(±)-*trans*-1,2,3,4,4a,9a-Hexahydroanthrone

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The title compound, $C_{14}H_{16}O$, is largely flat and rigid, with near coplanarity between the ketone and the aromatic ring. The packing includes two intermolecular C—H···O=C close contacts.

Comment

The title compound, (I), is the end product in a synthetic sequence designed for a senior chemistry majors' undergraduate laboratory course (see *Experimental*), the final step of which involves acid-catalyzed internal acylation in *trans*-2-benzylcyclohexanecarboxylic acid (Scribner & Miller, 1965). Both the *trans* and the *cis* diastereomers of the product are known, and the equilibrium between them has been shown to favor (I) by a ratio of 88:12 at 298 K (Thompson & Long, 1988). Thus (I) is isolated more easily than the *cis* epimer, and because (I) is also the higher melting of the pair by some 9 K, it is more easily purified as well.
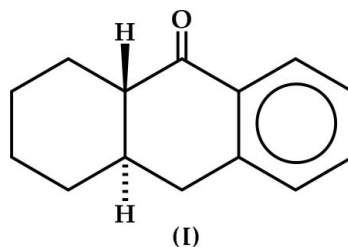

Fig. 1 shows the asymmetric unit for (I), with its numbering. The molecule has no significant flexibility and is largely flat except for the H atoms; the r.m.s. deviation for all non-H atoms from their average plane is 0.190 (3) Å; the partial flattening of the central ring in turn enforces a slight abnormal flattening in its fully saturated neighbor. Thus, the six internal tetrahedral bond angles for that ring are widened and vary from 110.9 (2) to 112.7 (3)°, while the ring-carbon torsion
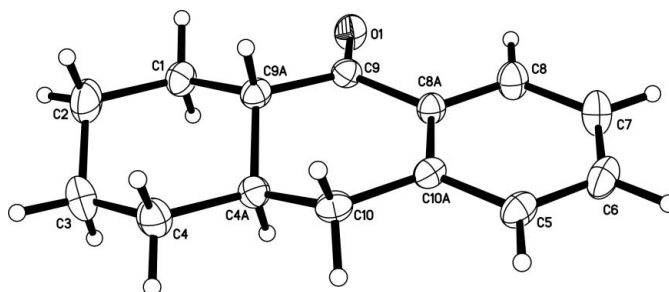

Figure 1
The molecular structure of (I), with its numbering. Displacement ellipsoids are drawn at the 20% probability level.

angles all have absolute values between 51.6 (3) and 56.5 (4)°, rather than the 60° expected for cyclohexane. The dihedral angle for the ketone (C8A/C9/C9A/O1) *versus* the aromatic ring is 8.69 (11)°. This coplanarity provides almost the fullest possible degree of conjugation, reflected in the C=O stretching frequency of the IR spectrum (KBr, 1676 cm^{-1}).

Fig. 2 shows the packing arrangement, involving centro-symmetric pairing of molecules. Despite the short interplanar separations for the aromatic rings (3.87 Å within the chosen cell, 3.67 Å across the *bc* face), π–π stacking is absent because of the offset of the aromatic rings from one another, evident in Fig. 2. Within the 2.7 Å range we routinely survey for non-bonded dipolar packing interactions (Steiner, 1997), two intermolecular C—H···O=C close contacts were found, involving H9A (2.66 Å) in a centrosymmetrically related molecule, and H5A (2.61 Å) in a molecule translationally related along *b* (Table 1).

Experimental

Friedel–Crafts acylation of benzene with *cis*-cyclohexane-1,2-dicar-boxylic acid anhydride (AlCl$_3$) yielded 2-benzoylcyclohexane-carboxylic acid, which was subjected to intentional base-catalyzed stereochemical equilibration to provide the *trans* epimer (Scribner & Miller, 1965; Lalancette *et al.*, 1996). Subsequent catalytic hydrogenolysis, employing Pd/C in acetic acid, gave *trans*-2-benzyl-cyclohexanecarboxylic acid, and this was then cyclized at room temperature with H$_2$SO$_4$ (Scribner & Miller, 1965). Sublimation of (I) and recrystallization from hexane provided material of X-ray quality (m.p. 382 K).

Crystal data

C$_{14}$H$_{16}$O	Z = 2
M_r = 200.27	D_x = 1.212 Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
a = 7.533 (5) Å	Cell parameters from 25
b = 8.067 (7) Å	reflections
c = 9.317 (5) Å	θ = 3.4–9.7°
α = 82.06 (6)°	μ = 0.07 mm^{-1}
β = 80.95 (3)°	T = 296 (2) K
γ = 81.31 (7)°	Parellelepiped, colourless
V = 548.9 (7) Å^3	0.50 × 0.25 × 0.07 mm

Data collection

Siemens *P*4 diffractometer	R_{int} = 0.035
ω/2θ scans	θ_{max} = 25.0°
Absorption correction: numerical	h = $-8 \rightarrow 1$
(*SHELXTL*; Sheldrick, 1997)	k = $-9 \rightarrow 9$
T_{min} = 0.981, T_{max} = 0.989	l = $-11 \rightarrow 11$
2406 measured reflections	3 standard reflections
1926 independent reflections	every 97 reflections
1101 reflections with $I > 2\sigma(I)$	intensity decay: variation <2.5%

Refinement

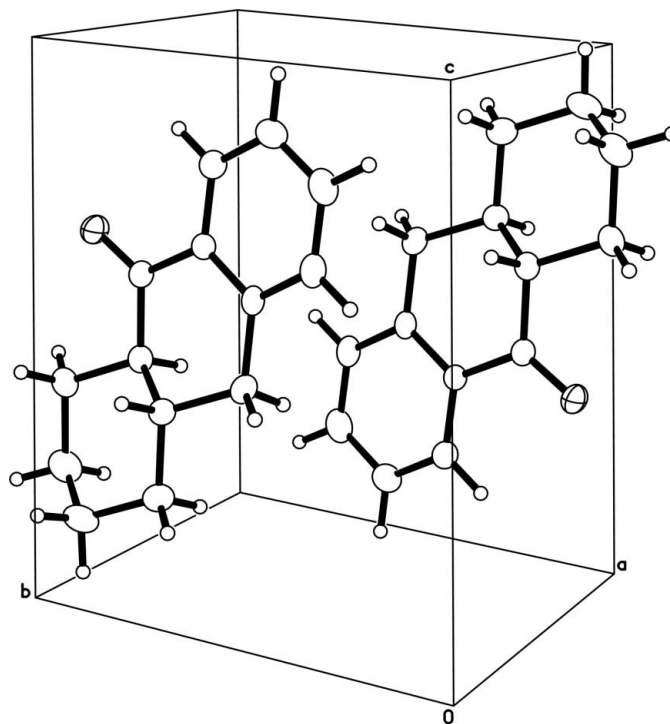|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0559P)^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.064	$+ 0.1357P]$
$wR(F^2)$ = 0.162	where $P = (F_o^2 + 2F_c^2)/3$
S = 1.03	$(\Delta/\sigma)_{max}$ <0.001
1926 reflections	$\Delta\rho_{max}$ = 0.13 e Å^{-3}
136 parameters	$\Delta\rho_{min}$ = -0.14 e Å^{-3}
H-atom parameters constrained	

Figure 2
A packing diagram for (I). Displacement ellipsoids are drawn at the 20% probability level.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9A—H9A···O1^i	0.98	2.66	3.413 (4)	134
C5—H5A···O1^{ii}	0.98	2.61	3.354 (4)	133

Symmetry codes: (i) $-x + 1, -y + 2, -z + 1$; (ii) $x, y - 1, z$.

All H atoms were found in electron density difference maps but were placed in calculated positions and allowed to refine as riding on their respective C atoms [C—H = 0.98 Å for the aromatic and methine H atoms, C—H = 0.97 Å for the methylene H atoms, and U_{iso}(H) = 1.2U_{eq} (C)].

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*.

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