

## (±)-3-(3-Oxocyclohexyl)propionic acid: dual conformational selection and hydrogen bonding in an $\epsilon$ -keto acid

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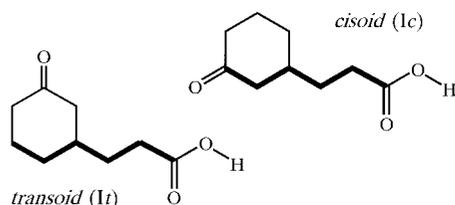
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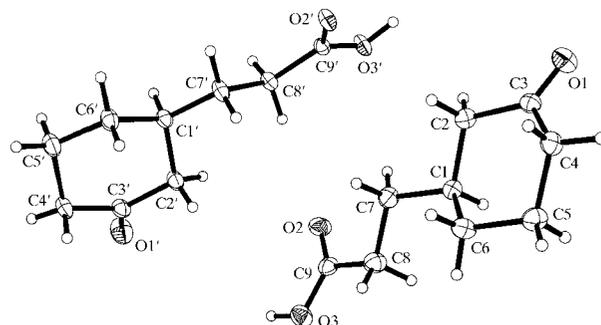
The asymmetric unit of the title compound,  $C_9H_{14}O_3$ , consists of two molecules having conformations that differ by a rotation of  $111.7 (5)^\circ$  about the equatorial substituent bond, so that the side chains of the two species extend away from the ring in different directions. Each conformer forms centrosymmetric hydrogen-bonded acid-to-acid dimers with its own enantiomer [ $O \cdots O = 2.681 (3)$  and  $2.698 (4) \text{ \AA}$ ]. There is an intermolecular  $C-H \cdots O$  close contact involving the ketone group of one of the conformers.

### Comment

The crystal structures of keto-carboxylic acids display five known hydrogen-bonding modes. Two of these lack ketone involvement, reflecting the common pairing and much rarer chain modes known for simple acids (Leiserowitz, 1976). Acid-to-ketone chains (catemers) constitute a sizable minority of cases, while intramolecular hydrogen bonds and acid-to-ketone dimers are rarely observed. We have previously provided and cited examples of many of these, along with discussions of the factors that appear to govern the choice of mode (Lalancette *et al.*, 1998, 1999; Brunskill *et al.*, 1999).



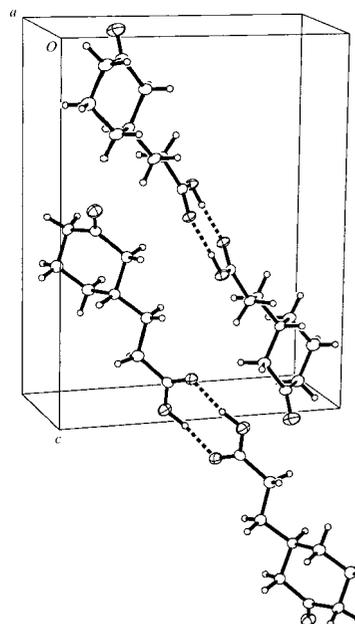
We report here the crystal structure of the title compound, (I). The category of  $\epsilon$ -keto acids to which (I) belongs includes catemers of the helical, translational and glide types, as well as dimers and hydrated patterns. Fig. 1 presents a view of the asymmetric unit of (I) with the atom numbering. The two molecules in this unit, (Ic) and (It), differ in the conformations of their side chains, as illustrated in the Scheme. Although the chain extends away from the ring equatorially in a standard staggered-*anti* fashion in both molecules, C7 has two options



**Figure 1**

A view of the asymmetric unit of (I) with the atom-numbering scheme; the two molecules differ in the direction of extension of the side chain away from the ring, producing *cisoid*, (Ic), and *transoid*, (It), arrangements of the two carbonyl groups, as illustrated in the Scheme. Displacement ellipsoids are drawn at the 20% probability level.

for the onward direction the chain can take, differing by a rotation of  $111.7 (5)^\circ$  about C1–C7. For both these conformations, the staggered-*anti* arrangement of the chain extends into the ring, but in one case [(Ic), '*cisoid*' carbonyls], this extension includes C2 and C3 (the ketone carbon), while in the other [(It), '*transoid*' carbonyls], it includes C6 and C5. Except for a  $35.5 (6)^\circ$  difference in the rotational conformations of the carboxyl groups relative to their chains [torsion angle O2–C9–C8–C7 =  $28.7 (5)^\circ$  for (Ic) and  $-6.8 (4)^\circ$  for (It)], the distinction between (Ic) and (It) would disappear in the absence of the ketone function. The ketone O atom is sufficiently remote from the side chain that, without packing forces, enthalpy differences between (Ic) and (It) are negligible; remarkably, of these isoenthalpic conformers, the crystal packing arrangement chooses both.



**Figure 2**

A partial packing diagram, showing the dimers formed by centrosymmetric hydrogen-bonded pairing of (Ic) and of (It). Dimers centered on the *b* edge are of the *cisoid* type, (Ic), and those on the *bc* face are of the *transoid* type, (It). All carbon-bound H atoms has been removed for clarity. Displacement ellipsoids are drawn at the 20% probability level.

Although averaging of the C—O bond lengths and C—C—O angles by disorder is common in dimeric carboxyls (Leiserowitz, 1976), neither (Ic) nor (It) displays significant carboxyl disorder. In (Ic), the C—O bond lengths are 1.234 (4)/1.297 (4) Å, with angles of 122.6 (3)/113.8 (3)°; the corresponding values for (It) are 1.228 (3)/1.324 (3) Å, with angles of 124.2 (3)/112.9 (2)°. Typical values cited for highly ordered dimeric carboxyls are 1.21/1.31 Å and 123/112°, respectively (Borthwick, 1980).

Fig. 2 illustrates the packing of the cell. Each of the two conformers pairs centrosymmetrically with its own enantiomer. Dimers of the *cisoid* type, (Ic), are centered on the *b* edge of the chosen cell, while dimers of the (It) type are centered on the *bc* face. The O···O distance and O—H···O angle are 2.698 (4) Å and 167 (4)° for (Ic), and 2.681 (3) Å and 177 (4)° for (It).

In the packing, a 2.64 Å intermolecular C—H···O close contact was found for the ketone function of the *transoid* species (It) to atom H8A of a neighboring molecule of type (Ic). This lies within the 2.7 Å range we usually employ for non-bonded C—H···O packing interactions (Steiner, 1997). Using compiled data for a large number of C—H···O contacts, Steiner & Desiraju (1998) have found 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.

The solid-state (KBr) IR spectrum of (I) has a broadened stretching absorption at 1709 cm<sup>-1</sup> for both C=O functions in both species, typical for acids having and ketones lacking hydrogen bonding; a shoulder appears at *ca* 1730 cm<sup>-1</sup>. In CHCl<sub>3</sub> solution, this broad peak appears at 1708 cm<sup>-1</sup>, with a typical carboxyl-dilution shoulder at *ca* 1740 cm<sup>-1</sup>.

## Experimental

Compound (I) was prepared by Rh-catalyzed hydrogenation of 3-hydroxycinnamic acid, followed by Jones oxidation. Crystals suitable for X-ray diffraction analysis were produced from a cyclohexane–Et<sub>2</sub>O solution (m.p. 315 K).

### Crystal data

|   |   |
|---|---|
| C <sub>9</sub> H <sub>14</sub> O <sub>3</sub> | <i>Z</i> = 4                                    |
| <i>M<sub>r</sub></i> = 170.20                 | <i>D<sub>x</sub></i> = 1.213 Mg m <sup>-3</sup> |
| Triclinic, <i>P</i> $\bar{1}$                 | Mo <i>K</i> α radiation                         |
| <i>a</i> = 5.429 (3) Å                        | Cell parameters from 31 reflections             |
| <i>b</i> = 12.005 (7) Å                       | <i>θ</i> = 4.0–10.1°                            |
| <i>c</i> = 14.570 (8) Å                       | <i>μ</i> = 0.09 mm <sup>-1</sup>                |
| <i>α</i> = 87.05 (2)°                         | <i>T</i> = 260 (2) K                            |
| <i>β</i> = 88.96 (2)°                         | Parallelepiped, colourless                      |
| <i>γ</i> = 79.39 (2)°                         | 0.46 × 0.16 × 0.07 mm                           |
| <i>V</i> = 932.1 (9) Å <sup>3</sup>           |   |

### Data collection

|   |                                  |
|---|----------------------------------|
| Siemens <i>P</i> 4 diffractometer                                     | <i>θ</i> <sub>max</sub> = 25.0°  |
| 2θ/θ scans  | <i>h</i> = -6 → 6                |
| Absorption correction: numerical ( <i>SHELXTL</i> ; Sheldrick, 1997b) | <i>k</i> = -14 → 14              |
| <i>T</i> <sub>min</sub> = 0.97, <i>T</i> <sub>max</sub> = 0.99        | <i>l</i> = 0 → 17                |
| 3303 measured reflections   | 3 standard reflections           |
| 3303 independent reflections  | every 97 reflections             |
| 2085 reflections with <i>I</i> > 2σ( <i>I</i> )                       | intensity decay: variation <1.2% |

### Refinement

|                                     |   |
|-------------------------------------|---|
| Refinement on <i>F</i> <sup>2</sup> | $w = 1/[\sigma^2(F_o^2) + (0.0751P)^2 + 0.3643P]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.063$     | where $P = (F_o^2 + 2F_c^2)/3$                    |
| $wR(F^2) = 0.175$                   | (Δ/σ) <sub>max</sub> < 0.001                      |
| <i>S</i> = 1.04                     | Δρ <sub>max</sub> = 0.42 e Å <sup>-3</sup>        |
| 3303 reflections                    | Δρ <sub>min</sub> = -0.18 e Å <sup>-3</sup>       |
| 223 parameters                      |   |
| H atoms: see below                  |   |

**Table 1**

Selected geometric parameters (Å, °).

|             |            |                 |           |
|-------------|------------|-----------------|-----------|
| O2—C9       | 1.234 (4)  | O2'—C9'         | 1.228 (3) |
| O3—C9       | 1.297 (4)  | O3'—C9'         | 1.324 (3) |
| O2—C9—C8    | 122.6 (3)  | O2'—C9'—C8'     | 124.2 (3) |
| O3—C9—C8    | 113.8 (3)  | O3'—C9'—C8'     | 112.9 (2) |
| C2—C1—C7—C8 | 175.0 (3)  | C2'—C1'—C7'—C8' | 63.3 (4)  |
| C1—C7—C8—C9 | -160.7 (3) | C1'—C7'—C8'—C9' | 172.3 (2) |
| C7—C8—C9—O2 | 28.7 (5)   | C7'—C8'—C9'—O2' | -6.8 (4)  |

**Table 2**

Hydrogen-bonding geometry (Å, °).

| <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 <sup>i</sup>     | 0.98 (4)    | 1.73 (4)      | 2.698 (4)             | 167 (4)                 |
| O3'—H3'···O2' <sup>ii</sup> | 0.91 (4)    | 1.77 (4)      | 2.681 (3)             | 177 (4)                 |

Symmetry codes: (i) -*x*, 1 - *y*, 2 - *z*; (ii) -*x*, 1 - *y*, 1 - *z*.

All H atoms were found in electron-density difference maps but were placed in calculated positions (0.97 Å for the methylene and 0.98 Å for the methine H atoms) and allowed to refine as riding models on their respective C atoms. Their displacement parameters were fixed at 120% of those of their attached C atoms. The positional parameters of the carboxyl H atoms were allowed to refine, but their displacement parameters were fixed at 150% of those of their attached O atoms.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 1997b).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1348). Services for accessing these data are described at the back of the journal.

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