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Methyl (2*RS*,4*aRS*,8*aRS*)-2-(4-methylbenzyl)-3-oxoperhydronaphthalene-2-carboxylate

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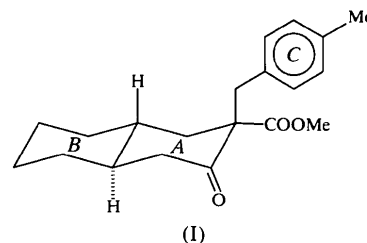
Abstract

In the title compound, C₂₀H₂₆O₃, the fused cyclohexane rings adopt the chair conformation. The dihedral angle between the two planes is 2.97 (8)°. The equatorially attached carboxylate group forms a dihedral angle of 69.97 (9)° with the cyclohexanone ring. The phenyl rings of the inversion-related molecules are involved in mutual C—H···π interactions.

Comment

The title compound, (I), was obtained during studies of stereoselectivity in cyclic β-ketoester alkylations (Surya Prakash Rao *et al.*, 1994). When methyl (4*aR*,8*aR*)-3-oxoperhydronaphthalene-2-carboxylate was alkylated with 4-methylbenzyl bromide in the presence of potassium carbonate, both *E*- and *Z*-benzylated products were

obtained. The X-ray structure determination of one of these products was carried out in order to elucidate the molecular conformation.



In general, the geometry values of the fused-ring system are comparable with those observed in a related structure (Chadwick & Dunitz, 1979). The C2—C19 [1.526 (2) Å] and C2—C3 [1.546 (2) Å] distances are longer than the normal Csp³—Csp² bond distance of 1.507 Å (Allen *et al.*, 1987). The *trans*-fused cyclohexanone and cyclohexane rings are in chair conformations, with a pseudo-twofold rotational axis bisecting the C2—C3, C6—C7 and C9—C10 bonds. The mean planes through the cyclohexanone and cyclohexane rings form a dihedral angle of 2.97 (8)°. The carboxylate group is attached equatorially and the C11—C2—C19—O2 torsion angle of 25.6 (2)° characterizes the synperiplanar conformation of the O2 and C11 atoms. The conformation of the attachment of the benzyl substituent to the decalin ring system is described by the torsion angle C3—C2—C11—C12 of -175.4 (1)°; the C2—C11—C12—C13 torsion angle of 86.0 (2)° shows how the phenyl ring of the benzyl moiety is oriented. A short intramolecular C1···O3 contact [2.713 (2) Å] is observed in this structure. The phenyl rings (C) of the

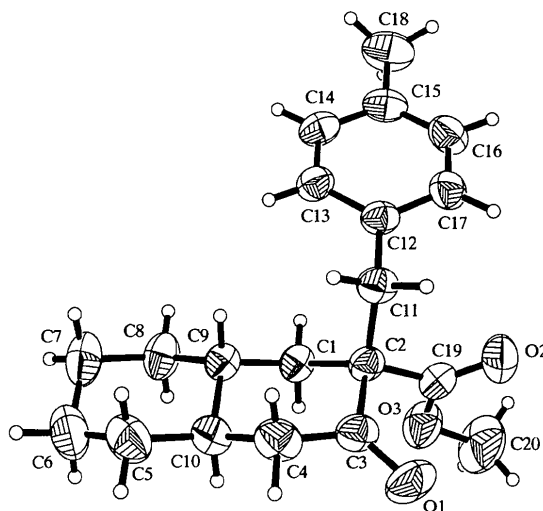


Fig. 1. The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

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inversion-related molecules are involved in mutual C8—H8B··· π interactions (Table 1) which, together with van der Waals forces, stabilize the crystal structure.

Experimental

To a stirred suspension of potassium carbonate (0.035 g, 2.5 mmol) in dry acetone (25 ml), a solution of methyl (4*aR*,8*aR*)-3-oxoperhydronaphthalene-2-carboxylate (0.105 mg, 0.5 mmol) in acetone (15 ml) was added under a nitrogen atmosphere. After stirring at room temperature for 20 min, freshly distilled 4-methylbenzyl bromide (0.463 g, 2.5 mmol) in dry acetone (25 ml) was added over a period of 10 min. The reaction mixture was stirred for 12 h. Solid particles were filtered off and the remaining solution was concentrated under reduced pressure. The residue in water was extracted with ether. After removal of the solvent, a mixture of *E* and *Z* isomers in 90% yield (0.421 g) was obtained. Individual isomers were separated by column chromatography on silica gel (100–200 mesh) using a hexane–ethyl acetate solvent mixture (90:1). The isomers were found to be in a 1:4 ratio (*E*:*Z*, ¹H NMR).

Crystal data

C₂₀H₂₆O₃
M_r = 314.41
 Triclinic
P $\bar{1}$
a = 8.9148 (3) Å
b = 10.1052 (3) Å
c = 10.8606 (3) Å
 α = 95.565 (1)°
 β = 108.976 (1)°
 γ = 101.414 (1)°
V = 893.08 (5) Å³
Z = 2
D_x = 1.169 Mg m⁻³
D_m not measured

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 4043 reflections
 θ = 2.09–28.29°
 μ = 0.077 mm⁻¹
T = 293 (2) K
 Parallelepiped
 0.48 × 0.40 × 0.34 mm
 Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 6208 measured reflections
 4265 independent reflections
 3207 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.015
 θ_{\max} = 28.29°
h = -11 → 11
k = -13 → 13
l = 0 → 14

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.049
wR(*F*²) = 0.147
S = 1.03
 4265 reflections
 210 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0745P)^2 + 0.1138P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.17 \text{ e } \text{Å}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters and hydrogen-bonding geometry (Å, °)

O1—C3	1.212 (2)	C2—C19	1.526 (2)	
O2—C19	1.196 (2)	C2—C3	1.546 (2)	
O3—C19	1.334 (2)	C3—C4	1.498 (2)	
O3—C20	1.440 (2)			
C9—C1—C2—C3	51.9 (1)	C2—C1—C9—C10	-60.1 (1)	
C1—C2—C3—C4	-47.5 (2)	C7—C8—C9—C10	53.6 (2)	
C2—C3—C4—C10	50.3 (2)	C6—C5—C10—C9	55.6 (2)	
C10—C5—C6—C7	-57.2 (2)	C8—C9—C10—C5	-53.6 (2)	
C5—C6—C7—C8	56.9 (2)	C1—C9—C10—C4	58.3 (1)	
C6—C7—C8—C9	-55.4 (2)	C3—C4—C10—C9	-53.6 (2)	
<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C8—H8B··· π (C ¹)	0.97	2.91	3.806 (2)	155

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

The data collection covered over a hemisphere of reciprocal space by a combination of three sets of exposures. Each set had a different φ angle (0, 88 and 180°) for the crystal and each exposure of 30 s covered 0.3° in ω . The crystal-to-detector distance was 4 cm and the detector swing angle was -30°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections; it was found to be negligible. After checking their presence in the difference map, all the H atoms were placed at geometrically calculated positions and a riding model was used for their refinement.

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* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1279). Services for accessing these data are described at the back of the journal.

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