

(±)-1-Tetralone-3-carboxylic acid and (±)-1-tetralone-2-acetic acid: hydrogen bonding in two γ -keto acids

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The crystal structure of (±)-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid ($C_{11}H_{10}O_3$) involves projection of the carboxyl group nearly orthogonal to the aromatic plane and hydrogen bonding of the acid groups by centrosymmetric pairing across the *a* edge and the center of the chosen cell [$O \cdots O = 2.705$ (2) Å]. Intermolecular $C-H \cdots O=C$ close contacts to translationally related molecules are found for both the ketone (2.55 Å) and the acid (2.67 Å). In (±)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-acetic acid ($C_{12}H_{12}O_3$), the aggregation involves centrosymmetric carboxyl dimers mutually hydrogen bonded across the *bc* face and the *a* edge of the chosen cell [$O \cdots O = 2.674$ (2) Å]. A 2.60 Å close $C-H \cdots O=C$ contact is found to the carboxyl group of centrosymmetrically related molecule.

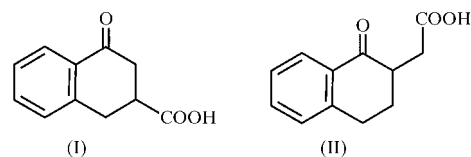
Comment

Beyond the dimerization that dominates the hydrogen bonding in functionally unadorned carboxylic acids lies a range of alternative hydrogen-bonding modes that expands as other functional groups are added. Our continuing study of the crystal structures of keto acids explores the molecular characteristics that control their five known hydrogen-bonding modes (Lalancette, Thompson & Brunskill, 1999). Two of these, including carboxyl dimerization, lack ketone involvement, but acid-to-ketone catemers constitute a sizable minority of cases, while intramolecular hydrogen bonds and acid-to-ketone dimers are rarely observed. In addition, more than a dozen hydrates are known, having more complex hydrogen-bonding patterns.

We report here the structures and hydrogen-bonding behavior of the two tetralone acids of the title. The category of γ -keto acids is especially rich in hydrogen-bonding types, embracing internal hydrogen bonds and catemers of the helical, translational and glide types, as well as dimers and hydrated patterns. The two compounds presented here are part of a series of indanone and tetralone acids we have examined, in which the indanone species have been found to be

predominantly catemers (Lalancette *et al.*, 1997; Lalancette, Brunskill & Thompson, 1999; Thompson, Brunskill & Lalancette, 1998; Thompson, Lalancette & Brunskill, 1998).

Fig. 1 shows the asymmetric unit of (±)-1-tetralone-3-carboxylic acid [(±)-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylic acid, $C_{11}H_{10}O_3$, (I)] with the atomic numbering. The ketone ring adopts a conformation resembling a folded envelope, in which the dihedral angle for $C1-C2-C3$ versus the tetralone ring system excluding $C2$ is 49.92 (14)°, placing $C2$ above the average aromatic plane by 0.703 (3) Å, while $C3$ lies 0.059 (3) Å above it. This allows the ketone to lie nearly coplanar with the aromatic ring [torsion angle $O1-C4-C4A-C5 = -3.4$ (3)°], while the carboxyl group is positioned pseudo-axially and turned so that it is nearly coplanar with the $C2-C3$ bond, with its carbonyl toward the ketone. The torsion angle $O2-C9-C2-C3$ is -1.7 (3)° and the vector angle for $C2-C9$ versus the tetralone ring system without $C2$ is 80.22 (8)°. The ketone-carboxyl dihedral angle ($C3/C4/C4A/O1$ versus $C9/O2/O3$) is 82.3 (2)°.



This angular carboxyl conformation seems surprising, but its resemblance to the usual axial arrangements is both superficial and deceptive. Even apart from the flattening of the ketone ring, the H atoms responsible for unfavorable 1,3-diaxial interactions in cyclohexane systems are absent in (I). The *gauche* arrangements created along the $C1-C2$ and $C2-C3$ bonds by the pseudo-axial carboxyl group are $C9-C2-C1-C8A$ and $C9-C2-C3-C4$, but the terminal atoms, $C9$, $C8A$ and $C4$, are all trigonal. These atoms therefore lack much of the three-dimensional character that creates the steric strain in alkylcyclohexanes, a situation also seen with halo- and cyano-substituted cyclohexanes (Hirsch, 1967). The result is that the pseudo-axial and pseudo-equatorial conformations for (I) are energetically closer than in systems fully populated by tetrahedral C atoms. Although semi-empirical molecular

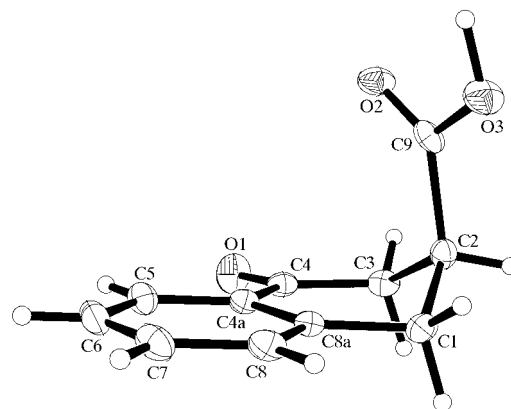


Figure 1

The asymmetric unit of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

(AM1) modeling (Wavefunction, 1995; Dewar *et al.*, 1985) indicated the pseudo-equatorial conformation to be slightly more stable, any such advantage is obviously overbalanced by other forces in the crystal.

The disorder commonly detected in carboxyl dimers as an averaging of C—O distances and C—C—O angles (Leiserowitz, 1976) is not seen in (I), where these values are 1.214 (3)/1.313 (3) Å and 123.3 (2)/114.3 (2)°, respectively. Values cited as typical for highly ordered dimeric carboxyls are 1.21/1.31 Å and 123/112°, respectively (Borthwick, 1980).

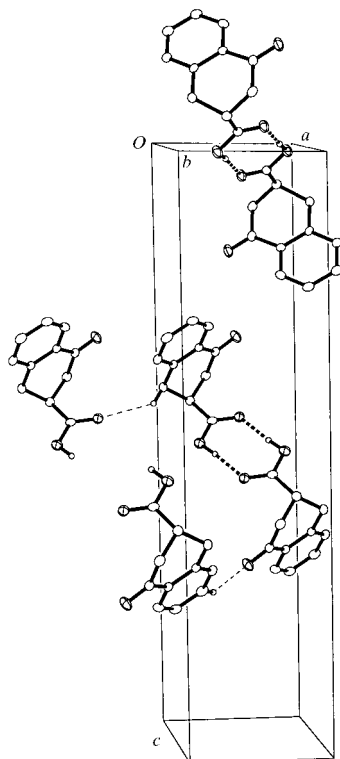


Figure 2

A partial packing diagram for (I), with extracellular molecules, showing acid dimers centered on the *a* edge and at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. Close contacts found between O1 and H7 (2.55 Å), and between O2 and H1B (2.67 Å) of separate translationally related molecules are indicated by dotted lines. Displacement ellipsoids are drawn at the 20% probability level and carbon-bound H atoms have been removed for clarity.

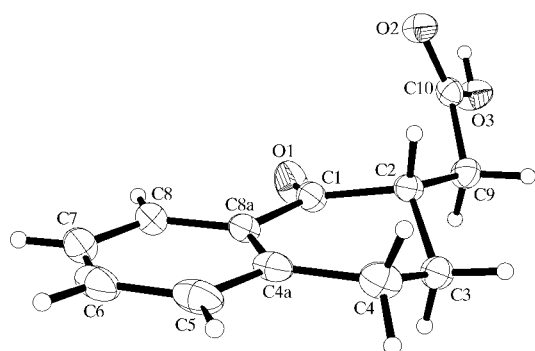


Figure 3

The asymmetric unit of (II), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

Fig. 2 shows the packing arrangement for (I), involving centrosymmetric dimers centered on the *a* edge of the chosen cell and at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ [$O \cdots O = 2.705 (2)$ Å and $O-H \cdots O = 173 (3)^\circ$]. Translationally related molecules stack with an interplanar distance of 3.48 Å, but the aromatic portions do not stack directly together, and the overlap between stacked aromatic and ketone rings involves only about half of each ring. Close C—H \cdots O=C contacts are found to separate translational neighbors between the ketone and H7 (2.55 Å), and between the acid and H1B (2.67 Å). These distances lie within the 2.7 Å range we often employ for non-bonded H \cdots O packing interactions (Steiner, 1997). Using data compiled from a large number of C—H \cdots O contacts, Steiner & Desiraju (1998) find significant statistical directionality even as far out as 3.0 Å and conclude that these are legitimately viewed as 'weak hydrogen bonds', with a greater contribution to packing forces than simple van der Waals attractions.

Fig. 3 shows the asymmetric unit of (\pm)-1-tetralone-2-acetic acid [(\pm)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-acetic acid, $C_{12}H_{12}O_3$, (II)] with the atomic numbering. The flexible ketone ring adopts a significantly more twisted conformation than in (I), placing C2 0.358 (3) Å above the average aromatic plane, while C3 lies 0.440 (3) Å below it. The ketone is significantly less coplanar with the aromatic ring than in the case of (I) [torsion angle $O1-C1-C8A-C8 = -14.3 (3)^\circ$]. Free rotation is possible about only two bonds, and the

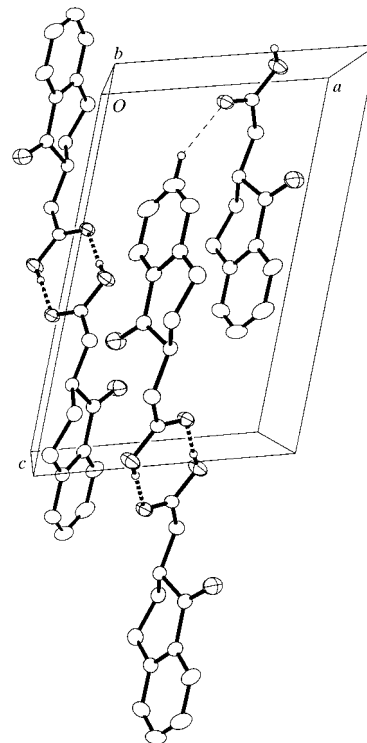


Figure 4

A partial packing diagram for (II), with extracellular molecules, showing acid dimers centered on the *a* edge and the *bc* face. A reciprocal close contact found between the acid carbonyl and the H6 atom of a centrosymmetrically related neighbor is indicated by dotted lines. Displacement ellipsoids are set at the 20% probability level and carbon-bound H atoms have been removed for clarity.

conformational arrangement at C2—C9 is staggered, with C9 forming a pseudo-equatorial bond so that the torsion angle C9—C2—C3—C4 is 171.3 (2)°. The C9—C10 bond is rotated so that the O2—C10—C9—C2 torsion angle is 23.4 (3)°, placing the two carboxyl O atoms at similar distances from the ketone O atom [O1···O2 = 3.173 (2) Å and O1···O3 = 3.670 (2) Å]. The ketone—carboxyl dihedral angle (C2/C1/C8A/O1 versus C10/O2/O3) is 79.1 (1)°. No carboxyl disorder was detected in (II), where the C—O distances are 1.216 (2)/1.311 (2) Å and the C—C—O angles are 123.7 (2)/114.1 (2)°.

Fig. 4 shows the packing arrangement for (II), involving centrosymmetric dimers centered on the *bc* face and the *a* edge of the chosen cell [O···O = 2.674 (2) Å and O—H···O = 176°]. Centrosymmetrically related molecules stack with their aromatic rings significantly overlapped, at an interplanar distance of 3.65 Å, and a 2.60 Å close C—H···O=C contact is found between the acid and H6 of a centrosymmetrically related neighbor (to which it is not hydrogen bonded).

Compound (I) in KBr has a single IR peak at 1691 cm⁻¹ for both C=O groups. In CHCl₃ solution, where dimers are known to predominate, the presence of two peaks, at 1687 and 1713 cm⁻¹, suggests the presence in solution of a different (or more than one) conformation. The KBr spectrum of (II) has discrete C=O absorptions at 1692 (ketone) and 1704 cm⁻¹ (acid). In CHCl₃ solution, only slight shifts occur, and these peaks appear at 1683 and 1712 cm⁻¹, with a typical carboxyl-dilution shoulder *ca* 1740 cm⁻¹.

Experimental

Compound (I) was prepared from the Stobbe-condensation product of benzaldehyde with diethyl succinate by sequential saponification, hydrogenation (Pd/C) and acid-catalyzed cyclization (Horning & Walker, 1952). Crystals of (I) (m.p. 420 K) were obtained from ethyl acetate/cyclohexane. For compound (II), 2-carbomethoxy-1-tetralone was alkylated with ethyl bromoacetate and the product was hydrolyzed and decarboxylated under acidic conditions, as described by Bachman & Johnson (1949). After sublimation of the crude product, crystals of (II) (m.p. 383 K) were obtained from diethyl ether.

Compound (I)

Crystal data

C ₁₁ H ₁₀ O ₃	$D_x = 1.416 \text{ Mg m}^{-3}$
$M_r = 190.19$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 52 reflections
$a = 6.2645 (7) \text{ \AA}$	$\theta = 4.5\text{--}20.2^\circ$
$b = 5.4440 (12) \text{ \AA}$	$\mu = 0.103 \text{ mm}^{-1}$
$c = 26.170 (3) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 91.339 (11)^\circ$	Trapezoid, colourless
$V = 892.2 (2) \text{ \AA}^3$	$0.56 \times 0.52 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Siemens <i>P4</i> diffractometer	$R_{\text{int}} = 0.036$
$2\theta/\theta$ scans	$\theta_{\text{max}} = 25.01^\circ$
Absorption correction: numerical (<i>XPREP</i> ; Sheldrick, 1997)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.952, T_{\text{max}} = 0.990$	$k = 0 \rightarrow 6$
2499 measured reflections	$l = 0 \rightarrow 30$
1582 independent reflections	3 standard reflections every 97 reflections
1118 reflections with $I > 2\sigma(I)$	intensity variation: <0.7%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0365P)^2 + 0.2370P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.106$	$(\Delta/\sigma)_{\text{max}} = 0.02$
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.16 \text{ e \AA}^{-3}$
1582 reflections	$\Delta\rho_{\text{min}} = -0.12 \text{ e \AA}^{-3}$
141 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.007 (2)

Table 1

Selected geometric parameters (Å, °) for (I).

O2—C9	1.214 (3)	O3—C9	1.313 (3)
O2—C9—C2	123.3 (2)	O3—C9—C2	114.3 (2)

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O3—H3···O2 ⁱ	0.94 (3)	1.77 (3)	2.705 (2)	173 (3)
C1—H1B···O2 ⁱⁱ	0.97	2.67	3.471 (3)	140
C7—H7···O1 ⁱⁱⁱ	0.93	2.55	3.368 (3)	147

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

Compound (II)

Crystal data

C ₁₂ H ₁₂ O ₃	$D_x = 1.312 \text{ Mg m}^{-3}$
$M_r = 204.22$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 21 reflections
$a = 8.0008 (10) \text{ \AA}$	$\theta = 4.6\text{--}15.0^\circ$
$b = 10.579 (2) \text{ \AA}$	$\mu = 0.094 \text{ mm}^{-1}$
$c = 12.6789 (13) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 105.616 (8)^\circ$	Block, colorless
$V = 1033.5 (3) \text{ \AA}^3$	$0.60 \times 0.34 \times 0.24 \text{ mm}$
$Z = 4$	

Data collection

Siemens <i>P4</i> diffractometer	$R_{\text{int}} = 0.022$
$2\theta/\theta$ scans	$\theta_{\text{max}} = 24.99^\circ$
Absorption correction: numerical (<i>XPREP</i> ; Sheldrick, 1997)	$h = -9 \rightarrow 9$
$T_{\text{min}} = 0.981, T_{\text{max}} = 0.997$	$k = 0 \rightarrow 12$
2503 measured reflections	$l = 0 \rightarrow 15$
1822 independent reflections	3 standard reflections every 97 reflections
1305 reflections with $I > 2\sigma(I)$	intensity variation: <1%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0330P)^2 + 0.2742P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.109$	$(\Delta/\sigma)_{\text{max}} = 0.00$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.13 \text{ e \AA}^{-3}$
1822 reflections	$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$
149 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 3

Selected geometric parameters (Å, °) for (II).

O2—C10	1.216 (2)	O3—C10	1.311 (2)
O2—C10—C9	123.69 (18)	O3—C10—C9	114.05 (18)

Table 4

Hydrogen-bonding geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3...O2 ⁱ	0.90	1.77	2.674 (2)	176
C6—H6...O2 ⁱⁱ	0.93	2.60	3.418 (3)	147
C9—H9A...O1 ⁱⁱⁱ	0.97	2.71	3.336 (3)	122

 Symmetry codes: (i) $2 - x, 1 - y, 1 - z$; (ii) $2 - x, 1 - y, -z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$.

For both (I) and (II), all H atoms were found in electron-density difference maps but were placed in calculated positions and allowed to refine as riding models, with C—H distances of 0.97 Å for CH₂, 0.98 Å for methine and 0.93 Å for aromatic C atoms. All U_{iso} values for H atoms were refined. The carboxyl H atoms was also found in difference maps, but their positional and isotropic displacement parameters were allowed to fully refine.

For both compounds, data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1312). Services for accessing these data are described at the back of the journal.

References

- Bachman, W. E. & Johnson, G. D. (1949). *J. Am. Chem. Soc.* **71**, 3463–3468.
- Borthwick, P. W. (1980). *Acta Cryst.* **B36**, 628–632.
- Dewar, M. J. S., Zebisch, E. G., Healy, E. F. & Stewart, J. J. P. (1985). *J. Am. Chem. Soc.* **107**, 3902–3909.
- Hirsch, J. A. (1967). *Table of Conformational Energies*, in *Topics in Stereochemistry*, Vol. 1, edited by N. L. Allinger & E. L. Eliel, pp. 199–222. New York: Wiley-Interscience.
- Horning, E. C. & Walker, G. N. (1952). *J. Am. Chem. Soc.* **74**, 5147–5151.
- Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1997). *Acta Cryst.* **C53**, 1838–1842.
- Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1999). *Acta Cryst.* **C55**, 568–572.
- Lalancette, R. A., Thompson, H. W. & Brunskill, A. P. J. (1999). *Acta Cryst.* **C55**, 1908–1911.
- Leiserowitz, L. (1976). *Acta Cryst.* **B32**, 775–802.
- Sheldrick, G. M. (1997). *SHELXTL*. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.
- Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Steiner, T. (1997). *Chem. Commun.* pp. 727–734.
- Steiner, T. & Desiraju, G. R. (1998). *Chem. Commun.* pp. 891–892.
- Thompson, H. W., Brunskill, A. P. J. & Lalancette, R. A. (1998). *Acta Cryst.* **C54**, 829–831.
- Thompson, H. W., Lalancette, R. A. & Brunskill, A. P. J. (1998). *Acta Cryst.* **C54**, 1180–1182.
- Wavefunction (1995). *SPARTAN*. Version 4.0. Wavefunction Inc., 18401 Von Karman Avenue, Irvine, CA 92715, USA.