

8a-Ethyl 2-methyl (4a*R*,8a*S*)-3-oxoperhydro-2,8a-naphthalenedicarboxylate

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## Key indicators

Single-crystal X-ray study

$T = 293$  K

Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å

$R$  factor = 0.056

$wR$  factor = 0.112

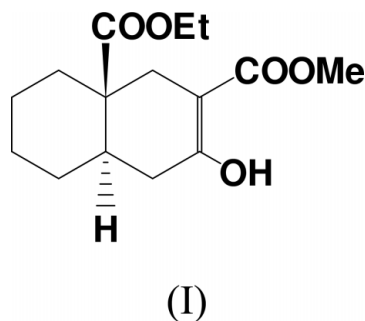
Data-to-parameter ratio = 19.2

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

In the title compound,  $\text{C}_{15}\text{H}_{22}\text{O}_5$ , the cyclohexane ring *A* adopts a screw-boat conformation and ring *B* adopts a chair conformation. The carboxylate groups are in a synclinal orientation with respect to each other.

## Comment

The title compound, (I), was prepared in connection with studies on the effect of remote functional groups on the stereoselectivity of cyclic  $\beta$ -keto-ester alkylations (Rao *et al.*, 1994). Spectroscopic data for the title compound indicate predominance of the enol form, which in solution is in equilibrium with the corresponding keto form. In order to elucidate the molecular conformation, the structure analysis was carried out.



The bond lengths and angles observed are comparable with those observed in related structures (Rajamathe *et al.*, 1999; Rao *et al.*, 1999). The C8—C13 bond distance [1.528 (2) Å] is longer than the normal  $\text{Csp}^3-\text{Csp}^2$  bond distance of 1.507 Å (Allen *et al.*, 1987). Ring *A* adopts a screw-boat conformation and ring *B* adopts a chair conformation. The substituents at the fusion adopt an axial orientation. The carboxylate group attached to the ring *A* is in an equatorial orientation and the C1—C10—C11—O2 torsion angle of 172.2 (2)° characterizes the antiperiplanar conformation of atoms C1 and O2. The carboxylate groups are in a synclinal orientation with respect to each other. The X-ray crystal structure shows a clear preference for the enol form. The stabilization of the enol form is due to intramolecular hydrogen bonding between a carbonyl-O and the H atom on the enol oxygen.

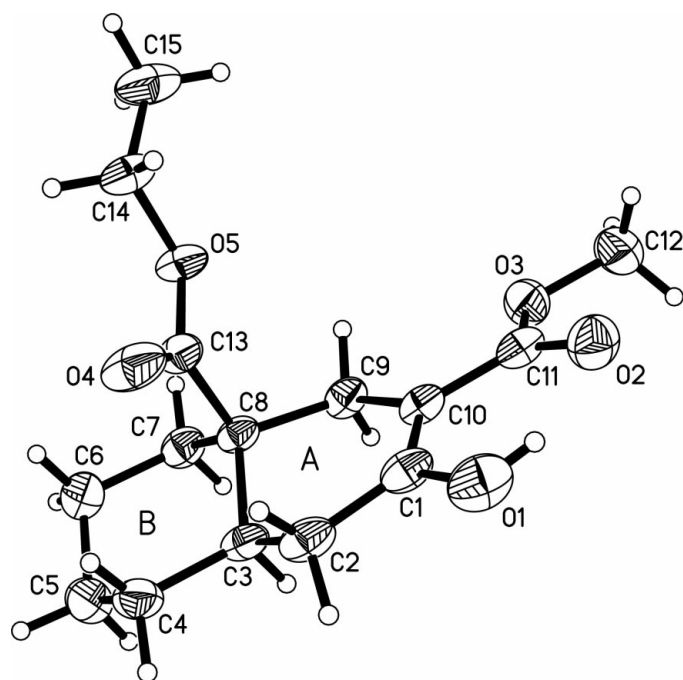
## Experimental

To 0.110 g (2.6 mmol) of a 57% mineral oil dispersion of sodium hydride (twice washed with anhydrous benzene) in 2 ml of dry dimethyl carbonate, 0.224 g (1 mmol) of ethyl (4a*S*,8a*R*)-2-oxoperhydro-4a-naphthalenedicarboxylate in 5 ml of dry dimethyl carbonate was added. The mixture was refluxed for 10 h, after which it was

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**Figure 1**  
The structure of title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme.

poured into 50 ml of water. The aqueous layer was acidified to pH 4 and extracted with ether. The combined ether layers were washed with water, then brine, dried over anhydrous sodium sulfate, and concentrated, to give 0.280 g of crude product, which was chromatographed over silica gel (100–200 mesh) using a hexane–ethyl acetate solvent mixture (90:10) to yield 0.226 g (80%) of crystalline solid. Diffraction-quality crystals were obtained by further recrystallization from an ether–hexane solvent mixture.

#### Crystal data

$C_{15}H_{22}O_5$   
 $M_r = 282.33$   
 Triclinic,  $P\bar{1}$   
 $a = 6.8206$  (3) Å  
 $b = 9.5663$  (4) Å  
 $c = 11.9330$  (4) Å  
 $\alpha = 97.092$  (1)°  
 $\beta = 97.502$  (1)°  
 $\gamma = 100.954$  (2)°  
 $V = 749.03$  (5) Å<sup>3</sup>

#### Data collection

Siemens SMART CCD area detector diffractometer  
 $\omega$  scans  
 Absorption correction: none  
 5358 measured reflections  
 3500 independent reflections

$Z = 2$   
 $D_x = 1.252$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 2709 reflections  
 $\theta = 1.7$ – $56.7^\circ$   
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, colourless  
 $0.46 \times 0.34 \times 0.30$  mm  
 1893 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.048$   
 $\theta_{max} = 28.3^\circ$   
 $h = -9 \rightarrow 8$   
 $k = -12 \rightarrow 12$   
 $l = -15 \rightarrow 10$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.056$   
 $wR(F^2) = 0.112$   
 $S = 0.89$   
 3500 reflections  
 182 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0937P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.27$  e Å<sup>-3</sup>  
 Extinction correction: *SHELXTL*  
 Extinction coefficient: 0.091 (13)

**Table 1**

Selected interatomic distances (Å).

O1–C1	1.343 (2)	O4–C13	1.204 (2)
O2–C11	1.225 (2)	O5–C13	1.328 (2)
O3–C11	1.338 (3)	O5–C14	1.453 (2)
O3–C12	1.443 (3)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1–H1A $\cdots$ O2	0.82	1.86	2.584 (2)	146

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; 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*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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