Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

(±)-12-Oxotricyclo[6.2.2.$0^{1,6}$]dodecane-10-carboxylic acid: hydrogen bonding in a tricyclic δ-keto acid

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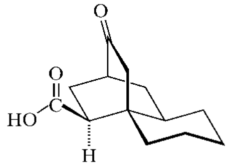
Received 13 February 2002
Accepted 17 April 2002
Online 11 May 2002

The ring system of the title compound, $C_{13}H_{18}O_3$, was synthesized by addition of ethyl acrylate to the dienamine of 2-octalone. The keto acid aggregates in the solid as acid-to-acid dimers [O···O = 2.663 (2) Å and O—H···O = 170 (3)°] whose centrosymmetric hydrogen bonds lie across the *a* edges and the center of the chosen cell. Three intermolecular C—H···O close contacts within 2.7 Å were found involving the ketone group.

Comment

Of the five hydrogen-bonding modes known for crystalline keto carboxylic acids, only three involve the ketone function; the remainder correspond to the common pairing and rare chain modes of simple acids (Leiserowitz, 1976). As part of our study of factors governing the choice of hydrogen-bonding mode, we have examined the structure of (±)-12-oxotricyclo[6.2.2.$0^{1,6}$]dodecane-10-carboxylic acid, (I), which belongs to the category of δ-keto acids, a category generally rich in hydrogen-bonding types.



(I)

Fig. 1 presents a view of the asymmetric unit of (I), which was synthesized by addition of ethyl acrylate to the dienamine of 2-octalone (see *Experimental*). Compound (I) is a 'Diels–Alder-type' product and the arrangement of reactants required for the observed stereochemistry does, indeed, appear to be the most favorable of all the candidate [4+2] electrocyclic processes. Moreover, a study by House *et al.* (1965) indicates that the cross-conjugated homoannular diene required for such a [4+2] addition is a significant component of the mixture of isomers present in this dienamine. However, we have no actual evidence as to whether the bridged portion of the molecule arises from such a [4+2] electrocyclic reaction or from a polar stepwise one. Compound (I) has not previously been reported, but several studies have been carried out on the addition of vinyl ketones to the dienamine involved in our synthesis and to closely analogous dienamines. These have concluded that both [4+2] electrocyclic and polar stepwise processes can operate, with the observed mix dependent on specific conditions of reactant, solvent, *etc.* (Hickmott & Simpson, 1992). Despite the alternative configurational options available at C6 and C10, compound (I) was the only crystalline material isolated from the reaction sequence involved, and whether the configurations in (I) are the result of kinetic or thermodynamic processes is unknown.

Simple bicyclo[2.2.2]octane systems are not entirely rigid, and the nominally parallel ethylene bridges are often significantly skewed, presumably to relieve eclipsing strain (Deutsch, 1972; Blackstock *et al.*, 1987; Zimmerman *et al.*, 1992). In (I), this bridged portion of the molecule displays a modest conformational twist, described by the torsion angles C1—C6—C7—C8 [−0.5 (2)°], C1—C10—C9—C8 [8.5 (2)°] and C1—C11—C12—C8 [4.2 (2)], which would all be 0° in the absence of any twist. The relatively small size of this twist is probably attributable in part to the lack of eclipsing strain in the ketone bridge and in part to restraint presented by the appended cyclohexane ring, which adopts the expected chair conformation. Full rotation is possible only about C10—C13, and the carboxyl group is rotated so that its carbonyl lies on the same face of the molecule as the ketone, with an O2—C13—C10—C9 torsion angle of −37.8 (2)°. The dihedral angle between the carboxyl and ketone planes is 58.58 (12)°.

Averaging of the C—O bond lengths and C—C—O angles by disorder is common in carboxylic acids, but is seen only in dimers (Leiserowitz, 1976), whose geometry can support the averaging mechanisms. In (I), these C—O bond lengths and C—C—O angles are 1.229 (2)/1.313 (2) Å and 123.5 (2)/114.1 (2)°, respectively; in comparison, typical values cited for highly ordered dimeric carboxyls are 1.21/1.31 Å and 123/112° (Borthwick, 1980). The observed lengths and angles, therefore, appear to represent only a slight degree of carboxyl disordering, and we were unable to find any electron density

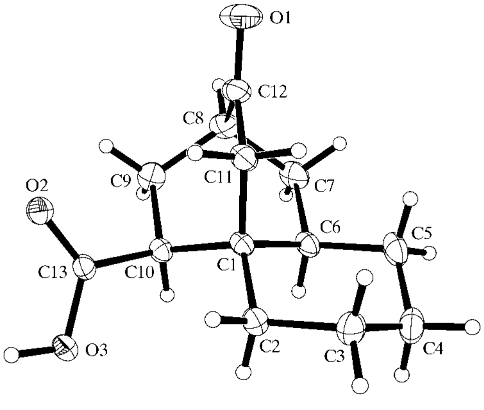


Figure 1
A view of the asymmetric unit of (I) with the atom-numbering scheme. Displacement ellipsoids are shown at the 20% probability level.

DOI: 10.1107/S0108270102006893 © 2002 International Union of Crystallography

representing the minority disorder species in electron-density difference maps.

The packing of the cell involves acid-to-acid dimers [O···O = 2.663 (2) Å and O—H···O = 170 (3)°], which pair centrosymmetrically across the *a* edges and the center of the chosen cell. Lying within the 2.7 Å range we usually employ for non-bonded C—H···O packing interactions (Steiner, 1997), were found three intermolecular close contacts to the ketone O atom: 2.61 Å to H7*A*, related through a center of symmetry on the *b* edge, and 2.70 Å to H9*A* and 2.68 Å to H10, both to a molecule screw-related in *c*. Using compiled data for a large number of such C—H···O contacts, Steiner & Desiraju (1998) have found significant statistical directionality even as far out as 3.0 Å, and conclude that these are legitimately viewed as 'weak hydrogen bonds', with a greater contribution to packing forces than simple van der Waals attractions.

The solid-state (KBr) IR spectrum of (I) has C═O stretching absorptions at 1722 and 1691 cm^{-1} for ketone and acid, respectively. In $CHCl_3$ solution, these bands coalesce to a single broad absorption at 1720 cm^{-1}, with a typical carboxyl-dilution shoulder at *ca* 1740 cm^{-1}.

Experimental

The pyrrolidine enamine of cyclohexanone was treated with methyl vinyl ketone to generate the expected mixture of octalone dienamines. The mixture was isolated and purified by distillation (Stork *et al.*, 1963), and then treated with ethyl acrylate as described by Szmuszkovicz (1963). The isolated alkylation product in that reference was an ester assigned a bicyclic structure; that assignment is now cast into doubt by our results. Here, the ester product was isolated by distillation and saponified to yield (I). Material suitable for X-ray analysis (m.p. 416 K) was obtained from diethyl ether.

Crystal data

$C_{13}H_{18}O_3$
$M_r = 222.27$
Monoclinic, $P2_1/c$
$a = 12.832$ (4) Å
$b = 7.961$ (3) Å
$c = 11.809$ (4) Å
$\beta = 99.79$ (2)°
$V = 1188.8$ (7) Å^3
$Z = 4$

$D_x = 1.242$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 27 reflections
$\theta = 3.0$–8.4°
$\mu = 0.09$ mm^{-1}
$T = 296$ (2) K
Hexagonal rod, colorless
0.38 × 0.28 × 0.24 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: numerical (Sheldrick, 1997)
$T_{min} = 0.96$, $T_{max} = 0.97$
2775 measured reflections
2083 independent reflections
1539 reflections with $I > 2\sigma(I)$

$R_{int} = 0.034$
$\theta_{max} = 25.0°$
$h = -15 \rightarrow 15$
$k = -9 \rightarrow 1$
$l = -1 \rightarrow 14$
3 standard reflections every 97 reflections intensity variation: <1%

Table 1
Selected geometric parameters (Å, °).

O2—C13	1.229 (2)	O3—C13	1.313 (2)
O2—C13—C10	123.50 (16)	O3—C13—C10	114.10 (16)

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.114$
$S = 1.04$
2083 reflections
150 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0429P)^2 + 0.3022P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.13$ e Å^{-3}
$\Delta\rho_{min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.026 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3···O2^{i}	0.92 (3)	1.75 (3)	2.663 (2)	170 (3)

Symmetry code: (i) $1 - x, -y, 2 - z$.

All H atoms were found in electron-density difference maps but were placed in calculated positions (0.98 Å for methine H atoms and 0.97 Å for methylene H atoms) and, except for the carboxyl H atom, were allowed to refine as riding models on their attached C atoms. The displacement parameters were fixed at 120% of those of their attached C atoms. The carboxyl H atom was allowed to refine fully.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1370). Services for accessing these data are described at the back of the journal.

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