Crystal structure of (2*S*, 3*S*, 4*R*, 5*S*)-2-(4-iodophenyl)-3,4-O-isopropylidene-5-methyl-1,3,4-trihydroxypyrrolidine, $C_{14}H_{18}INO_3$

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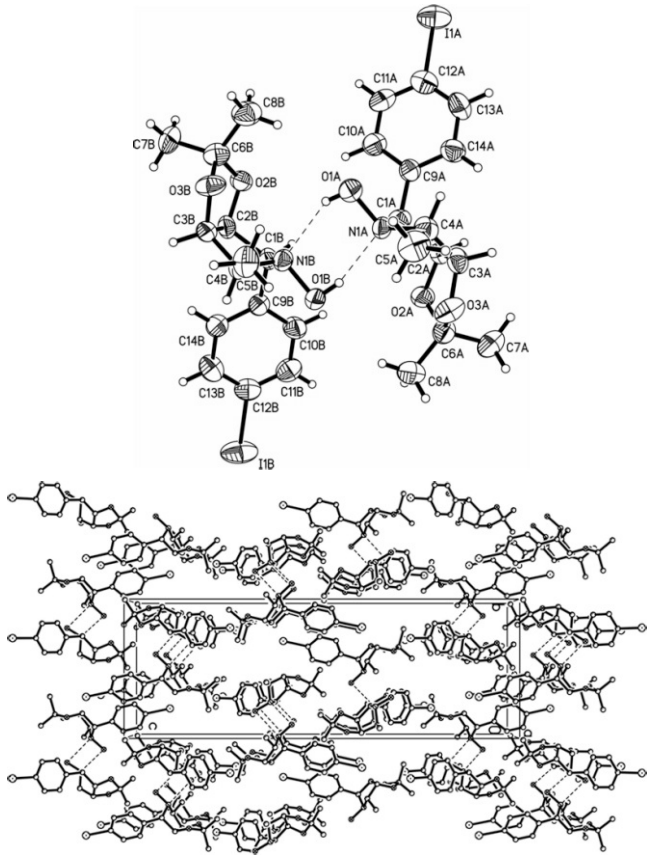

Abstract

$C_{14}H_{18}INO_3$, orthorhombic, $P2_12_12_1$ (no. 19), a = 8.925(2) Å, b = 11.141(2) Å, c = 31.595(5) Å, V = 3141.9 Å^3, Z = 8, $R_{gt}(F)$ = 0.0648, $wR_{ref}(F^2)$ = 0.1052, T = 295 K.

Table 1. Data collection and handling.

Crystal:	colourless blocks, size 0.25×0.45×0.60 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	20.42 cm^{-1}
Diffractometer, scan mode:	Nicolet P3, Wyckoff-Scan
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6199, 5529
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3528
$N(param)_{refined}$:	352
Programs:	SHELXS-97 [6]

Source of material

The title compound was obtained by reduction of the bromomethyl group of (2*R*,3*R*,4*S*,5*S*)-2-bromomethyl-3,4-O-isopropylidene-5-(4-iodophenyl)-1,3,4,-trihydroxypyrrolidine with lithium aluminium hydride $LiAlH_4$ [1]. The pyrrolidine derivate was derived from the Grignard addition of 4-iodophenylmagnesium chloride to (3*S*,4*R*,5*R*)-5-bromomethyl-3,4-isopropylidenedioxy-3,4-dihydro-5*H*-pyrrole-1-oxide [2-5]. The purification of the crude product by column chromatography (ethyl actetate / petroleum ether) afforded the title product as colourless, analytically pure crystals.

Analysis: m.p. 144-146°C, $[\alpha]_D20$ = 27 (c = 0.28, CH_2Cl_2).

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Experimental details

H atoms were located in the difference fourier map, but refined with fixed individual displacement parameters, using a riding model with d(C–H) ranging from 0.93 to 0.98 Å. The hydrogen atoms attached at the hydroxy functions were refined free with slight support of restraints, because of their relevance to hydrogen bond interactions. The Flack parameter is -0.14(4) [7], which is in accordance with the absolute configuration resulting from the synthetic pathway. For better overview the displacement parameters are drawn with 40 % probability.

Discussion

The title compound (figure, top) crystallizes with two independent molecules in the asymmetric unit of the acentric space group $P2_12_12_1$. The bond lengths N1A–O1A and N1B–O1B of the hydroxyaminofunctions were 1.419(9) Å and 1.442(9) Å. One hydroxylamino moiety establishes an intermolecular hydrogen bond to another one and works as OH-donor and also as N-acceptor vice versa (figure, top). The distances H1AA···N1B and H1BB···N1A are 2.12(4) Å and 1.96(3) Å and the related angles O1A–H1AA···N1B and O1B–H1BB···N1A are 149(7)° and 162(8)° which indicates a nearly linear interaction. The pyrrolidine and dioxolane ring systems of molecules A and B were showing an envelope conformation, where the nitrogen (N1A, N1B) and carbon atoms (C6A, C6B) are out-of-plane. The nitrogen atoms show a larger deviation (0.66 Å) than the carbon atoms (0.48 Å). The cell plot of the packing diagram shows an alternate stacking of polar and non-polar layers along the c-axis (figure, bottom). The non-polar layers are formed by the phenyl and the methyl groups and the polar ones are built up by the iodine and the hydroxylamino moieties. The view is along the *a*-axis.

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

Atom	Site	x	y	z	U_{iso}
H(1AA)	4*a*	0.560(9)	0.370(3)	0.342(2)	0.02(2)
H(1A)	4*a*	0.3338	0.3153	0.3946	0.065
H(2A)	4*a*	0.2543	0.0971	0.4128	0.053
H(3A)	4*a*	0.4506	–0.0256	0.3981	0.070
H(4A)	4*a*	0.5125	0.0791	0.3394	0.071
H(5A1)	4*a*	0.7643	0.1319	0.3356	0.121
H(5A2)	4*a*	0.7550	0.0117	0.3613	0.121
H(5A3)	4*a*	0.7781	0.1339	0.3850	0.121

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(7A1)	4*a*	0.4738	–0.0435	0.5087	0.124
H(7A2)	4*a*	0.3488	–0.0368	0.4739	0.124
H(7A3)	4*a*	0.3345	0.0402	0.5153	0.124
H(8A1)	4*a*	0.6512	0.1293	0.5178	0.135
H(8A2)	4*a*	0.5209	0.2222	0.5237	0.135
H(8A3)	4*a*	0.6389	0.2403	0.4875	0.135
H(10A)	4*a*	0.2512	0.4063	0.3301	0.075
H(11A)	4*a*	0.0877	0.3976	0.2730	0.086
H(13A)	4*a*	0.0628	0.0445	0.2844	0.090
H(14A)	4*a*	0.2266	0.0495	0.3415	0.080
H(1BB)	4*a*	0.624(9)	0.338(5)	0.412(2)	0.06(3)
H(1B)	4*a*	0.4158	0.5336	0.4014	0.057
H(2B)	4*a*	0.5145	0.7483	0.3836	0.062
H(3B)	4*a*	0.7590	0.7318	0.3629	0.064

Table 2. continued.

Atom	Site	x	y	z	U_{iso}
H(4B)	4*a*	0.8046	0.5846	0.4106	0.057
H(5B1)	4*a*	0.9184	0.4184	0.3814	0.109
H(5B2)	4*a*	0.9711	0.5328	0.3567	0.109
H(5B3)	4*a*	0.8496	0.4480	0.3369	0.109
H(7B1)	4*a*	0.4452	0.8127	0.2772	0.127
H(7B2)	4*a*	0.6157	0.8088	0.2654	0.127
H(7B3)	4*a*	0.5664	0.8434	0.3115	0.127
H(8B1)	4*a*	0.4097	0.5985	0.2548	0.120
H(8B2)	4*a*	0.5053	0.4967	0.2758	0.120
H(8B3)	4*a*	0.5790	0.5833	0.2427	0.120
H(10B)	4*a*	0.4061	0.4737	0.4743	0.078
H(11B)	4*a*	0.4363	0.5204	0.5458	0.086
H(13B)	4*a*	0.6928	0.8014	0.5139	0.083
H(14B)	4*a*	0.6610	0.7548	0.4430	0.068

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}
I(1A)	4*a*	–0.0915(1)	0.21803(9)	0.22295(2)	0.0845(5)	0.1334(8)	0.0722(5)	0.0187(6)	–0.0211(5)	–0.0035(5)
O(1A)	4*a*	0.5511(8)	0.3024(7)	0.3318(2)	0.085(5)	0.064(5)	0.049(4)	–0.015(5)	0.003(3)	0.003(4)
N(1A)	4*a*	0.5208(8)	0.2391(6)	0.3698(2)	0.061(5)	0.036(5)	0.045(4)	–0.001(4)	0.004(3)	0.000(3)
C(1A)	4*a*	0.356(1)	0.2397(8)	0.3801(2)	0.070(6)	0.053(6)	0.039(4)	0.008(5)	0.002(4)	–0.004(4)
O(2A)	4*a*	0.3844(7)	0.1886(5)	0.4533(2)	0.077(5)	0.058(4)	0.047(3)	0.005(4)	–0.002(3)	–0.005(3)
C(2A)	4*a*	0.3501(9)	0.1400(8)	0.4130(3)	0.037(5)	0.044(5)	0.052(5)	0.000(4)	0.000(4)	–0.002(4)
O(3A)	4*a*	0.5751(8)	0.0648(6)	0.4399(2)	0.058(4)	0.085(5)	0.060(4)	0.026(4)	0.013(4)	0.015(4)
C(3A)	4*a*	0.483(1)	0.0570(9)	0.4034(3)	0.068(7)	0.046(6)	0.061(6)	–0.004(5)	0.011(6)	–0.010(5)
C(4A)	4*a*	0.560(1)	0.1105(9)	0.3651(3)	0.066(7)	0.057(7)	0.054(6)	0.001(6)	0.008(5)	–0.010(5)
C(5A)	4*a*	0.730(1)	0.096(1)	0.3614(3)	0.067(8)	0.10(1)	0.078(8)	0.011(7)	0.021(6)	–0.003(7)
C(6A)	4*a*	0.486(1)	0.1098(9)	0.4735(3)	0.067(7)	0.059(7)	0.062(7)	–0.002(6)	0.003(6)	0.006(6)
C(7A)	4*a*	0.403(2)	0.0082(9)	0.4948(3)	0.098(9)	0.077(8)	0.073(7)	0.013(9)	0.006(8)	0.019(6)
C(8A)	4*a*	0.583(1)	0.182(1)	0.5033(3)	0.100(8)	0.101(9)	0.070(6)	–0.020(9)	–0.025(7)	0.008(7)
C(9A)	4*a*	0.249(1)	0.2297(9)	0.3429(3)	0.058(6)	0.047(7)	0.053(6)	0.005(6)	0.003(4)	–0.005(5)
C(10A)	4*a*	0.212(1)	0.333(1)	0.3215(3)	0.079(8)	0.054(7)	0.054(6)	0.014(6)	0.003(6)	–0.006(5)
C(11A)	4*a*	0.115(1)	0.328(1)	0.2871(3)	0.083(8)	0.077(8)	0.054(6)	0.015(7)	0.004(6)	0.014(5)
C(12A)	4*a*	0.060(1)	0.221(1)	0.2742(3)	0.050(6)	0.087(8)	0.059(6)	0.003(7)	0.010(5)	–0.012(7)
C(13A)	4*a*	0.100(1)	0.118(1)	0.2940(3)	0.068(7)	0.064(8)	0.093(8)	–0.010(7)	–0.012(7)	–0.014(6)
C(14A)	4*a*	0.197(1)	0.120(1)	0.3284(3)	0.068(7)	0.067(8)	0.065(7)	0.003(6)	–0.011(6)	–0.003(6)
I(1B)	4*a*	0.6058(1)	0.70339(9)	0.60034(2)	0.1285(7)	0.1277(7)	0.0528(4)	0.0556(7)	–0.0095(5)	–0.0278(5)
O(1B)	4*a*	0.6609(8)	0.3957(6)	0.4244(2)	0.086(5)	0.042(4)	0.047(4)	–0.007(4)	–0.007(4)	0.003(3)
N(1B)	4*a*	0.6318(8)	0.4824(6)	0.3916(2)	0.061(5)	0.039(4)	0.048(4)	0.001(4)	0.002(4)	0.001(3)
C(1B)	4*a*	0.515(1)	0.5697(8)	0.4053(3)	0.056(6)	0.040(5)	0.047(5)	–0.008(5)	0.006(5)	–0.005(4)
C(2B)	4*a*	0.538(1)	0.6684(8)	0.3723(3)	0.059(6)	0.037(6)	0.058(6)	–0.009(5)	0.002(5)	–0.003(5)
O(2B)	4*a*	0.4532(7)	0.6416(6)	0.3354(2)	0.053(4)	0.062(4)	0.047(4)	–0.006(4)	–0.002(3)	–0.003(3)
O(3B)	4*a*	0.6950(7)	0.6294(7)	0.3150(2)	0.055(4)	0.106(6)	0.039(4)	0.005(4)	0.006(3)	0.006(4)
C(3B)	4*a*	0.703(1)	0.6573(9)	0.3580(3)	0.050(6)	0.060(7)	0.050(5)	–0.015(5)	–0.008(5)	0.006(5)
C(4B)	4*a*	0.767(1)	0.5536(8)	0.3836(3)	0.047(6)	0.041(6)	0.055(6)	0.002(5)	0.004(5)	0.001(5)
C(5B)	4*a*	0.887(1)	0.4818(8)	0.3628(3)	0.062(7)	0.064(7)	0.091(8)	0.001(6)	0.011(7)	0.001(6)
C(6B)	4*a*	0.550(1)	0.662(1)	0.3003(3)	0.058(7)	0.074(8)	0.052(6)	0.008(6)	0.007(5)	–0.003(5)
C(7B)	4*a*	0.544(1)	0.7940(9)	0.2874(3)	0.11(1)	0.055(7)	0.091(8)	–0.008(7)	–0.013(7)	0.027(7)
C(8B)	4*a*	0.507(1)	0.577(1)	0.2653(3)	0.099(9)	0.083(9)	0.058(7)	0.012(7)	0.004(7)	–0.008(6)
C(9B)	4*a*	0.532(1)	0.6088(8)	0.4509(3)	0.060(6)	0.043(6)	0.047(5)	0.007(5)	0.005(5)	–0.005(4)
C(10B)	4*a*	0.464(1)	0.540(1)	0.4821(3)	0.076(8)	0.074(7)	0.046(6)	–0.013(6)	0.007(5)	–0.008(5)
C(11B)	4*a*	0.482(1)	0.567(1)	0.5252(3)	0.076(8)	0.078(8)	0.060(7)	0.010(7)	0.009(6)	0.006(6)
C(12B)	4*a*	0.569(1)	0.664(1)	0.5363(3)	0.064(7)	0.078(8)	0.049(5)	0.013(6)	0.005(5)	–0.010(5)
C(13B)	4*a*	0.636(1)	0.735(1)	0.5061(3)	0.077(8)	0.055(7)	0.076(7)	0.010(6)	0.007(6)	–0.027(6)
C(14B)	4*a*	0.616(1)	0.7068(8)	0.4635(2)	0.074(6)	0.047(5)	0.048(5)	0.007(6)	0.006(5)	–0.007(5)

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