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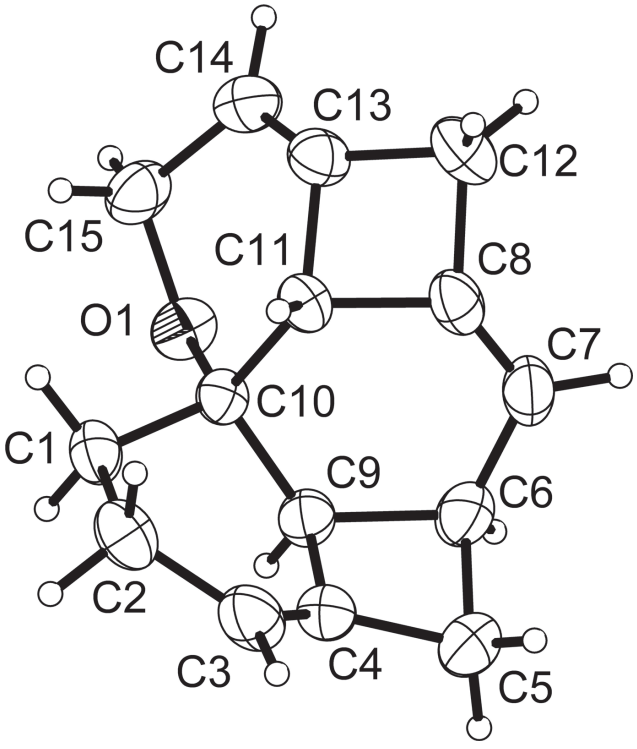
Crystal structure of (6*aR*,6*a*^{1}*S*,10*aS*)-2,4*a*,6*a*,6*a*^{1},9,10-hexahydro-7*H*-4,5-methanocyclobuta[4,5]naphtho[8*a*,1-*b*]pyran, $C_{15}H_{16}O$



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Abstract

$C_{15}H_{16}O$, monoclinic, $P2_1/c$ (no. 14), $a = 5.4371(7)$ Å, $b = 17.567(2)$ Å, $c = 11.8840(18)$ Å, $\beta = 101.043(9)°$, $V = 1114.1(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0422$, $wR_{ref}(F^2) = 0.1155$, $T = 296(2)$ K.

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The asymmetric unit of the molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.21 × 0.14 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.08 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	10178, 2747, 0.021
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2314
$N(param)_{refined}$:	145
Programs:	Bruker [1], Olex2 [2]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5780(2)	0.37047(7)	0.56543(9)	0.0364(3)
H1A	0.6140	0.3276	0.5197	0.044*
H1B	0.4116	0.3888	0.5324	0.044*
O1	0.38400(14)	0.28689(5)	0.68690(7)	0.0370(2)
C2	0.7677(2)	0.43389(8)	0.55803(10)	0.0441(3)
H2A	0.9292	0.4111	0.5559	0.053*
H2B	0.7147	0.4616	0.4869	0.053*
C3	0.7975(3)	0.48893(8)	0.65613(12)	0.0476(3)
H3	0.9045	0.5304	0.6580	0.057*
C4	0.6728(3)	0.47884(7)	0.73964(11)	0.0423(3)
C5	0.6903(4)	0.50384(8)	0.86299(13)	0.0610(4)
H5A	0.5720	0.5434	0.8733	0.073*
H5B	0.8587	0.5165	0.9022	0.073*
C6	0.6041(3)	0.42121(8)	0.88802(11)	0.0457(3)
H6	0.4638	0.4216	0.9290	0.055*

Table 2 (continued)

Atom	x	y	z	U_{iso}*/U_{eq}
C7	0.8048(3)	0.36707(8)	0.94025(10)	0.0447(3)
H7	0.8554	0.3654	1.0195	0.054*
C8	0.9119(2)	0.32140(7)	0.87562(10)	0.0377(3)
C9	0.5133(2)	0.41098(7)	0.75495(10)	0.0348(3)
H9	0.3350	0.4235	0.7324	0.042*
C10	0.57851(18)	0.34258(6)	0.68846(9)	0.0287(2)
C11	0.83073(19)	0.31034(6)	0.74726(9)	0.0304(2)
H11	0.9644	0.3243	0.7063	0.037*
C12	1.0343(3)	0.24295(8)	0.88981(12)	0.0458(3)
H12A	1.0075	0.2147	0.9566	0.055*
H12B	1.2082	0.2417	0.8814	0.055*
C13	0.8437(2)	0.22714(7)	0.77995(11)	0.0386(3)
C14	0.6581(3)	0.17947(7)	0.74542(12)	0.0459(3)
H14	0.6593	0.1299	0.7729	0.055*
C15	0.4435(2)	0.21056(7)	0.65847(12)	0.0447(3)
H15A	0.4879	0.2101	0.5832	0.054*
H15B	0.2976	0.1784	0.6557	0.054*

Source of material

All reactions were carried out under argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially, and used without further purification. To a solution of (4*aS*,5*S*,6*aS*,6*a*^{1}*S*,10*aS*)-4*a*,5,6*a*,6*a*^{1},9,10-hexahydro-7*H*-4,5-methanocyclobuta[4,5]naphtho[8*a*,1-*b*]pyran-6(2*H*)-one (456.0 mg, 2.0 mmol) in absolute dry MeOH (10 mL) was added $NaBH_4$ (151.32 mg, 4,0 mmol, 2.0 equiv) at 0 °C. The reaction mixture was stirred at this temperature for another 1 h, then the reaction mixture was warmed to room temperature. After the starting material disappeared (detected by TLC), the reaction was quenched with saturated aq. NH_4Cl, and the mixture was extracted with ethyl acetate three times, and the organic layer was washed with saturated aq. NaCl solution. This organic mixture was dried over anhydrous Na_2SO_4, then concentrated under reduced pressure. The resulting residue was purified by flash column chromatography using petroleum ether/ethyl acetate eluent to afford the alcohol (414.5 mg, 90% yield) as a colorless sticky oil.

To a stirred solution of the intermediate alcohol (230 mg, 1.0 mmol) obtained above, and PPh_3 (1310.2 mg, 5.0 mmol) in THF (20.0 mL) was added DEAD (870.7 mg, 5.0 mmol) dropwise at 0 °C. The resulting mixture was stirred at room temperature overnight before it was quenched with saturated aq. $NaHCO_3$ solution (20 mL) and extracted with ethyl acetate (3×10 mL). The combined organic phases were washed with brine (20 mL) and dried over anhydrous Na_2SO_4. After filtration and evaporation of the solvent, the residue so obtained was purified by flash column chromatography with petroleum ether/EtOAc (15:1 to 10:1) to give the desired product (180 mg, 85%) as a foam solid. The titled crystal could be afforded by slowly evaporation of the foam solid obtained above in petroleum ether/ethyl acetate mixture.

Experimental details

Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms.

Comment

The polycyclic compounds are widely found in natural products [3], drug molecules [4] and bioactive compounds, [5] and due to the complicated structure and potential biological activity, the development of new methods for the synthesis of novel polycyclic compounds is of great insterest. As part of our continuing efforts on the efficient synthetic methods for cyclic compounds synthesis, [6] herein, we report a useful method and the crystal structure of the titled compound.

There is one molecule in the asymmetric unit of the title structure (see the figure). The single crystal structure verifies that all bond lengths are in normal ranges. Furthermore, the crystal packing doesn't exhibit intramolecular or intermolecular hydrogen bonds.

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