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Structure of 10-Hydroxy-4-methoxy-5,9-dimethyltricyclo[7.3.1.0^{2,7}]trideca-2,4,6-trien-13-one†

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Abstract

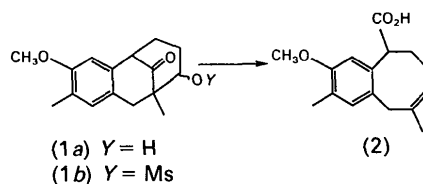
This X-ray diffraction study establishes the molecular structure of the title compound. The carbon skeleton of the molecule comprises a system of three six-membered rings, *A*, *B* and *C*; *A* is aromatic and almost planar. The *A* and *B* rings are *cis*-fused. The *A*, *B* and *C* rings adopt twist-chair ³T₁, envelope ⁶E and chair ⁴C₁ conformations, respectively. The *C* ring hydroxyl and methyl groups occupy axial and equatorial positions, respectively. The crystal structure is stabilized by an intermolecular hydrogen bond and two C—H⋯O hydrogen-bond interactions.

Comment

An important method for medium-size ring formation involves fragmentation (Grob & Schiess, 1967; Grob, 1969) of appropriately functionalized bicyclic systems. In our laboratory, the NaOH-induced fragmentation of the benzobicyclic ketomesylates (*1b*) were studied. Although both isomers gave the expected benzocyclooctene product (2), yields were strikingly different depending of the isomer used as starting material. Thus, the ketomesylate derived from the oily ketol isomer fragmented in nearly 90% yield, while the ketomesylate derived from the other (crystalline) ketol isomer proceeded in only about 40% yield.

In this paper, the stereochemistry of the OH group in the crystalline ketol (*1a*) has been established to be axial by X-ray crystal analysis. The oily ketol is the isomer with the equatorial OH, a result consistent

with a favourable antiperiplanar bonding arrangement for optimal fragmentation (Clayton, Henbest & Smith, 1957) in this isomer.



The *A* and *B* rings are *cis*-fused at the C(2)—C(7) bond and the *B* ring is fused at C(1)—C(13)—C(9) to the *C* ring. The ring-puckering parameters (Cremer & Pople, 1975) are $\varphi = -25$ (7), $\theta = 88$ (6) $^\circ$, $Q = 0.023$ (3) Å for *A*, $\varphi = -60.6$ (4), $\theta = 47.1$ (3) $^\circ$, $Q = 0.478$ (3) Å for *B*, and $\varphi = 68$ (6), $\theta = 2.8$ (3) $^\circ$, $Q = 0.584$ (3) Å for *C*, indicating twist-chair ³T₁, envelope ⁶E and chair ⁴C₁ conformations, respectively. The substituents at C(9) and C(10) are in equatorial and axial positions with torsion angles C(15)—C(9)—C(13)—C(1) = -179.8 (3) and O(2)—C(10)—C(11)—C(12) = -62.4 (4) $^\circ$, respectively. The crystal structure is stabilized by an intermolecular hydrogen bond between the O(2)—H hydroxyl group and the O(3) carbonyl group [O(2)—H⋯O(3)(0.5 + *x*, $-y$, *z*) 2.871 (4) Å] and two C—H⋯O interactions < 3.5 Å [C(12)⋯O(2)($-x$, $-y$, 0.5 + *z*) 3.499 (6) and C(16)⋯O(3)($-0.5 - x$, *y*, 0.5 + *z*) 3.435 (5) Å].

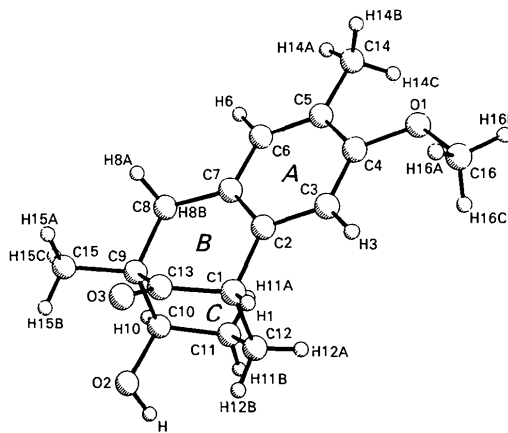


Fig. 1. The molecular structure of the title compound with atom numbering.

Experimental

Crystal data

C₁₆H₂₀O₃
M_r = 260.3
 Orthorhombic
*Pca*2₁
a = 8.594 (2) Å
b = 14.045 (6) Å
c = 11.509 (6) Å

Cu *K*α radiation
 $\lambda = 1.5418$ Å
 Cell parameters from 25
 reflections
 $\theta = 3.15 - 14.6^\circ$
 $\mu = 0.645$ mm⁻¹
T = 293 K

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$V = 1389 (1) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.24 \text{ Mg m}^{-3}$

Data collection

Nicolet P3/F diffractometer
 $2\theta/\theta$ scans
 Absorption correction:
 none
 1052 measured reflections
 930 independent reflections
 878 observed reflections
 $[I > 2.5\sigma(I)]$

Needle
 $0.46 \times 0.32 \times 0.14 \text{ mm}$
 Colourless

$\theta_{\max} = 55^\circ$
 $h = 0 \rightarrow 9$
 $k = 0 \rightarrow 14$
 $l = 0 \rightarrow 12$
 2 standard reflections
 monitored every 50
 reflections
 intensity variation: 3%

Refinement

Refinement on F
 $R = 0.034$
 $wR = 0.046$
 $S = 1.30$
 878 reflections
 175 parameters
 $w = [\sigma^2(F_o) + 0.07(F_o)^2]^{-1}$

$(\Delta/\sigma)_{\max} = 0.70$
 $\Delta\rho_{\max} = 0.13 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.11 \text{ e \AA}^{-3}$
 Atomic scattering factors
 from *International Tables*
 for *X-ray Crystallography*
 (1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	B_{eq}
O(1)	0.0425 (2)	0.3937 (2)	0.3419	4.8 (1)
O(2)	0.0870 (3)	0.0234 (2)	-0.1977 (4)	7.2 (2)
O(3)	-0.2376 (3)	0.1382 (1)	-0.1192 (3)	5.3 (1)
C(1)	-0.0583 (3)	0.1515 (2)	0.0375 (4)	4.0 (1)
C(2)	-0.0004 (3)	0.2482 (2)	0.0765 (4)	3.3 (1)
C(3)	-0.0134 (3)	0.2761 (2)	0.1934 (4)	3.6 (1)
C(4)	0.0505 (3)	0.3610 (2)	0.2294 (3)	3.6 (1)
C(5)	0.1301 (3)	0.4202 (2)	0.1529 (3)	3.6 (1)
C(6)	0.1387 (3)	0.3918 (2)	0.0379 (3)	3.6 (1)
C(7)	0.0744 (3)	0.3077 (2)	-0.0029 (3)	3.4 (1)
C(8)	0.0818 (3)	0.2844 (2)	-0.1304 (4)	4.1 (1)
C(9)	0.0228 (3)	0.1857 (2)	-0.1692 (4)	3.9 (1)
C(10)	0.1517 (4)	0.1096 (2)	-0.1551 (4)	4.9 (2)
C(11)	0.2048 (3)	0.0992 (2)	-0.0304 (4)	4.9 (2)
C(12)	0.0703 (4)	0.0766 (2)	0.0498 (4)	4.8 (2)
C(13)	-0.1057 (3)	0.1567 (2)	-0.0869 (4)	3.8 (1)
C(14)	0.2045 (4)	0.5104 (2)	0.1950 (4)	5.3 (2)
C(15)	-0.0295 (5)	0.1907 (3)	-0.2951 (4)	5.5 (2)
C(16)	-0.0430 (5)	0.3396 (3)	0.4234 (4)	6.2 (2)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

O(1)—C(4)	1.376 (4)	C(5)—C(6)	1.384 (5)
O(1)—C(16)	1.413 (5)	C(5)—C(14)	1.499 (4)
O(2)—C(10)	1.419 (5)	C(6)—C(7)	1.387 (4)
O(3)—C(13)	1.221 (3)	C(7)—C(8)	1.505 (4)
C(1)—C(2)	1.514 (4)	C(8)—C(9)	1.542 (5)
C(1)—C(12)	1.532 (5)	C(9)—C(10)	1.548 (4)
C(1)—C(13)	1.490 (5)	C(9)—C(13)	1.512 (5)
C(2)—C(3)	1.406 (5)	C(9)—C(15)	1.519 (6)
C(2)—C(7)	1.395 (4)	C(10)—C(11)	1.513 (6)
C(3)—C(4)	1.376 (4)	C(11)—C(12)	1.513 (6)
C(4)—C(5)	1.392 (4)		
C(4)—O(1)—C(16)	118.1 (3)	C(6)—C(7)—C(8)	119.9 (3)
C(2)—C(1)—C(12)	110.6 (2)	C(7)—C(8)—C(9)	117.6 (3)
C(2)—C(1)—C(13)	109.3 (3)	C(8)—C(9)—C(10)	110.8 (2)
C(12)—C(1)—C(13)	108.6 (3)	C(8)—C(9)—C(13)	107.5 (3)
C(1)—C(2)—C(3)	120.6 (3)	C(8)—C(9)—C(15)	109.4 (3)
C(1)—C(2)—C(7)	119.6 (3)	C(10)—C(9)—C(13)	105.7 (3)
C(3)—C(2)—C(7)	119.7 (3)	C(10)—C(9)—C(15)	110.1 (3)
C(2)—C(3)—C(4)	119.9 (3)	C(13)—C(9)—C(15)	113.2 (3)
O(1)—C(4)—C(3)	123.6 (3)	O(2)—C(10)—C(9)	105.9 (2)

O(1)—C(4)—C(5)	114.9 (2)	O(2)—C(10)—C(11)	111.3 (3)
C(3)—C(4)—C(5)	121.5 (3)	C(9)—C(10)—C(11)	112.5 (3)
C(4)—C(5)—C(6)	117.3 (2)	C(10)—C(11)—C(12)	111.6 (2)
C(4)—C(5)—C(14)	120.7 (3)	C(1)—C(12)—C(11)	110.5 (3)
C(6)—C(5)—C(14)	122.1 (3)	O(3)—C(13)—C(1)	122.5 (3)
C(5)—C(6)—C(7)	123.3 (3)	O(3)—C(13)—C(9)	123.0 (3)
C(2)—C(7)—C(6)	118.1 (3)	C(1)—C(13)—C(9)	114.5 (2)
C(2)—C(7)—C(8)	121.9 (3)		

Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods (TEXSAN; Molecular Structure Corporation, 1990). The H-atom positions in the CH, CH₂ and CH₃ groups were allowed to ride on the bonded C atoms and refined. The H atom bonded to the O atom was located on a difference Fourier map at an advanced stage of anisotropic refinement and its coordinates refined.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71343 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HA1049]

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Structure of 2,4,6-Tri(tert-butyl)aniline at 153 K

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Abstract

The structure of 2,4,6-tri(tert-butyl)aniline is reported. The molecule lies on a crystallographic twofold axis.