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(*E*)-(1-Oxoindan-2-ylidene)acetic acid: catemeric hydrogen bonding in an unsaturated γ-keto acid

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The title compound, $C_{11}H_8O_3$, displays catemeric aggregation, involving hydrogen bonds progressing from the carboxyl of one molecule to the ketone of a glide-related neighbor [$O\cdots O = 2.6952\ (12)$ Å and $O-H\cdots O = 177.7\ (16)°$]. The molecule is highly planar and inherently achiral, but a slight conformational enantiomerism generated by the packing creates alternating conformational chirality in the chain units. Hydrogen-bonding chains, all aligned in the *a*-axis direction, occur in parallel counter-directional pairs related by centrosymmetry. Significant overlap of the aromatic rings occurs in the molecular stacking, at an average distance of 3.354 Å. Two $C-H\cdots O{=}C$ close contacts exist.

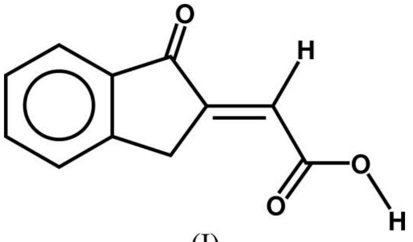
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.091
Data-to-parameter ratio = 11.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Our survey of hydrogen bonding in ketocarboxylic acids includes numerous examples of carboxyl-to-ketone catemers. These overwhelmingly involve homochiral chains, having either a screw or translational internal relationship. Far rarer are heterochiral chains resulting from glide-related chain members (Hickmott *et al.*, 1985; Watson *et al.*, 1990; Abell *et al.*, 1991; Kashyap *et al.*, 1995; Dobrzynska & Turowska-Tyrk, 1997; Thompson *et al.*, 1998; Barcon *et al.*, 1998, 2002). The present instance of the latter behavior involves an inherently achiral molecule, (I), with nearly imperceptible conformational enantiomerism generated by the packing.



(I)

Fig. 1 shows the molecular structure of (I) with the numbering scheme. The entire molecule is skeletally rigid and highly planar, with carboxyl coplanarity enforced by conjugation. The very slight conformational chirality is indicated by the largest non-H atom torsion-angle deviation from planarity present in the molecule, 2.38 (13)° (C7a—C3a—C3—C2), which, significantly, involves the only sp^3 C atom present.

Averaging of C—O bond lengths and C—C—O angles by disorder is invariably absent in catemers, like (I), whose geometry cannot support the averaging processes available to carboxyl dimers (Table 1).

Fig. 2 shows the packing arrangement. The hydrogen bonds progress catemerically between glide-related molecules, so

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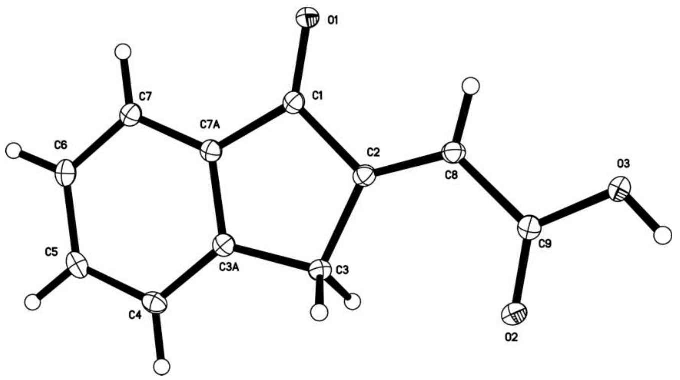

Figure 1
The molecular structure of (I) with the numbering scheme. The slight conformational chirality of the molecule is not visually apparent. Displacement ellipsoids are drawn at the 30% probability level.

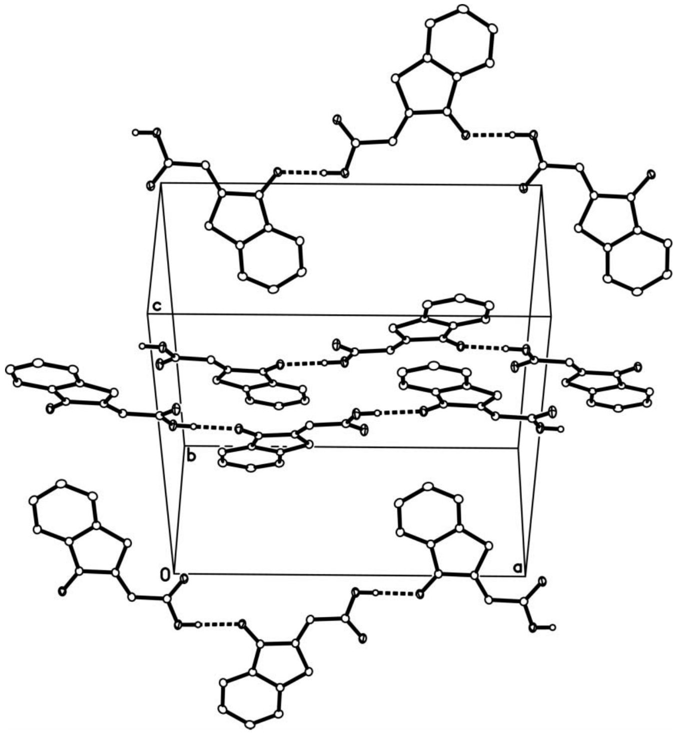

Figure 2
A partial packing diagram for (I), illustrating the hydrogen-bonded chains aligned along *a*. Shown are two counter-directional pairs, centrosymmetrically arranged around ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$) and composed of molecules of alternating chirality. Displacement ellipsoids are drawn at the 30% probability level. Carbon-bound H atoms have been omitted.

that chain-members are of alternating chirality. Centrosymmetrically related hydrogen-bonding chains proceed in counter-directional pairs parallel to the *a* axis. The flat zigzag chains are stacked nearly parallel to one another, in two general orientations in a herringbone pattern. Within each separate stack of ribbon-like catemers, alternate layers are mutually parallel by translation, but each layer has a dihedral angle of 3.35 (2)° with the adjacent ones sandwiching it; significant π overlap occurs among aromatic rings in adjacent layers, at an average distance of 3.354 Å.

Within the 2.6 Å range we routinely survey, two C—H$\cdots$O=C close intermolecular contacts were found (Table 2).

We characterize the geometry of hydrogen bonding to carbonyls using a combination of H$\cdots$O=C angle and H$\cdots$O=C—C torsion angle. These describe the approach of the acid H atom to the O atom in terms of its deviation from, respectively, C=O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). In (I), the values for these two angles are 128.10 (9) and 2.58 (10)°, respectively.

Experimental

Compound (I) (m.p. 483 K) was synthesized from 1-indanone and glyoxylic acid by the method of Tanaka *et al.* (1994); the stereochemistry probably results from equilibration under the reaction conditions (H_2SO_4 catalysis, 373 K). The crystal used was obtained from acetonitrile. The solid-state (KBr) infrared spectrum of (I) displays C=O absorptions at 1678 and 1721 cm^{-1}, with shifts typical of catemers, due, respectively, to addition of H bonding to the ketone and its removal from carboxyl C=O. In $CHCl_3$ solution, where dimers predominate, these absorptions coalesce to a single broader peak for both carbonyls, centered at 1698 cm^{-1}.

Crystal data

$C_{11}H_8O_3$
M_r = 188.17
Orthorhombic, *Pbcn*
a = 14.9634 (2) Å
b = 7.18210 (10) Å
c = 15.9359 (2) Å
V = 1712.61 (4) Å^3
Z = 8
Cu *Kα* radiation
μ = 0.89 mm^{-1}
T = 100 (2) K
0.26 × 0.26 × 0.16 mm

Data collection

Bruker SMART CCD APEXII area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
T_{min} = 0.802, T_{max} = 0.871
9720 measured reflections
1548 independent reflections
1473 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.091
S = 1.08
1548 reflections
131 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.26 e Å^{-3}
$\Delta\rho_{min}$ = −0.16 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O2—C9	1.2089 (15)	O3—C9	1.3333 (14)
O2—C9—C8	123.94 (11)	O3—C9—C8	112.56 (10)

Table 2
Hydrogen-bond and close-contact geometry (Å, °).

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O3—H3*C*$\cdots$O1^{i}	0.91 (2)	1.78 (2)	2.6952 (12)	177.7 (16)
C4—H4*A*$\cdots$O2^{ii}	0.95	2.56	3.2584 (15)	131
C5—H5*A*$\cdots$O1^{iii}	0.95	2.50	3.4531 (15)	180

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

All H atoms were found in electron-density difference maps. The O—H hydrogen was allowed to refine positionally, with $U_{iso}(H) = 1.5U_{eq}(O)$. The methylene, vinyl, and phenyl H atoms were placed in geometrically idealized positions and constrained to ride on their parent C atoms, with C—H distances of 0.99 Å for the methylene and 0.95 Å for both the vinyl and phenyl H atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2004); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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