Crystal structure of (2*S*,3*S*)-3-(1-adamantyl)-3-aminopropane-1,2-diol hydrochloride monohydrate, $[C_{13}H_{24}NO_2]Cl \cdot H_2O$

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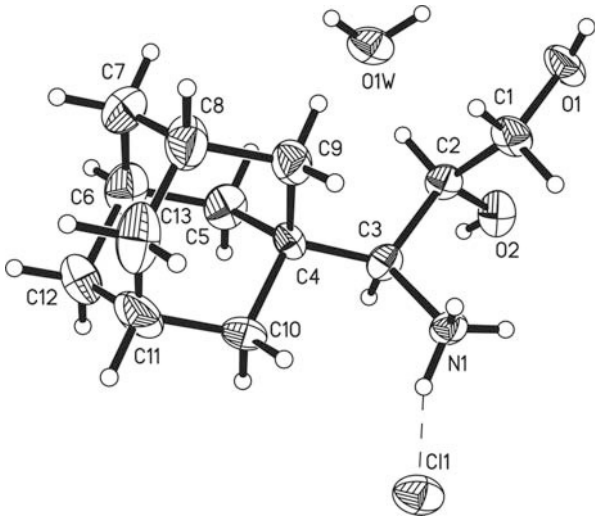

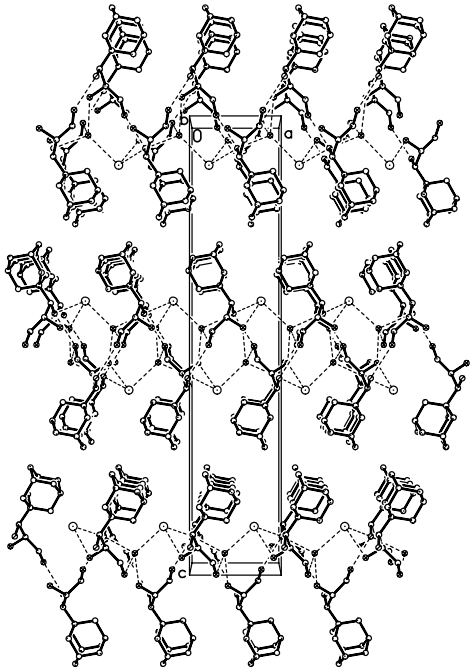

Abstract

$C_{13}H_{26}ClNO_3$, orthorhombic, $P2_12_12_1$ (no. 19), a = 6.532(2) Å, b = 6.746(2) Å, c = 32.690(9) Å, V = 1440.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.076, $wR_{ref}(F^2)$ = 0.187, T = 293 K.

Source of material

The title compound was prepared from 2,3-*O*-cyclohexylidene-*D*-glyceraldehyde *N*-benzylnitrone [1] by Grignard addition, hydrogenation, and finally treatment of the intermediate (2*S*,3*S*)-3-(1-adamantyl)-3-amino-1,2-*O*-cyclohexylidene-1,2-propanediol with concentrated hydrochloric acid [2,3]. The resulting colourless solid was purified by recrystallization from methanol/diethyl ether [2], mp. 235 °C (decomposition), $[\alpha]_D^{20} = 13$ (c = 0.91, MeOH).

Experimental detasils

H atoms were located on difference Fourier map, but refined with fixed individual displacement parameters using a riding model with d(C—H) ranging from 0.82 to 0.98 Å. In addition, the ammonium ion is allowed to rotate but not to tip and the H atoms of the hydroxy functions were allowed to rotate with respect to their typically geometric properties. The H atoms of the solvent water were refined free with a weak support of constraints for better convergence of the refinement and with respect of their relevance in hydrogen bond interaction. The refinement was converged with a short H1···H1C contact of 1.55 Å between the hydroxy function O1–H1 and the ammonium ion N1. This could be a result of the barely sufficient crystal quality indicated by R(int) = 0.106. The Flack's parameter is: x = 0.20(19). Possible twinnig effects could be not confirmed, because twin refinement strategies yields in no better results.

Discussion

The title compound crystallizes with one independent molecule and one water solvent molecule in the asymmetric unit of the acentric space group $P2_12_12_1$ (figure, top). The observed absolute configuration of the crystal structure, indicated by the absolute structure parameter of 0.20(19), is in accordance with the asymmetric direction of the synthetic pathway. The view along [010] (figure, bottom) shows a layer-type packing pattern in the *a*,*b*-plane. The non-polar layers are formed by the adamantyl moieties, and the polar ones by a complex network of intermolecular hydrogen bonds built up by hydroxy functions, chloride ions, and water molecules which are essential for the packing. The chloride anion acts as an acceptor showing a threefold coordination. Three types of donors build up nearly linear hydrogen bonds involved in this coordination. The H2A···Cl1 distance is 2.30 Å and the angle O2–H2A···Cl1 is 152°. The H1D···Cl distance of the ammonium ion donor is also 2.30 Å with an angle N1–H1D···Cl1 of 160°. The distance H1W···Cl1 of the water donor to the chloride acceptor is 2.22(2) Å and the relevant angle O1W–H1W···Cl1 is characterized by 160(6)°. The tetrahedral hydrogen bond coordination of the water molecule is completed by the contacts with the hydroxy functions and the ammonium ion. The relevant distances and an-

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gles are: N1–H1E···O1W (2.06 Å, 157°), O1W–H2W···O2 (2.04 Å, 154°), O1W–H2W···O1 (2.60 Å, 120°), respectively. The hydroxy group O1–H1 and the nitrogen N1 of the ammonium ion also establish a synergetic interaction. The H1···N1 distance is 2.37 Å with an angle O1–H1···N1 of 118°, the H1C···O1 distance is 2.00 Å, the relevant angle N1–H1C···O1 is 157°.

Table 1. Data collection and handling.

Crystal:	colorless block, size 0.15 × 0.25 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	2.67 cm^{-1}
Diffractometer, scan mode:	Nicolet P3, Wyckoff
$2\theta_{max}$:	49.94°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5918, 2514
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1825
$N(param)_{refined}$:	174
Programs:	SHELXS-97 [4], SHELXL-97 [5], SHELXTL-Plus [6]

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

Atom	Site	x	y	z	U_{iso}
H(1)	4*a*	1.4132	–0.0047	1.0032	0.060
H(1C)	4*a*	0.9662	0.4346	0.9530	0.042
H(1D)	4*a*	0.9422	0.5353	0.9140	0.042
H(1E)	4*a*	1.1451	0.5086	0.9314	0.042
H(1A)	4*a*	1.3834	0.1853	0.9552	0.040
H(1B)	4*a*	1.2125	0.2756	0.9833	0.040
H(2A)	4*a*	0.8281	0.0060	0.9452	0.056
H(2)	4*a*	1.1426	–0.0205	0.9237	0.033
H(3)	4*a*	0.9034	0.2245	0.8968	0.031
H(5A)	4*a*	1.1615	–0.0287	0.8549	0.047
H(5B)	4*a*	0.9776	0.0865	0.8351	0.047
H(6)	4*a*	1.2039	–0.0173	0.7837	0.055
H(7A)	4*a*	1.5411	0.1107	0.7823	0.075
H(7B)	4*a*	1.5088	–0.0160	0.8221	0.075
H(8)	4*a*	1.6653	0.2890	0.8396	0.063
H(9A)	4*a*	1.4398	0.3907	0.8914	0.045
H(9B)	4*a*	1.4446	0.1580	0.8896	0.045
H(10A)	4*a*	0.9712	0.4632	0.8375	0.046
H(10B)	4*a*	1.1514	0.5780	0.8587	0.046
H(11)	4*a*	1.1954	0.5875	0.7871	0.057
H(12A)	4*a*	1.2491	0.2923	0.7503	0.055
H(12B)	4*a*	1.0313	0.2872	0.7709	0.055
H(13A)	4*a*	1.4930	0.5883	0.8260	0.066
H(13B)	4*a*	1.5335	0.4750	0.7847	0.066
H(1W)	4*a*	1.495(5)	–0.34(1)	0.946(1)	0.09(3)
H(2W)	4*a*	1.419(8)	–0.382(9)	0.9871(7)	0.06(2)

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*	0.7074(2)	0.7775(2)	0.89891(4)	0.0436(7)	0.0279(6)	0.0519(7)	–0.0008(6)	–0.0080(6)	0.0024(6)
O(1)	4*a*	1.2903(7)	0.0040(5)	0.9984(1)	0.062(2)	0.024(2)	0.034(2)	0.006(2)	–0.018(2)	0.006(2)
N(1)	4*a*	1.0217(7)	0.4544(5)	0.9284(1)	0.034(2)	0.018(2)	0.032(2)	0.004(2)	0.004(2)	0.003(2)
C(1)	4*a*	1.2561(9)	0.1562(7)	0.9693(2)	0.049(3)	0.020(2)	0.032(3)	–0.002(2)	–0.004(3)	0.007(2)
O(2)	4*a*	0.9160(6)	0.0483(5)	0.9608(1)	0.047(2)	0.032(2)	0.034(2)	–0.011(2)	0.004(2)	–0.000(2)
C(2)	4*a*	1.0953(8)	0.0983(7)	0.9382(1)	0.038(3)	0.015(2)	0.030(3)	–0.001(2)	0.005(2)	0.004(2)
C(3)	4*a*	1.0417(7)	0.2571(6)	0.9063(1)	0.031(2)	0.017(2)	0.031(2)	–0.004(2)	0.000(2)	–0.006(2)
C(4)	4*a*	1.1728(7)	0.2734(7)	0.8673(1)	0.030(3)	0.020(2)	0.021(2)	–0.005(2)	–0.005(2)	0.003(2)
C(5)	4*a*	1.124(1)	0.0913(8)	0.8404(2)	0.056(4)	0.020(3)	0.043(3)	–0.007(2)	–0.005(3)	–0.010(2)
C(6)	4*a*	1.238(1)	0.0999(8)	0.8000(2)	0.067(5)	0.027(3)	0.044(3)	–0.005(3)	0.006(3)	–0.009(3)
C(7)	4*a*	1.467(1)	0.104(1)	0.8080(2)	0.080(6)	0.059(4)	0.048(4)	0.032(4)	0.010(4)	–0.006(3)
C(8)	4*a*	1.5177(9)	0.286(1)	0.8343(2)	0.036(3)	0.088(5)	0.034(3)	0.002(4)	0.001(2)	–0.003(4)
C(9)	4*a*	1.4043(7)	0.2765(9)	0.8749(2)	0.035(3)	0.047(3)	0.029(3)	0.000(3)	–0.005(2)	–0.003(3)
C(10)	4*a*	1.117(1)	0.4613(7)	0.8428(2)	0.051(4)	0.024(3)	0.040(3)	0.012(3)	0.000(3)	0.009(2)
C(11)	4*a*	1.234(1)	0.4669(8)	0.8020(2)	0.071(5)	0.032(3)	0.040(3)	0.002(3)	–0.006(3)	0.018(2)
C(12)	4*a*	1.1773(9)	0.2878(9)	0.7763(2)	0.051(3)	0.056(4)	0.032(3)	–0.003(3)	–0.009(3)	0.003(3)
C(13)	4*a*	1.459(1)	0.471(1)	0.8104(2)	0.067(5)	0.060(4)	0.037(4)	–0.024(4)	0.014(3)	–0.009(3)
O(1W)	4*a*	1.3819(6)	–0.3530(5)	0.9614(1)	0.047(2)	0.022(2)	0.049(2)	0.002(2)	–0.008(2)	0.003(2)

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