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Hydrogen-Bonding Pattern of an α,β-Unsaturated δ-Keto Acid: 1′,3′-Dihydro-2-methyl-6-oxospiro[2-cyclohexene-1,2′-2′*H*-indene]-3-carboxylic Acid

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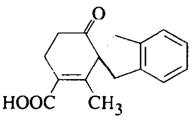
Abstract

The title compound, $C_{16}H_{16}O_3$, adopts a chiral conformation incorporating a flattened cyclohexene ring, with pairs of molecules forming centrosymmetric carboxyl dimers. The acid group is rotated 18 (1)° from coplanarity with the alkene and displays typical carboxyl disorder; the methyl group is rotationally disordered.

Comment

Our continuing study of the X-ray structures of simple keto carboxylic acids concerns their hydrogen-bonding motifs, of which four are known. The commonest has acid dimers in which the ketone is not involved (Coté, Thompson & Lalancette, 1996). Less frequently, intermolecular carboxyl-to-ketone hydrogen bonds repeat, often along a screw axis, to yield a catemer (Coté, Thompson & Lalancette, 1997). A third rare arrangement has an internal hydrogen bond (Coté, Lalancette & Thompson, 1996) and one instance is known of acid-to-ketone dimerization (Abell, Trent & Morris, 1991). The title compound, (I), is a δ-keto acid, a class found to contain examples of both dimeric and catemeric, as well as internal, hydrogen bonding.



(I)

The atom-numbering scheme for (I) and the chiral conformation it adopts are shown in Fig. 1. Around the planar alkene, whose C1—C2=C3—C4 torsion angle is −0.9 (4)°, the six-membered ring assumes a conformation which is more flattened than a standard cyclohexene half-chair because of the sp^2 hybridization at the C6 atom. The ketonic C6 atom lies only 0.282 (2) Å out of the average plane of this ring [the C3=C2—C1—C6 torsion angle is 9.4 (3)°], while C5 lies 0.332 (1) Å from this plane, on the opposite face [torsion angle C2=C3—C4—C5 is 21.5 (3)°]. The indane system is planar, with a mean deviation from planarity of 0.016 Å, and nearly orthogonal to the plane defined by the C6, C1 and C2 atoms [dihedral angle 89.0 (1)°]. The methyl group H atoms are rotationally disordered, with contributions from two principal rotamers in a ratio of 76 (3):24 (3); the predominant rotamer is shown in Fig. 1.

The carboxyl group is rotated slightly out of the plane defined by the alkene and its two neighboring ring C atoms (C1—C2=C3—C4), forming a dihedral angle of 18 (1)°. Its C—O bond lengths and C—C—O angles are partially averaged by disordering, as is frequently found in dimeric carboxylic acids (Leiserowitz, 1976). The observed lengths here are C7—O2 1.229 (3) and C7—O3 1.263 (3) Å, and the angles are 116.6 (2) for C3—C7—O3 and 123.6 (3)° for C3—C7—O2. Typical values for highly ordered cases are 1.21 and 1.31 Å, and 112 and 123°, respectively (Borthwick, 1980).

It is possible that the disordering exhibited by both the methyl and carboxyl groups is coupled, since these two groups are physically quite close. Modeling with a fully ordered carboxyl (Borthwick, 1980) in the two orientations (differing by 180°) contributing to the carboxyl disorder shows that the modeled C—O oxygen approaches significantly closer to the methyl H atoms than does the modeled C=O oxygen. For the worst-case 'head-on' steric interaction involving the modeled C—O oxygen and the minor (24%) methyl conformer (not shown in Fig. 1), our model indicates an O···H distance on the order of 1.8 Å. The serious repulsion involved would force the staggering of the H atoms to either side of the C—O oxygen, as seen in the major methyl conformer (76%), where their modeled O···H distances become roughly 2.15 and 2.50 Å to H8*B* and H8*C*, respectively. For the modeled C=O oxy-

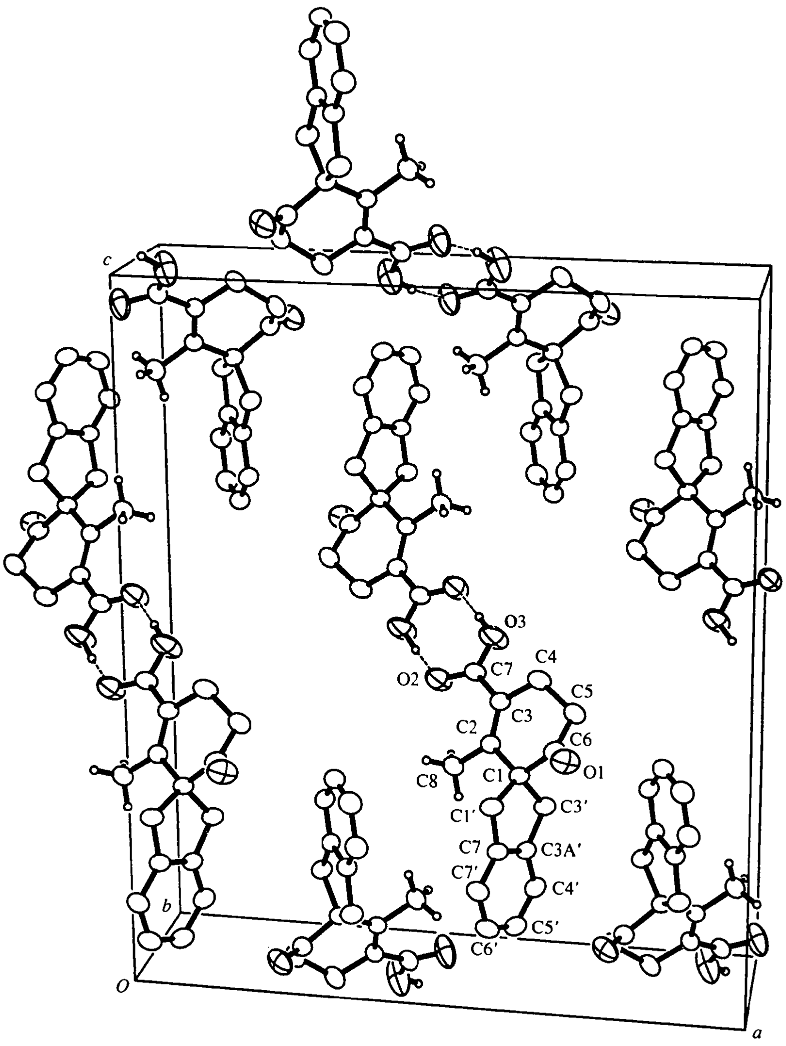


Fig. 1. A partial packing diagram of (I), with its numbering scheme. The molecule is inherently achiral but adopts a chiral conformation. Centrosymmetric carboxyl dimers are centered on the corners and center of the cell, plus the *c* edge and the *ab* face. Only the predominant methyl rotamer and carboxyl species are shown; all other non-carboxyl H atoms have been removed for clarity. The ellipsoids are drawn at the 40% probability level.

gen, the corresponding staggered distances to hydrogen, 2.5 and 2.9 Å, involve no serious strains. Hence, the staggered major methyl conformer evidently allows the presence of either C—O or C═O oxygen, while the minor methyl conformer would tolerate the proximity of only the C═O oxygen; in this case, the modeled 'head-on' O···H distance is *ca* 2.2 Å. Our observed O···H distances in the predominant conformers shown in Fig. 1 are 2.37 and 2.78 Å.

The packing of the centrosymmetric carboxyl dimers is illustrated in Fig 1. Translationally related sets of dimers are centered on the cell center and the *c* edge. Other sets translationally related to each other are also centered on the corners and the *ab* face.

The solid-state (KBr) IR spectrum of (I) has C═O absorptions at 1719 cm^{-1} (ketone), and at 1686 and 1664 cm^{-1} (acid). These values are in the normal range for a system with conjugated acid dimers and no ketone hydrogen bonding (Vanderhoff, Lalancette & Thompson, 1990; Coté, Lalancette & Thompson, 1995). The two carboxyl C═O assignments are based on the expectation that a carboxyl that is disordered in a strongly asymmetric environment may display more than one band, plus the fact that in $CHCl_3$, all the C═O absorptions coalesce to 1713 cm^{-1}. This latter value also indicates that in solution the carboxyl conformers that predominate lack conjugation.

Experimental

Compound (I) (m.p. 469 K) was synthesized by saponifying the condensation product of dibromo-*o*-xylene and Hagemann's ester, and was recrystallized from acetone.

Crystal data

$C_{16}H_{16}O_3$
$M_r = 256.29$
Monoclinic
$C2/c$
$a = 19.515\,(3)$ Å
$b = 5.8352\,(9)$ Å
$c = 22.854\,(3)$ Å
$\beta = 90.669\,(9)^\circ$
$V = 2602.3\,(7)$ Å^3
$Z = 8$
$D_x = 1.308$ Mg m^{-3}
$D_m = 1.30\,(1)$ Mg m^{-3}
D_m measured by flotation in cyclohexane/CCl_3Br

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 19 reflections
$\theta = 7.0–12.4^\circ$
$\mu = 0.090$ mm^{-1}
$T = 295\,(2)$ K
Rhombus
$0.60 \times 0.20 \times 0.10$ mm
Colorless

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: face-indexed numerical
$T_{\min} = 0.972$, $T_{\max} = 0.994$
3020 measured reflections
2276 independent reflections
1376 reflections with $F > 4\sigma(F)$

$R_{\rm int} = 0.047$
$\theta_{\max} = 25^\circ$
$h = -1 \rightarrow 22$
$k = -1 \rightarrow 6$
$l = -27 \rightarrow 27$
3 standard reflections every 97 reflections intensity decay: 2.5%

Refinement

Refinement on F^2
$R(F) = 0.0555$
$wR(F^2) = 0.148$
$S = 0.904$
2276 reflections
178 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.353$ e Å^{-3}
$\Delta\rho_{\min} = -0.193$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1994)
Extinction coefficient: 0.0133 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) and hydrogen-bonding geometry (Å, °)*

O1—C6	1.207 (3)	C1—C6	1.522 (3)
O2—C7	1.229 (3)	C3—C7	1.474 (3)
O3—C7	1.263 (3)	C5—C6	1.483 (3)
C7—O3—H3*C*	122 (2)	C5—C6—C1	114.4 (2)
C2—C3—C7	123.0 (2)	O2—C7—O3	119.8 (2)
C7—C3—C4	113.7 (2)	O2—C7—C3	123.6 (2)
O1—C6—C5	122.9 (2)	O3—C7—C3	116.6 (2)
O1—C6—C1	122.7 (2)		
C1—C2—C3—C7	175.8 (2)	C2—C3—C7—O2	19.7 (4)
C7—C3—C4—C5	−155.5 (2)	C4—C3—C7—O2	−163.3 (3)
C4—C5—C6—O1	−118.9 (2)	C2—C3—C7—O3	−160.7 (3)
C2—C1—C6—O1	140.0 (3)	C4—C3—C7—O3	16.3 (4)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*C*···O2$^{\rm i}$	0.98 (4)	1.66 (4)	2.622 (3)	169 (3)

Symmetry code: (i) $-x, 2-y, 1-z$.

All non-carboxyl H atoms, although found in electron-density difference maps, were replaced in calculated positions and allowed to refine as riding models. The displacement parameters of the methylene H atoms were refined as a group having a group $U_{\rm iso}$ of 0.063 (3). The aromatic H atoms refined to a group $U_{\rm iso}$ of 0.066 (4). The H atoms of the methyl group were treated as disordered with two different sets of three H atoms each [occupancy ratio 76 (3):24 (3)] and had a group $U_{\rm iso}$ of 0.058 (7). The carboxyl H3 atom was found in an electron-density difference map. Its positional parameters were refined but its isotropic temperature factor $U_{\rm iso}$ was held constant at 0.100.

Data collection: *XSCANS* (Siemens, 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*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1273). Services for accessing these data are described at the back of the journal.

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(+)-3-Oxoandrost-4-ene-17β-carboxylic Acid: Catemeric Hydrogen Bonding in a Steroidal Keto Acid

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Abstract

The title keto acid, $C_{20}H_{28}O_3$, forms translational carboxyl···ketone (O—H···O) hydrogen-bonding catemers [O···O 2.692 (3) Å], which follow no crystal-