Refinement

Table 1. *Puckering parameters (Å, °) (Cremer & Pople,*
1975)

	Ring B			Ring C		
	Q	φ	θ	Q	φ	θ
Molecule A	0.521	27.5	128.2	0.563	2.2	18.8
Molecule B	0.533	29.9	129.3	0.567	3.7	24.4
	Ring D			Ring E		
Molecule A	0.631	–	359.0	0.548	–	179.8
Molecule B	0.622	–	0.7	0.542	–	181.3

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3-Oxo-1-cyclohexene-1-carboxylic Acid: Catemeric Hydrogen Bonding and Flexional Ring Disorder in a γ-Keto Acid

ALAN BARCON, ANDREW P. J. BRUNSKILL, ROGER A. LALANCETTE* AND HUGH W. THOMPSON

Carl A. Olson Memorial Laboratories, Department of Chemistry, Rutgers University, Newark, NJ 07102, USA. E-mail: lalancette@hades.rutgers.edu

Abstract

The crystal structure of 3-oxo-1-cyclohexene-1-carboxylic acid, $C_7H_8O_3$, involves hydrogen-bonding catemers of an unusual type. Hydrogen bonds progress from the carboxyl H atom of one molecule to the ketone O atom of a glide-related molecule [O···O 2.703 (2) Å], resulting in heterochiral chains. Parallel counterdirectional pairs of hydrogen-bonding chains proceed through the chosen cell. There are mutual close contacts of 2.65 Å between the ketone O and vinyl H atoms of centrosymmetrically related chains. Two of the tetrahedral C atoms of the molecule are flexionally disordered, and three of their associated H atoms show attractive intermolecular close contacts to O atoms.

Comment

Keto carboxylic acids offer options for varying the standard pattern of dimeric hydrogen bonding that dominates functionally unadorned acids. Usually the ketone fails to participate, resulting in typical carboxyl dimers, but less commonly intermolecular carboxyl-to-ketone hydrogen bonds occur, yielding a catemer. A third, rare arrangement has an internal hydrogen bond, two instances are known of acid-to-ketone dimerization and one of carboxyl catemerization (see below). Several cases also exist of hydrates with more complex hydrogen-bonding patterns. We have referenced and discussed numerous examples of these hydrogen-bonding modes (Thompson *et al.*, 1992; Coté *et al.*, 1996). Part of our continuing interest in this hydrogen-bonding behavior lies in the discovery of new hydrogen-bonding patterns. We have recently reported an instance of carboxyl catemerization not previously observed in keto acids (Lalancette *et al.*, 1998), and we now report a hydrogen-bonding pattern of a heretofore rarely observed type.

The title compound, (I), belongs to the category of γ-keto acids, one especially rich in hydrogen-bonding types, embracing dimers, internal hydrogen bonds, and carboxyl-to-ketone catemers. We further categorize such catemers as either homo- or heterochiral to denote the

handedness of the intrachain units. With three exceptions (Watson et al., 1990; Dobrzynska & Turowska-Tyrk, 1997; Thompson et al., 1998), previously reported keto-acid catemers have been of either the screw-related or translational type, and hence homochiral. We report here a rare instance of a heterochiral carboxyl-to-ketone catemer, involving hydrogen bonding between molecules of alternating handedness, which are generated in this space group, $P2_1/n$, from a glide relationship.

(I)
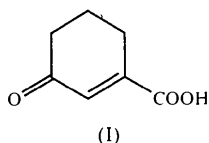
The asymmetric unit for (I) with the atomic numbering is shown in Fig. 1. The rotation of the carboxyl group from coplanarity with the enone system [torsion angle C2—C1—C7—O2 −165.8 (2)°] alone defines the conformational enantiomerism (handedness) of a particular molecule. 'Handedness' of a specific molecule is defined by conformation since this molecule has no chiral center. The ring system displays flexional disordering of both C4 and C5, and thus cannot be considered as defining the 'handedness' of a molecule.
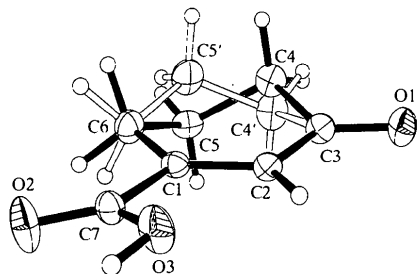
Semi-empirical molecular (AM1) modeling (Wavefunction, 1995; Dewar et al., 1985) finds negligible energy differences between the two flexional forms, with an activation energy in the order of 1.0 kcal mol^{-1} (1 kcal mol^{-1} = 4.184 kJ mol^{-1}). This value is significantly lower than the known liquid-state activation barriers of 5.3–5.4 kcal mol^{-1} for cyclohexene (Anet & Haq, 1965; Jensen & Bushweller, 1969) and 4.0 kcal mol^{-1} for cyclohexanone (Anet et al., 1973). Energy barriers of 1–2 kcal mol^{-1} have been found experimentally for tautomeric hydrogen exchange, which was also shown by solid-state NMR and IR to be dynamic (Meier et al., 1982; Nagaoka et al., 1983). Facey et al. (1996) have recently reported flexional disorder similar to that in (I) in the X-ray structures of two tetrahydronaphthalenes and have demonstrated by means of solid-state NMR that the disorder is dynamic, with an activation barrier of 2.9 kcal mol^{-1} estimated for one of them. These cases render it likely that the disorder observed in (I) is dynamic as well.

Averaging of C—O bond lengths and C—C—O angles by disorder, although common in carboxyl dimers (Leiserowitz, 1976), is not observed in catemers, whose geometry cannot support the mechanisms underlying the averaging processes involved. In (I), these C—O bond

Fig. 1. The asymmetric unit of (I), with its atom numbering. The flexional disordering of the ring is illustrated by the inclusion of C4′ and C5′, and their ghost bonds. Ellipsoids are set at the 20% probability level.

This disorder was observed originally as high anisotropy and additional electron density for C4 and C5; we have modeled this disorder, as shown in Fig. 1 (and described fully in the refinement details), by the inclusion of C4′ and C5′ and their attached H atoms (all shown by ghost bonds). In the model, the C5/C5′ pair has greater separation than does C4/C4′ [0.782 (6) versus 0.538 (12) Å], but neither pair is positioned equidistant from the C3—C2—C1—C6 plane; the torsion angles involved are: C4—C3—C2—C1 9.0 (4), C4′—C3—C2—C1 −14.0 (5)° and C5—C6—C1—C2 20.1 (3), C5′—C6—C1—C2 −12.7 (2)°. The alternative positions for C4 require a twist about C2—C3, which implies an accompanying wagging of the C3—O1 bond. This whould appear as unusual anisotropy in the ketone (O1), but it is not observed.

Fig. 2. A partial packing diagram for (I), with extracellular molecules, illustrating one counterdirectional pair of parallel hydrogen-bonding chains, centrosymmetrically related around $\frac{1}{2},\frac{1}{2},\frac{1}{2}$, and composed of units of alternating chirality. Molecules are shown with their disorder modeled as in Fig. 1 and displacement ellipsoids are set at the 20% probability level. All non-carboxyl H atoms have been omitted for clarity.

lengths are 1.191 (2) and 1.312 (2) Å, with angles of 122.3 (2) and 113.6 (2)°. Our survey of 28 catemeric keto-acid structures gives average values of 1.20 (1) and 1.32 (1) Å, and 124.5 (10) and 112.8 (14)° for these lengths and angles, in accord with typical values of 1.21 and 1.31 Å, and 123 and 112°, cited for highly ordered dimeric carboxyls (Borthwick, 1980).

The packing arrangement is shown in Fig. 2. Almost all previously observed carboxyl-to-ketone catemers involve intrachain units of a single handedness. In (I), the hydrogen bonding [O···O 2.703 (2) Å] progresses between molecules with a glide relationship, so that chain members are of alternating chirality. The resulting parallel centrosymmetrically related hydrogen-bonding chains proceed in counterdirectional pairs through the chosen cell. They follow no crystallographic cell axis, but advance simultaneously by one cell each in the **a** and **c** directions for each iteration of the two-molecule repeat sequence. The dihedral angles between the carboxyl group (C1, C7, O2, O3) and the ketone plane of each of the conformers of the adjacent hydrogen-bonded molecule (O1, C3, C2, C4 and O1, C3, C2, C4′) are 94.6 (2) and 82.1 (2)°, respectively.

A 2.65 Å reciprocal ketone-O···H—C close contact is found between O1 and the vinyl H2A atom in molecules centrosymmetrically related across the *ac* face. Additional close contacts are found between H atoms attached to the flexionally disordered C atoms; C4—H4B···O3 (2.68 Å), C5—H5B···O2 (2.62 Å) and C5′—H5B′···O1 (2.45 Å). These contacts probably represent polar attractions contributing materially to the packing forces (Jönsson, 1972; Leiserowitz, 1976; Berkovitch-Yellin & Leiserowitz, 1982). The fact that the flexional conformations have different close contacts has consequences in the solid-state vibrational spectrum.

The solid-state (KBr) IR spectrum of (I) has a complex of three peaks of comparable intensity (1657, 1649 and 1642 cm⁻¹) for the ketone C=O and a double peak (1720 and 1714 cm⁻¹) for the carboxyl C=O. These bands conform generally in position to the shifts typically seen in catemers, due to addition of hydrogen bonding to the ketone and removal of hydrogen bonding from carboxyl C=O (Coté *et al.*, 1997), but display multiplicity due to the several C=O environments present as a result of the flexional disorder (Lalancette *et al.*, 1997). In CHCl₃ solution, all the C=O absorptions coalesce to a single broader peak centered at 1688 cm⁻¹, with shoulders at 1682 and *ca* 1705 cm⁻¹, consistent with a carboxyl which is predominantly rotated out of the plane of conjugation and dimerically hydrogen bonded.

Experimental

Compound (I) was synthesized from 1,3-cyclohexanedione by the sequence described by Agosta & Lowrance (1970). Crystals of (I) (m.p. 398 K) were obtained from water.

Crystal data

$C_7H_8O_3$	Mo $K\alpha$ radiation
$M_r = 140.13$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 27
$P2_1/n$	reflections
$a = 9.703\,(1)$ Å	$\theta = 6.11–17.94°$
$b = 5.582\,(1)$ Å	$\mu = 0.107$ mm⁻¹
$c = 12.765\,(1)$ Å	$T = 295\,(2)$ K
$\beta = 97.90\,(1)°$	Parallelepiped
$V = 684.8\,(2)$ Å³	$0.56 \times 0.48 \times 0.24$ mm
$Z = 4$	Colorless
$D_x = 1.359$ Mg m⁻³	
$D_m = 1.36\,(1)$ Mg m⁻³	
D_m measured by flotation in cyclohexane/CCl₄	

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.038$
$2\theta/\theta$ scans	$\theta_{max} = 27.49°$
Absorption correction:	$h = -1 \rightarrow 12$
face-indexed numerical	$k = -7 \rightarrow 1$
(Sheldrick, 1994)	$l = -16 \rightarrow 16$
$T_{min} = 0.954$, $T_{max} = 0.976$	3 standard reflections
2221 measured reflections	every 97 reflections
1575 independent reflections	intensity decay: 0.30%
1028 reflections with $F > 4\sigma(F)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$\Delta\rho_{max} = 0.21$ e Å⁻³
$wR(F^2) = 0.137$	$\Delta\rho_{min} = -0.12$ e Å⁻³
$S = 1.06$	Extinction correction: none
1574 reflections	Scattering factors from
112 parameters	*International Tables for*
H atoms: see below	*Crystallography* (Vol. C)
$w = 1/[\sigma^2(F_o^2) + (0.0521P)^2 + 0.1539P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1. *Selected geometric parameters (Å, °)*

O1—C3	1.225 (2)	C4—C5	1.535 (14)
O2—C7	1.191 (2)	C4′—C5′	1.483 (15)
O3—C7	1.312 (2)	C5—C6	1.515 (6)
C3—C4	1.485 (13)	C5′—C6	1.499 (6)
C3—C4′	1.523 (12)		
O2—C7—C1	122.3 (2)	C3—C4′—C5′	110.2 (6)
O3—C7—C1	113.6 (2)	C4—C5—C6	109.0 (4)
C2—C3—C4	116.2 (5)	C4′—C5′—C6	116.6 (5)
C2—C3—C4′	117.2 (5)	C1—C6—C5′	113.48 (10)
C3—C4—C5	110.9 (7)	C1—C6—C5	112.2 (2)
C1—C2—C3—C4	9.0 (4)	C2—C1—C6—C5′	-12.7 (2)
C1—C2—C3—C4′	-14.0 (5)	C2—C1—C6—C5	20.1 (3)
C3—C4—C5—C6	59.1 (6)	C4′—C5′—C6—C1	38.1 (4)
C3—C4′—C5′—C6	-49.3 (7)	C4—C5—C6—C1	-48.9 (5)

Table 2. *Hydrogen-bonding and close-contact geometries (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3···O1ⁱ	0.85 (3)	1.86 (3)	2.703 (2)	169 (2)
C2—H2A···O1ⁱⁱ	0.93	2.65	3.569 (2)	169
C4—H4B···O3ⁱⁱⁱ	0.97	2.68	3.362 (10)	128

C5—H5B···O2^{iv}	0.97	2.62	3.585 (6)	173
C5'—H5B'···O1^{v}	0.97	2.45	3.368 (7)	157

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

The initial solution of the structure located C4 and C5 in positions approximately coplanar with the other C atoms and at a distance from each other much shorter than for a known C—C single bond. Initial cycles of refinement showed areas of high residual electron density above and below both C4 and C5, and subsequent anisotropic refinement of these C atoms caused them to show extremely large and prolated displacement ellipsoids. Atoms C4 and C5 were then refined isotropically with their displacement parameters held at 0.05 Å^2. The positions of maximum residual electron density above and below C4 and C5 were then chosen as the sites for the disordered C atoms. Occupancies for C4, C4', C5 and C5' were each initially set to 50%. Subsequent isotropic and anisotropic refinement continued smoothly. Occupancies for C4, C4', C5 and C5' were then allowed to refine but remained at 50% within error and so were again fixed at 50%. Several non-carboxyl H atoms were found in electron-density difference maps, but were replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms. Disordered H atoms were added in calculated positions to C4, C4', C5 and C5', and also to C6, with occupancies set at 50%. The displacement parameters for these methylene H atoms were refined as two groups relating to the flexional disorder. The carboxyl H3 atom was found in an electron-density difference map and was allowed to refine both positionally and isotropically.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS* (Siemens, 1996). Data reduction: *XSCANS* (Siemens, 1996). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1448). Services for accessing these data are described at the back of the journal.

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10,16-Dioxatetracyclo[7.6.1.0^{1,11}.0^{4,9}]hexadecan-11-ol

Masood Parvez,[a] Naheed Sultana,[b] Tahira B. Sarfaraz[b] and Shaheen A. Husain[b]

[a]*Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4, and [b]Pharmaceutical and Fine Chemicals Research Centre, PCSIR Laboratories Complex, Karachi 75280, Pakistan. E-mail: parvez@acs.ucalgary.ca*

Abstract

The crystal structure of the title compound, $C_{14}H_{22}O_3$, consists of independent molecules in each of which three six-membered rings and a five-membered ring are fused together. All the six-membered rings display chair conformations, while the five-membered ring has an envelope conformation. The molecular dimensions are normal with mean bond distances C_{sp^3}—C_{sp^3} 1.523 (10) and C_{sp^3}—O 1.44 (2) Å. Pairs of molecules lying about inversion centers are linked by O—H···O hydrogen bonds [O···O 2.806 (3) Å].