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# (±)-*trans*-2-Benzoylcyclohexanecarboxylic Acid. Structure and Hydrogen-Bonding Pattern of a γ-Keto Acid

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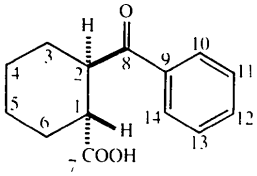
## Abstract

In the title compound, $C_{14}H_{16}O_3$, enantiomeric pairs of molecules form dimers by mutual hydrogen bonding of carboxyl groups, with the ketone group not involved in the hydrogen bonding. The components of the dimer differ in conformation, so that the dimer is the asymmetric unit.

## Comment

Our interest in simple keto carboxylic acids arises from their four known crystalline hydrogen-bonding states. The commonest retains the dimer pattern characteristic of almost all functionally unelaborated acids in which the ketone is not involved. Less commonly, intermolecular carboxyl-to-ketone hydrogen bonds repeat infinitely along one cell axis to yield a chain or catemer. A third rare arrangement is an internal hydrogen bond and one instance is known of acid-to-ketone dimerization. We have previously referenced and discussed many examples of these (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

γ-Keto acids constitute a class particularly rich in hydrogen-bonding types, with examples of dimers, internal hydrogen bonds and catemers of both the helical and translational type. Despite the expectation of an intramolecular hydrogen bond for the *cis* counterpart of the title compound (Pourahmady & Eisenbraun, 1982), it was found to crystallize as a centrosymmetric dimer (Choney, Holt, Pourahmady & Eisenbraun, 1983). We report here that the *trans* epimer, (I), also adopts the common carboxylic acid dimer motif, but that the dimer components are crystallographically unrelated, leading to an unusually long cell dimension [40.748 (6) Å] for such a small molecule (17 non-H atoms).



(I)

Friedel–Crafts acylation of benzene with *cis*-1,2-cyclohexanedicarboxylic anhydride yields, as the immediate product, the less stable *cis*-keto acid (m.p. 413 K). Aqueous base epimerizes this to the more stable *trans* diastereomer (m.p. 427 K) (Scribner & Miller, 1965).

Fig. 1 presents a view of the asymmetric unit with its numbering scheme. The cell contains four asymmetric units ($Z = 8$), each consisting of a pair of conformationally distinct molecules of opposite chirality, reciprocally hydrogen bonded through their carboxyl groups, with no ketone participation in the hydrogen bonding. Each molecule, as expected, has its substituents equatorial to a chair cyclohexane and the two molecules in the asymmetric unit differ almost entirely in the rotational orientation of the benzene ring. The carboxyl group adopts a conformation relative to its ring H atom whose torsion angle is 31.9° for molecule *A* and 30.1° for molecule *B*. The torsion angle for the benzoyl C=O relative to its axial ring H atom is 138.9° for molecule *A* and 141.0° for molecule *B*. Hence, the dihedral angles between the ketone and carboxyl planes are nearly identical in the two molecules, 73.0° in *A* and 70.2° in *B*. In molecule *A*, however, the dihedral angle of the aromatic ring relative to the ketone is 31.9°, whereas this angle is 9.7° in molecule *B*.

The carboxyl C—O bond lengths and C—C—O angles are found to be only slightly disordered, although

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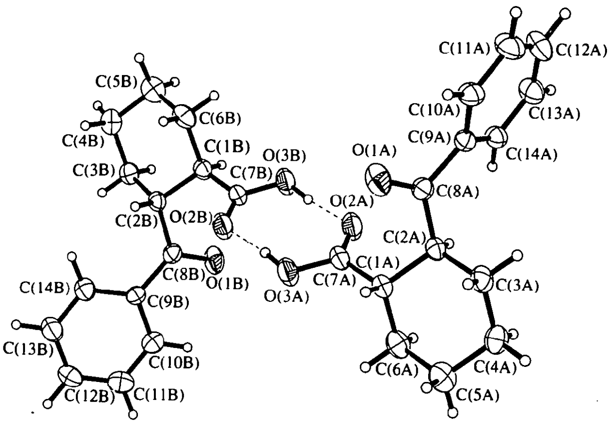

Fig. 1. A view of the asymmetric unit with its numbering scheme. Each unit consists of a pair of conformationally distinct molecules of opposite chirality, reciprocally hydrogen bonded through their carboxyl groups. The ellipsoids are drawn at the 30% probability level.

disorder is common in dimeric acids (Dieterich, Paul & Curtin, 1974). The lengths here average 1.228 and 1.300 Å, with angles 114.9 and 122.6°, in contrast to typical lengths of 1.21 and 1.31 Å, and angles of 112 and 123° in highly ordered carboxyl dimers (Borthwick, 1980).

Fig. 2 is a packing diagram utilizing extracellular molecules to illustrate the arrangement of the asymmetric units.

The solid-state (KBr) IR spectrum of the title compound displays C=O stretching absorptions at 1704 and 1673 $cm^{-1}$ for carboxyl and ketone, respectively, which is normal for such compounds showing the dimeric hydrogen-bonding motif (Vanderhoff, Lalancette & Thompson, 1990; Thompson, Vanderhoff & Lalancette, 1991).

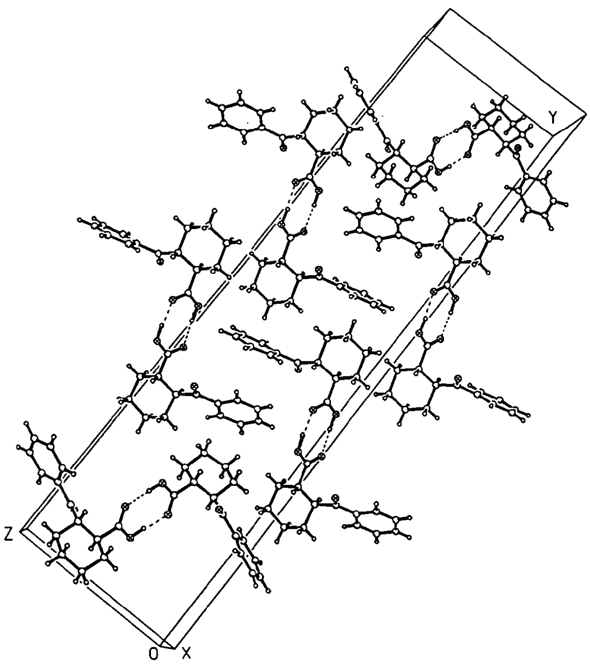

Fig. 2. A packing diagram of the title compound. Extracellular molecules illustrate the arrangement of the asymmetric unit.

## Experimental

The title compound was crystallized at room temperature from a 250:4:1 solution of absolute ethanol, water and acetic acid.

*Crystal data*

$C_{14}H_{16}O_3$
$M_r = 232.3$
Monoclinic
$P2_1/n$
$a = 5.774\,(1)$ Å
$b = 40.748\,(6)$ Å
$c = 10.648\,(1)$ Å
$\beta = 99.053\,(9)°$
$V = 2474.2\,(6)$ Å$^3$
$Z = 8$
$D_x = 1.247$ Mg m$^{-3}$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 22 reflections
$\theta = 7.95–14.77°$
$\mu = 0.086$ mm$^{-1}$
$T = 297$ K
Flattened hexagonal prism
0.82 × 0.60 × 0.40 mm
Colorless

*Data collection*

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: analytical
$T_{\min} = 0.948$, $T_{\max} = 0.974$
3596 measured reflections
3227 independent reflections
2289 observed reflections $[F > 4\sigma(F)]$

$R_{\rm int} = 0.021$
$\theta_{\max} = 22.5°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 43$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 47 reflections
intensity decay: 2.97%

*Refinement*

Refinement on $F$
$R = 0.053$
$wR = 0.063$
$S = 1.56$
2289 reflections
311 parameters
$w = 1/[\sigma^2(F) + 0.0007F^2]$
$(\Delta/\sigma)_{\max} = 0.138$
$\Delta\rho_{\max} = 0.15$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.14$ e Å$^{-3}$

Extinction correction: $F^* = F/(1 + 0.002F^2 \times \chi/\sin 2\theta)^{1/4}$
Extinction coefficient: $\chi = 0.0012$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å$^2$)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | $x$ | $y$ | $z$ | $U_{\rm eq}$ |
|---|---|---|---|---|
| O(1*A*) | 0.6839 (4) | 0.0634 (1) | 0.6385 (2) | 0.069 (1) |
| O(2*A*) | 0.3925 (4) | 0.1067 (1) | 0.8313 (2) | 0.072 (1) |
| O(3*A*) | 0.6681 (4) | 0.0817 (1) | 0.9663 (2) | 0.066 (1) |
| C(1*A*) | 0.4161 (5) | 0.0482 (1) | 0.8245 (2) | 0.046 (1) |
| C(2*A*) | 0.3075 (5) | 0.0490 (1) | 0.6838 (2) | 0.043 (1) |
| C(3*A*) | 0.2366 (5) | 0.0146 (1) | 0.6369 (3) | 0.057 (1) |
| C(4*A*) | 0.0704 (6) | −0.0014 (1) | 0.7158 (3) | 0.061 (1) |
| C(5*A*) | 0.1752 (6) | −0.0017 (1) | 0.8562 (3) | 0.069 (1) |
| C(6*A*) | 0.2452 (6) | 0.0328 (1) | 0.9032 (3) | 0.064 (1) |
| C(7*A*) | 0.4920 (5) | 0.0813 (1) | 0.8736 (3) | 0.049 (1) |
| C(8*A*) | 0.4727 (5) | 0.0631 (1) | 0.6014 (3) | 0.046 (1) |

| | | | | |
|---|---|---|---|---|
| C(9A) | 0.3782 (5) | 0.0747 (1) | 0.4710 (2) | 0.044 (1) |
| C(10A) | 0.5195 (5) | 0.0717 (1) | 0.3773 (3) | 0.057 (1) |
| C(11A) | 0.4422 (7) | 0.0829 (1) | 0.2560 (3) | 0.074 (2) |
| C(12A) | 0.2270 (7) | 0.0979 (1) | 0.2268 (3) | 0.072 (1) |
| C(13A) | 0.0884 (6) | 0.1014 (1) | 0.3184 (3) | 0.064 (1) |
| C(14A) | 0.1611 (5) | 0.0896 (1) | 0.4401 (3) | 0.051 (1) |
| O(1B) | −0.5164 (4) | 0.1857 (1) | 0.2330 (2) | 0.072 (1) |
| O(2B) | −0.2231 (4) | 0.1416 (1) | 0.0544 (2) | 0.067 (1) |
| O(3B) | −0.4897 (4) | 0.1662 (1) | −0.0867 (2) | 0.073 (1) |
| C(1B) | −0.2383 (5) | 0.2002 (1) | 0.0518 (2) | 0.047 (1) |
| C(2B) | −0.1398 (5) | 0.2021 (1) | 0.1934 (2) | 0.044 (1) |
| C(3B) | −0.0833 (5) | 0.2381 (1) | 0.2279 (3) | 0.055 (1) |
| C(4B) | 0.0961 (6) | 0.2520 (1) | 0.1506 (3) | 0.063 (1) |
| C(5B) | 0.0183 (6) | 0.2475 (1) | 0.0085 (3) | 0.068 (1) |
| C(6B) | −0.0527 (6) | 0.2126 (1) | −0.0260 (3) | 0.062 (1) |
| C(7B) | −0.3179 (5) | 0.1666 (1) | 0.0081 (3) | 0.048 (1) |
| C(8B) | −0.3080 (5) | 0.1877 (1) | 0.2754 (3) | 0.048 (1) |
| C(9B) | −0.2195 (5) | 0.1765 (1) | 0.4075 (3) | 0.045 (1) |
| C(10B) | −0.3706 (5) | 0.1592 (1) | 0.4726 (3) | 0.057 (1) |
| C(11B) | −0.2980 (6) | 0.1489 (1) | 0.5957 (3) | 0.067 (1) |
| C(12B) | −0.0751 (6) | 0.1558 (1) | 0.6563 (3) | 0.067 (1) |
| C(13B) | 0.0764 (6) | 0.1726 (1) | 0.5935 (3) | 0.068 (1) |
| C(14B) | 0.0071 (5) | 0.1825 (1) | 0.4690 (3) | 0.057 (1) |

Table 2. *Selected geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O(1A)—C(8A) | 1.221 (3) | O(1B)—C(8B) | 1.220 (3) |
| O(2A)—C(7A) | 1.232 (4) | O(2B)—C(7B) | 1.225 (4) |
| O(3A)—C(7A) | 1.301 (3) | O(3B)—C(7B) | 1.299 (3) |
| C(1A)—C(2A) | 1.531 (3) | C(1B)—C(2B) | 1.527 (3) |
| C(1A)—C(6A) | 1.526 (4) | C(1B)—C(6B) | 1.540 (4) |
| C(1A)—C(7A) | 1.490 (4) | C(1B)—C(7B) | 1.494 (4) |
| C(2A)—C(3A) | 1.524 (4) | C(2B)—C(3B) | 1.535 (4) |
| C(2A)—C(8A) | 1.507 (4) | C(2B)—C(8B) | 1.521 (4) |
| C(3A)—C(4A) | 1.519 (5) | C(3B)—C(4B) | 1.530 (5) |
| C(4A)—C(5A) | 1.522 (4) | C(4B)—C(5B) | 1.519 (4) |
| C(5A)—C(6A) | 1.523 (5) | C(5B)—C(6B) | 1.511 (5) |
| C(8A)—C(9A) | 1.487 (4) | C(8B)—C(9B) | 1.491 (4) |
| C(9A)—C(10A) | 1.389 (4) | C(9B)—C(10B) | 1.388 (4) |
| C(9A)—C(14A) | 1.385 (5) | C(9B)—C(14B) | 1.390 (4) |
| C(10A)—C(11A) | 1.377 (4) | C(10B)—C(11B) | 1.378 (4) |
| C(12A)—C(13A) | 1.363 (5) | C(11B)—C(12B) | 1.375 (5) |
| C(11A)—C(12A) | 1.377 (5) | C(12B)—C(13B) | 1.367 (5) |
| C(13A)—C(14A) | 1.384 (4) | C(13B)—C(14B) | 1.383 (4) |
| O(3A)···O(2B$^{i}$) | 2.655 (5) | O(3B)···O(2A$^{ii}$) | 2.630 (5) |
| H(16)···O(2A$^{ii}$) | 1.634 (4) | H(15)···O(2B$^{i}$) | 1.663 (4) |
| H(15)—O(3A) | 0.997(4) | H(16)—O(3B) | 1.000 (4) |

| | | | |
|---|---|---|---|
| C(2A)—C(1A)—C(6A) | 110.3 (2) | C(2B)—C(1B)—C(6B) | 109.4 (2) |
| C(2A)—C(1A)—C(7A) | 112.0 (2) | C(2B)—C(1B)—C(7B) | 113.7 (2) |
| C(6A)—C(1A)—C(7A) | 111.1 (2) | C(6B)—C(1B)—C(7B) | 109.8 (2) |
| C(1A)—C(2A)—C(3A) | 110.3 (2) | C(1B)—C(2B)—C(3B) | 108.4 (2) |
| C(1A)—C(2A)—C(8A) | 112.3 (2) | C(1B)—C(2B)—C(8B) | 112.1 (2) |
| C(3A)—C(2A)—C(8A) | 108.8 (2) | C(3B)—C(2B)—C(8B) | 111.1 (2) |
| C(2A)—C(3A)—C(4A) | 112.0 (2) | C(2B)—C(3B)—C(4B) | 111.2 (3) |
| C(3A)—C(4A)—C(5A) | 111.0 (3) | C(3B)—C(4B)—C(5B) | 111.9 (3) |
| C(4A)—C(5A)—C(6A) | 111.1 (3) | C(4B)—C(5B)—C(6B) | 112.4 (3) |
| C(1A)—C(6A)—C(5A) | 111.1 (3) | C(1B)—C(6B)—C(5B) | 111.3 (3) |
| O(2A)—C(7A)—O(3A) | 122.2 (3) | O(2B)—C(7B)—O(3B) | 122.6 (3) |
| O(2A)—C(7A)—C(1A) | 122.5 (2) | O(2B)—C(7B)—C(1B) | 122.8 (2) |
| O(3A)—C(7A)—C(1A) | 115.3 (3) | O(3B)—C(7B)—C(1B) | 114.5 (3) |
| O(1A)—C(8A)—C(2A) | 120.4 (2) | O(1B)—C(8B)—C(2B) | 119.7 (2) |
| O(1A)—C(8A)—C(9A) | 120.0 (3) | O(1B)—C(8B)—C(9B) | 120.0 (3) |
| C(2A)—C(8A)—C(9A) | 119.5 (2) | C(2B)—C(8B)—C(9B) | 120.3 (2) |
| C(8A)—C(9A)—C(10A) | 118.1 (3) | C(8B)—C(9B)—C(10B) | 118.5 (2) |
| C(8A)—C(9A)—C(14A) | 123.1 (3) | C(8B)—C(9B)—C(14B) | 123.2 (3) |
| C(10A)—C(9A)—C(14A) | 118.7 (2) | C(10B)—C(9B)—C(14B) | 118.3 (3) |
| C(9A)—C(10A)—C(11A) | 120.2 (3) | C(9B)—C(10B)—C(11B) | 120.6 (3) |
| C(10A)—C(11A)—C(12A) | 120.5 (3) | C(10B)—C(11B)—C(12B) | 120.4 (3) |
| C(11A)—C(12A)—C(13A) | 119.7 (3) | C(11B)—C(12B)—C(13B) | 119.8 (3) |
| C(12A)—C(13A)—C(14A) | 120.6 (3) | C(12B)—C(13B)—C(14B) | 120.3 (3) |
| C(9A)—C(14A)—C(13A) | 120.3 (3) | C(9B)—C(14B)—C(13B) | 120.6 (3) |
| O(2A$^{ii}$)···H(16)—O(3B) | 173.8 (2) | O(2B$^{i}$)···H(15)—O(3A) | 172.4 (2) |
| C(7A)—O(2A)···H(16$^{ii}$) | 122.5 (2) | C(7B)—O(2B)···H(15$^{ii}$) | 121.0 (2) |
| C(7A)—O(3A)—H(15) | 108.4 (3) | C(7B)—O(3B)—H(16) | 109.5 (3) |

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

All diffractometer software was provided by Siemens Analytical X-ray Instruments Inc., including *SHELXTL/PC* (Sheldrick, 1990). The structure was solved by direct methods. Integrated intensities were corrected for Lorentz and polarization effects. Full-matrix least-squares refinement was performed. All non-H atoms were refined anisotropically. Both carboxyl H atoms were located in difference maps and allowed to refine as riding models on their associated O atoms. All other H atoms were placed in calculated positions and allowed to refine as riding models on their associated C atoms for optimum *R* factor and goodness-of-fit.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: PT1013). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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# (2*E*,4′*S*)-2-(4′-Benzyl-2′-oxo-3′-oxazolidinylcarbonyl)-3-phenylacrylic Acid Methyl Ester

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## Abstract

The crystal structure of the title compound, $C_{21}H_{19}NO_5$, has been determined at 153 K in order to confirm the configuration of the double bond.

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