini & Sacconi, 1973; Elerman, Fuess & Paulus, 1992). Complexes of Schiff