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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···N2^{i}	0.94 (2)	2.56 (2)	3.318 (2)	137 (1)
C12—H12···N4^{ii}	1.01 (2)	2.60 (2)	3.382 (2)	134 (2)
C14—H14···π(phenyl^{iii})	0.98 (2)	3.06 (2)	3.876 (2)	141 (2)
C18—H18···π(pyridyl^{ii})	0.99 (2)	2.87 (2)	3.682 (2)	140 (2)

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

The data collection covered 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 3 cm and the detector swing angle was −40°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections, and was found to be negligible.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were located from a difference map and refined isotropically.

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: SK1269). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). C**55**, 772–774

2-Ethyl-2-(3-oxobutyl)cycloheptane-1,3-dione

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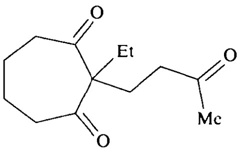
Abstract

In the title compound, $C_{13}H_{20}O_3$, the cycloheptane ring adopts a twist-chair conformation. The molecules are packed as layers parallel to the $(\bar{2}02)$ plane. The planar oxobutyl group forms a dihedral angle of 48.3 (1)° with the best plane through the cycloheptane ring.

Comment

The title compound, (I), is the first solid prochiral triketone system in carbocyclic chemistry. It serves as an important precursor for the synthesis of homo-Wieland Miescher ketone which is a potential building block for the synthesis of terpenes (Ireland & Aristoff, 1979) and other natural-product intermediates. It can also be used for the study of oxy-cope rearrangement (Selvarajan, 1966) and synthesis of optically active carbocyclic intermediates (Rajagopal & Swaminathan, 1998). The X-ray structure determination of the compound was carried out to study the molecular conformation.



(I)

Some of the bond lengths and intra-annular valence angles in the cycloheptane ring that deviate significantly from the reported mean values (Allen *et al.*, 1993) may be due to the presence of the extended oxobutyl substituent at C1, and Csp^2 atoms C2 and C7. The cycloheptane ring adopts a twist-chair conformation with a twofold axis running through C1 and the mid-point of the C4—C5 bond. The Cremer & Pople puckering parameters (Cremer & Pople, 1975) are $q_2 = 0.540$ (2) Å,

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$\varphi_2 = 87.4\,(2)^\circ$, $q_3 = 0.673\,(2)$ Å and $\varphi_3 = 90.2\,(1)^\circ$. The atoms C1, C2 and C5 of this ring deviate by 0.953 (1), 1.254 (1) and −0.720 (2) Å, respectively, from the mean plane through C3, C4, C6 and C7. The oxobutyl group forms a planar extended configuration giving a dihedral angle of 48.3 (1)° with the mean plane passing through the cycloheptane ring. In the crystal, the molecules are packed as layers parallel to the ($\bar{2}02$) plane. Inversion-related molecules in the adjacent layers have very weak C3—H3$A\cdots$O3($-x$, $-y$, $1-z$) contacts (Table 2).

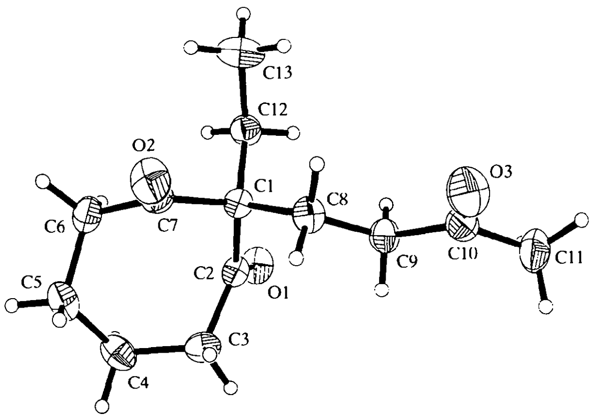

Fig. 1. The structure of (I), showing 30% probability displacement ellipsoids and the atom-numbering scheme.

Experimental

The title compound was prepared by the Michael addition of methyl vinyl ketone (0.7 g, 0.01 mol) with 2-ethylcycloheptane-1,3-dione in the presence of a catalytic amount of acetic acid in an aqueous medium. The reaction mixture was stirred for 7 h under a nitrogen atmosphere. The crude Michael adduct was purified using flash silica-gel chromatography with chloroform as eluant. Single crystals were obtained by slow evaporation of the compound in hexane (82% yield based on recovered starting material, m.p. 337–338 K).

Crystal data

$C_{13}H_{20}O_3$
$M_r = 224.29$
Monoclinic
$P2_1/c$
$a = 11.9991\,(2)$ Å
$b = 9.0405\,(2)$ Å
$c = 12.0566\,(2)$ Å
$\beta = 99.472\,(1)^\circ$
$V = 1290.04\,(4)$ Å^3
$Z = 4$
$D_x = 1.155$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 5035 reflections
$\theta = 1.72–28.33^\circ$
$\mu = 0.080$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
0.52 × 0.50 × 0.40 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
10 233 measured reflections
3182 independent reflections

2021 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.051$
$\theta_{\rm max} = 28.33^\circ$
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.057$
$wR(F^2) = 0.172$
$S = 0.981$
3182 reflections
147 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2) + (0.1032P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.39$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C2	1.213 (2)	C2—C3	1.499 (2)
O2—C7	1.211 (2)	C3—C4	1.530 (3)
O3—C10	1.206 (2)	C4—C5	1.518 (3)
C1—C2	1.531 (2)	C5—C6	1.521 (3)
C1—C7	1.533 (2)	C6—C7	1.506 (2)
C7—C1—C2—C3	−43.5 (2)	C5—C6—C7—C1	94.1 (2)
C1—C2—C3—C4	93.2 (2)	C2—C1—C7—C6	−41.4 (2)
C2—C3—C4—C5	−71.0 (2)	C8—C9—C10—O3	−6.2 (3)
C3—C4—C5—C6	55.1 (2)	C8—C9—C10—C11	175.4 (2)
C4—C5—C6—C7	−74.3 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$A\cdots$O3$^{\rm i}$	0.96	2.54	3.453 (2)	156

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

The data collection covered 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 10 s covered 0.3° in ω. The crystal-to-detector distance was 3 cm and the detector swing angle was −20°. Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections, and was found to be negligible.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. After checking their presence in the difference map, all the H atoms were placed at the geometrically calculated positions and the riding model was used for their refinement; rotating group refinement was used for the methyl groups.

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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Acta Cryst. (1999). C**55**, 774–776

5a,6,9,9a-Tetrahydro-4-hydroxy-6,9-methano-5*H*-fluoreno[2,3-*b*]furan-5-one and 5a,6,9,9a-tetrahydro-6,9-methano-4-methoxy-5*H*-fluoreno[2,3-*b*]furan-5-ol

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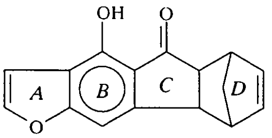
Abstract

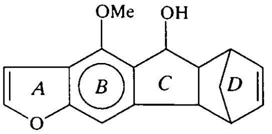
In the title compounds, $C_{16}H_{12}O_3$ and $C_{17}H_{16}O_3$, the six-membered ring of the norbornene moiety adopts a boat conformation and the five-membered rings formed by the methylene bridge adopt envelope conformations; the other rings in the molecules are nearly coplanar. In the solid state, both compounds exhibit O—H···O and C—H···O hydrogen bonds.

Comment

The title compounds, 5a,6,9,9a-tetrahydro-4-hydroxy-6,9-methano-5*H*-fluoreno[2,3-*b*]furan-5-one, (I), and 5a,6,9,9a-tetrahydro-6,9-methano-4-methoxy-5*H*-fluoreno[2,3-*b*]furan-5-ol, (II), were prepared for the purpose of generating new analogues of photodynamic drugs, *i.e.* psoralens (Shim, 1984). Both the title intermediates have been successfully transformed into their respective psoralens (Mal *et al.*, 1998). The X-ray structure determinations were carried out in order to establish the relative stereochemistries.



(I)



(II)

The bond lengths and angles observed in fused rings *A*, *B* and *C* of compounds (I) and (II) agree with each other, and those in the norbornene ring system are comparable with reported values (Beddoes *et al.*, 1993; Chinnakali *et al.*, 1999). The asymmetric unit of (II) consists of two independent molecules [(II*A*) and (II*B*)] which have different orientations of the methoxy group [C3*A*—C4*A*—O2*A*—C17*A* 49.8 (4) and C3*B*—C4*B*—O2*B*—C17*B* −54.9 (4)°].

In the molecules of (I) and (II), the fused rings *A*, *B* and *C* are nearly coplanar. The fused five-membered ring *C* in (II*A*) adopts a flattened envelope conformation, and in (II*B*) it is in the half-chair conformation; asymmetry parameters ΔC_s(C6*A*) = 0.004 (1) and ΔC_2(C13*B*) = 0.005 (1) (Nardelli, 1983).

In both compounds, the six-membered ring (*D*) of the norbornene ring system is a fairly symmetrical boat, with asymmetry parameters ΔC_s(C7—C12) = 0.001 (1) (I), 0.025 (1) (II*A*) and 0.021 (1) (II*B*), and ΔC_s(C8) = 0.012 (1) (I), 0.030 (1) (II*A*) and 0.025 (1) (II*B*); the five-membered rings in the norbornene moiety formed by the methylene bridge adopt envelope conformations. The C7/C9/C10/C12 plane is nearly perpendicular to the five-membered ring *C*, with a dihedral angle of 87.50 (7) in (I), 89.7 (1) in (II*A*) and 89.08 (8)° in (II*B*). In both compounds, the *C*/*D* ring junction is *cis*.

In (I), the hydroxyl- and carbonyl-O atoms are involved in a weak O—H···O intramolecular hydrogen bond. In the crystal, the screw-related molecules are linked by weak C1—H1*A*···O3$(1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$ hydrogen bonds along the *a* direction (Table 2). In (II), the two independent molecules in the asymmetric unit are linked by O3*B*—H3*BA*···O2*A* and O3*A*—H3*AA*···O2*B* intermolecular hydrogen bonds. In the solid state, weak C—H···O contacts are observed for (II*A*) along the *b* direction and for (II*B*) along the *a* direction (Table 4).

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