Crystal structure of 1*R*,5*S*,8*R*,9*S*-8-azidomethyl-2-benzyl-6,6-dimethyl-3,7-dioxo-2-aza-bicyclo[3.3.1]nonan-9-ol, C₁₆H₂₂N₄O₃

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Abstract

C₁₆H₂₂N₄O₃, orthorhombic, *P*2₁2₁2₁ (no. 19), *a* = 5.959(5) Å, *b* = 8.099(5) Å, *c* = 33.942(5) Å, *V* = 1638.1 Å³, *Z* = 4, *R*_{gt}(*F*) = 0.051, *wR*_{ref}(*F*²) = 0.113, *T* = 173 K.

Source of material

The title compound was obtained by reaction of the corresponding mesylated bicyclic alcohol with sodium azide as described in [1,2], purified by chromatography on silica gel and recrystallized from hexane/ethyl acetate (m.p. 420–422 K).

Experimental details

The relevant hydrogen positions H1, H5 and H8 were located in the Fourier difference map and refined, whereas all other hydrogen positions were calculated with idealized distances (*d*(C—H) = 0.93 Å or 0.97 Å) and constrained to ride on their parent atoms with *U*_{iso}(H) = 1.2 *U*_{eq}(C) for the methylene and *U*_{iso}(H) = 1.5 *U*_{eq}(C) for the methyl H atoms. The low *N*_{gt}/*N*_{param} ratio is due to the poor quality of the crystals.

Discussion

The crystal structure proves the constitution and configuration of the four stereogenic centres (C1, C5, C8 and C9) and also shows interesting details of the conformation of the tetrahydropyran

bridged bicyclic 1,2-oxazine derivative with two chair conformations of both six-membered rings. Bonding distances and bond angles show normal values.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.02 × 0.05 × 0.4 mm
Wavelength:	Mo <i>K</i> _α radiation (0.71069 Å)
<i>μ</i> :	0.91 cm ^{−1}
Diffractometer, scan mode:	Bruker SMART CCD, <i>φ/ω</i>
2 θ _{max} :	41.62°
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} :	8672, 1690
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ (<i>I</i> _{obs}), 1281
<i>N</i> (<i>param</i>) _{refined} :	227
Programs:	SHELXS-97 [3], SHELXL-97 [4], ORTEP-3 [5]

Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso}
H(4A)	4a	0.3833	−0.1919	0.1935	0.030
H(4B)	4a	0.2309	−0.2343	0.1571	0.030
H(9)	4a	−0.0369	−0.0716	0.1327	0.035
H(10A)	4a	−0.0241	0.2873	0.2032	0.069
H(10B)	4a	0.1615	0.3486	0.2325	0.069
H(10C)	4a	0.0121	0.1960	0.2434	0.069
H(11A)	4a	0.4870	0.1897	0.2455	0.063
H(11B)	4a	0.5550	0.0379	0.2195	0.063
H(11C)	4a	0.3693	0.0187	0.2519	0.063
H(12A)	4a	0.5860	0.2924	0.1119	0.037
H(12B)	4a	0.3930	0.3598	0.0849	0.037
H(13A)	4a	0.1793	−0.1669	0.0844	0.046
H(13B)	4a	0.4318	−0.2227	0.0838	0.046
H(15)	4a	0.0708	−0.1632	0.0177	0.038
H(16)	4a	0.1175	−0.0714	−0.0474	0.043
H(17)	4a	0.4252	0.0891	−0.0635	0.051
H(18)	4a	0.6903	0.1563	−0.0161	0.044
H(19)	4a	0.6432	0.0595	0.0470	0.036
H(3O)	4a	−0.31(1)	0.077(9)	0.158(2)	0.13(3)
H(1)	4a	0.137(7)	0.127(5)	0.096(1)	0.00(1)
H(5)	4a	0.036(7)	−0.067(5)	0.202(1)	0.01(1)
H(8)	4a	0.14(1)	0.337(7)	0.140(2)	0.05(2)

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
O(1)	4a	0.4782(6)	−0.0769(4)	0.14421(9)	0.027(2)	0.019(2)	0.022(2)	0.003(2)	−0.003(2)	0.006(2)
O(2)	4a	0.3841(5)	0.2347(4)	0.1742(1)	0.025(2)	0.026(2)	0.023(2)	−0.004(2)	0.003(2)	0.001(2)
O(3)	4a	−0.1548(7)	0.1466(5)	0.1485(1)	0.024(3)	0.055(3)	0.065(3)	0.005(3)	0.001(3)	0.003(2)

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Table 3. Continued.

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
N(1)	4a	0.3862(7)	−0.0022(5)	0.1088(1)	0.032(3)	0.017(3)	0.020(2)	0.006(2)	−0.008(2)	0.004(2)
N(2)	4a	0.4925(9)	0.5225(5)	0.1256(1)	0.054(4)	0.025(3)	0.041(3)	−0.001(3)	−0.011(3)	0.002(3)
N(3)	4a	0.661(1)	0.5410(6)	0.1463(2)	0.049(4)	0.026(3)	0.038(3)	0.008(3)	0.008(3)	−0.002(3)
N(4)	4a	0.812(1)	0.5777(7)	0.1654(2)	0.059(5)	0.057(4)	0.084(5)	−0.001(4)	−0.027(4)	−0.022(3)
C(1)	4a	0.195(1)	0.1059(7)	0.1181(2)	0.023(4)	0.023(4)	0.023(4)	−0.002(3)	−0.012(3)	0.000(3)
C(4)	4a	0.3105(9)	−0.1459(7)	0.1704(2)	0.031(4)	0.022(3)	0.022(3)	0.001(3)	−0.001(3)	0.007(3)
C(5)	4a	0.145(1)	−0.0131(7)	0.1830(2)	0.027(4)	0.027(4)	0.021(3)	−0.008(3)	0.000(3)	0.006(3)
C(6)	4a	0.2550(9)	0.1389(7)	0.2028(2)	0.027(4)	0.031(4)	0.023(3)	0.009(3)	0.004(3)	0.002(3)
C(8)	4a	0.278(1)	0.2690(7)	0.1369(2)	0.028(4)	0.024(4)	0.023(4)	0.001(3)	−0.004(3)	−0.002(3)
C(9)	4a	0.0212(9)	0.0296(7)	0.1447(2)	0.019(3)	0.029(3)	0.039(4)	−0.008(3)	−0.002(3)	0.002(3)
C(10)	4a	0.086(1)	0.2533(7)	0.2223(2)	0.050(5)	0.046(4)	0.042(4)	−0.004(4)	0.013(4)	−0.016(3)
C(11)	4a	0.433(1)	0.0920(7)	0.2327(2)	0.043(4)	0.059(4)	0.023(3)	−0.001(4)	0.000(3)	0.004(3)
C(12)	4a	0.447(1)	0.3552(6)	0.1118(2)	0.051(4)	0.015(3)	0.028(3)	−0.005(3)	−0.006(3)	−0.005(3)
C(13)	4a	0.332(1)	−0.1292(7)	0.0803(1)	0.066(5)	0.027(3)	0.021(3)	0.001(4)	0.007(3)	−0.005(3)
C(14)	4a	0.357(1)	−0.0609(6)	0.0388(2)	0.031(4)	0.021(3)	0.028(3)	0.000(3)	−0.001(3)	−0.002(3)
C(15)	4a	0.195(1)	−0.1004(6)	0.0108(2)	0.035(4)	0.021(4)	0.038(4)	0.000(3)	0.004(4)	−0.004(3)
C(16)	4a	0.223(1)	−0.0443(7)	−0.0282(2)	0.045(4)	0.035(4)	0.028(4)	0.001(4)	−0.010(3)	0.000(3)
C(17)	4a	0.408(1)	0.0515(7)	−0.0378(2)	0.064(5)	0.037(4)	0.027(3)	−0.006(4)	−0.005(4)	0.000(3)
C(18)	4a	0.567(1)	0.0917(7)	−0.0097(2)	0.039(4)	0.039(4)	0.033(4)	−0.010(3)	0.011(3)	−0.010(3)
C(19)	4a	0.536(1)	0.0335(7)	0.0280(2)	0.030(4)	0.037(4)	0.022(4)	0.001(3)	−0.003(3)	−0.003(3)

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References

1. Al-Harrasi, A.; Reissig, H.-U.: Synthesis of Enantiopure Carbohydrate Mimetics by Lewis Acid Catalyzed Rearrangement of 1,3-Dioxolanyl-Substituted 1,2-Oxazines. *Angew. Chem.* **117** (2005) 6383–6387, *Angew. Chem. Int. Ed.* **44** (2005) 6227–6231.
2. Al-Harrasi, A.: New Transformations of Enantiopure 3,6-Dihydro-2H-1,2-oxazines: Ring Cleavages, Ring Enlargements and a Novel Approach to Carbohydrate Mimetics. Dissertation, Freie Universität Berlin 2005.
3. Sheldrick, G. M.: Phase Annealing in SHELX-90: Direct Methods for Larger Structures. *Acta Crystallogr. A* **46** (1990) 467–473.
4. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
5. Farrugia, L. J.: ORTEP-3 for Windows – a version of ORTEP-III with a Graphical User Interface (GUI). *J. Appl. Crystallogr.* **30** (1997) 565.