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(1α,2β,5β,6α)-5,6-Dichloro-3-cyclohexene-1,2-diyl diacetate

Sema Öztürk,[a] Mehmet Akkurt,[a]* Arif Baran,[b] Hasan Seçen[b] and Orhan Büyükgüngör[c]

[a]Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey, [b]Department of Chemistry, Faculty of Arts and Sciences, Atatürk University, 25240 Erzurum, Turkey, and [c]Department of Physics, Ondokuz Mayıs University, 55139 Samsun, Turkey

Correspondence e-mail: akkurt@erciyes.edu.tr

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.049
wR factor = 0.149
Data-to-parameter ratio = 17.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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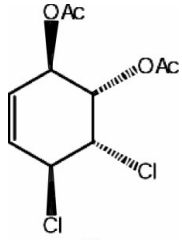
The reaction of *endo-cis*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-diol with BCl_3 followed by acetylation with acetyl chloride gives dichloroconduritol derivatives. The crystal structure of the title compound, $C_{10}H_{12}Cl_2O_4$, has been investigated. The cyclohexene ring adopts a distorted half-chair conformation.

Comment

Glycosidase inhibitors have become interesting as anti-obesity drugs, antidiabetics, antifungals, insecticides and antivirals, including substances active against the human immunodeficiency virus (HIV) and metastasis (Tatsuta, 1998). Bromoconduritol, a diastereomeric mixture of (1α,2β,3α,6β)-6-bromo-4-cyclohexene-1,2,3-triol and (1α,2β,3α,6α)-6-bromo-4-cyclohexene-1,2,3-triol, has been commonly used as a covalent irreversible active-site-directed glycosidase inhibitor (Elbein, 1987*a*,*b*, 1991; Legler, 1977; Salvucci, 2000; Trudel *et al.*, 1988, Alonso *et al.*, 1993). Other halogenated compounds (Guo *et al.*, 1993, 1994; Haines *et al.*, 1998; Hudlicky *et al.*, 1991) related to bromoconduritol have been synthesized. As part of an ongoing research program to design and synthesize novel haloconduritol compounds, we successfully used the diacetate and reported (Baran *et al.*, 2003, 2004) the efficient preparation of (1α,2α,3β,6β)-6-halo-4-cyclohexene-1,2,3-triols (halo = Cl or Br).



(I)

In this study, we report the crystal structure of the title compound, (I) (Fig. 1). The average C—Cl bond length is 1.796 (3) Å. All bond distances and angles agree with normal values in the literature (Allen *et al.*, 1987).

The two acetate groups are nearly coplanar [C3—O1—C7—O3 = 6.6 (4)° and C4—O2—C9—O4 = 3.6 (5)°]. The cyclohexene ring adopts a distorted half-chair conformation. The puckering parameters (Cremer & Pople, 1975) for the cyclohexene ring are Q = 0.511 (4) Å, θ = 49.2 (6)° and φ = 148.8 (7)°.

No hydrogen bonds are found in this structure.

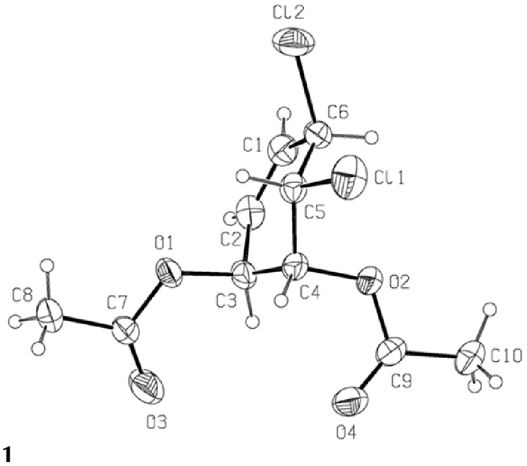


Figure 1
An view of the molecule of (I), with the atom-numbering scheme and 30% probability displacement ellipsoids.

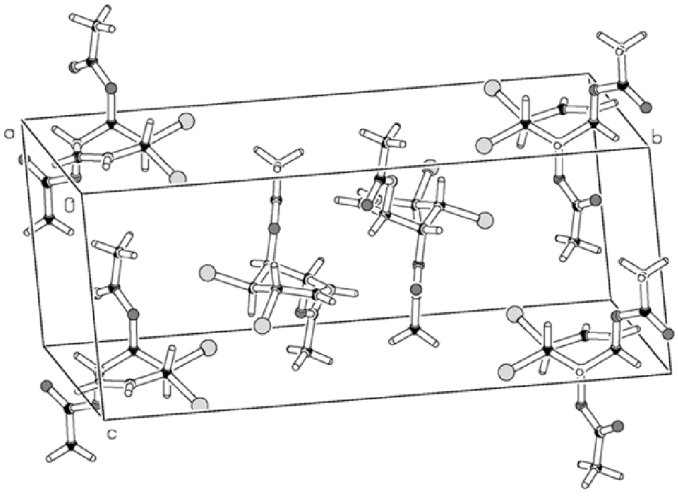


Figure 2
The packing of (I).

Experimental

Under a nitrogen atmosphere, to a stirred solution of *endo-cis*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-diol (1.00 g, 7.8 mmol) in 50 ml of CH_2Cl_2 was added BCl_3 (1.29 g, 11 mmol) at 195 K over 20 min. After the BCl_3 addition was complete, the mixture was stirred at 273 K for 5 h. To the reaction mixture was added 1 ml of water. The solvent was evaporated. To the residue was added 30 ml of CH_2Cl_2 and 3 ml of acetyl chloride. The reaction mixture was stirred at room temperature for 12 h. The solvents and excess acetyl chloride were evaporated. The mixture was chromatographed on basic Al_2O_3 (Active 1: 40 g), eluting with $CHCl_3$ (0.83 g, 40%); m.p. 359–361 K (from hexane–EtOAc). ^{1}H NMR (200 MHz, $CDCl_3$): δ 5.95–5.87 (*A* part of *AB* system, *ddt*, 1H, H_4, $J_{3,4}$ = 10.0 Hz, $J_{4,5}$ = 3.8 Hz, ^4J = 1.1 Hz), 5.81–5.75 (*B* part of *AB* system, *bdd*, 1H, H_3, $J_{3,4}$ = 10.0 Hz, $J_{2,3}$ = 2.5 Hz), 5.56–5.51 (*A* part of *AB* system, *dm*, 1H, H_2, $J_{1,2}$ = 6.8 Hz), 5.51–5.46 (*B* part of *AB* system, *bdd*, 1H, H_1, $J_{1,2}$ = 6.8 Hz, $J_{1,6}$ = 2.5 Hz), 4.66 (*A* part of *AX* system, *bddd*, 1H, H_5, $J_{5,6}$ = 4.4 Hz, $J_{4,5}$ = 3.8 Hz, ^4J = 0.8 Hz), 4.48 (*X* part of *AX* system, *ddd*, 1H, H_6, $J_{5,6}$ = 4.4 Hz, $J_{1,6}$ = 2.5 Hz, ^4J = 0.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.6 (C═O), 169.4 (C═O), 127.9 (C_3 or C_4), 126.8 (C_3 or C_4), 69.4 (C_1 or C_2), 68.3 (C_1 or C_2), 59.6 (C_5 or C_6), 56.0 (C_5 or C_6), 20.6 (CH_3), 20.5 (CH_3). Analysis calculated for $C_{10}H_{12}Cl_2O_4$: C 44.97, H 4.53%; found: C 44.76, H 4.45%.

Crystal data

$C_{10}H_{12}Cl_2O_4$	D_x = 1.477 Mg m^{-3}
M_r = 267.10	Mo Kα radiation
Monoclinic, $P2_1/n$	Cell parameters from 2616 reflections
a = 7.4270 (6) Å	θ = 1.9–26.9°
b = 21.6166 (15) Å	μ = 0.54 mm^{-1}
c = 8.3108 (7) Å	T = 293 K
β = 115.768 (6)°	Block, colorless
V = 1201.59 (17) Å^3	0.65 × 0.52 × 0.36 mm
Z = 4	

Data collection

Stoe IPDS-II diffractometer	2616 independent reflections
ω scans	1839 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)	R_{int} = 0.046
	θ_{max} = 27.2°
T_{min} = 0.722, T_{max} = 0.831	$h = -9 \rightarrow 9$
18742 measured reflections	$k = -27 \rightarrow 27$
	$l = -10 \rightarrow 10$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0871P)^2 + 0.1417P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.049	
$wR(F^2)$ = 0.149	
S = 1.07	$(\Delta/\sigma)_{max} < 0.001$
2616 reflections	$\Delta\rho_{max}$ = 0.48 e Å^{-3}
146 parameters	$\Delta\rho_{min}$ = −0.44 e Å^{-3}
H-atom parameters constrained	Extinction correction: *SHELXL*97
	Extinction coefficient: 0.013 (4)

Table 1
Selected geometric parameters (Å, °).

Cl1—C5	1.788 (2)	O2—C9	1.349 (3)
Cl2—C6	1.804 (3)	O3—C7	1.185 (4)
O1—C3	1.457 (3)	O4—C9	1.192 (4)
O1—C7	1.322 (4)	C3—C4	1.522 (4)
O2—C4	1.441 (3)		
C3—O1—C7	119.4 (2)	Cl2—C6—C1	108.21 (18)
C4—O2—C9	117.15 (18)	Cl2—C6—C5	109.35 (16)
O1—C3—C2	107.04 (19)	O1—C7—O3	122.5 (2)
O1—C3—C4	106.58 (19)	O1—C7—C8	111.5 (2)
O2—C4—C3	109.04 (19)	O3—C7—C8	126.0 (3)
O2—C4—C5	106.71 (19)	O2—C9—O4	122.4 (2)
Cl1—C5—C4	111.37 (17)	O2—C9—C10	111.3 (3)
Cl1—C5—C6	110.01 (17)	O4—C9—C10	126.4 (3)
C3—O1—C7—O3	6.6 (4)	C1—C2—C3—C4	−15.3 (3)
C7—O1—C3—C4	−119.3 (2)	O1—C3—C4—O2	170.22 (19)
C4—O2—C9—O4	3.6 (5)	O2—C4—C5—C6	57.9 (2)
C9—O2—C4—C3	−83.7 (3)		

H atoms were placed geometrically (C—H = 0.93–0.98 Å) and refined with a riding model, with U_{iso} = 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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