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rac-(1*R*,1a*R*,4*S*,6a*S*)-Ethyl 4-carboxy-1,1a,2,3,4,5,6,6a-octahydrocyclopropa[*f*]-indene-1-carboxylate

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In the title compound, $C_{14}H_{18}O_4$, the central six-membered ring subtends interplanar angles of 3.5 (1), 78.4 (1) and 78.73 (4)°, respectively, with the five-membered ring, the cyclopropane ring and the ester side chain. The C—C bond distal to the carbonyl substituent is shortened compared to the other two bonds of the cyclopropane moiety. The carboxylic acid groups form inversion–symmetric dimers by hydrogen bonding.

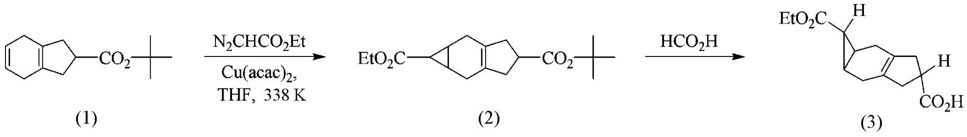
Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.003 Å
R factor = 0.045
wR factor = 0.108
Data-to-parameter ratio = 15.6

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

Comment

On cyclopropanation of *tert*-butyl 4,7-dihydro-2-indenecarboxylate, (1), with ethyl diazoacetate in the presence of a copper catalyst, a cycloadduct was obtained in 45% yield to which the structure (2) was assigned, *i.e.* the less substituted double bond of the substrate had been attacked (Zindel *et al.*, 1996). In our studies of novel core units for liquid crystalline materials (Hussain *et al.*, 2005), we were interested in these cycloadducts but needed exact stereochemical information with respect to the functional groups and the tricyclic carbon framework. We therefore hydrolysed (2) with formic acid and obtained the mono acid (3), the structure of which we report here.



The molecule of (3) is shown in Fig. 1. The relative configurations of the various asymmetric centres are established as given in the title. The central six-membered ring is almost planar (mean deviation 0.06 Å) but is slightly folded, by 12.9 (1)°, about the axis C2···C6; the five-membered ring is essentially planar (mean deviation 0.01 Å). The two larger

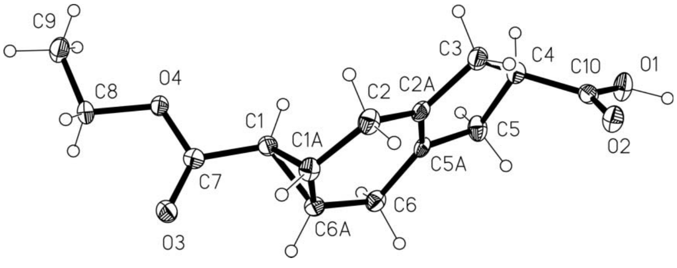


Figure 1
The molecule of compound (3) in the crystal. Displacement ellipsoids are drawn at the 50% probability level.

rings are approximately coplanar [interplanar angle = 3.5 (1)°], but the three- and six-membered rings subtend an interplanar angle of 78.4 (1)°. The six atoms of the ester side chain are coplanar (r.m.s. deviation = 0.018 Å) and this plane subtends an angle of 78.73 (4)° with the central ring.

Molecular dimensions may be regarded as normal. In the three-membered ring, the bond distal to the electron-withdrawing carbonyl substituent is shortened (Table 1), an effect discussed by Allen (1980).

The molecules are linked to form dimers across inversion centres by the standard pattern of hydrogen bonding in carboxylic acids. There is no evidence for disorder of the COOH group. Five further C—H···O interactions (Table 2) link the molecules into a three-dimensional packing pattern.

Experimental

The bis-ester (2) was prepared according to the literature procedure of Zindel *et al.* (1996). For the hydrolysis, compound (2) (0.31 g, 1.0 mmol) was stirred in formic acid (50 ml) at room temperature for 15 h. The solvent was removed and the crude product recrystallized from hexane to provide (3) (0.25 g, 98%). The usual spectroscopic and analytical data were recorded (Hussain, 2003).

Crystal data

$C_{14}H_{18}O_4$
$M_r = 250.28$
Monoclinic, $P2_1/c$
$a = 21.075$ (2) Å
$b = 7.4723$ (7) Å
$c = 8.2054$ (7) Å
$\beta = 97.524$ (2)°
$V = 1281.1$ (2) Å^3
$Z = 4$

$D_x = 1.298$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2297 reflections
$\theta = 2.9$–27.9°
$\mu = 0.09$ mm^{-1}
$T = 133$ (2) K
Lath, colourless
0.45 × 0.14 × 0.10 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: none
7734 measured reflections
2622 independent reflections

1437 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.064$
$\theta_{\rm max} = 26.4°$
$h = -26 \rightarrow 21$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.108$
$S = 0.78$
2622 reflections
168 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 0.0846P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.015$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—C6*A*	1.518 (3)	C10—O2	1.222 (2)
C1—C1*A*	1.526 (3)	C10—O1	1.317 (3)
C1*A*—C6*A*	1.496 (3)		
C6*A*—C1—C1*A*	58.85 (12)	C1*A*—C6*A*—C1	60.85 (13)
C6*A*—C1*A*—C1	60.30 (13)		
C3—C4—C10—O1	−161.26 (17)	C9—C8—O4—C7	179.50 (16)
C1—C7—O4—C8	−176.36 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H01···O2$^{\rm i}$	0.94 (3)	1.71 (3)	2.6540 (19)	177 (3)
C4—H4···O2$^{\rm ii}$	1.00	2.54	3.348 (3)	138
C8—H8*A*···O3$^{\rm iii}$	0.99	2.62	3.588 (3)	166
C8—H8*B*···O3$^{\rm iv}$	0.99	2.49	3.358 (2)	147
C9—H9*B*···O3$^{\rm v}$	0.98	2.63	3.545 (2)	155
C6*A*—H6*A*1···O4$^{\rm vi}$	1.00	2.56	3.417 (2)	144

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

The H atom of the COOH group was refined freely. The methyl H atoms were identified in a difference synthesis, idealized (C—H = 0.98 Å and H—C—H = 109.5°) and refined as a rigid group allowed to rotate but not tip. Other H atoms were included using a riding model, starting from calculated positions, with C—H = 0.99 (CH_2) or 1.00 Å (CH) and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C).

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

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