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L-Nebivololinium chloride dihydrate

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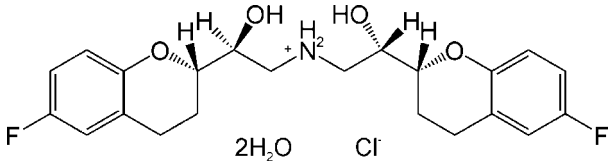
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.005 Å; R factor = 0.041; wR factor = 0.113; data-to-parameter ratio = 11.3.

The hydrochloride salt of chiral L-nebivolol {systematic name: (+)−(*R*,*S*,*S*,*S*)-bis[2-(6-fluoro-3,4-dihydro-2*H*-1-benzopyran-2-yl)-2-hydroxyethyl]ammonium chloride dihydrate}, $C_{22}H_{26}F_2NO_4^+\cdot Cl^-\cdot 2H_2O$, was obtained by chiral liquid chromatography as a dihydrate. The pyran rings adopt half-chair conformations. Hydrogen bonds between the cation, anions and water molecules contribute to the formation of layers parallel to the *ac* plane.

Related literature

For related literature, see: Cini *et al.* (1990); van Lommen *et al.* (1990); Peeters *et al.* (1993); Tuchalski *et al.* (2006).



Experimental

Crystal data

$C_{22}H_{26}F_2NO_4^+\cdot Cl^-\cdot 2H_2O$
M_r = 477.92
Orthorhombic, $P2_12_12_1$
a = 4.8026 (4) Å
b = 14.5781 (12) Å
c = 33.261 (3) Å
V = 2328.7 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.22 mm^{-1}
T = 291 (2) K
0.60 × 0.12 × 0.09 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.865, T_{max} = 0.981
26222 measured reflections
3401 independent reflections
2857 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.113
S = 1.05
3401 reflections
301 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: Flack (1983), 608 Friedel pairs
Flack parameter: −0.04 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1W^{i}	0.90	2.12	2.794 (3)	131
N1—H1···O4^{ii}	0.90	2.37	3.056 (4)	133
N1—H2···O4′^{iii}	0.90	2.19	3.061 (4)	162
O4—H9···Cl1^{i}	0.82	2.67	3.142 (2)	118
O4′—H10···O2W^{ii}	0.82	2.04	2.701 (4)	137
O1W—H1B···Cl1	0.89 (4)	2.47 (4)	3.242 (2)	146 (4)
O1W—H2B···N1^{iv}	0.88 (3)	2.47 (4)	2.794 (3)	102 (3)
O2W—H1A···Cl1	0.89 (4)	2.29 (4)	3.175 (3)	175 (3)
O2W—H2A···Cl1^{iii}	0.88 (4)	2.37 (4)	3.242 (3)	171 (3)
C2′—H4···O6′	0.97	2.26	2.708 (4)	107
C2—H5···O6	0.97	2.35	2.738 (4)	103
C2—H6···O6^{ii}	0.97	2.49	3.457 (4)	172
C14′—H26···F1^{v}	0.93	2.34	3.213 (5)	156

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXTL* (Bruker, 2001).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB2656).

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L-Nebiviololinium chloride dihydrate

Gisbert Tuchalski, Andre Hänsicke, Günther Reck and Franziska Emmerling

S1. Comment

L-Nebivolol is one enantiomer of the active pharmaceutical ingredient DL-nebivolol. DL-Nebivolol is a *β*-blocker of the third generation exhibiting a unique activity profile (van Lommen, *et al.*, 1990). Here we report the title compound, (I), the hydrochloride salt of *L*-nebivolol, obtained by chiral liquid chromatography.

The overall shape of the cation in (I) is strongly influenced by the conformation of the bridging C—C—N—C—C chain between the two benzopyran moieties. This conformation is stabilized by two intramolecular N—H···O hydrogen bonds, depicted in Figure 1. Two non-classical C—H···O intramolecular hydrogen bonds align the torsion angles C2—C3—C5—O6 and C2′-C3′-C5′-O6′ in a synclinal (*sc*) arrangement. The length of the bridging chain defined by the distance between the carbon atoms C5 and C5′ amounts to 7.434 (2) Å. O6 and O6′ are in *cis*-position. The average C—N, C—C and C—O distances in the title compound (Fig. 1) are in good agreement with those in other nebivolol derivatives (Peeters *et al.*, 1993; Tuchalski *et al.*, 2006).

Figure 2 shows the packing in (I). Like in the other nebivolol isomers the molecular packing of l-nebivolol is directed by classical intermolecular hydrogen bonds. Nine unique hydrogen bonds between nitrogen and hydroxyl groups, nitrogen and water molecules, hydroxyl groups and water molecules, hydroxyl groups and chlorine as well as between water and chlorine can be observed (Table 1). Together, these result in layers propagating in (010).

S2. Experimental

The title compound was synthesized by a subsequent ring-opening addition reaction (Cini *et al.*, 1990) of two different oxiran isomers with benzylamine leading to the individual benzyl-nebivolol isomers endowed with 4 chiral centers. The *L*-nebivolol isomer was isolated after hydrogenation and preparative chiral chromatography as its corresponding hydrochloride.

Colourless needles of (I) were grown by solvent evaporation from ethanol/ethyl acetate (1:1 *v*/*v*) at room temperature. NMR data: ^{1}H *NMR* (DMSO-d_6), δ(p.p.m.): 1.70 (1*H*, m); 1.77 (1*H*, m); 1.93 (1*H*, m); 2.11 (1*H*, m); 2.79 (4*H*, m); 3.05 (1*H*, m); 3.17 (1*H*, m); 3.22 (1*H*, m); 3.33 (1*H*, m); 3.89 (1*H*, m); 3.99 (1*H*, m); 3.99 (1*H*, m); 4.09 (1*H*, m); 5.75 (1*H*, d); 5.94 (1*H*, d); 6.76 (2*H*, dd); 6.91 (2*H*, m); 6.94 (2*H*, m); 8.63 (2*H*, broad) ^{13}C *NMR* (DMSO -d_6) δ(p.p.m.): 22.1; 22.3; 23.4; 24.0; 49.4; 49.8; 67.3; 67.4; 76.7; 77.0; 113.6 (23.0); 113.6 (23.1); 115.2 (22.5); 115.3 (22.5); 117.3 (8.1); 117.3 (8.1); 123.6 (7.7); 123.7 (7.8); 150.0 (1.4); 150.4 (1.6); 155.8 (235.5); 155.9 (235.5); $[\alpha l]^{29}_{D}$= - 20.5° (c = 1, THF/water = 4/1) chiral LC: 99.9 area-%

S3. Refinement

The water H atoms were located in a difference map and their positions were freely refined with U_{iso}(H) = 1.5U_{eq}(O).

The other hydrogen atoms were located in difference maps, repositioned with idealized geometry (C—H = 0.93–0.97 Å, N—H = 0.89 Å, O—H = 0.82 Å) and refined as riding with U_{iso}(H) = 1.2U_{eq}(parent atom).

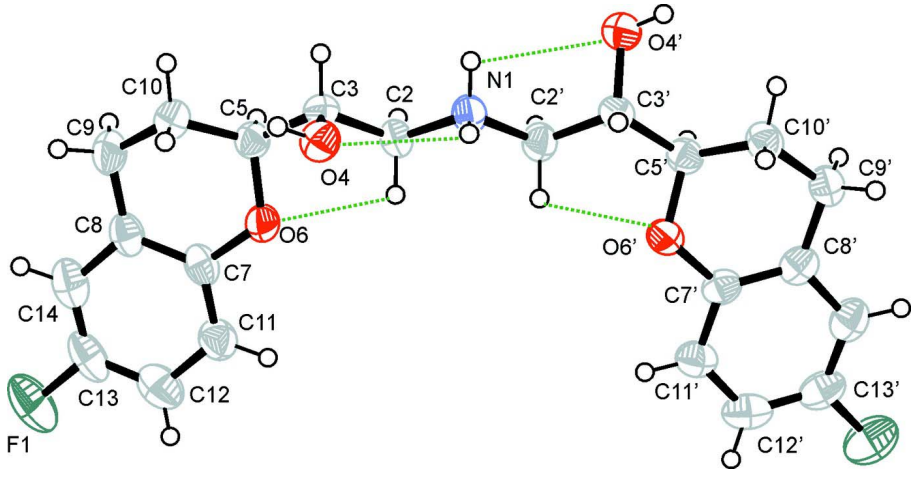

Figure 1

View of the molecular structure of (I) with 50% probability displacement ellipsoids for the non-hydrogen atoms.

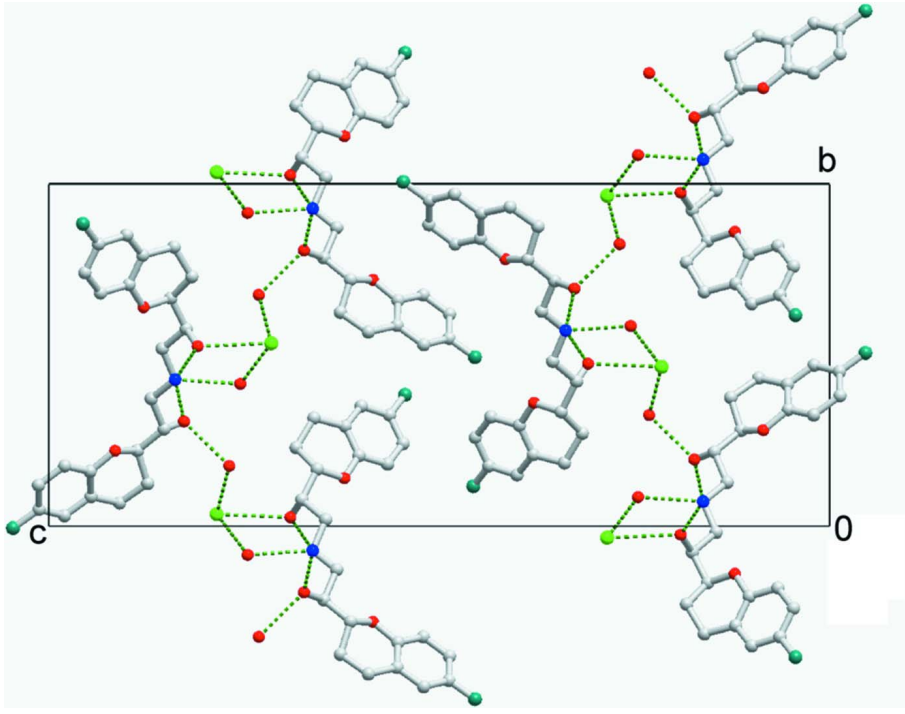

Figure 2

View of the layers array of (I), formed *via* hydrogen-bonding interactions (indicated by green lines).

(+)-(*R*,*S*,*S*,*S*)-bis[2-(6-fluoro-3,4-dihydro-2*H*-1-benzopyran-2-yl)-2-\ hydroxyethyl]ammonium chloride dihydrate

Crystal data

$C_{22}H_{26}F_2NO_4^+\cdot Cl^-\cdot 2H_2O$
M_r = 477.92
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
a = 4.8026 (4) Å
b = 14.5781 (12) Å
c = 33.261 (3) Å
V = 2328.7 (3) Å^3
Z = 4
F(000) = 1008
D_x = 1.363 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å

Cell parameters from 120 reflections
θ = 1.2–25.4°
μ = 0.22 mm^{-1}
T = 291 K
Needle, colourless
0.60 × 0.12 × 0.09 mm

Data collection

APEX CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω–scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.865, T_{max} = 0.981
26222 measured reflections
3401 independent reflections
2857 reflections with $I > 2\sigma(I)$
R_{int} = 0.054
θ_{max} = 26.4°, θ_{min} = 1.2°
h = −6→6
k = −18→18
l = −41→41

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.113
S = 1.05
3401 reflections
301 parameters
6 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 0.978P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}
Absolute structure: Flack (1983), xx Friedel pairs
Absolute structure parameter: −0.04 (12)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.7060 (2)	0.96561 (9)	0.28493 (3)	0.0826 (4)
O1W	0.2063 (8)	1.0846 (2)	0.24528 (8)	0.0899 (10)
H1A	0.348 (7)	0.866 (3)	0.2722 (19)	0.135*
H1B	0.348 (8)	1.075 (3)	0.2618 (13)	0.135*
O2W	0.2154 (7)	0.8243 (2)	0.26894 (9)	0.0772 (8)
H2A	0.064 (6)	0.858 (3)	0.2719 (18)	0.116*
H2B	0.191 (10)	1.0312 (17)	0.2332 (13)	0.116*
N1	0.7326 (6)	0.57169 (17)	0.33807 (7)	0.0461 (7)
H1	0.8475	0.5622	0.3171	0.069*
H2	0.5829	0.6026	0.3290	0.069*
C2′	0.8776 (7)	0.6276 (2)	0.36873 (9)	0.0435 (8)

H3	1.0288	0.5918	0.3800	0.052*
H4	0.7484	0.6414	0.3903	0.052*
C2	0.6415 (7)	0.4814 (2)	0.35470 (9)	0.0397 (8)
H5	0.5196	0.4920	0.3775	0.048*
H6	0.8035	0.4483	0.3643	0.048*
C3	0.4905 (7)	0.4230 (2)	0.32411 (9)	0.0390 (8)
H7	0.6169	0.4092	0.3018	0.058*
C3′	0.9940 (7)	0.7165 (2)	0.35241 (9)	0.0403 (8)
H8	0.8498	0.7478	0.3367	0.048*
O4	0.2600 (5)	0.47447 (14)	0.30934 (6)	0.0449 (5)
H9	0.1744	0.4437	0.2928	0.067*
O4′	1.2211 (5)	0.69428 (15)	0.32678 (6)	0.0508 (6)
H10	1.2871	0.7415	0.3174	0.076*
C5	0.3984 (7)	0.3337 (2)	0.34381 (9)	0.0403 (8)
H11	0.5645	0.3008	0.3530	0.060*
C5′	1.0904 (7)	0.7793 (2)	0.38644 (9)	0.0390 (8)
H12	1.2551	0.7521	0.3991	0.047*
O6	0.2381 (5)	0.36036 (13)	0.37856 (6)	0.0455 (6)
O6′	0.8676 (5)	0.78023 (15)	0.41512 (6)	0.0473 (6)
C7	0.0810 (7)	0.2942 (2)	0.39725 (9)	0.0421 (8)
C7′	0.8967 (7)	0.8404 (2)	0.44712 (9)	0.0411 (8)
C8	0.0283 (7)	0.2085 (2)	0.37968 (11)	0.0457 (9)
C8′	1.0804 (7)	0.9139 (2)	0.44601 (10)	0.0431 (8)
C9	0.1485 (8)	0.1844 (2)	0.33954 (11)	0.0571 (10)
H13	0.0117	0.1508	0.3239	0.069*
H14	0.3097	0.1452	0.3432	0.069*
C9′	1.2565 (8)	0.9325 (2)	0.40927 (9)	0.0461 (8)
H15	1.4495	0.9183	0.4152	0.055*
H16	1.2451	0.9971	0.4025	0.055*
C10	0.2340 (9)	0.2710 (2)	0.31677 (9)	0.0506 (9)
H17	0.3460	0.2543	0.2936	0.061*
H18	0.0692	0.3026	0.3072	0.061*
C10′	1.1607 (7)	0.8755 (2)	0.37343 (9)	0.0455 (8)
H19	0.9982	0.9038	0.3614	0.055*
H20	1.3072	0.8736	0.3534	0.055*
C11	−0.0325 (8)	0.3188 (3)	0.43371 (10)	0.0527 (9)
H21	0.0097	0.3756	0.4449	0.063*
C11′	0.7255 (8)	0.8244 (2)	0.47963 (9)	0.0499 (9)
H22	0.6006	0.7757	0.4791	0.060*
C12	−0.2092 (9)	0.2592 (3)	0.45375 (12)	0.0668 (11)
H23	−0.2908	0.2753	0.4781	0.080*
C12′	0.7387 (9)	0.8806 (3)	0.51317 (10)	0.0578 (10)
H24	0.6242	0.8707	0.5353	0.069*
C13	−0.2590 (9)	0.1757 (3)	0.43632 (13)	0.0660 (11)
C13′	0.9266 (9)	0.9516 (3)	0.51263 (10)	0.0581 (10)
C14	−0.1492 (8)	0.1495 (3)	0.40030 (13)	0.0615 (11)
H25	−0.1928	0.0924	0.3895	0.092*
C14′	1.0930 (8)	0.9700 (3)	0.48011 (10)	0.0551 (9)

H26	1.2141	1.0198	0.4807	0.066*
F1	−0.4347 (6)	0.11636 (19)	0.45634 (9)	0.1020 (9)
F1′	0.9452 (7)	1.00610 (18)	0.54589 (7)	0.0957 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0593 (7)	0.1298 (10)	0.0587 (6)	−0.0099 (7)	−0.0044 (5)	0.0150 (6)
O1W	0.098 (3)	0.120 (3)	0.0524 (17)	0.013 (2)	−0.0059 (17)	−0.0197 (17)
O2W	0.0740 (19)	0.095 (2)	0.0626 (16)	−0.0110 (18)	0.0067 (18)	0.0175 (16)
N1	0.0506 (17)	0.0464 (15)	0.0414 (14)	−0.0137 (15)	0.0035 (14)	−0.0038 (13)
C2′	0.0459 (19)	0.0432 (19)	0.0414 (18)	−0.0070 (16)	−0.0018 (16)	−0.0028 (15)
C2	0.0390 (18)	0.0357 (17)	0.0444 (17)	−0.0061 (15)	0.0004 (15)	0.0030 (14)
C3	0.0357 (18)	0.0401 (17)	0.0411 (17)	0.0007 (16)	0.0039 (15)	−0.0046 (15)
C3′	0.0384 (18)	0.0422 (18)	0.0403 (17)	−0.0039 (16)	0.0044 (15)	0.0003 (15)
O4	0.0432 (12)	0.0465 (13)	0.0450 (12)	0.0013 (13)	−0.0060 (12)	−0.0019 (10)
O4′	0.0512 (14)	0.0442 (12)	0.0569 (13)	−0.0016 (12)	0.0125 (13)	−0.0022 (11)
C5	0.0404 (18)	0.0349 (17)	0.0456 (18)	0.0003 (15)	0.0008 (17)	−0.0006 (15)
C5′	0.0348 (17)	0.0430 (19)	0.0393 (17)	−0.0010 (15)	−0.0008 (15)	0.0007 (15)
O6	0.0562 (14)	0.0394 (12)	0.0410 (11)	−0.0112 (12)	0.0060 (12)	−0.0027 (10)
O6′	0.0437 (13)	0.0532 (14)	0.0449 (12)	−0.0116 (11)	0.0076 (11)	−0.0069 (11)
C7	0.0403 (18)	0.044 (2)	0.0424 (19)	−0.0079 (17)	−0.0072 (16)	0.0112 (16)
C7′	0.0400 (19)	0.0469 (19)	0.0365 (17)	0.0051 (17)	−0.0033 (16)	−0.0046 (15)
C8	0.0412 (19)	0.0370 (18)	0.059 (2)	−0.0038 (17)	−0.0063 (17)	0.0082 (17)
C8′	0.0386 (19)	0.0441 (19)	0.0467 (19)	0.0081 (17)	−0.0071 (16)	−0.0029 (16)
C9	0.060 (3)	0.0351 (18)	0.076 (3)	−0.0089 (18)	0.005 (2)	−0.0075 (18)
C9′	0.0445 (19)	0.0416 (18)	0.0522 (19)	−0.0056 (18)	−0.0005 (18)	0.0015 (16)
C10	0.056 (2)	0.046 (2)	0.0500 (19)	−0.008 (2)	0.003 (2)	−0.0102 (16)
C10′	0.049 (2)	0.0463 (19)	0.0408 (18)	−0.0076 (16)	−0.0002 (16)	0.0044 (15)
C11	0.058 (2)	0.055 (2)	0.045 (2)	−0.012 (2)	0.0019 (19)	0.0034 (18)
C11′	0.051 (2)	0.055 (2)	0.0446 (19)	0.0013 (19)	0.0068 (18)	0.0017 (16)
C12	0.060 (3)	0.078 (3)	0.062 (2)	−0.011 (2)	0.007 (2)	0.016 (2)
C12′	0.058 (2)	0.072 (2)	0.0435 (19)	0.016 (2)	0.0081 (19)	0.0023 (19)
C13	0.055 (2)	0.060 (2)	0.084 (3)	−0.020 (2)	0.001 (2)	0.027 (2)
C13′	0.068 (3)	0.065 (3)	0.041 (2)	0.008 (2)	−0.001 (2)	−0.0143 (19)
C14	0.054 (2)	0.048 (2)	0.082 (3)	−0.0118 (19)	−0.008 (2)	0.009 (2)
C14′	0.059 (2)	0.051 (2)	0.056 (2)	−0.002 (2)	−0.007 (2)	−0.0113 (18)
F1	0.090 (2)	0.0920 (18)	0.124 (2)	−0.0404 (17)	0.0217 (17)	0.0312 (17)
F1′	0.124 (2)	0.1009 (19)	0.0617 (14)	−0.0078 (18)	0.0089 (15)	−0.0367 (14)

Geometric parameters (Å, º)

O1W—H1B	0.89 (4)	C7—C8	1.402 (5)
O1W—H2B	0.88 (3)	C7′—C11′	1.378 (5)
O2W—H1A	0.89 (4)	C7′—C8′	1.388 (5)
O2W—H2A	0.92 (5)	C8—C14	1.391 (5)
N1—C2′	1.479 (4)	C8—C9	1.496 (5)
N1—C2	1.493 (4)	C8′—C14′	1.400 (5)

N1—H1	0.9000	C8′—C9′	1.511 (5)
N1—H2	0.9000	C9—C10	1.528 (5)
C2′—C3′	1.512 (4)	C9—H13	0.9700
C2′—H3	0.9700	C9—H14	0.9700
C2′—H4	0.9700	C9′—C10′	1.525 (4)
C2—C3	1.512 (4)	C9′—H15	0.9700
C2—H5	0.9700	C9′—H16	0.9700
C2—H6	0.9700	C10—H17	0.9700
C3—O4	1.424 (4)	C10—H18	0.9700
C3—C5	1.524 (4)	C10′—H19	0.9700
C3—H7	0.9800	C10′—H20	0.9700
C3′—O4′	1.422 (4)	C11—C12	1.385 (5)
C3′—C5′	1.528 (4)	C11—H21	0.9300
C3′—H8	0.9800	C11′—C12′	1.386 (5)
O4—H9	0.8200	C11′—H22	0.9300
O4′—H10	0.8200	C12—C13	1.370 (6)
C5—O6	1.442 (4)	C12—H23	0.9300
C5—C10	1.506 (5)	C12′—C13′	1.372 (5)
C5—H11	0.9800	C12′—H24	0.9300
C5′—O6′	1.434 (4)	C13—C14	1.363 (6)
C5′—C10′	1.505 (4)	C13—F1	1.379 (4)
C5′—H12	0.9800	C13′—C14′	1.371 (5)
O6—C7	1.373 (4)	C13′—F1′	1.365 (4)
O6′—C7′	1.386 (4)	C14—H25	0.9300
C7—C11	1.377 (5)	C14′—H26	0.9300

H1B—O1W—H2B	102 (4)	C14—C8—C7	117.1 (3)
H1A—O2W—H2A	101 (4)	C14—C8—C9	122.1 (3)
C2′—N1—C2	111.6 (2)	C7—C8—C9	120.7 (3)
C2′—N1—H1	109.3	C7′—C8′—C14′	117.2 (3)
C2—N1—H1	109.3	C7′—C8′—C9′	121.1 (3)
C2′—N1—H2	109.3	C14′—C8′—C9′	121.7 (3)
C2—N1—H2	109.3	C8—C9—C10	110.6 (3)
H1—N1—H2	108.0	C8—C9—H13	109.5
N1—C2′—C3′	113.5 (3)	C10—C9—H13	109.5
N1—C2′—H3	108.9	C8—C9—H14	109.5
C3′—C2′—H3	108.9	C10—C9—H14	109.5
N1—C2′—H4	108.9	H13—C9—H14	108.1
C3′—C2′—H4	108.9	C8′—C9′—C10′	111.4 (3)
H3—C2′—H4	107.7	C8′—C9′—H15	109.3
N1—C2—C3	112.8 (2)	C10′—C9′—H15	109.3
N1—C2—H5	109.0	C8′—C9′—H16	109.3
C3—C2—H5	109.0	C10′—C9′—H16	109.3
N1—C2—H6	109.0	H15—C9′—H16	108.0
C3—C2—H6	109.0	C5—C10—C9	110.3 (3)
H5—C2—H6	107.8	C5—C10—H17	109.6
O4—C3—C2	108.0 (2)	C9—C10—H17	109.6
O4—C3—C5	111.9 (3)	C5—C10—H18	109.6

C2—C3—C5	109.3 (2)	C9—C10—H18	109.6
O4—C3—H7	109.2	H17—C10—H18	108.1
C2—C3—H7	109.2	C5′—C10′—C9′	110.5 (3)
C5—C3—H7	109.2	C5′—C10′—H19	109.5
O4′—C3′—C2′	107.7 (3)	C9′—C10′—H19	109.5
O4′—C3′—C5′	110.4 (3)	C5′—C10′—H20	109.5
C2′—C3′—C5′	111.1 (2)	C9′—C10′—H20	109.5
O4′—C3′—H8	109.2	H19—C10′—H20	108.1
C2′—C3′—H8	109.2	C7—C11—C12	120.2 (3)
C5′—C3′—H8	109.2	C7—C11—H21	119.9
C3—O4—H9	109.5	C12—C11—H21	119.9
C3′—O4′—H10	109.5	C7′—C11′—C12′	120.3 (4)
O6—C5—C10	111.3 (3)	C7′—C11′—H22	119.9
O6—C5—C3	105.6 (2)	C12′—C11′—H22	119.9
C10—C5—C3	114.5 (3)	C13—C12—C11	117.5 (4)
O6—C5—H11	108.4	C13—C12—H23	121.3
C10—C5—H11	108.4	C11—C12—H23	121.3
C3—C5—H11	108.4	C13′—C12′—C11′	117.7 (4)
O6′—C5′—C10′	110.5 (3)	C13′—C12′—H24	121.1
O6′—C5′—C3′	105.8 (2)	C11′—C12′—H24	121.1
C10′—C5′—C3′	114.4 (3)	C14—C13—C12	123.5 (4)
O6′—C5′—H12	108.7	C14—C13—F1	119.1 (4)
C10′—C5′—H12	108.7	C12—C13—F1	117.4 (4)
C3′—C5′—H12	108.7	C14′—C13′—F1′	119.1 (4)
C7—O6—C5	117.8 (2)	C14′—C13′—C12′	122.7 (3)
C7′—O6′—C5′	116.2 (2)	F1′—C13′—C12′	118.1 (3)
O6—C7—C11	115.7 (3)	C13—C14—C8	119.9 (4)
O6—C7—C8	122.4 (3)	C13—C14—H25	120.1
C11—C7—C8	121.8 (3)	C8—C14—H25	120.1
C11′—C7′—O6′	115.8 (3)	C13′—C14′—C8′	120.0 (4)
C11′—C7′—C8′	122.0 (3)	C13′—C14′—H26	120.0
O6′—C7′—C8′	122.1 (3)	C8′—C14′—H26	120.0

C2—N1—C2′—C3′	175.4 (3)	O6′—C7′—C8′—C9′	0.8 (5)
C2′—N1—C2—C3	179.6 (3)	C14—C8—C9—C10	157.4 (4)
N1—C2—C3—O4	−56.6 (3)	C7—C8—C9—C10	−19.6 (5)
N1—C2—C3—C5	−178.5 (3)	C7′—C8′—C9′—C10′	11.8 (4)
N1—C2′—C3′—O4′	−70.0 (4)	C14′—C8′—C9′—C10′	−167.6 (3)
N1—C2′—C3′—C5′	169.0 (3)	O6—C5—C10—C9	−59.5 (4)
O4—C3—C5—O6	−64.8 (3)	C3—C5—C10—C9	−179.1 (3)
C2—C3—C5—O6	54.8 (3)	C8—C9—C10—C5	47.3 (4)
O4—C3—C5—C10	58.0 (4)	O6′—C5′—C10′—C9′	61.2 (4)
C2—C3—C5—C10	177.5 (3)	C3′—C5′—C10′—C9′	−179.6 (3)
O4′—C3′—C5′—O6′	−167.0 (2)	C8′—C9′—C10′—C5′	−41.4 (4)
C2′—C3′—C5′—O6′	−47.6 (3)	O6—C7—C11—C12	175.8 (3)
O4′—C3′—C5′—C10′	71.1 (4)	C8—C7—C11—C12	−1.5 (5)
C2′—C3′—C5′—C10′	−169.5 (3)	O6′—C7′—C11′—C12′	179.9 (3)
C10—C5—O6—C7	41.9 (4)	C8′—C7′—C11′—C12′	−2.0 (5)

C3—C5—O6—C7	166.7 (3)	C7—C11—C12—C13	1.5 (6)
C10′—C5′—O6′—C7′	−49.5 (4)	C7′—C11′—C12′—C13′	−0.1 (5)
C3′—C5′—O6′—C7′	−173.9 (2)	C11—C12—C13—C14	−1.4 (7)
C5—O6—C7—C11	170.0 (3)	C11—C12—C13—F1	179.9 (3)
C5—O6—C7—C8	−12.7 (4)	C11′—C12′—C13′—C14′	1.9 (6)
C5′—O6′—C7′—C11′	−163.3 (3)	C11′—C12′—C13′—F1′	−178.6 (3)
C5′—O6′—C7′—C8′	18.7 (4)	C12—C13—C14—C8	1.3 (7)
O6—C7—C8—C14	−175.8 (3)	F1—C13—C14—C8	180.0 (3)
C11—C7—C8—C14	1.3 (5)	C7—C8—C14—C13	−1.2 (5)
O6—C7—C8—C9	1.4 (5)	C9—C8—C14—C13	−178.3 (4)
C11—C7—C8—C9	178.5 (3)	F1′—C13′—C14′—C8′	178.8 (3)
C11′—C7′—C8′—C14′	2.2 (5)	C12′—C13′—C14′—C8′	−1.7 (6)
O6′—C7′—C8′—C14′	−179.8 (3)	C7′—C8′—C14′—C13′	−0.4 (5)
C11′—C7′—C8′—C9′	−177.2 (3)	C9′—C8′—C14′—C13′	179.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1*W*^{i}	0.90	2.12	2.794 (3)	131
N1—H1···O4^{ii}	0.90	2.37	3.056 (4)	133
N1—H2···O4′^{iii}	0.90	2.19	3.061 (4)	162
O4—H9···Cl1^{i}	0.82	2.67	3.142 (2)	118
O4′—H10···O2*W*^{ii}	0.82	2.04	2.701 (4)	137
O1*W*—H1*B*···Cl1	0.89 (4)	2.47 (4)	3.242 (2)	146 (4)
O1*W*—H2*B*···N1^{iv}	0.88 (3)	2.47 (4)	2.794 (3)	102 (3)
O2*W*—H1*A*···Cl1	0.89 (4)	2.29 (4)	3.175 (3)	175 (3)
O2*W*—H2*A*···Cl1^{iii}	0.88 (4)	2.37 (4)	3.242 (3)	171 (3)
C2′—H4···O6′	0.97	2.26	2.708 (4)	107
C2—H5···O6	0.97	2.35	2.738 (4)	103
C2—H6···O6^{ii}	0.97	2.49	3.457 (4)	172
C14′—H26···F1^{v}	0.93	2.34	3.213 (5)	156

Symmetry codes: (i) −*x*+1, *y*−1/2, −*z*+1/2; (ii) *x*+1, *y*, *z*; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, *y*+1/2, −*z*+1/2; (v) *x*+2, *y*+1, *z*.