

1,4-Methano-11a-methyl-4,4a,11,11a-tetrahydro-1H-benzo[*b*]fluoren-11-one

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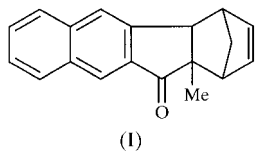
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The title compound, C₁₉H₁₆O, crystallizes with two molecules of opposite chirality in the asymmetric unit. In both molecules, the naphthalene and cyclopentanone moieties are individually planar. The two cyclopentane rings adopt envelope conformations, while the cyclohexane ring adopts a boat conformation.

Comment

Isocoumarins are of interest because to their various biological and pharmacological properties (Hill, 1986). Recently, Mal *et al.* (2000) reported a new synthesis of isocoumarin and isolated the title compound, (I), in order to extend the scope of the preparation to substituted isocoumarins. However, it was not possible to determine the stereochemistry of the molecule by NMR analysis alone. To confirm the structure assignments and stereochemistry, an X-ray structure determination of (I) was undertaken.



In the asymmetric unit of (I), there are two independent molecules with opposite chirality. The observed bond lengths and angles of both molecules agree with one another. Within the phenyl rings, the average C—C bond lengths are 1.390 (3) and 1.392 (3) Å for molecules *A* and *B*, respectively. The bond lengths and angles observed for the benzo[*b*]fluorene moiety are only slightly different from those reported for a related structure, *i.e.* an azabeno[*b*]fluorene derivative (Kubicki & Borowiak, 1995).

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In both molecules, the naphthalene and cyclopentanone rings are both individually planar and coplanar, exhibiting dihedral angles of 1.2 (1) and 2.5 (1)° in molecules *A* and *B*, respectively. Atom O1 deviates slightly from the attached least-squares plane through the naphthalene and cyclopentanone moieties, with deviations of −0.133 (2) and 0.211 (2) Å for molecules *A* and *B*, respectively.

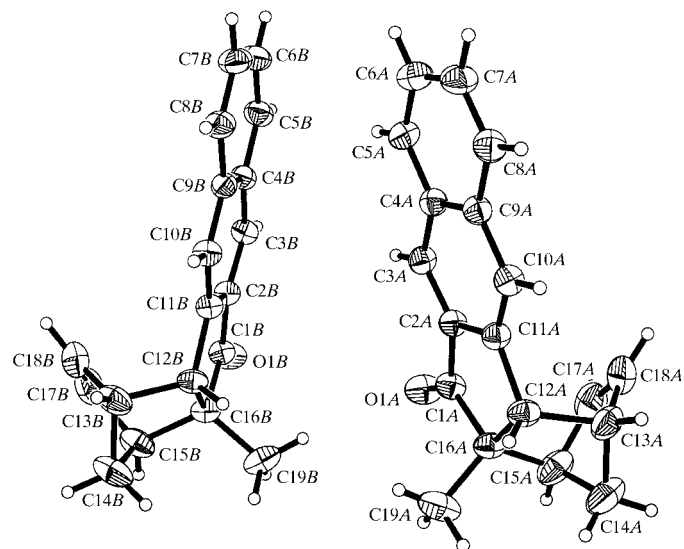


Figure 1
The structure of the title compound showing 50% probability displacement ellipsoids and the atom-numbering scheme.

The C12–C16 cyclopentane ring adopts an envelope conformation, with puckering parameters (Cremer & Pople, 1975) $Q_2 = 0.631$ (4) Å and $\varphi_2 = 72.2$ (3)° for molecule *A*, and $Q_2 = 0.625$ (3) Å and $\varphi_2 = -71.1$ (3)° for molecule *B*. The least-squares planes through the cyclopentane rings make dihedral angles of 42.9 (2) and 42.2 (2)° with the cyclopentanone rings in molecules *A* and *B*, respectively. The other cyclopentane ring (C13–C18) also adopts an envelope conformation, with puckering parameters (Cremer & Pople, 1975) $Q_2 = 0.550$ (4) Å and $\varphi_2 = 36.2$ (4)° for molecule *A*, and $Q_2 = 0.552$ (3) Å and $\varphi_2 = -36.4$ (3)° for molecule *B*. The dihedral angles between the least-squares planes through the two cyclopentane rings are 80.8 (2) and 81.1 (2)° for molecules *A* and *B*, respectively. The C12–C16 cyclohexane rings have total puckering amplitudes (Q_T) of 0.944 (3) and 0.947 (3) Å in molecules *A* and *B*, respectively, revealing boat conformations.

Experimental

To a lithium diisopropylamide solution [2.9 mmol in 5 ml tetrahydrofuran (THF)] at 195 K was added a 1,4-methano-4,4a,11,11a-tetrahydro-1H-benzo[*b*]fluoren-11-one solution (2.03 mmol in 20 ml THF). After stirring for 1 h, the enolate was quenched with MeI (1.3 g, 10.4 mmol, 5 equivalents). The mixture was stirred for an additional 1 h at 195 K and was then allowed to warm to 298 K before being acidified with 15 ml 15% HCl solution. Treatment with diethyl ether and column chromatography of the reaction mixture furnished the desired product, (I) (91% yield), as a white solid which was crystallized from a mixture of ethyl acetate and petroleum ether.

Crystal data

$C_{19}H_{16}O$	$D_x = 1.264 \text{ Mg m}^{-3}$
$M_r = 260.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 7052 reflections
$a = 6.23030 (10) \text{ \AA}$	$\theta = 1.9\text{--}28.3^\circ$
$b = 20.5610 (3) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 10.7476 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 96.6650 (10)^\circ$	Block, colourless
$V = 1367.48 (4) \text{ \AA}^3$	$0.48 \times 0.42 \times 0.36 \text{ mm}$
$Z = 4$	

Data collection

Siemens SMART CCD area-detector	$R_{\text{int}} = 0.066$
ω scans	$\theta_{\text{max}} = 28.4^\circ$
9941 measured reflections	$h = -7 \rightarrow 8$
3470 independent reflections	$k = -27 \rightarrow 27$
2677 reflections with $I > 2\sigma(I)$	$l = -14 \rightarrow 12$
	Intensity decay: negligible

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1A—C1A	1.214 (3)	O1B—C1B	1.225 (3)
C1A—C16A	1.512 (4)	C1B—C16B	1.512 (3)
C2A—C3A	1.363 (4)	C2B—C3B	1.374 (3)
C12A—C16A	1.557 (4)	C12B—C16B	1.546 (3)
C14A—C15A	1.533 (5)	C14B—C15B	1.531 (5)
C15A—C17A	1.497 (6)	C15B—C17B	1.522 (5)
C16A—C19A	1.515 (4)	C16B—C19B	1.518 (4)
O1A—C1A—C2A	126.0 (3)	O1B—C1B—C2B	126.4 (2)
C12A—C13A—C14A	99.8 (3)	C12B—C13B—C14B	99.4 (3)
C13A—C14A—C15A	93.3 (3)	C13B—C14B—C15B	93.7 (2)
C14A—C15A—C17A	100.5 (3)	C14B—C15B—C17B	99.7 (3)
C16A—C15A—C17A	107.2 (3)	C16B—C15B—C17B	106.9 (2)
C14A—C15A—C16A	100.1 (3)	C14B—C15B—C16B	100.5 (3)
C1A—C16A—C15A	113.0 (2)	C1B—C16B—C15B	113.2 (2)
C12A—C16A—C19A	113.7 (2)	C12B—C16B—C19B	114.3 (2)
C15A—C17A—C18A	107.8 (3)	C15B—C17B—C18B	107.5 (3)
C1A—C2A—C11A—C12A	−1.1 (3)	C1B—C2B—C11B—C12B	1.7 (3)
C13A—C12A—C16A—C15A	−0.1 (3)	C13B—C12B—C16B—C15B	−1.0 (3)
C14A—C15A—C16A—C1A	150.1 (3)	C14B—C15B—C16B—C1B	−148.8 (3)
C14A—C15A—C16A—C12A	37.5 (3)	C14B—C15B—C16B—C12B	−36.2 (3)
C15A—C17A—C18A—C13A	0.1 (4)	C15B—C17B—C18B—C13B	−0.4 (4)

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.052$	$w = 1/[\sigma^2(F_o^2) + (0.074P)^2]$
$wR(F^2) = 0.131$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.99$	$(\Delta/\sigma)_{\text{max}} < 0.001$
3470 reflections	$\Delta\rho_{\text{max}} = 0.25 \text{ e \AA}^{-3}$
363 parameters	$\Delta\rho_{\text{min}} = -0.23 \text{ e \AA}^{-3}$

After checking their presence in the difference map, all H atoms were fixed geometrically (C—H = 0.93–0.98 \AA) and allowed to ride on their attached atoms.

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1493). Services for accessing these data are described at the back of the journal.

References

- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1348.
 Hill, R. A. (1986). *Fortschr. Chem. Org. Naturst.* **49**, 1–78.
 Kubicki, M. & Borowiak, T. (1995). *Acta Cryst.* **C51**, 462–465.
 Mal, D., Bandyopandhyay, M., Ghorai, S. K. & Datta, K. (2000). *Tetrahedron Lett.* **41**, 3677–3680.
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
 Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
 Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.