Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2-Hydroxycyclohexene-1-carboxylic acid: the enol isomer of 2-oxocyclohexane-1-carboxylic acid

A. Jerry Kresge, Alan J. Lough* and Yu Zhu

Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6

Correspondence e-mail:
alough@chem.utoronto.ca

Received 10 February 2003
Accepted 13 February 2003
Online 21 February 2003

There are four independent molecules in the asymmetric unit of the title compound, $C_7H_{10}O_3$, and two of the molecules are disordered. Molecules form two independent O—H$\cdots$O hydrogen-bonded dimers, through the carboxyl groups, with O$\cdots$O distances of 2.669 (3), 2.661 (3), 2.653 (3) and 2.654 (3) Å. Each hydrogen-bonded dimer contains a disordered molecule.

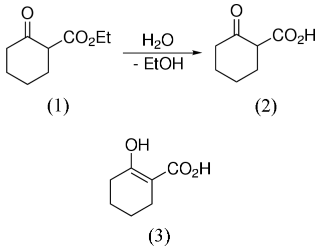
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.005 Å
Disorder in main residue
R factor = 0.046
wR factor = 0.118
Data-to-parameter ratio = 8.1

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

Comment

A traditional method of preparing β-oxocarboxylic acids is hydrolysis of the corresponding carboxylic acid esters, and application of this reaction to ethyl 2-oxocyclohexane-1-carboxylate, (1), has produced a colourless solid (m.p. 353 K) commonly believed to be 2-oxocyclohexane-1-carboxylic acid, (2) (see, for example, Dieckmann, 1901; Corey, 1953). However, in the course of our study of the 2-oxocyclohexane-1-carboxylic acid keto–enol system (Chang *et al.*, 2003), we began to suspect that this solid substance might be the enol isomer of 2-oxocyclohexane-1-carboxylic acid, (3), and not the oxoacid itself. We therefore carried out the present X-ray diffraction analysis, which shows that the solid (m.p. 353 K) is, in fact, the enol isomer.



(1)

(2)

(3)

In the asymmetric unit of (3), there are four independent molecules (A, B, C and D). The bond lengths and angles in each molecule are the same, within experimental error. In two of the molecules, namely C and D, ring atoms C4 and C5 are disordered over two sites. The two disorder positions for C4 and C5 in each molecule correspond to an up/down or down/up arrangement of the out-of-plane atoms in the half-chair conformation of the six-membered ring. The independent molecules form two O—H$\cdots$O hydrogen-bonded dimers (see Figs. 1 and 2), each of which contains a disordered molecule (see Table 1 for hydrogen-bonding distances). Each hydrogen-bonded pair shows the characteristic $R_2^2(8)$ (Bernstein *et al.*, 1995) carboxyl dimer motif. Furthermore, in molecules A–D, there is an $S(6)$ O—H$\cdots$O intramolecular hydrogen bond formed *via* the hydroxyl group and the carbonyl group. In order to facilitate both intermolecular and intramolecular hydrogen bonding, all of the O atoms are required to be

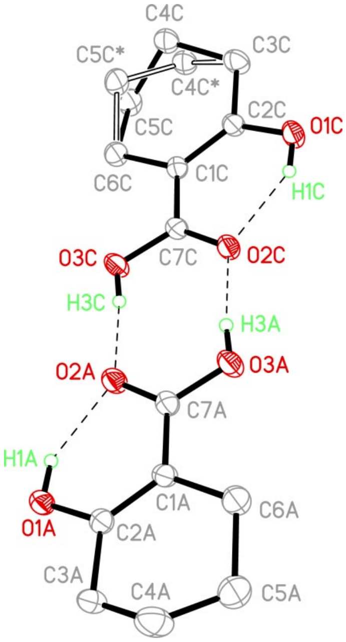


Figure 1
View of the hydrogen-bonded dimer involving molecules *A* and *C*, with hydrogen bonds shown as dashed lines. The open bonds indicate the minor component of the disorder. Ellipsoids are at the 30% probability level.

almost planar. In fact, the O atoms and the other atoms in a unique hydrogen-bonded dimer (except for C4 and C5) form a least-squares plane with maximum deviations of 0.108 (3) Å for O2*C* (in the *A*···*C* dimer) and 0.110 (3) Å for C3*D* (in the *B*···*D* dimer).

In the cyclohexene ring, an analysis (Cremer & Pople, 1975) of the puckering in the ring (C1–C6) gives Q_T = 0.451 (3), 0.461 (3), 0.509 (3) [0.503 (14) Å] and 0.526 (3) Å [0.529 (10) Å] for molecules *A*, *B*, *C* and *D*, respectively (the values in square brackets are for the ring conformations which contain the minor component of disorder). In all molecules, the conformational analysis of that ring (Duax *et al.*, 1976) shows that the conformation is a half-chair, with a local pseudo-twofold axis running through the mid-points of the C1—C2 and C4—C5 bonds.

Experimental

Saponification of ethyl 2-oxocyclohexane-1-carboxylate (Aldrich), according to a reported procedure (Sato *et al.*, 1983), produced a colourless solid (m.p. 355–356 K). Crystals suitable for X-ray analysis were obtained by keeping a dilute ethyl ether–hexanes solution of this solid in a refrigerator until crystals appeared; these were then collected, washed with pentane, and dried.

Crystal data

$C_7H_{10}O_3$
M_r = 142.15
Monoclinic, *Cc*
a = 11.1360 (4) Å
b = 11.1049 (3) Å
c = 22.8774 (9) Å
β = 91.9072 (12)°
V = 2827.55 (17) Å^3
Z = 16

D_x = 1.336 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 2659 reflections
θ = 2.6–27.5°
μ = 0.10 mm^{-1}
T = 150 (1) K
Block, colourless
0.40 × 0.35 × 0.30 mm

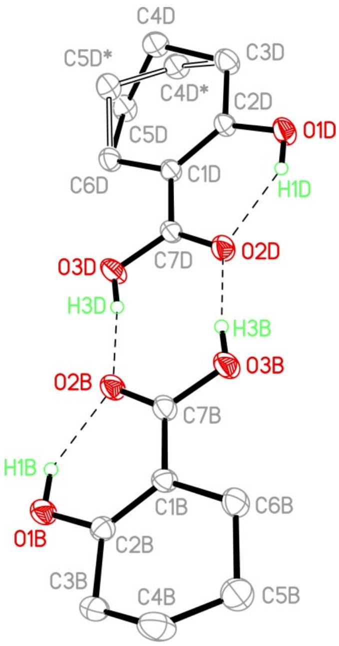


Figure 2
View of the hydrogen-bonded dimer involving molecules *B* and *D*, with hydrogen bonds shown as dashed lines. The open bonds indicate the minor component of the disorder. Ellipsoids are at the 30% probability level.

Data collection

Nonius KappaCCD diffractometer
φ scans and *ω* scans with *κ* offsets
Absorption correction: none
8426 measured reflections
3220 independent reflections
2554 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.039
$\theta_{\rm max}$ = 27.5°
$h = -14 \rightarrow 14$
$k = -14 \rightarrow 14$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.118
S = 1.03
3220 reflections
400 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.052P)^2 + 1.6672P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.41 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0047 (12)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···O2*A*	0.84	1.84	2.570 (3)	145
O3*A*—H3*A*···O2*C*	0.84	1.83	2.669 (3)	173
O1*B*—H1*B*···O2*B*	0.84	1.84	2.576 (3)	145
O3*B*—H3*B*···O2*D*	0.84	1.83	2.661 (3)	173
O1*C*—H1*C*···O2*C*	0.84	1.85	2.582 (3)	145
O3*C*—H3*C*···O2*A*	0.84	1.82	2.653 (3)	174
O1*D*—H1*D*···O2*D*	0.84	1.86	2.591 (3)	145
O3*D*—H3*D*···O2*B*	0.84	1.82	2.654 (3)	173

In the final refinement cycles, geometric restraints were applied to the bonds lengths (but not angles) of the disordered regions of molecules *C* and *D*. The final ratios for the occupancies of the disordered atoms (C4 and C5) are 0.762 (7):0.238 (7) and 0.661 (6):0.339 (6) for molecules *C* and *D*, respectively. In order to restrain the major and minor components of the disorder to refine to similar geometry, the SADI command in *SHELXTL/PC* (Sheldrick, 2001) was used. Dummy disordered atoms were included on the same sites as C3 and C6 (using EXYZ in *SHELXTL/PC*) to allow for the disorder of the H atoms bonded to C3 and C6. All H atoms were included in calculated positions, with C—H and O—H distances of 0.99 and 0.84 Å, respectively. They were then included in the refinement in riding-motion approximation, with $U_{\rm iso} = 1.2U_{\rm eq}$ of the carrier atom ($U_{\rm iso} = 1.5U_{\rm eq}$ for hydroxyl). Due to the lack of anomalous scatterers, the enantiomer was not determined from the X-ray diffraction data and Friedel pairs were merged. The absolute configuration of the molecule is not known.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The authors acknowledge NSERC Canada and the University of Toronto for funding.

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Chang, J. A., Kresge, A. J., Nikolaev, V. A. & Popik, V. V. (2003). *J. Am. Chem. Soc.* Submitted.

Corey, E. J. (1953). *J. Am. Chem. Soc.* **75**, 3297–3299.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Dieckmann, W. (1901). *Justus Liebigs Ann. Chem.* **317**, 27–109.

Duax, W. L., Weeks, C. M. & Roher, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by E. L. Eliel and N. Allinger, pp. 271–383. New York: John Wiley.

Nonius (1997–2002). *COLLECT*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.

Sato, M., Ogasawara, H., Oi, K. & Kato, T. (1983). *Chem. Pharm. Bull.* **31**, 1896–1901.

Sheldrick, G. M. (2001). *SHELXTL/PC*. Version 6.12 for Windows NT. Bruker AXS Inc., Madison, Wisconsin, USA.