

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.064$
 $wR(F^2) = 0.161$
 $S = 0.972$
 3987 reflections
 525 parameters
 H atoms not refined
 $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.014$
 $\Delta\rho_{\max} = 0.417 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.285 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from
*International Tables for
 Crystallography* (Vol. C)
 Absolute structure: assigned
 from the estrone precursor

Acta Cryst. (1998). **C54**, 1282–1285

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

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(Received 30 January 1998; accepted 30 March 1998)

Table 1. Puckering parameters (Å , $^\circ$) (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		
	Q	φ	θ	Q	φ	θ
Molecule A	0.631	–	359.0	0.548	–	179.8
Molecule B	0.622	–	0.7	0.542	–	181.3

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989).
 Cell refinement: *CAD-4 Software*. Data reduction: *CAD-4
 Software*. Program(s) used to solve structure: *SHELXS86*
 (Sheldrick, 1990). Program(s) used to refine structure:
SHELXL93 (Sheldrick, 1993). Molecular graphics: *ZORTEP*
 (Zsolnai & Pritzkow, 1994). Software used to prepare material
 for publication: *SHELXL93*.

Our thanks are extended to Professor M. R. Caira for
 the preliminary photography and to Drs L. R. Barbour
 and S. A. Bourne for their assistance in solving the
 structure and preparing the CIF file. We would also
 like to acknowledge financial and material support from
 the FRD (Pretoria, South Africa), Schering AG (Berlin,
 Germany) and the University of Cape Town, South
 Africa.

Supplementary data for this paper are available from the IUCr
 electronic archives (Reference: SX1056). Services for accessing these
 data are described at the back of the journal.

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Abstract

The crystal structure of 3-oxo-1-cyclohexene-1-carboxylic acid, C₇H₈O₃, 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