Crystal structure of (1*S*,2*R*,4*S*)-1-[(morpholin-4-yl)-methyl]-4-(prop-1-en-2-yl)cyclohexane-1,2-diol

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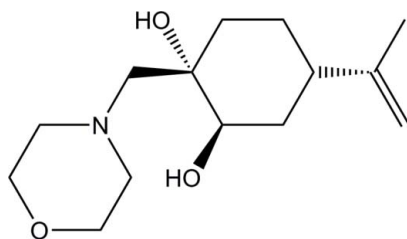
The asymmetric unit of the title compound, $C_{14}H_{25}NO_3$, contains two independent molecules with similar geometry. The morpholine and cyclohexane rings of both molecules adopt a chair conformation. Intramolecular O—H···N hydrogen bonds are observed. In the crystal, molecules are linked by O—H···O hydrogen bonds into chains parallel to the [101] direction. The chains are further connected through C—H···O hydrogen bonds forming undulating layers parallel to the ($\bar{1}$01) plane. The absolute configuration was assigned by reference to an unchanging chiral centre in the synthetic procedure.

1. Chemical context

1,2-Aminoalcohols are important building blocks in the synthesis of natural products, pharmaceuticals and other materials (Möller, 1957). The classical synthetic approach towards aminoalcohols involves aminolysis of epoxides with an excess of amines. There are some limitations to this classical approach, such as the requirement of elevated reaction temperatures in the case of less reactive amines, lower reactivity for sterically crowded amines/epoxides, and poor regioselectivity of the epoxide ring opening (Sello *et al.*, 2006). To obviate these problems, various methodologies to undertake epoxide opening under milder conditions have been developed (Surendra *et al.*, 2005), but there are still many limitations, such as the formation of bisalkylated products, longer reaction times, stoichiometric amounts of catalysts and harsh reaction conditions.

Recently, we have shown that calcium(II) compounds are very useful, environmentally friendly catalysts for several acid-catalysed reactions (Harrad *et al.*, 2010). Moreover, calcium triflate works under almost neutral conditions. In a continuation of our ongoing program on the aminolysis of 1,2-epoxides using a mild, practical and efficient method under solvent-free conditions (Outouch, Boualy, Ali *et al.*, 2011; Outouch, Boualy, El Firdoussi *et al.*, 2011; Outouch *et al.*, 2014), we report herein the synthesis and crystal structure of a new aminodiol from epoxyperillyl alcohol, which can be used as a chiral ligand for catalytic enantioselective transformations. The title compound was prepared by condensation of epoxyperillyl alcohol with morpholine using a catalytic amount of $Ca(CF_3COO)_2$ under solvent-free conditions according to the procedure described previously (Outouch, Boualy, Ali *et al.*, 2011; Outouch, Boualy, El Firdoussi *et al.*, 2011).

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O2—H2A$\cdots$N1	0.86 (2)	1.91 (2)	2.7118 (19)	154 (2)
O5—H5A$\cdots$N2	0.83 (3)	1.90 (3)	2.6697 (18)	155 (3)
O1—H1A$\cdots$O5^{i}	0.84 (3)	1.95 (3)	2.7595 (18)	164 (3)
O4—H4A$\cdots$O2	0.84 (3)	2.00 (3)	2.8249 (17)	167 (2)
C9—H9B$\cdots$O6^{ii}	0.99	2.35	3.269 (2)	155
C24—H24A$\cdots$O3^{iii}	0.99	2.45	3.344 (2)	150

Symmetry codes: (i) $x + 1, y, z + 1$; (ii) $-x, y + \frac{1}{2}, -z + 1$; (iii) $-x, y - \frac{1}{2}, -z + 1$.
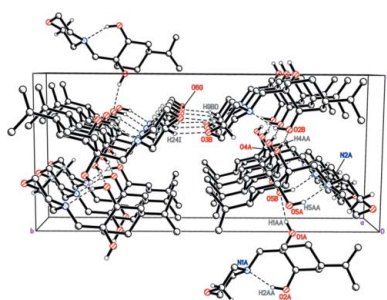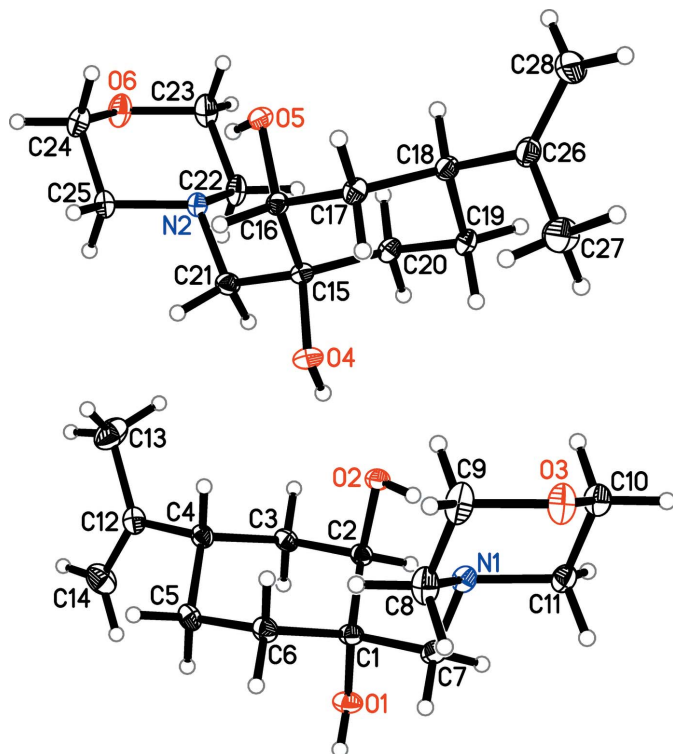
2. Structural commentary

As shown in Fig. 1, there are two molecules in the asymmetric unit of the title compound. In both molecules, the cyclohexane rings adopt a chair conformation, with atoms C1/C4 and C15/C18 as flaps. The hydroxyl groups are all in axial positions. A chair conformation is also observed for the morpholine rings, with the N and O atoms as flaps. The molecular conformation is enforced by an intramolecular O—H$\cdots$N hydrogen bond (Table 1).

3. Supramolecular features

In the crystal, molecules are linked by O—H$\cdots$O hydrogen bonds (Table 1) involving the hydroxyl groups into chains running parallel to the [101] direction (Fig. 2). Moreover, the chains are further connected *via* C—H$\cdots$O hydrogen bonds, forming undulating layers parallel to the ($\bar{1}$01) plane.
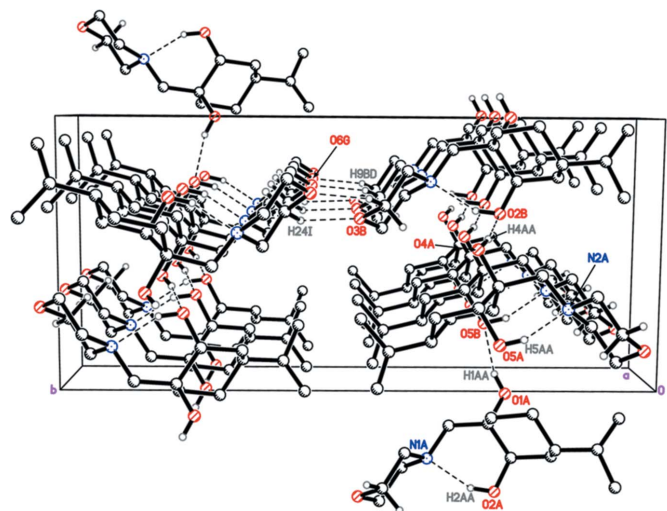
4. Database survey

The structures of related 1,4-substituted cyclohexane-1,2-diols have been reported recently by Byrne *et al.* (2004), Blair *et al.* (2007, 2010), Dams *et al.* (2004), Outouch, Boualy, Ali *et al.* (2011) and Outouch, Boualy, El Firdoussi *et al.* (2011). As found for the title compound, the cyclohexane-1,2-diol rings of these compounds adopt a chair conformation.

5. Synthesis and crystallization

A mixture of morpholine (5.1 mmol) and epoxyperillyl alcohol (5 mmol), prepared by epoxidation of (S)-$(-)$ perillyl alcohol, was added to 5 mol% of $Ca(CF_3CO_2)_2$ under solvent-free conditions. The mixture was stirred at 313 K for 72 h. After the reaction had finished, the mixture was extracted with ethyl acetate (3 × 10 ml), dried over Na_2SO_4 and the solvent was removed at reduced pressure. The title compound was purified by column chromatography on silica gel using hexane/ ethyl acetate (1:1 *v/v*) as eluent (yield 49%). Single crystals suitable for X-ray analysis were obtained by slow evaporation of the solvents.

^{1}H NMR (CDCl$_3$): δ [p.p.m.] 1.8 (*s*, 3H), 2.3 (*m*, 1H), 2.59 (*m*, 2H), 2.66 (*s*, 2H), 3.31 (*m*, 1H), 3.67 (*m*, 4H), 4.68 (*s*, 2H); ^{13}CNMR (CDCl$_3$) δ [p.p.m.] 16.9, 21.4, 27.1, 29.4, 32, 51, 62.5, 63.4, 65.9, 67.9, 104.6, 144.9.

Figure 1
The molecular structure of the two independent molecules of the title compound, with displacement ellipsoids drawn at the 30% probability level.

Figure 2
A packing diagram of the title compound showing hydrogen bonds as dashed lines (see Table 1 for details).

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{25}NO_3$
M_r	255.35
Crystal system, space group	Monoclinic, $P2_1$
Temperature (K)	150
a, b, c (Å)	6.3300 (1), 22.0241 (5), 10.1179 (2)
β (°)	95.2083 (12)
V (Å^3)	1404.74 (5)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	$0.44 \times 0.42 \times 0.28$
Data collection	
Diffractometer	Bruker Kappa APEXII DUO
Absorption correction	Multi-scan (*SADABS*; Bruker, 2008)
T_{min}, T_{max}	0.92, 0.98
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	42775, 6792, 6514
R_{int}	0.027
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.082, 1.06
No. of reflections	6792
No. of parameters	343
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.24, −0.15
Absolute structure	Flack x determined using 3097 quotients [$(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.21 (19)

Computer programs: *APEX2* (Bruker, 2011), *SAINT* (Bruker, 2009), *SHELXS97*, *SHELXL2014* and *SHELXTL* (Sheldrick, 2008).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms attached to oxygen could be found in a difference Fourier map and were freely refined. All other H atoms were placed in idealized positions with d(C—H) = 0.95–0.99 Å and refined using a riding model, with U_{iso}(H) = 1.2 U_{eq}(C) or 1.5 U_{eq}(C) for methyl H atoms. A rotating model was adopted for the methyl groups. The absolute configuration was not established by anomalous scattering effects, the enantiomer was assigned by reference to an unchanging chiral center in the synthetic procedure.

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Computing details

Data collection: *APEX2* (Bruker, 2011); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(1*S*,2*R*,4*S*)-1-[(Morpholin-4-yl)methyl]-4-(prop-1-en-2-yl)cyclohexane-1,2-diol

Crystal data

$C_{14}H_{25}NO_3$	$F(000) = 560$
$M_r = 255.35$	$D_x = 1.207$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 6.3300$ (1) Å	Cell parameters from 9947 reflections
$b = 22.0241$ (5) Å	$\theta = 2.7–28.8°$
$c = 10.1179$ (2) Å	$\mu = 0.08$ mm^{-1}
$\beta = 95.2083$ (12)°	$T = 150$ K
$V = 1404.74$ (5) Å^3	Prism, colourless
$Z = 4$	$0.44 \times 0.42 \times 0.28$ mm

Data collection

Bruker Kappa APEXII DUO diffractometer	42775 measured reflections
Radiation source: fine-focus sealed tube	6792 independent reflections
Curved graphite monochromator	6514 reflections with $I > 2\sigma(I)$
Detector resolution: 8.3333 pixels mm^{-1}	$R_{int} = 0.027$
φ and ω scans	$\theta_{max} = 28.0°$, $\theta_{min} = 1.9°$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$h = -8 \rightarrow 7$
	$k = -29 \rightarrow 29$
	$l = -13 \rightarrow 13$
$T_{min} = 0.92$, $T_{max} = 0.98$	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.031$	
$wR(F^2) = 0.082$	$w = 1/[\sigma^2(F_o^2) + (0.0479P)^2 + 0.1776P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
6792 reflections	$(\Delta/\sigma)_{max} < 0.001$
343 parameters	$\Delta\rho_{max} = 0.24$ e Å^{-3}
1 restraint	$\Delta\rho_{min} = -0.15$ e Å^{-3}

Absolute structure: Flack x determined using 3097 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.21 (19)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.7333 (2)	0.28883 (8)	0.90710 (15)	0.0222 (3)
C2	0.7379 (2)	0.25014 (8)	0.78061 (15)	0.0212 (3)
H2B	0.8889	0.2453	0.7609	0.025*
C3	0.6442 (3)	0.18737 (8)	0.79751 (16)	0.0231 (3)
H3A	0.7398	0.1640	0.8616	0.028*
H3B	0.6369	0.1658	0.7113	0.028*
C4	0.4205 (3)	0.18895 (8)	0.84677 (16)	0.0228 (3)
H4B	0.3248	0.2105	0.7780	0.027*
C5	0.4259 (3)	0.22604 (8)	0.97478 (17)	0.0258 (3)
H5B	0.2813	0.2285	1.0044	0.031*
H5C	0.5187	0.2057	1.0454	0.031*
C6	0.5091 (3)	0.28994 (8)	0.95188 (17)	0.0249 (3)
H6A	0.5096	0.3136	1.0352	0.030*
H6B	0.4128	0.3106	0.8835	0.030*
C7	0.8332 (3)	0.35171 (8)	0.88857 (18)	0.0268 (4)
H7A	0.8264	0.3750	0.9718	0.032*
H7B	0.9850	0.3458	0.8756	0.032*
C8	0.5642 (3)	0.42779 (8)	0.8175 (2)	0.0333 (4)
H8A	0.6201	0.4555	0.8895	0.040*
H8B	0.4525	0.4023	0.8517	0.040*
C9	0.4707 (3)	0.46446 (8)	0.7005 (2)	0.0359 (4)
H9A	0.4120	0.4367	0.6296	0.043*
H9B	0.3531	0.4898	0.7280	0.043*
C10	0.7961 (3)	0.46608 (8)	0.61057 (19)	0.0291 (4)
H10A	0.9052	0.4926	0.5766	0.035*
H10B	0.7409	0.4390	0.5374	0.035*
C11	0.8970 (3)	0.42814 (8)	0.72373 (18)	0.0267 (3)
H11A	1.0109	0.4027	0.6918	0.032*
H11B	0.9615	0.4551	0.7946	0.032*
C12	0.3362 (3)	0.12475 (8)	0.85890 (19)	0.0278 (3)
C13	0.2009 (4)	0.10122 (10)	0.7415 (3)	0.0477 (6)
H13A	0.1600	0.0592	0.7580	0.072*
H13B	0.2808	0.1027	0.6629	0.072*
H13C	0.0733	0.1264	0.7263	0.072*
C14	0.3850 (4)	0.08997 (9)	0.9646 (2)	0.0404 (5)

H14A	0.3336	0.0495	0.9662	0.048*
H14B	0.4712	0.1056	1.0386	0.048*
C15	0.1605 (2)	0.29160 (7)	0.44014 (15)	0.0190 (3)
C16	−0.0367 (2)	0.32633 (7)	0.37967 (15)	0.0188 (3)
H16	−0.1437	0.3279	0.4465	0.023*
C17	0.0177 (2)	0.39080 (7)	0.34182 (16)	0.0219 (3)
H17A	0.0615	0.4141	0.4235	0.026*
H17B	−0.1106	0.4104	0.2978	0.026*
C18	0.1962 (2)	0.39340 (7)	0.24867 (16)	0.0216 (3)
H18	0.1467	0.3708	0.1659	0.026*
C19	0.3920 (2)	0.36029 (7)	0.31378 (17)	0.0221 (3)
H19A	0.5057	0.3606	0.2527	0.026*
H19B	0.4453	0.3818	0.3960	0.026*
C20	0.3380 (2)	0.29471 (7)	0.34709 (16)	0.0213 (3)
H20A	0.4662	0.2745	0.3897	0.026*
H20B	0.2932	0.2726	0.2641	0.026*
C21	0.1026 (3)	0.22662 (7)	0.48039 (16)	0.0233 (3)
H21A	0.2351	0.2051	0.5115	0.028*
H21B	0.0150	0.2293	0.5564	0.028*
C22	0.1256 (3)	0.14898 (8)	0.30774 (19)	0.0280 (4)
H22A	0.1939	0.1195	0.3720	0.034*
H22B	0.2385	0.1728	0.2703	0.034*
C23	−0.0033 (3)	0.11532 (9)	0.1975 (2)	0.0344 (4)
H23A	−0.0649	0.1448	0.1309	0.041*
H23B	0.0907	0.0876	0.1528	0.041*
C24	−0.3040 (3)	0.12046 (8)	0.3148 (2)	0.0295 (4)
H24A	−0.4185	0.0963	0.3498	0.035*
H24B	−0.3706	0.1503	0.2507	0.035*
C25	−0.1826 (3)	0.15376 (8)	0.42746 (17)	0.0245 (3)
H25A	−0.2796	0.1808	0.4715	0.029*
H25B	−0.1206	0.1243	0.4939	0.029*
C26	0.2417 (3)	0.45830 (8)	0.20956 (19)	0.0277 (4)
C27	0.3227 (4)	0.50158 (9)	0.3166 (2)	0.0448 (5)
H27A	0.3413	0.5418	0.2780	0.067*
H27B	0.4592	0.4870	0.3582	0.067*
H27C	0.2206	0.5042	0.3836	0.067*
C28	0.2082 (4)	0.47606 (11)	0.0848 (2)	0.0479 (6)
H28A	0.2356	0.5169	0.0616	0.057*
H28B	0.1568	0.4480	0.0182	0.057*
N1	0.7366 (2)	0.38889 (7)	0.77770 (14)	0.0231 (3)
N2	−0.0127 (2)	0.18982 (6)	0.37589 (13)	0.0201 (3)
O1	0.8751 (2)	0.25829 (6)	1.00335 (13)	0.0293 (3)
O2	0.62372 (19)	0.27966 (6)	0.66952 (11)	0.0238 (2)
O3	0.6273 (2)	0.50262 (6)	0.65029 (16)	0.0343 (3)
O4	0.2236 (2)	0.32243 (6)	0.56239 (12)	0.0256 (3)
O5	−0.12856 (18)	0.29577 (6)	0.26338 (11)	0.0218 (2)
O6	−0.1697 (2)	0.08119 (6)	0.24837 (15)	0.0340 (3)
H1A	0.876 (4)	0.2765 (12)	1.076 (3)	0.041 (7)*

H2A	0.657 (4)	0.3175 (11)	0.678 (2)	0.028 (5)*
H4A	0.334 (4)	0.3044 (11)	0.593 (3)	0.037 (6)*
H5A	−0.121 (4)	0.2593 (14)	0.282 (3)	0.046 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0204 (7)	0.0277 (8)	0.0183 (7)	0.0030 (6)	−0.0002 (5)	−0.0015 (6)
C2	0.0194 (7)	0.0260 (8)	0.0185 (7)	0.0024 (6)	0.0031 (6)	0.0000 (6)
C3	0.0257 (7)	0.0241 (8)	0.0201 (7)	0.0035 (6)	0.0052 (6)	−0.0001 (6)
C4	0.0222 (7)	0.0243 (8)	0.0222 (7)	0.0020 (6)	0.0031 (6)	0.0032 (6)
C5	0.0256 (8)	0.0288 (8)	0.0243 (8)	0.0026 (6)	0.0089 (6)	0.0011 (6)
C6	0.0251 (7)	0.0272 (8)	0.0233 (7)	0.0033 (6)	0.0067 (6)	−0.0032 (6)
C7	0.0244 (8)	0.0298 (9)	0.0255 (8)	−0.0022 (6)	−0.0018 (6)	−0.0032 (6)
C8	0.0315 (9)	0.0240 (8)	0.0468 (11)	0.0021 (7)	0.0166 (8)	−0.0044 (8)
C9	0.0263 (9)	0.0216 (8)	0.0612 (13)	0.0044 (7)	0.0115 (8)	0.0018 (8)
C10	0.0266 (8)	0.0264 (8)	0.0351 (9)	0.0023 (6)	0.0082 (7)	−0.0019 (7)
C11	0.0207 (7)	0.0285 (8)	0.0311 (9)	−0.0024 (6)	0.0030 (6)	−0.0033 (7)
C12	0.0259 (8)	0.0263 (8)	0.0318 (9)	0.0007 (6)	0.0061 (7)	0.0037 (7)
C13	0.0461 (12)	0.0315 (10)	0.0621 (15)	−0.0090 (9)	−0.0141 (11)	0.0070 (10)
C14	0.0572 (13)	0.0283 (9)	0.0367 (10)	0.0008 (9)	0.0094 (9)	0.0068 (8)
C15	0.0187 (6)	0.0196 (7)	0.0183 (7)	0.0005 (6)	−0.0005 (5)	−0.0021 (6)
C16	0.0162 (6)	0.0213 (7)	0.0191 (7)	0.0008 (5)	0.0020 (5)	−0.0009 (5)
C17	0.0182 (7)	0.0202 (7)	0.0273 (8)	0.0024 (6)	0.0017 (6)	−0.0007 (6)
C18	0.0203 (7)	0.0213 (7)	0.0229 (7)	−0.0022 (6)	0.0005 (6)	−0.0007 (6)
C19	0.0160 (6)	0.0225 (7)	0.0280 (8)	−0.0013 (5)	0.0033 (6)	−0.0021 (6)
C20	0.0167 (7)	0.0206 (7)	0.0267 (8)	0.0020 (6)	0.0023 (5)	−0.0030 (6)
C21	0.0260 (8)	0.0226 (8)	0.0209 (8)	−0.0003 (6)	−0.0006 (6)	0.0029 (6)
C22	0.0224 (7)	0.0227 (8)	0.0406 (10)	−0.0017 (6)	0.0127 (7)	−0.0030 (7)
C23	0.0385 (10)	0.0277 (9)	0.0397 (10)	−0.0078 (7)	0.0172 (8)	−0.0096 (8)
C24	0.0216 (7)	0.0253 (8)	0.0421 (10)	−0.0036 (6)	0.0052 (7)	−0.0026 (7)
C25	0.0225 (7)	0.0229 (7)	0.0291 (8)	−0.0008 (6)	0.0083 (6)	0.0027 (6)
C26	0.0241 (8)	0.0252 (8)	0.0334 (9)	−0.0041 (6)	0.0008 (7)	0.0035 (7)
C27	0.0647 (15)	0.0237 (9)	0.0440 (12)	−0.0115 (9)	−0.0061 (10)	0.0017 (8)
C28	0.0576 (14)	0.0441 (12)	0.0398 (12)	−0.0206 (10)	−0.0071 (10)	0.0147 (9)
N1	0.0197 (6)	0.0220 (6)	0.0277 (7)	0.0012 (5)	0.0034 (5)	−0.0034 (5)
N2	0.0195 (6)	0.0186 (6)	0.0225 (6)	−0.0013 (5)	0.0040 (5)	−0.0002 (5)
O1	0.0291 (6)	0.0371 (7)	0.0207 (6)	0.0061 (5)	−0.0041 (5)	0.0004 (5)
O2	0.0275 (6)	0.0245 (6)	0.0188 (5)	−0.0021 (4)	−0.0013 (4)	0.0011 (4)
O3	0.0307 (7)	0.0207 (6)	0.0533 (9)	0.0033 (5)	0.0136 (6)	0.0011 (6)
O4	0.0268 (6)	0.0272 (6)	0.0218 (6)	0.0015 (5)	−0.0047 (5)	−0.0056 (5)
O5	0.0203 (5)	0.0220 (6)	0.0223 (6)	−0.0013 (4)	−0.0032 (4)	−0.0001 (5)
O6	0.0328 (7)	0.0229 (6)	0.0478 (8)	−0.0077 (5)	0.0124 (6)	−0.0082 (6)

Geometric parameters (Å, º)

C1—O1	1.4308 (19)	C15—C21	1.541 (2)
C1—C6	1.529 (2)	C15—C16	1.543 (2)

C1—C2	1.540 (2)	C16—O5	1.4321 (18)
C1—C7	1.541 (2)	C16—C17	1.518 (2)
C2—O2	1.4355 (19)	C16—H16	1.0000
C2—C3	1.520 (2)	C17—C18	1.537 (2)
C2—H2B	1.0000	C17—H17A	0.9900
C3—C4	1.543 (2)	C17—H17B	0.9900
C3—H3A	0.9900	C18—C26	1.518 (2)
C3—H3B	0.9900	C18—C19	1.534 (2)
C4—C12	1.520 (2)	C18—H18	1.0000
C4—C5	1.529 (2)	C19—C20	1.529 (2)
C4—H4B	1.0000	C19—H19A	0.9900
C5—C6	1.528 (2)	C19—H19B	0.9900
C5—H5B	0.9900	C20—H20A	0.9900
C5—H5C	0.9900	C20—H20B	0.9900
C6—H6A	0.9900	C21—N2	1.472 (2)
C6—H6B	0.9900	C21—H21A	0.9900
C7—N1	1.476 (2)	C21—H21B	0.9900
C7—H7A	0.9900	C22—N2	1.470 (2)
C7—H7B	0.9900	C22—C23	1.515 (3)
C8—N1	1.472 (2)	C22—H22A	0.9900
C8—C9	1.509 (3)	C22—H22B	0.9900
C8—H8A	0.9900	C23—O6	1.428 (2)
C8—H8B	0.9900	C23—H23A	0.9900
C9—O3	1.428 (2)	C23—H23B	0.9900
C9—H9A	0.9900	C24—O6	1.424 (2)
C9—H9B	0.9900	C24—C25	1.506 (2)
C10—O3	1.424 (2)	C24—H24A	0.9900
C10—C11	1.511 (3)	C24—H24B	0.9900
C10—H10A	0.9900	C25—N2	1.470 (2)
C10—H10B	0.9900	C25—H25A	0.9900
C11—N1	1.476 (2)	C25—H25B	0.9900
C11—H11A	0.9900	C26—C28	1.320 (3)
C11—H11B	0.9900	C26—C27	1.498 (3)
C12—C14	1.329 (3)	C27—H27A	0.9800
C12—C13	1.493 (3)	C27—H27B	0.9800
C13—H13A	0.9800	C27—H27C	0.9800
C13—H13B	0.9800	C28—H28A	0.9500
C13—H13C	0.9800	C28—H28B	0.9500
C14—H14A	0.9500	O1—H1A	0.84 (3)
C14—H14B	0.9500	O2—H2A	0.86 (2)
C15—O4	1.4354 (18)	O4—H4A	0.84 (3)
C15—C20	1.531 (2)	O5—H5A	0.83 (3)
O1—C1—C6	110.33 (13)	O5—C16—C17	108.46 (12)
O1—C1—C2	104.34 (13)	O5—C16—C15	110.28 (12)
C6—C1—C2	110.06 (13)	C17—C16—C15	111.69 (12)
O1—C1—C7	105.45 (13)	O5—C16—H16	108.8
C6—C1—C7	115.08 (14)	C17—C16—H16	108.8

C2—C1—C7	110.94 (13)	C15—C16—H16	108.8
O2—C2—C3	109.03 (13)	C16—C17—C18	112.70 (13)
O2—C2—C1	110.74 (13)	C16—C17—H17A	109.1
C3—C2—C1	111.89 (13)	C18—C17—H17A	109.1
O2—C2—H2B	108.4	C16—C17—H17B	109.1
C3—C2—H2B	108.4	C18—C17—H17B	109.1
C1—C2—H2B	108.4	H17A—C17—H17B	107.8
C2—C3—C4	113.24 (13)	C26—C18—C19	113.25 (13)
C2—C3—H3A	108.9	C26—C18—C17	111.25 (14)
C4—C3—H3A	108.9	C19—C18—C17	109.22 (13)
C2—C3—H3B	108.9	C26—C18—H18	107.6
C4—C3—H3B	108.9	C19—C18—H18	107.6
H3A—C3—H3B	107.7	C17—C18—H18	107.6
C12—C4—C5	114.17 (14)	C20—C19—C18	110.82 (12)
C12—C4—C3	110.14 (13)	C20—C19—H19A	109.5
C5—C4—C3	109.58 (14)	C18—C19—H19A	109.5
C12—C4—H4B	107.6	C20—C19—H19B	109.5
C5—C4—H4B	107.6	C18—C19—H19B	109.5
C3—C4—H4B	107.6	H19A—C19—H19B	108.1
C6—C5—C4	110.19 (13)	C19—C20—C15	111.65 (13)
C6—C5—H5B	109.6	C19—C20—H20A	109.3
C4—C5—H5B	109.6	C15—C20—H20A	109.3
C6—C5—H5C	109.6	C19—C20—H20B	109.3
C4—C5—H5C	109.6	C15—C20—H20B	109.3
H5B—C5—H5C	108.1	H20A—C20—H20B	108.0
C5—C6—C1	111.87 (13)	N2—C21—C15	115.84 (13)
C5—C6—H6A	109.2	N2—C21—H21A	108.3
C1—C6—H6A	109.2	C15—C21—H21A	108.3
C5—C6—H6B	109.2	N2—C21—H21B	108.3
C1—C6—H6B	109.2	C15—C21—H21B	108.3
H6A—C6—H6B	107.9	H21A—C21—H21B	107.4
N1—C7—C1	116.42 (13)	N2—C22—C23	109.96 (14)
N1—C7—H7A	108.2	N2—C22—H22A	109.7
C1—C7—H7A	108.2	C23—C22—H22A	109.7
N1—C7—H7B	108.2	N2—C22—H22B	109.7
C1—C7—H7B	108.2	C23—C22—H22B	109.7
H7A—C7—H7B	107.3	H22A—C22—H22B	108.2
N1—C8—C9	110.15 (16)	O6—C23—C22	110.94 (15)
N1—C8—H8A	109.6	O6—C23—H23A	109.5
C9—C8—H8A	109.6	C22—C23—H23A	109.5
N1—C8—H8B	109.6	O6—C23—H23B	109.5
C9—C8—H8B	109.6	C22—C23—H23B	109.5
H8A—C8—H8B	108.1	H23A—C23—H23B	108.0
O3—C9—C8	111.02 (16)	O6—C24—C25	111.56 (14)
O3—C9—H9A	109.4	O6—C24—H24A	109.3
C8—C9—H9A	109.4	C25—C24—H24A	109.3
O3—C9—H9B	109.4	O6—C24—H24B	109.3
C8—C9—H9B	109.4	C25—C24—H24B	109.3

H9A—C9—H9B	108.0	H24A—C24—H24B	108.0
O3—C10—C11	112.01 (15)	N2—C25—C24	109.51 (14)
O3—C10—H10A	109.2	N2—C25—H25A	109.8
C11—C10—H10A	109.2	C24—C25—H25A	109.8
O3—C10—H10B	109.2	N2—C25—H25B	109.8
C11—C10—H10B	109.2	C24—C25—H25B	109.8
H10A—C10—H10B	107.9	H25A—C25—H25B	108.2
N1—C11—C10	110.28 (14)	C28—C26—C27	121.16 (18)
N1—C11—H11A	109.6	C28—C26—C18	120.70 (18)
C10—C11—H11A	109.6	C27—C26—C18	118.13 (16)
N1—C11—H11B	109.6	C26—C27—H27A	109.5
C10—C11—H11B	109.6	C26—C27—H27B	109.5
H11A—C11—H11B	108.1	H27A—C27—H27B	109.5
C14—C12—C13	120.99 (18)	C26—C27—H27C	109.5
C14—C12—C4	122.92 (18)	H27A—C27—H27C	109.5
C13—C12—C4	116.03 (16)	H27B—C27—H27C	109.5
C12—C13—H13A	109.5	C26—C28—H28A	120.0
C12—C13—H13B	109.5	C26—C28—H28B	120.0
H13A—C13—H13B	109.5	H28A—C28—H28B	120.0
C12—C13—H13C	109.5	C8—N1—C11	108.20 (14)
H13A—C13—H13C	109.5	C8—N1—C7	112.39 (14)
H13B—C13—H13C	109.5	C11—N1—C7	110.78 (13)
C12—C14—H14A	120.0	C22—N2—C25	108.76 (13)
C12—C14—H14B	120.0	C22—N2—C21	113.35 (13)
H14A—C14—H14B	120.0	C25—N2—C21	111.93 (13)
O4—C15—C20	110.29 (12)	C1—O1—H1A	109.2 (18)
O4—C15—C21	105.41 (12)	C2—O2—H2A	104.9 (15)
C20—C15—C21	114.16 (13)	C10—O3—C9	109.32 (13)
O4—C15—C16	105.01 (12)	C15—O4—H4A	104.7 (17)
C20—C15—C16	110.28 (13)	C16—O5—H5A	105.3 (19)
C21—C15—C16	111.20 (13)	C24—O6—C23	110.02 (13)
O1—C1—C2—O2	−172.39 (12)	C16—C17—C18—C26	178.24 (13)
C6—C1—C2—O2	69.23 (17)	C16—C17—C18—C19	−56.02 (17)
C7—C1—C2—O2	−59.30 (17)	C26—C18—C19—C20	−178.30 (14)
O1—C1—C2—C3	65.74 (16)	C17—C18—C19—C20	57.12 (17)
C6—C1—C2—C3	−52.63 (17)	C18—C19—C20—C15	−58.41 (17)
C7—C1—C2—C3	178.83 (12)	O4—C15—C20—C19	−60.07 (16)
O2—C2—C3—C4	−69.99 (16)	C21—C15—C20—C19	−178.51 (13)
C1—C2—C3—C4	52.85 (18)	C16—C15—C20—C19	55.46 (16)
C2—C3—C4—C12	179.02 (13)	O4—C15—C21—N2	166.67 (13)
C2—C3—C4—C5	−54.58 (17)	C20—C15—C21—N2	−72.14 (18)
C12—C4—C5—C6	−179.04 (14)	C16—C15—C21—N2	53.40 (18)
C3—C4—C5—C6	56.89 (17)	N2—C22—C23—O6	−58.5 (2)
C4—C5—C6—C1	−59.77 (18)	O6—C24—C25—N2	59.16 (19)
O1—C1—C6—C5	−57.93 (18)	C19—C18—C26—C28	120.7 (2)
C2—C1—C6—C5	56.68 (18)	C17—C18—C26—C28	−115.8 (2)
C7—C1—C6—C5	−177.09 (14)	C19—C18—C26—C27	−60.1 (2)

O1—C1—C7—N1	170.17 (14)	C17—C18—C26—C27	63.4 (2)
C6—C1—C7—N1	−67.99 (18)	C9—C8—N1—C11	57.64 (19)
C2—C1—C7—N1	57.78 (18)	C9—C8—N1—C7	−179.71 (14)
N1—C8—C9—O3	−60.3 (2)	C10—C11—N1—C8	−56.23 (18)
O3—C10—C11—N1	57.89 (18)	C10—C11—N1—C7	−179.86 (14)
C5—C4—C12—C14	−40.6 (2)	C1—C7—N1—C8	89.85 (18)
C3—C4—C12—C14	83.2 (2)	C1—C7—N1—C11	−148.98 (14)
C5—C4—C12—C13	142.11 (19)	C23—C22—N2—C25	57.74 (18)
C3—C4—C12—C13	−94.1 (2)	C23—C22—N2—C21	−177.07 (14)
O4—C15—C16—O5	−173.83 (12)	C24—C25—N2—C22	−57.80 (17)
C20—C15—C16—O5	67.37 (16)	C24—C25—N2—C21	176.19 (13)
C21—C15—C16—O5	−60.32 (16)	C15—C21—N2—C22	97.33 (17)
O4—C15—C16—C17	65.49 (16)	C15—C21—N2—C25	−139.20 (14)
C20—C15—C16—C17	−53.31 (17)	C11—C10—O3—C9	−58.3 (2)
C21—C15—C16—C17	179.00 (13)	C8—C9—O3—C10	59.2 (2)
O5—C16—C17—C18	−66.97 (15)	C25—C24—O6—C23	−58.9 (2)
C15—C16—C17—C18	54.76 (17)	C22—C23—O6—C24	58.2 (2)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2A···N1	0.86 (2)	1.91 (2)	2.7118 (19)	154 (2)
O5—H5A···N2	0.83 (3)	1.90 (3)	2.6697 (18)	155 (3)
O1—H1A···O5[i]	0.84 (3)	1.95 (3)	2.7595 (18)	164 (3)
O4—H4A···O2	0.84 (3)	2.00 (3)	2.8249 (17)	167 (2)
C9—H9B···O6[ii]	0.99	2.35	3.269 (2)	155
C24—H24A···O3[iii]	0.99	2.45	3.344 (2)	150

Symmetry codes: (i) $x+1, y, z+1$; (ii) $-x, y+1/2, -z+1$; (iii) $-x, y-1/2, -z+1$.