Crystal structure of (2*S*, 3*R*, 4*S*, 5*R*)-2-methylpiperidine-1,3,4,5-tetrol hydrochloride, $C_6H_{14}ClNO_4$

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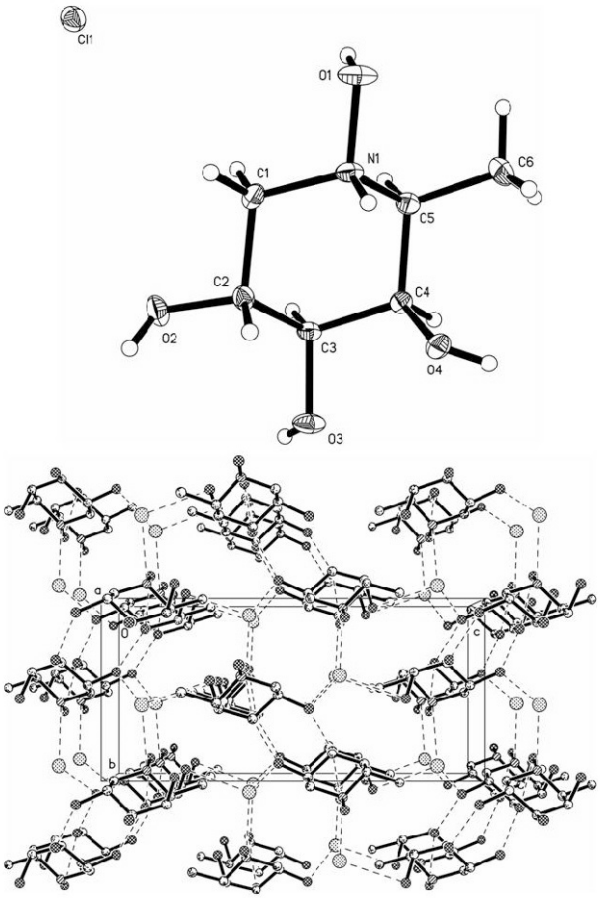
Received December 15, 2011, accepted May 30, 2012, available online July 19, 2012, CCDC no. 1267/3772



Abstract

$C_6H_{14}ClNO_4$, orthorhombic, $P2_12_12_1$ (no. 19), a = 6.4374(5) Å, b = 8.0297(6) Å, c = 16.811(1) Å, V = 868.9 Å^3, Z = 4, $R_{gt}(F)$ = 0.0251, $wR_{ref}(F^2)$ = 0.0615, T = 100 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.16×0.21×0.39 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	4.17 cm^{-1}
Diffractometer, scan mode:	Bruker Kappa APEX II Duo, ω and φ
$2\theta_{max}$:	61.1°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9571, 2664
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2520
$N(param)_{refined}$:	126
Programs:	SHELXS-97

Source of material

The 2-methylpiperidine framework was obtained by Cope-House cyclization of the respective 5-hexenose, derived from *L*-galactose [1-3]. The title compound was obtained by hydrolysis of this fully protected intermediate, the (2*S*, 3*R*, 4*R*, 5*R*)-5-O-tert-butyl-dimethylsilyl-2-methyl-3,4-O-isopropylidenpiperidine-1,3,4,5-tetraol [4, 5] in methanol and conc. hydrochloric acid. The crude product was recrystallized from methanol and dichloromethane to give colourless crystals (m.p. 418 K (decomp.)) [4]. The enantiomerically pure compound has $[\alpha]_D20$ = -7.8 (c = 1.02, CH_3OH).

Experimental details

H atoms were located by difference fourier techniques, but refined with fixed individual displacement parameters, using a riding model with d(C–H) ranging from 0.93 to 1.00 Å. H atoms of hydroxy functions were refined free, because of their relevance in hydrogen bond interactions. In addition, the methyl group is allowed to rotate but not to tip. The Flack parameter is 0.01(4) [7], which is in accordance with the absolute configuration resulting from the synthetic pathway.

Discussion

The title compound (figure, top) crystallizes with one independent ion pair in the asymmetric unit of the acentric space group $P2_12_12_1$. As expected, the piperidine ring system shows a chair conformation. The packing diagram (figure, bottom) shows a complex network of intermolecular hydrogen bonds, where the chloride anion works as threefold acceptor. The H1···Cl1 distance is 2.22 Å and the related angle N1–H1···Cl1 is 151°. The distances of H2A···Cl1 and H4A···Cl1 are 2.23(2) Å and 2.32(2) Å and the related angles O2–H2A···Cl1 and O4–H4A···Cl1 are 177(2)° and 165(2)°, respectively. Two more intermolecular hydrogen bonds are built up between two hydroxy functions, with distances H1C···O3 of 1.80(2) Å and H3A···O2 of 2.06(2) Å. The related angles O1-H1C···O3 and O3-H3A···O2 are 175(2)° and 158(2)°, respectively. The *bc*-view of the cell plot (figure, bottom) shows an alternate layer-type organization of the structure, built up by the piperidine moieties and the chloride anions. The layers have a diagonal orientation in the *ab*-plane and the stacking vector extends along the *bc*-diagonal.

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1C)	4*a*	0.394(3)	0.530(3)	0.878(1)	0.032(5)
H(1A)	4*a*	0.6502	0.4140	0.9715	0.018
H(1B)	4*a*	0.6971	0.6036	0.9953	0.018
H(1)	4*a*	0.7600	0.6589	0.8627	0.017
H(2A)	4*a*	1.087(3)	0.450(3)	1.061(1)	0.038(5)
H(2)	4*a*	1.0463	0.5792	0.9572	0.016
H(3A)	4*a*	1.287(3)	0.268(2)	0.916(1)	0.021(4)
H(3)	4*a*	0.9710	0.2387	0.9116	0.015
H(4A)	4*a*	1.098(2)	0.531(2)	0.746(1)	0.023(4)
H(4)	4*a*	0.9872	0.3101	0.7780	0.015
H(5)	4*a*	0.6456	0.3303	0.8300	0.018
H(6A)	4*a*	0.4924	0.4960	0.7333	0.035
H(6B)	4*a*	0.6878	0.4062	0.6930	0.035
H(6C)	4*a*	0.7037	0.5971	0.7196	0.035

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}
Cl(1)	4*a*	0.35480(4)	0.57813(3)	1.11903(1)	0.0153(1)	0.0141(1)	0.0142(1)	0.0012(1)	–0.0021(1)	–0.0016(1)
O(1)	4*a*	0.4673(1)	0.6234(1)	0.87288(6)	0.0086(4)	0.0192(4)	0.0366(5)	0.0023(3)	0.0008(4)	0.0029(4)
C(1)	4*a*	0.7318(2)	0.5140(2)	0.95709(7)	0.0159(5)	0.0184(6)	0.0119(5)	0.0009(4)	0.0032(4)	0.0003(4)
N(1)	4*a*	0.6764(1)	0.5681(1)	0.87509(6)	0.0090(4)	0.0143(4)	0.0186(4)	–0.0001(4)	0.0013(3)	0.0022(4)
O(2)	4*a*	0.9944(1)	0.4022(1)	1.03869(5)	0.0216(4)	0.0243(5)	0.0121(4)	–0.0097(4)	–0.0045(3)	0.0049(3)
C(2)	4*a*	0.9633(2)	0.4744(2)	0.96216(6)	0.0140(5)	0.0143(5)	0.0109(4)	–0.0033(4)	–0.0011(4)	0.0023(4)
O(3)	4*a*	1.2506(1)	0.3408(1)	0.89574(6)	0.0103(4)	0.0172(4)	0.0298(5)	0.0019(3)	–0.0004(3)	0.0089(4)
C(3)	4*a*	1.0289(2)	0.3509(1)	0.89838(6)	0.0090(5)	0.0117(5)	0.0161(5)	–0.0006(4)	–0.0003(4)	0.0019(4)
O(4)	4*a*	1.0634(1)	0.5475(1)	0.79209(5)	0.0141(4)	0.0132(4)	0.0138(3)	–0.0023(3)	0.0022(3)	0.0016(3)
C(4)	4*a*	0.9545(2)	0.4019(1)	0.81616(6)	0.0122(5)	0.0113(5)	0.0129(4)	–0.0010(4)	0.0006(3)	–0.0002(4)
C(5)	4*a*	0.7201(2)	0.4345(2)	0.81414(7)	0.0116(4)	0.0174(5)	0.0150(5)	–0.0020(4)	–0.0010(4)	–0.0005(5)
C(6)	4*a*	0.6443(2)	0.4882(2)	0.73285(7)	0.0177(5)	0.0361(7)	0.0163(5)	–0.0025(6)	–0.0062(5)	0.0030(5)

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