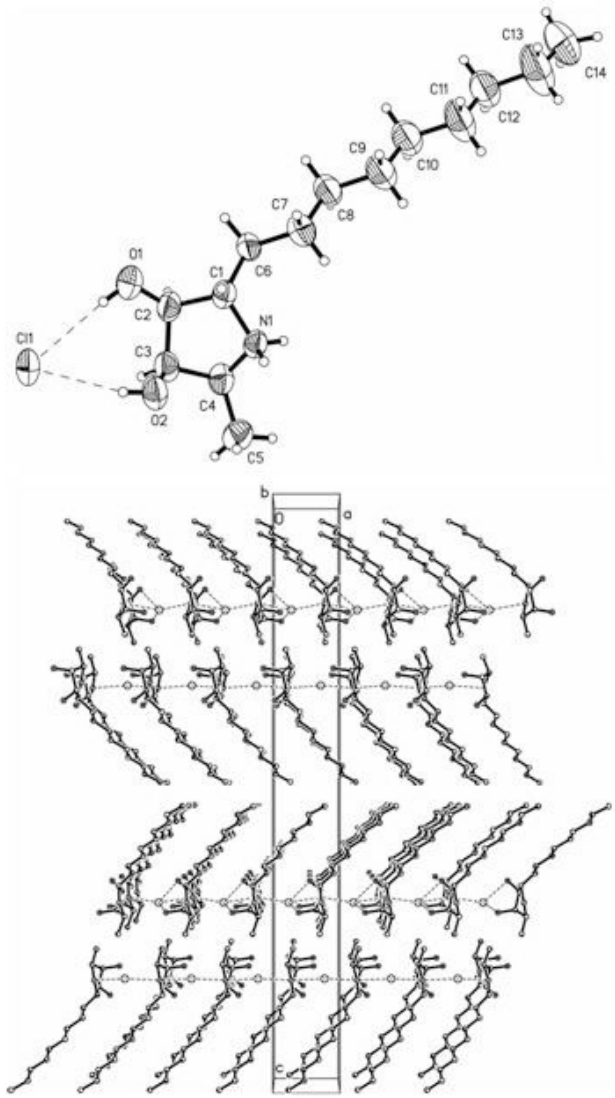
Crystal structure of (2*S*, 3*S*, 4*R*, 5*S*)-3,4-dihydroxy-5-methyl-2-nonyl-pyrrolidine hydrochloride, $C_{14}H_{30}ClNO_2$

Wolfgang Frey, Amélie Castiglia and Volker Jäger*

Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany

Received December 15, 2011, accepted May 30, 2012, available online July 19, 2012, CCDC no. 1267/3770



Abstract

$C_{14}H_{30}ClNO_2$, orthorhombic, $P2_12_12_1$ (no. 19), a = 5.268(1) Å, b = 6.786(1) Å, c = 46.941(9) Å, V = 1678.0 Å^3, Z = 4, $R_{gt}(F)$ = 0.0790, $wR_{ref}(F^2)$ = 0.1742, T = 295 K.

Source of material

The title compound was obtained by acidic cleavage in methanol of (2*S*,3*S*,4*R*,5*S*)-3,4-dihydroxy-3,4-O-isopropylidene-5-methyl-2-nonyl-pyrrolidine [1], which was derived from Grignard addition of *n*-nonylmagnesium bromide to (3*S*, 4*R*, 5*R*)-5-bromomethyl-3,4-isopropylidenedioxy-3,4-dihydro-5*H*-pyrrole-1-oxide [2-5]. The product was purified by recrystallization from a mixture of MeOH/EtO_2 to give spectroscopically pure, colourless crystals.

Analysis: m.p. 205-207°C, $[\alpha]_D20$ = -37.5 (c = 1.03, CH_3OH).

Table 1. Data collection and handling.

Crystal:	colourless needles, size 0.15×0.3×0.8 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.25 cm^{-1}
Diffractometer, scan mode:	Nicolet P3, Wyckoff-Scan
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4542, 3837
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2285
$N(param)_{refined}$:	181
Programs:	SHELXS-97 [6]

Experimental details

H atoms were located by inspection of the difference fourier map, but refined with fixed individual displacement parameters, using a riding model with d(C–H) ranging from 0.96 to 0.98 Å. In addition, the methyl group is allowed to rotate but not to tip. The hydrogen atoms attached to the hydroxy functions and to the ammonium ion are refined free with slight support of restraints. The Flack parameter is 0.00(17) [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 $P2_12_12_1$. A complex pattern of intermolecular hydrogen bonds is evident, where the chloride ion works as acceptor with a tetrahedral geometry. The donor functions are the hydroxy groups and the ammonium ion, which build up linear interactions. The distances are: H1A···Cl1, 2.25(3) Å; H1B···Cl1, 2.31(3) Å; H1C···Cl1, 2.43(3) Å and H2A···Cl1, 2.38(3) Å. The related angles are: N1–H1A···Cl1, 174(5)°; N1–H1B···Cl1, 170(5)°; O1–H1C···Cl1, 171(6)° and O2–H2A···Cl1, 156(6)°. We also observe a weak intramolecular hydrogen bond interaction between the hydroxy moieties. The distance H1C···O2 is 2.60(6) Å and the related angle O1–H1C···O2 is 97(4)°. The pyrrolidinium ion shows an envelope conformation where carbon C3 is out-of-plane (0.62 Å). The packing diagram of the cell plot (figure, bottom) is showing a bilayer-type stacking of alternate polar and non-polar regions with a stacking vector along the *c*-axis and layers which have their positions in the *ab*-plane. The polar interactions of the hydrogen atoms establish only single layers. In contrast, the non-polar moieties build up two types of bi-layers: The first type is formed by the methyl groups and the second type is generated by the nonyl moieties.

* Correspondence author (e-mail: jager.ioc@oc.uni-stuttgart.de)

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	4*a*	–0.364(8)	–0.150(7)	0.183(1)	0.09(2)
H(1B)	4*a*	–0.081(7)	–0.128(8)	0.185(1)	0.09(2)
H(1)	4*a*	–0.0360	0.0315	0.1458	0.055
H(1C)	4*a*	0.01(1)	0.466(7)	0.158(1)	0.08(2)
H(2A)	4*a*	0.20(1)	0.337(6)	0.199(1)	0.10(2)
H(2)	4*a*	–0.3902	0.3165	0.1629	0.072
H(3)	4*a*	–0.2179	0.3718	0.2070	0.065
H(4)	4*a*	–0.4662	0.0960	0.2066	0.068
H(5A)	4*a*	–0.2978	–0.1356	0.2377	0.127
H(5B)	4*a*	–0.2327	0.0753	0.2492	0.127
H(5C)	4*a*	–0.0244	–0.0490	0.2335	0.127
H(6A)	4*a*	–0.4022	0.1026	0.1178	0.065
H(6B)	4*a*	–0.5709	0.0155	0.1422	0.065
H(7A)	4*a*	–0.2310	–0.2022	0.1080	0.075
H(7B)	4*a*	–0.3582	–0.2943	0.1351	0.075

Table 2. continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(8A)	4*a*	–0.7580	–0.2498	0.1142	0.087
H(8B)	4*a*	–0.6274	–0.1636	0.0870	0.087
H(9A)	4*a*	–0.4534	–0.4664	0.0766	0.094
H(9B)	4*a*	–0.5649	–0.5546	0.1047	0.094
H(10A)	4*a*	–0.9680	–0.5211	0.0865	0.101
H(10B)	4*a*	–0.8539	–0.4368	0.0583	0.101
H(11A)	4*a*	–0.6745	–0.7349	0.0485	0.122
H(11B)	4*a*	–0.7822	–0.8197	0.0769	0.122
H(12A)	4*a*	–1.1836	–0.7988	0.0595	0.110
H(12B)	4*a*	–1.0802	–0.7080	0.0312	0.110
H(13A)	4*a*	–0.9002	–0.9964	0.0193	0.169
H(13B)	4*a*	–0.9823	–1.0889	0.0482	0.169
H(14A)	4*a*	–1.2231	–1.2140	0.0145	0.188
H(14B)	4*a*	–1.2987	–1.0043	0.0034	0.188
H(14C)	4*a*	–1.3966	–1.0771	0.0331	0.188

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*	0.2751(2)	0.6742(2)	0.18827(3)	0.0579(7)	0.0395(5)	0.0857(8)	–0.0122(6)	0.0020(7)	–0.0001(6)
N(1)	4*a*	–0.2272(8)	–0.0676(5)	0.18138(8)	0.044(2)	0.039(2)	0.060(2)	–0.005(2)	–0.006(2)	0.007(2)
C(1)	4*a*	–0.2028(9)	0.0552(6)	0.15439(9)	0.042(2)	0.040(2)	0.057(3)	–0.004(2)	–0.002(2)	0.005(2)
O(1)	4*a*	–0.056(1)	0.3849(7)	0.1484(1)	0.169(5)	0.077(3)	0.079(3)	–0.069(3)	–0.019(3)	0.021(3)
O(2)	4*a*	0.1122(7)	0.2385(5)	0.20105(8)	0.051(2)	0.044(2)	0.089(3)	–0.006(2)	–0.013(2)	0.000(2)
C(2)	4*a*	–0.216(1)	0.2686(6)	0.1650(1)	0.067(3)	0.037(2)	0.075(3)	–0.002(2)	–0.018(3)	0.008(2)
C(3)	4*a*	–0.1508(9)	0.2573(7)	0.1968(1)	0.055(3)	0.040(2)	0.068(3)	0.001(2)	–0.006(2)	–0.004(2)
C(4)	4*a*	–0.283(1)	0.0712(6)	0.2060(1)	0.058(3)	0.048(2)	0.064(3)	–0.007(3)	0.008(3)	–0.002(2)
C(5)	4*a*	–0.202(1)	–0.0177(8)	0.2342(1)	0.124(6)	0.069(3)	0.061(3)	–0.019(4)	0.005(4)	0.010(3)
C(6)	4*a*	–0.407(1)	0.0056(6)	0.1330(1)	0.064(3)	0.041(2)	0.057(3)	–0.002(2)	–0.010(3)	–0.004(2)
C(7)	4*a*	–0.381(1)	–0.1989(7)	0.1199(1)	0.062(3)	0.057(3)	0.068(3)	–0.002(3)	0.004(3)	–0.013(3)
C(8)	4*a*	–0.608(1)	–0.2584(8)	0.1023(1)	0.085(4)	0.057(3)	0.074(4)	–0.001(3)	–0.020(3)	–0.010(3)
C(9)	4*a*	–0.598(1)	–0.4613(8)	0.0895(1)	0.084(4)	0.068(4)	0.083(4)	0.001(3)	–0.015(4)	–0.020(3)
C(10)	4*a*	–0.823(1)	–0.5289(9)	0.0737(1)	0.093(5)	0.068(4)	0.091(4)	0.005(3)	–0.023(4)	–0.017(3)
C(11)	4*a*	–0.817(1)	–0.7285(9)	0.0615(2)	0.103(5)	0.071(4)	0.131(6)	0.008(4)	–0.043(5)	–0.037(4)
C(12)	4*a*	–1.042(1)	–0.8015(9)	0.0463(1)	0.104(5)	0.073(4)	0.097(5)	0.001(4)	–0.009(4)	–0.023(4)
C(13)	4*a*	–1.034(2)	–0.998(1)	0.0334(2)	0.135(8)	0.094(6)	0.194(9)	0.012(6)	–0.063(7)	–0.065(6)
C(14)	4*a*	–1.257(2)	–1.080(1)	0.0200(2)	0.128(7)	0.111(6)	0.137(6)	–0.026(6)	–0.013(6)	–0.050(5)

References

1. Castiglia, A.: Synthesis of Aryl-Substituted Pyrrolidinediols with Potent Activity as α-L-Fucosidase Inhibitors. Synthesis and Characterization of a new Chiral Guanidine and its Derived Guanidinium Salts. Dissertation, Universität Stuttgart (2011).
2. Frey, W.; Bierer, L.; Jäger, V.: Crystal structure of the (3*S*, 4*R*, 5*R*)-5-bromomethyl-3,4-isopropylidenedioxy-3,4-dihydro-5*H*-pyrrole-1-oxide, $C_8H_{12}BrNO_3$. Z. Kristallogr. NCS **218** (2003) 107-108.
3. Jäger, V.; Bierer, L.; Dong, H-D.; Palmer, A.; Shaw, D.; Frey, W.: New Heterocyclic Structures from Unsaturated Aldehyde Derivatives. Inhibition of α-L-Fucosidases. J. Heterocyclic Chem. **37** (2000) 455-465.
4. Gulla, M.; Bierer, L.; Schmidt, S.; Redcliffe, L.; Jäger, V.: Bromocyclization of Unsaturated Oximes. Synthesis of Five-Membered Cyclic Nitrones (Pyrroline N-Oxides). Z. Naturforsch. **61b** (2006) 471-485.
5. Gulla; M.; Bierer, L.; Redcliffe, L.; Schmidt, S.; Jäger, V.: Synthesis of cyclic nitrones by bromocyclization of unsaturated oximes. ARKIVOC **2006** (Vii), 76-88.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
7. Flack, H. D.: On enantiomorph-polarity estimation. Acta Crystallogr. **A39** (1983) 876-881.