Crystal structure of 1-hydroxy-2′-methoxy-bicyclohexyl-1′-ene-2,3′-dione, $C_{13}H_{18}O_4$

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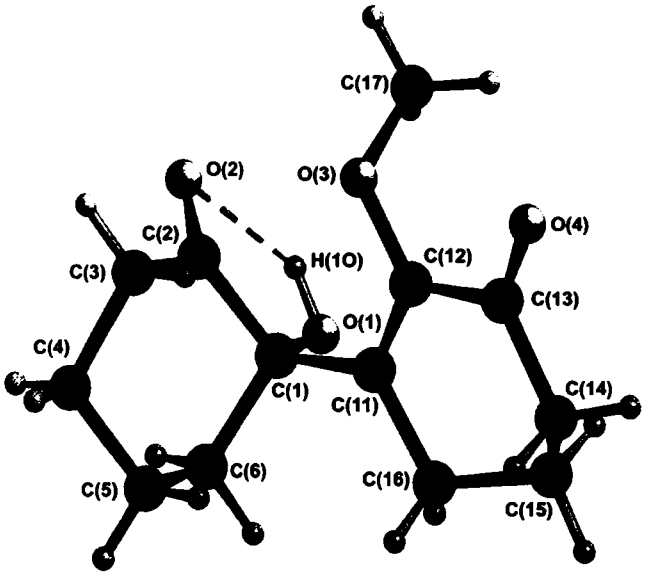

Abstract

$C_{13}H_{18}O_4$, triclinic, $P\bar{1}$ (No. 2), $a = 6.982(1)$ Å, $b = 7.457(1)$ Å, $c = 12.251(1)$ Å, $\alpha = 73.71(1)°$, $\beta = 81.32(1)°$, $\gamma = 86.11(1)°$, $V = 605.0$ Å^3, $Z = 2$, $R_{gt}(F) = 0.038$, $wR_{ref}(F^2) = 0.101$, $T = 293$ K.

Source of material

The title compound was formed as a side-product via barium oxide/hydroxide mediated coupling of 1,2-cyclohexanedione, followed by in situ methylation with dimethyl sulfate [1,2]. Recrystallization from *n*-hexane gave 11% of colorless prisms (mp 398 K – 400 K). Main product of this transformation was the methylated monoenolate of the dione in 54% yield.

Discussion

This compound was prepared in context with studies on the dimerization of cyclic 1,2-diones [3]. The dimerization depends on the ring-size, and is especially pronounced for medium sized 7- and 8-membered cyclic diones [4]. The reaction parallels similar findings reported by Gibson (who used K_2CO_3/MeI) [5], but gave better results in terms of conversion, purity and product yields.

The structure contains two directly linked substituted six-membered rings with different conformations. The ring C1 to C6 forms an almost perfect chair conformation (dihedral angles 52.3° to 60.1°) whereas the second C11 to C16 ring exists as a half-chair. The atoms C11 to C14 and C16 lie within a plane with the atom C15 above it (angle 131.0°). The oxygen atom O2 takes part in an intramolecular hydrogen bond with the proton H1O of the O–H group (d(O2–H1O) = 2.03 Å, ∠O1–H1O–O2 = 124.1°). As a result of this hydrogen bridge the atoms C1, C2, O2, H1O and O1 form a planar five-membered ring.

Table 1. Data collection and handling.

Crystal:	colorless prism, size 0.15 × 0.15 × 0.20 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.96 cm^{-1}
Diffractometer, scan mode:	Nonius KappaCCD, φ/ω
$2\theta_{max}$:	54°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5190, 2635
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2242
$N(param)_{refined}$:	226
Programs:	SHELXS-97 [6], SHELXL-97 [7], SCHAKAL97 [8]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(3A)	2*i*	0.549(2)	0.398(2)	0.112(1)	0.058(4)
H(3B)	2*i*	0.567(2)	0.420(2)	0.236(1)	0.055(4)
H(4A)	2*i*	0.874(3)	0.271(2)	0.102(2)	0.070(5)
H(4B)	2*i*	0.752(3)	0.152(3)	0.219(2)	0.073(5)
H(5A)	2*i*	1.060(3)	0.241(3)	0.248(2)	0.071(5)
H(5B)	2*i*	0.887(2)	0.326(2)	0.322(2)	0.061(5)
H(6A)	2*i*	1.088(2)	0.530(2)	0.107(2)	0.060(4)
H(6B)	2*i*	1.129(2)	0.559(2)	0.223(1)	0.056(4)
H(14A)	2*i*	0.662(2)	0.609(3)	0.560(2)	0.068(5)
H(14B)	2*i*	0.589(2)	0.815(2)	0.573(1)	0.064(5)
H(15A)	2*i*	0.936(2)	0.804(2)	0.511(1)	0.059(4)
H(15B)	2*i*	0.830(2)	0.954(2)	0.415(1)	0.058(4)
H(16A)	2*i*	0.955(2)	0.577(2)	0.410(1)	0.056(4)
H(16B)	2*i*	1.042(3)	0.766(2)	0.326(1)	0.059(4)
H(17A)	2*i*	0.300(3)	0.910(3)	0.140(2)	0.080(6)
H(17B)	2*i*	0.349(3)	0.995(3)	0.240(2)	0.083(6)
H(17C)	2*i*	0.515(3)	0.990(3)	0.130(2)	0.079(6)
H(1O)	2*i*	0.881(3)	0.879(3)	0.047(2)	0.079(6)

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Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.8642(2)	0.6748(2)	0.17286(9)	0.0368(6)	0.0327(5)	0.0282(5)	-0.0023(4)	-0.0037(4)	-0.0048(4)
C(2)	2*i*	0.7177(2)	0.6135(2)	0.1096(1)	0.0463(7)	0.0380(6)	0.0297(5)	0.0017(5)	-0.0079(5)	-0.0101(5)
C(3)	2*i*	0.6388(2)	0.4212(2)	0.1610(1)	0.0633(9)	0.0405(7)	0.0441(7)	-0.0104(6)	-0.0123(6)	-0.0127(6)
C(4)	2*i*	0.8062(3)	0.2759(2)	0.1773(1)	0.089(1)	0.0340(7)	0.0469(8)	0.0009(7)	-0.0089(7)	-0.0120(6)
C(5)	2*i*	0.9510(2)	0.3280(2)	0.2433(1)	0.0656(9)	0.0416(7)	0.0475(8)	0.0161(6)	-0.0115(7)	-0.0083(6)
C(6)	2*i*	1.0274(2)	0.5228(2)	0.1838(1)	0.0435(7)	0.0502(7)	0.0404(7)	0.0080(5)	-0.0024(5)	-0.0134(6)
C(11)	2*i*	0.7791(2)	0.7041(1)	0.28952(9)	0.0349(6)	0.0290(5)	0.0282(5)	-0.0015(4)	-0.0072(4)	-0.0049(4)
C(12)	2*i*	0.5899(2)	0.7376(2)	0.31803(9)	0.0346(6)	0.0312(5)	0.0339(6)	-0.0023(4)	-0.0075(4)	-0.0085(4)
C(13)	2*i*	0.5074(2)	0.7568(2)	0.4339(1)	0.0424(7)	0.0409(6)	0.0443(7)	-0.0050(5)	0.0025(5)	-0.0166(5)
C(14)	2*i*	0.6483(2)	0.7458(2)	0.5171(1)	0.0617(8)	0.0511(8)	0.0340(6)	-0.0053(6)	-0.0016(6)	-0.0166(6)
C(15)	2*i*	0.8448(2)	0.8157(2)	0.4558(1)	0.0534(8)	0.0535(8)	0.0388(7)	-0.0061(6)	-0.0152(6)	-0.0159(6)
C(16)	2*i*	0.9218(2)	0.7089(2)	0.3692(1)	0.0384(7)	0.0592(8)	0.0372(6)	0.0004(6)	-0.0128(5)	-0.0155(6)
C(17)	2*i*	0.3988(2)	0.9243(2)	0.1831(2)	0.0491(8)	0.0503(8)	0.071(1)	0.0051(6)	-0.0263(8)	-0.0021(7)
O(1)	2*i*	0.9432(1)	0.8490(1)	0.10475(8)	0.0544(6)	0.0417(5)	0.0369(5)	-0.0136(4)	-0.0020(4)	-0.0022(4)
O(2)	2*i*	0.6915(2)	0.7118(1)	0.01532(7)	0.0705(6)	0.0519(6)	0.0329(5)	-0.0011(5)	-0.0183(4)	-0.0048(4)
O(3)	2*i*	0.4572(1)	0.7398(1)	0.24497(7)	0.0363(4)	0.0429(5)	0.0468(5)	-0.0010(3)	-0.0160(4)	-0.0104(4)
O(4)	2*i*	0.3339(2)	0.7736(2)	0.4597(1)	0.0425(6)	0.105(1)	0.0749(7)	-0.0027(6)	0.0088(5)	-0.0459(7)

References

1. Reuvers, J. T. A.; de Groot, A.: Total Synthesis of (±)-3β-Hydroxynagilactone F. J. Org. Chem. **51** (1986) 4594-4599.
2. Kuhn, R.; Egge, H.; Brossmaner, R.; Gauhe, A.; Klesse, P.; Lochinger, W.; Röhm, E.; Trischmann, H.; Tschampel, D.: Über die Ganglioside des Gehirns. Angew. Chem. **72** (1960) 805-811.
3. Kawada, K.; Gross, R. S.; Watt, D. S.: Swern Oxidation of α-Ketols to α-Diketones. Synth. Commun. **19** (1989) 777-785.
4. Rao, D. V.; Stuber, F. A.; Ulrich, H.: Base-Catalyzed Autoxidation of Cyclic Ketones. J. Org. Chem. **44** (1979) 456-458.
5. Gibson, M. S.: The O-Alkylation of Cyclohexane-1,2-dione. J. Chem. Soc. (1962) 681-682.
6. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
7. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
8. Keller, E.: Schakal 97/Windows 32. Universität Freiburg, Germany 1997.