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5-Methoxy-3,3a,8,8a-tetrahydro-1*H*-cyclopenta[*a*]inden-2-one

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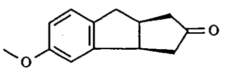
Abstract

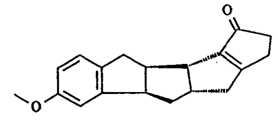
In the title compound the two five-membered rings are *cis* connected. The torsion angle C(1)—C(8a)—C(3a)—C(3) about the bond common to the two five-membered rings is unexpectedly large, 26.7 (3)°. The angle formed by the least-squares plane of the indene subunit with the least-squares plane of the terminal cyclopentane ring is 67.7 (1)°.

Comment

The title compound (1) was synthesized as a precursor to the target polyquinane (2), a potential steroid analogue (Trachsel & Keese, 1988). Molecular-modelling calculations showed that the cyclopentane units of (2) should be connected *cis–anti–cis* to obtain a flat backbone similar to that of steroids. The structure determination of (1) was undertaken to determine the stereochemistry of the junction between the five-membered rings and the general structural appearance of the molecule. No structure of a cyclopenta[*a*]indene has been reported previously.



(1)



(2)

Compound (1) was synthesized from 6-methoxyindene by cycloaddition with dichloroketene (Krepski & Hassner, 1978), ring enlargement with diazomethane (Greene & Deprés, 1979) and reduction with zinc in acetic acid (Sugihara, Sugimura & Murata, 1983). Crystals were obtained from ether (Aebi, 1992).

The aromatic ring of (1) is planar and the methoxy group is nearly coplanar with it (Table 2). The angle C(6)—C(5)—O(2) is 9° larger than C(4)—C(5)—O(2) as a result of repulsion between C(6) and C(9) (Sakaki, Sogo, Wakahara, Kanai, Fujiwara & Tomita, 1976; Hummel, Huml & Bürgi, 1988). The five-membered ring of the indene unit shows an envelope conformation, with C(8a) 0.411 (3) Å out of the plane formed by C(3a)—C(3b)—C(7a)—C(8).

The torsion angles about the C(8a)—C(3a) bond deviate by about 26° from the ecliptic conformation. A search in the Cambridge Structural Database showed an average deviation of only about 10° for *cis*-[3.3.0]bicyclooctane units. The bond C(8a)—C(3a) is 1.550 (4) Å. It is the longest in the molecule, as expected from the synclinical C–C repulsions [*e.g.* C(1)–C(3)]. The terminal cyclopentane ring shows a twist-envelope conformation. The deviations of the atoms from the least-squares plane of the entire carbon backbone range from 0.114 (2) Å for C(7a) to 0.948 (3) Å for C(2), which is more than in a normal steroid, for example, estrone (Busetta, Courseille & Hospital, 1973).

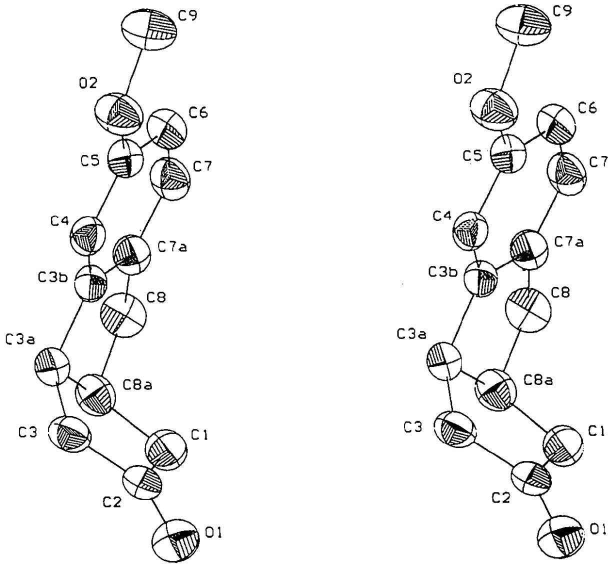


Fig. 1. Stereoscopic view of 5-methoxy-3,3a,8,8a-tetrahydro-1*H*-cyclopenta[*a*]inden-2-one (1), with thermal ellipsoids representing 50% probability density (295 K) and atomic numbering.

Experimental

Crystal data

$C_{13}H_{14}O_2$

M_r = 202.25

Monoclinic

D_x = 1.2738 Mg m^{-3}

Mo $K\alpha$ radiation

λ = 0.71069 Å

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$P2_1/c$
$a = 10.622$ (1) Å
$b = 11.249$ (2) Å
$c = 9.654$ (1) Å
$\beta = 113.90$ (1)°
$V = 1054.6$ (2) Å^3
$Z = 4$

Cell parameters from 24 reflections
$\theta = 7.24$–13.14°
$\mu = 0.079$ mm^{-1}
$T = 295$ K
Plate
0.4 × 0.25 × 0.2 mm
Colourless

Data collection

Enraf-Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
2180 measured reflections
1174 independent reflections
1040 observed reflections [$I > 3\sigma(I)$]

$R_{\text{int}} = 0.015$
$\theta_{\text{max}} = 25$°
$h = -12 \rightarrow 11$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 11$
3 standard reflections
frequency: 120 min
intensity variation: 0.05%

Refinement

Refinement on F
Final $R = 0.039$
$wR = 0.058$
$S = 0.875$
1040 reflections
137 parameters
Only H-atom U's refined
$w = 0.8586/[\sigma^2(F) + 0.00298F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.001$
$\Delta\rho_{\text{max}} = 0.145$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.163$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{\text{eq}} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
O(1)	0.0515 (2)	0.6645 (2)	−0.0349 (2)	0.0618 (9)
O(2)	0.7590 (2)	0.5321 (2)	0.2293 (2)	0.0540 (8)
C(1)	0.1876 (3)	0.7301 (2)	0.2193 (3)	0.0495 (11)
C(2)	0.1407 (3)	0.6447 (2)	0.0890 (3)	0.0439 (11)
C(3)	0.2203 (3)	0.5305 (2)	0.1376 (3)	0.0472 (11)
C(3a)	0.3245 (3)	0.5500 (2)	0.3005 (3)	0.0426 (10)
C(3b)	0.4660 (2)	0.5893 (2)	0.3187 (3)	0.0370 (9)
C(4)	0.5516 (3)	0.5389 (2)	0.2587 (3)	0.0405 (9)
C(5)	0.6814 (3)	0.5875 (2)	0.2942 (3)	0.0408 (10)
C(6)	0.7239 (3)	0.6865 (2)	0.3878 (3)	0.0460 (11)
C(7)	0.6371 (3)	0.7367 (2)	0.4471 (3)	0.0476 (11)
C(7a)	0.5085 (3)	0.6881 (2)	0.4135 (3)	0.0412 (10)
C(8)	0.4011 (3)	0.7229 (3)	0.4702 (3)	0.0513 (13)
C(8a)	0.2715 (3)	0.6581 (2)	0.3608 (3)	0.0457 (12)
C(9)	0.8965 (3)	0.5697 (3)	0.2729 (4)	0.0663 (15)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

O(1)—C(2)	1.208 (3)	C(3b)—C(3a)	1.507 (4)
O(2)—C(5)	1.372 (3)	C(7a)—C(8)	1.503 (5)
O(2)—C(9)	1.411 (4)	C(8)—C(8a)	1.537 (3)
C(1)—C(2)	1.499 (4)	C(8a)—C(1)	1.526 (4)
C(2)—C(3)	1.505 (4)	C(8a)—C(3a)	1.550 (4)
C(3)—C(3a)	1.528 (3)		
O(2)—C(5)—C(4)	115.3 (2)	C(5)—O(2)—C(9)	118.0 (2)
O(2)—C(5)—C(6)	124.4 (3)	C(7)—C(7a)—C(8)	129.5 (2)
C(1)—C(2)—C(3)	109.4 (2)	C(7a)—C(3b)—C(3a)	110.7 (2)
C(1)—C(8a)—C(3a)	104.5 (2)	C(7a)—C(8)—C(8a)	103.1 (2)
C(2)—C(3)—C(3a)	106.3 (2)	C(8)—C(8a)—C(1)	113.5 (2)
C(3b)—C(3a)—C(3)	115.8 (2)	C(8)—C(8a)—C(3a)	105.7 (2)
C(3b)—C(3a)—C(8a)	102.9 (2)	C(8a)—C(1)—C(2)	106.6 (2)
C(3b)—C(7a)—C(8)	110.8 (2)	C(8a)—C(3a)—C(3)	106.1 (2)
C(4)—C(3b)—C(3a)	128.7 (2)		

Table 3. *Torsion angles* (°)

C(9)—O(2)—C(5)—C(6)	7.2 (4)
C(8a)—C(1)—C(2)—C(3)	−13.8 (3)
C(1)—C(2)—C(3)—C(3a)	−3.1 (3)
C(2)—C(3)—C(3a)—C(8a)	18.6 (3)
C(2)—C(3)—C(3a)—C(3b)	−94.8 (3)
C(7a)—C(3b)—C(3a)—C(8a)	14.9 (3)
C(7a)—C(3b)—C(3a)—C(3)	130.1 (3)
C(3a)—C(3b)—C(7a)—C(8)	1.2 (3)
C(7)—C(7a)—C(8)—C(8a)	165.8 (3)
C(7a)—C(8)—C(8a)—C(3a)	25.4 (3)
C(7a)—C(8)—C(8a)—C(1)	−88.5 (3)
C(1)—C(8a)—C(3a)—C(3)	−26.7 (3)
C(1)—C(8a)—C(3a)—C(3b)	95.3 (2)
C(3a)—C(8a)—C(1)—C(2)	24.8 (3)
C(8)—C(8a)—C(1)—C(2)	139.4 (2)
C(8)—C(8a)—C(3a)—C(3)	−146.7 (2)
C(8)—C(8a)—C(3a)—C(3b)	−24.7 (3)

H atoms were placed at geometrically determined positions and held fixed during the least-squares refinement, but were periodically recalculated. Refinement was by full-matrix least-squares methods. Data collection: *CAD*-4 *Software* (Enraf-Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Structure Determination Package* (Enraf-Nonius, 1985). Program used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program used to refine structure: *SHELX*76 (Sheldrick, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1983); *PEANUT* (Hummel, Hauser & Bürgi, 1990).

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71210 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1043]

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