Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

1-Oxoindan-6-carboxylic acid: catemeric hydrogen bonding in an aromatic δ-keto acid

Roger A. Lalancette, Elizabeth M. Kikolski and Hugh W. Thompson*

Carl A. Olson Memorial Laboratories,
Department of Chemistry, Rutgers University,
Newark, NJ 07102, USA

Correspondence e-mail:
rogerlal@andromeda.rutgers.edu

Received 11 May 2006
Accepted 15 May 2006

The title compound, $C_{10}H_8O_3$, aggregates in the crystal structure as catemers, whose hydrogen bonding progresses from the carboxyl to the ketone of a neighboring screw-related molecule along the *b* axis [O···O = 2.6481 (12) Å and O—H···O = 169°]. Four hydrogen-bonding chains in centrosymmetric pairs pass through the cell in the *b*-axis direction. Two intermolecular C—H···O═C close contacts are found, involving both the ketone and acid functions.

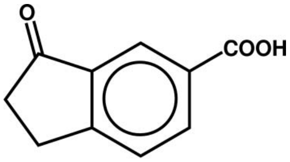
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.002 Å
R factor = 0.032
wR factor = 0.094
Data-to-parameter ratio = 10.6

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

Comment

Of the five hydrogen-bonding modes known for simple keto-carboxylic acids, acid dimerization is found to be disfavored by low molecular flexibility. This effect appears to involve a reduced repertoire of low-energy centrosymmetric conformations for the dimer. A simple measure of flexibility for small molecules is the number of full bond rotations possible; in this accounting we omit bonds to carboxyl, which is invariably present, and to methyl, whose rotation gives conformations trivially different for packing purposes. The 1-indanone system has an observed tendency to produce catemers in the solid state (Brunskill *et al.*, 1997; Lalancette *et al.*, 1997, 1999; Thompson *et al.*, 1998). We present here the crystal structure of an indanone, (I), that has the lowest possible degree of molecular flexibility and is found to associate catemerically.



(I)

Fig. 1 shows the molecular structure of (I) which is skeletally rigid and planar; the C atoms have an r.m.s. deviation of 0.012 (9) Å from their mean plane. Despite the strain, the eclipsing of H atoms at C2 and C3 is essentially perfect; the two calculated H—C2—C3—H torsion eclipsing angles are 1.3 and 2.1°. The only available rotation, about C6—C8, generates a dihedral angle between the carboxyl and the mean C-atom plane of 13.48 (2)°. Although (I) is inherently achiral, this produces a chiral conformation. As (I) is not dimeric, averaging of C—O bond lengths and C—C—O angles by disorder is precluded, and the values here (Table 1) resemble ones typical for highly ordered carboxyls (Borthwick, 1980).

Fig. 2 shows the packing arrangement for (I). Carboxyl-to-ketone catemers are formed by hydrogen bonds that progress *via* screw-related molecules. Centrosymmetrically related

doi:10.1107/S1600536806018022

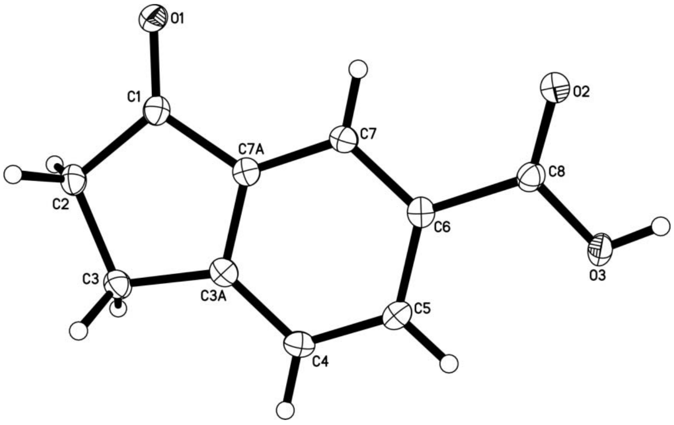


Figure 1
The molecular structure of (I), with the numbering scheme. Displacement ellipsoids are drawn at the 40% probability level.

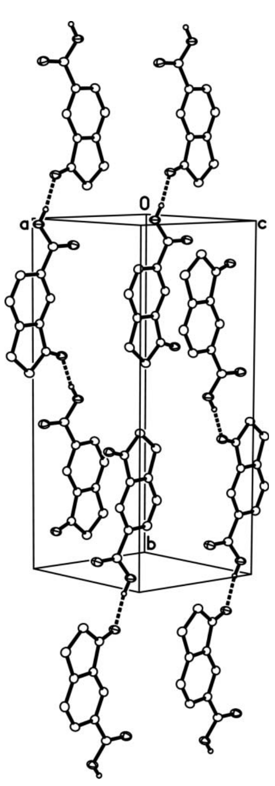


Figure 2
A partial packing diagram for (I), showing the hydrogen-bonded (dashed lines) chains. For clarity, all carbon-bound H atoms have been omitted. Displacement ellipsoids are drawn at the 50% probability level.

pairs of chains proceed counterdirectionally along axes parallel to the *b* axis. Within the 2.7 Å range we surveyed (Steiner, 1997), two intermolecular C—H···O close contacts were found, involving both carbonyl groups present (Table 2). Some degree of π-stacking is present in the packing, in which each aromatic ring is approximately half-overlapped with ones *ca* 3.5 Å distant in the two adjacent layers.

We characterize the geometry of hydrogen bonding to carbonyls with a combination of H···O═C angle and H···O═C—C torsion angle. These describe the approach of the acid H atom to the receptor O atom in terms of its deviation from, respectively, C═O axiality (ideal = 120°) and planarity with the carbonyl (ideal = 0°). In (I), these two angles are 132.4 and −3.2°.

Experimental

Compound (I) was purchased from Sigma–Aldrich Inc., St Louis, Missouri, USA. Material of X-ray quality (mp 533 K) was obtained by recrystallization from methanol. The solid-state (KBr) IR spectrum of (I) has C═O peaks at 1726 and 1676 cm^{-1}. This separation conforms to the shifts seen typically in catemers, due to removal of hydrogen bonding from carboxyl C═O and its addition to the ketone. In CHCl$_3$ solution, where dimers predominate, these coalesce to a single broad absorption centered at 1715 cm^{-1}.

Crystal data

$C_{10}H_8O_3$
$M_r = 176.16$
Monoclinic, $P2_1/c$
$a = 6.6457\ (1)$ Å
$b = 17.4657\ (3)$ Å
$c = 7.0105\ (1)$ Å
$\beta = 105.068\ (1)^\circ$
$V = 785.74\ (2)$ Å^3
$Z = 4$
$D_x = 1.489$ Mg m^{-3}
Cu $K\alpha$ radiation
$\mu = 0.93$ mm^{-1}
$T = 100\ (2)$ K
Block, colorless
0.25 × 0.22 × 0.15 mm

Data collection

Bruker SMART CCD APEX-II area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{\min} = 0.799$, $T_{\max} = 0.874$
4303 measured reflections
1273 independent reflections
1241 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.012$
$\theta_{\max} = 64.8^\circ$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.094$
$S = 1.07$
1273 reflections
120 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.2662P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.23$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0022 (6)

Table 1
Selected geometric parameters (Å, °).

O3—C8	1.3290 (15)	O2—C8	1.2103 (16)
O2—C8—C6	123.21 (11)	O3—C8—C6	113.02 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1$^{\rm i}$	0.84	1.82	2.6481 (12)	169
C3—H3B···O1$^{\rm ii}$	0.99	2.50	3.4009 (16)	152
C3—H3A···O2$^{\rm iii}$	0.99	2.46	3.3603 (15)	152

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

All H atoms for (I) were found in electron-density difference maps but were placed in calculated positions and refined as riding on their respective C or O atoms. The O—H distance was fixed at 0.84 Å; for methyl, methylene and methine H atoms, C—H distances were fixed at 0.98, 0.99 and 1.00 Å, respectively, with $U_{\rm iso}(\rm H) = 1.2U_{\rm eq}(\rm C)$ or $1.5U_{\rm eq}(\rm O)$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Borthwick, P. W. (1980). *Acta Cryst.* B**36**, 628–632.

Bruker (2000). *SHELXTL* (Version 6.10), *SMART* WNT/2000 (Version 5.622) and *SAINT-Plus* (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.

Brunskill, A. P. J., Thompson, H. W. & Lalancette, R. A. (1997). *Acta Cryst.* C**53**, 599–601.

Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1997). *Acta Cryst.* C**53**, 1838–1842.

Lalancette, R. A., Brunskill, A. P. J. & Thompson, H. W. (1999). *Acta Cryst.* C**55**, 568–572.

Sheldrick, G. M. (1997). *SHELXL97*. Release 97-2. University of Göttingen, Germany.

Steiner, T. (1997). *Chem. Commun.* pp. 727–734.

Thompson, H. W., Brunskill, A. P. J. & Lalancette, R. A. (1998). *Acta Cryst.* C**54**, 829–831.