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3-*O*-Benzhydryl-2,5-dideoxy-2,5-imino-2-*C*-methyl-L-lyxono-1,4-lactone

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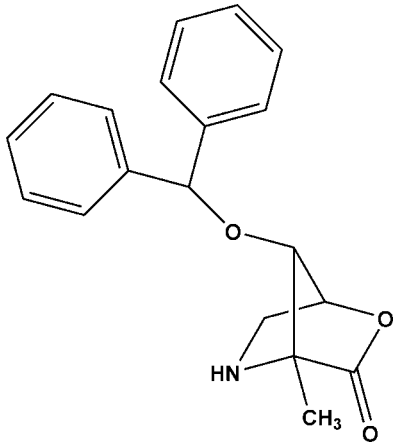
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; R factor = 0.029; wR factor = 0.102; data-to-parameter ratio = 9.8.

The title bicyclic lactone, $C_{19}H_{19}NO_3$, is an intermediate in the synthesis of chiral α-methylprolines and branched *C*-methyl pyrrolidines; the absolute configuration was determined by the use of D-erythronolactone as the starting material. It exhibits no unusual crystal packing features, and each molecule acts as a donor and acceptor for one C—H···O hydrogen bond.

Related literature

For use of carbohydrates in synthesis see: Monneret & Florent (1994); Ireland *et al.* (1983); Hotchkiss *et al.* (2006, 2007*a*,*b*); Dukhan *et al.* (2005); Rao *et al.* (2008); Punzo *et al.* (2005*a*,*b*); Da Cruz *et al.* (2008). For related crystallographic literature see: Larson (1970); Prince (1982); Watkin (1994).



Experimental

Crystal data

$C_{19}H_{19}NO_3$
M_r = 309.36
Orthorhombic, $P2_12_12_1$
a = 9.0336 (2) Å
b = 10.0498 (2) Å
c = 17.5941 (4) Å
V = 1597.30 (6) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 150 K
0.30 × 0.25 × 0.25 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.94, T_{max} = 0.98
25603 measured reflections
2071 independent reflections
1411 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.101
S = 0.86
2071 reflections
212 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C20—H201···O10^{i}	0.93	2.36	3.293 (3)	174

Symmetry code: (i) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$.

Data collection: *COLLECT* (Nonius, 1997-2001).; cell refinement: *DENZO*/*SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO*/*SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *CAMERON* (Watkin *et al.*, 1996); software used to prepare material for publication: *CRYSTALS*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CS2089).

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supporting information

Acta Cryst. (2008). E**64**, o1902–o1903 [doi:10.1107/S1600536808027888]

3-*O*-Benzhydryl-2,5-dideoxy-2,5-imino-2-*C*-methyl-L-lyxono-1,4-lactone

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S1. Comment

Carbon-branched sugar lactones have hitherto been rarely used for the synthesis of enantiopure chiral targets (Monneret & Florent, 1994; Ireland *et al.*, 1983). 2-*C*-Methyl-D-ribonolactone has become readily available in large amounts (Hotchkiss *et al.*, 2007*a*) and has been used in the synthesis of branched *α*-*C*-nucleosides (Dukhan *et al.*, 2005), 4-*C*-methylpentuloses (Rao *et al.*, 2008) and branched imino sugars (Hotchkiss *et al.*, 2007*b*). Derivatives of 2-*C*-methyl-D-arabinonolactone, such as **2**, are accessible from D-erythronolactone **1** by addition of methyl magnesium bromide followed by further reaction with sodium cyanide (Hotchkiss *et al.*, 2006; Punzo *et al.*, 2005*a*). The tertiary alcohol **2** may be efficiently converted into the *ribo*-azide **3**, the structure of which has been confirmed by X-ray crystallographic analysis (Da Cruz *et al.*, 2008; Punzo *et al.*, 2005*b*). The relative stereochemistry of **4** is firmly established in this paper by X-ray crystallographic analysis and the absolute configuration is defined by the use of D-erythronolactone **1** as the starting material.

The title compound exhibits no unusual crystal packing features. Each molecule acts as a donor and acceptor for one hydrogen bond, forming chains approximately parallel to the *a*-axis. A suggested hydrogen bond [N7 - H1 - O10] has been ignored in the packing diagram as it exceeds the limits of standard hydrogen bond length (2.52 Å)

S2. Experimental

The title compound was recrystallized from cyclohexane and diethyl ether: m.p. 116–118°C; $[\alpha]_D^{21}$ -26.0 (*c*, 1.0 in MeCN).

S3. Refinement

In the absence of significant anomalous scattering, Friedel pairs were merged. The H atoms were all located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98, N—H in the range 0.86–0.89 N—H to 0.86 O—H = 0.82 Å) and U_{iso}(H) (in the range 1.2–1.5 times U_{eq} of the parent atom), after which the positions were refined with riding constraints.

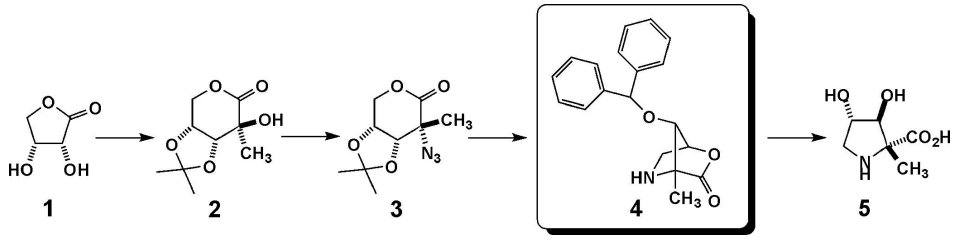

Figure 1

Synthetic scheme.

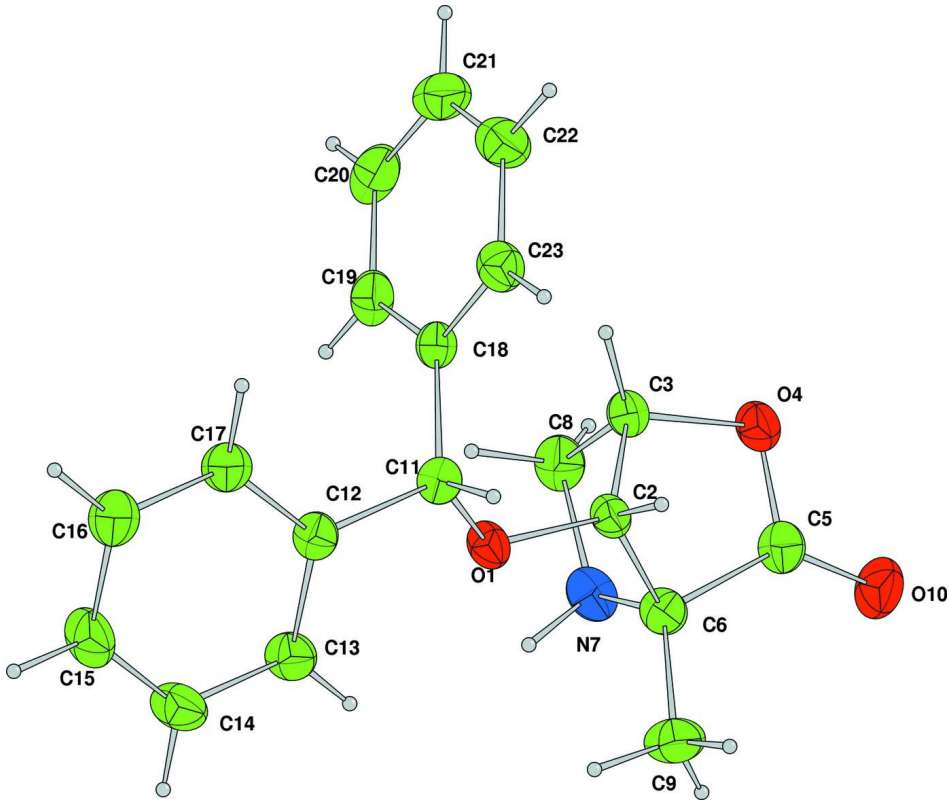

Figure 2

The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.

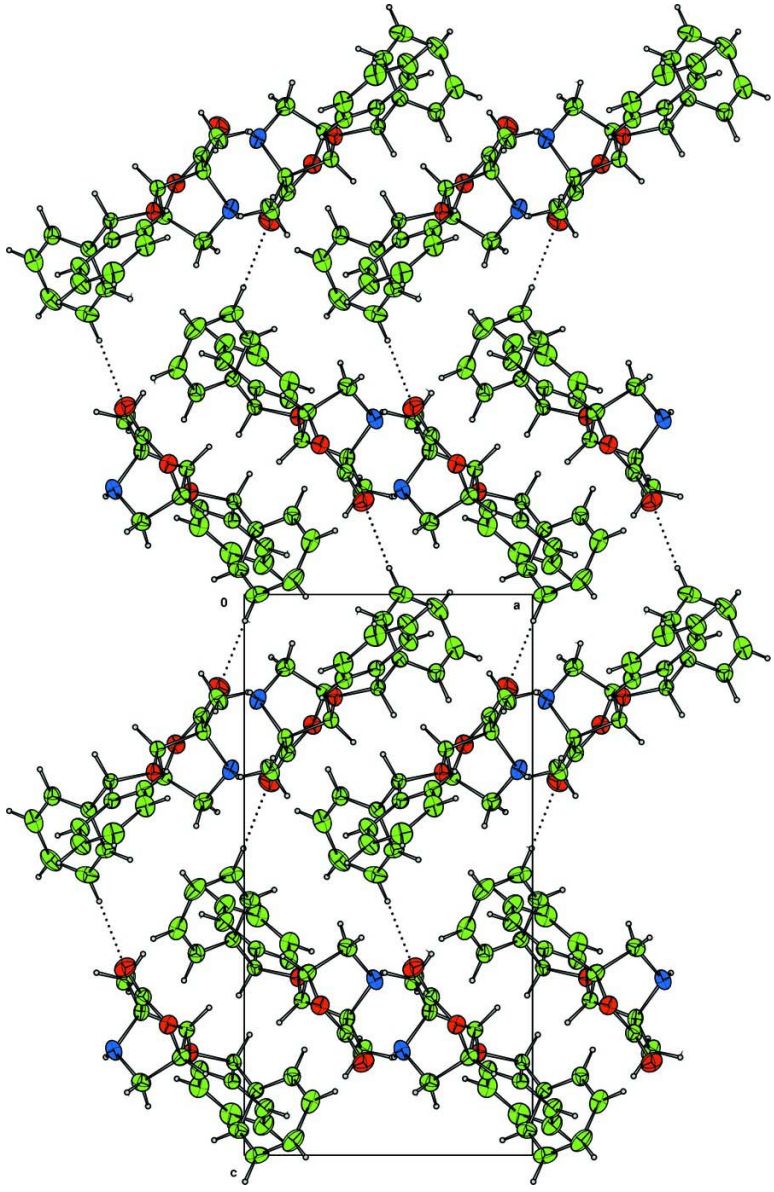

Figure 3

Packing diagram showing hydrogen bonded chains running parallel to the *a*-axis.

(I)

Crystal data

$C_{19}H_{19}NO_3$
$M_r = 309.36$
Orthorhombic, $P2_12_12_1$
Hall symbol: P 2ac 2ab
$a = 9.0336\ (2)$ Å
$b = 10.0498\ (2)$ Å
$c = 17.5941\ (4)$ Å
$V = 1597.30\ (6)$ Å^3
$Z = 4$
$F(000) = 656$
$D_x = 1.286$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 6711 reflections
$\theta = 5$–27°
$\mu = 0.09$ mm^{-1}
$T = 150$ K
Block, colourless
0.30 × 0.25 × 0.25 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Graphite monochromator
ω scans
Absorption correction: multi-scan (*DENZO*/*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.94, T_{max} = 0.98
25603 measured reflections
2071 independent reflections
1411 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.5°, θ_{min} = 5.2°
h = −11→11
k = −13→12
l = −22→22

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.101
S = 0.86
2071 reflections
212 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
Method, part 1, Chebychev polynomial, (Watkin, 1994) [*w*eight] = 1.0/[A_0*T_0(x) + A_1*T_1(x) ··· + A_{n-1}]*T_{n-1}(x)] where A_i are the Chebychev coefficients listed below and x = *F* /*F*max Method = Robust Weighting (*P*rince, 1982) W = [*w*eight] * [1-(delta*F*/6*sigma*F*)^2]^2 A_i are: 16.5 25.4 13.4 3.97
$(\Delta/\sigma)_{max}$ = 0.000186
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Extinction correction: Larson (1970), Equation 22
Extinction coefficient: 420 (70)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.68597 (16)	0.81026 (14)	0.31734 (9)	0.0272
C2	0.6994 (2)	0.69016 (19)	0.27608 (12)	0.0242
C3	0.7190 (3)	0.5647 (2)	0.32511 (13)	0.0286
O4	0.76321 (17)	0.46691 (14)	0.26720 (9)	0.0310
C5	0.8514 (3)	0.5332 (2)	0.21745 (12)	0.0301
C6	0.8569 (2)	0.6776 (2)	0.24385 (12)	0.0281
N7	0.9525 (2)	0.6653 (2)	0.31282 (12)	0.0325
C8	0.8577 (3)	0.5979 (2)	0.37011 (13)	0.0337
C9	0.9106 (3)	0.7768 (3)	0.18667 (15)	0.0392
O10	0.9132 (2)	0.47855 (18)	0.16574 (10)	0.0420
C11	0.5358 (2)	0.8483 (2)	0.33392 (12)	0.0251
C12	0.5418 (2)	0.9877 (2)	0.36769 (12)	0.0266
C13	0.6550 (3)	1.0751 (2)	0.34846 (13)	0.0315
C14	0.6565 (3)	1.2033 (2)	0.37762 (14)	0.0370
C15	0.5459 (3)	1.2459 (2)	0.42665 (15)	0.0406
C16	0.4328 (3)	1.1595 (2)	0.44577 (15)	0.0402
C17	0.4305 (3)	1.0309 (2)	0.41629 (13)	0.0344
C18	0.4604 (2)	0.74727 (19)	0.38447 (11)	0.0253
C19	0.5194 (3)	0.7164 (2)	0.45543 (12)	0.0322
C20	0.4554 (3)	0.6179 (3)	0.50012 (13)	0.0405
C21	0.3303 (3)	0.5504 (2)	0.47385 (16)	0.0422
C22	0.2698 (3)	0.5832 (2)	0.40451 (16)	0.0397

C23	0.3342 (3)	0.6812 (2)	0.35977 (13)	0.0312
H21	0.6217	0.6791	0.2367	0.0282*
H31	0.6344	0.5365	0.3548	0.0341*
H81	0.8335	0.6581	0.4126	0.0399*
H82	0.9062	0.5176	0.3880	0.0400*
H91	1.0125	0.7635	0.1745	0.0585*
H92	0.9002	0.8665	0.2083	0.0596*
H93	0.8509	0.7721	0.1411	0.0587*
H111	0.4814	0.8523	0.2851	0.0297*
H131	0.7306	1.0474	0.3158	0.0374*
H141	0.7337	1.2628	0.3636	0.0445*
H151	0.5485	1.3315	0.4472	0.0487*
H161	0.3564	1.1873	0.4788	0.0478*
H171	0.3527	0.9733	0.4299	0.0420*
H191	0.6040	0.7642	0.4731	0.0384*
H201	0.4969	0.5968	0.5471	0.0498*
H211	0.2866	0.4832	0.5036	0.0514*
H221	0.1848	0.5371	0.3861	0.0482*
H231	0.2913	0.7017	0.3118	0.0394*
H1	0.980 (4)	0.748 (3)	0.3251 (17)	0.0433*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0237 (7)	0.0228 (7)	0.0350 (7)	0.0012 (6)	0.0009 (6)	−0.0054 (6)
C2	0.0247 (9)	0.0202 (9)	0.0278 (9)	−0.0005 (8)	0.0007 (8)	−0.0031 (8)
C3	0.0329 (11)	0.0225 (9)	0.0303 (10)	0.0008 (8)	0.0044 (9)	−0.0034 (8)
O4	0.0330 (8)	0.0242 (7)	0.0359 (8)	0.0010 (6)	0.0024 (7)	−0.0046 (7)
C5	0.0280 (10)	0.0300 (10)	0.0324 (10)	0.0045 (9)	−0.0011 (9)	−0.0022 (9)
C6	0.0243 (10)	0.0261 (9)	0.0340 (10)	0.0013 (8)	0.0015 (8)	−0.0012 (9)
N7	0.0264 (9)	0.0306 (9)	0.0404 (10)	0.0011 (8)	−0.0073 (8)	−0.0026 (8)
C8	0.0375 (12)	0.0306 (11)	0.0331 (11)	0.0063 (10)	−0.0040 (10)	0.0005 (9)
C9	0.0358 (12)	0.0361 (12)	0.0457 (13)	−0.0005 (10)	0.0122 (11)	0.0078 (11)
O10	0.0462 (10)	0.0399 (9)	0.0398 (9)	0.0087 (8)	0.0086 (8)	−0.0084 (8)
C11	0.0224 (9)	0.0270 (9)	0.0260 (9)	0.0031 (8)	−0.0017 (8)	−0.0001 (8)
C12	0.0285 (10)	0.0247 (9)	0.0265 (9)	0.0045 (8)	−0.0011 (8)	0.0008 (8)
C13	0.0307 (11)	0.0267 (10)	0.0372 (11)	0.0034 (9)	0.0025 (10)	0.0025 (9)
C14	0.0385 (12)	0.0246 (10)	0.0478 (13)	−0.0016 (10)	0.0034 (11)	0.0045 (10)
C15	0.0496 (15)	0.0239 (11)	0.0482 (14)	0.0065 (10)	0.0007 (12)	−0.0049 (9)
C16	0.0421 (14)	0.0335 (12)	0.0452 (13)	0.0062 (11)	0.0100 (11)	−0.0051 (10)
C17	0.0361 (12)	0.0289 (11)	0.0383 (12)	0.0023 (10)	0.0079 (10)	−0.0004 (9)
C18	0.0265 (10)	0.0230 (9)	0.0265 (10)	0.0029 (8)	0.0018 (9)	−0.0030 (8)
C19	0.0408 (13)	0.0287 (10)	0.0272 (10)	0.0053 (11)	−0.0017 (10)	−0.0039 (8)
C20	0.0570 (16)	0.0362 (12)	0.0283 (10)	0.0138 (11)	0.0069 (12)	0.0020 (10)
C21	0.0474 (14)	0.0292 (11)	0.0501 (14)	0.0055 (11)	0.0209 (13)	0.0051 (10)
C22	0.0348 (12)	0.0299 (11)	0.0544 (15)	−0.0019 (10)	0.0093 (12)	−0.0035 (11)
C23	0.0284 (10)	0.0295 (10)	0.0356 (10)	0.0009 (8)	0.0004 (9)	−0.0038 (9)

Geometric parameters (Å, º)

O1—C2	1.414 (2)	C12—C13	1.390 (3)
O1—C11	1.439 (2)	C12—C17	1.389 (3)
C2—C3	1.538 (3)	C13—C14	1.387 (3)
C2—C6	1.537 (3)	C13—H131	0.935
C2—H21	0.992	C14—C15	1.388 (4)
C3—O4	1.471 (2)	C14—H141	0.951
C3—C8	1.519 (3)	C15—C16	1.382 (4)
C3—H31	0.968	C15—H151	0.934
O4—C5	1.358 (3)	C16—C17	1.393 (3)
C5—C6	1.524 (3)	C16—H161	0.945
C5—O10	1.200 (3)	C17—H171	0.941
C6—N7	1.495 (3)	C18—C19	1.393 (3)
C6—C9	1.497 (3)	C18—C23	1.389 (3)
N7—C8	1.486 (3)	C19—C20	1.390 (4)
N7—H1	0.89 (3)	C19—H191	0.954
C8—H81	0.986	C20—C21	1.397 (4)
C8—H82	0.971	C20—H201	0.932
C9—H91	0.955	C21—C22	1.377 (4)
C9—H92	0.983	C21—H211	0.942
C9—H93	0.968	C22—C23	1.389 (4)
C11—C12	1.523 (3)	C22—H221	0.954
C11—C18	1.512 (3)	C23—H231	0.952
C11—H111	0.990		
C2—O1—C11	114.34 (15)	C12—C11—C18	113.84 (17)
O1—C2—C3	114.94 (16)	O1—C11—H111	107.6
O1—C2—C6	109.83 (16)	C12—C11—H111	108.5
C3—C2—C6	91.88 (16)	C18—C11—H111	108.3
O1—C2—H21	113.2	C11—C12—C13	120.81 (19)
C3—C2—H21	112.4	C11—C12—C17	120.2 (2)
C6—C2—H21	112.8	C13—C12—C17	119.0 (2)
C2—C3—O4	100.99 (16)	C12—C13—C14	120.3 (2)
C2—C3—C8	101.98 (17)	C12—C13—H131	119.9
O4—C3—C8	106.51 (17)	C14—C13—H131	119.8
C2—C3—H31	116.9	C13—C14—C15	120.6 (2)
O4—C3—H31	113.0	C13—C14—H141	119.7
C8—C3—H31	115.7	C15—C14—H141	119.7
C3—O4—C5	106.11 (16)	C14—C15—C16	119.4 (2)
O4—C5—C6	106.84 (17)	C14—C15—H151	120.5
O4—C5—O10	122.5 (2)	C16—C15—H151	120.2
C6—C5—O10	130.6 (2)	C15—C16—C17	120.2 (2)
C2—C6—C5	99.24 (16)	C15—C16—H161	120.3
C2—C6—N7	104.02 (17)	C17—C16—H161	119.5
C5—C6—N7	100.82 (17)	C16—C17—C12	120.6 (2)
C2—C6—C9	119.55 (18)	C16—C17—H171	119.2
C5—C6—C9	116.07 (19)	C12—C17—H171	120.3

N7—C6—C9	114.42 (19)	C11—C18—C19	120.3 (2)
C6—N7—C8	104.77 (16)	C11—C18—C23	120.47 (19)
C6—N7—H1	106 (2)	C19—C18—C23	119.2 (2)
C8—N7—H1	115 (2)	C18—C19—C20	120.4 (2)
C3—C8—N7	102.82 (18)	C18—C19—H191	119.1
C3—C8—H81	110.3	C20—C19—H191	120.5
N7—C8—H81	111.3	C19—C20—C21	119.7 (2)
C3—C8—H82	111.0	C19—C20—H201	119.8
N7—C8—H82	109.7	C21—C20—H201	120.5
H81—C8—H82	111.3	C20—C21—C22	119.9 (2)
C6—C9—H91	111.7	C20—C21—H211	120.3
C6—C9—H92	108.6	C22—C21—H211	119.9
H91—C9—H92	107.9	C21—C22—C23	120.4 (3)
C6—C9—H93	110.2	C21—C22—H221	120.3
H91—C9—H93	110.1	C23—C22—H221	119.3
H92—C9—H93	108.2	C18—C23—C22	120.4 (2)
O1—C11—C12	106.90 (17)	C18—C23—H231	120.5
O1—C11—C18	111.45 (16)	C22—C23—H231	119.1

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C20—H201···O10^{i}	0.93	2.36	3.293 (3)	174
N7—H1···O10^{ii}	0.89 (2)	2.52 (3)	3.395 (3)	168

Symmetry codes: (i) −*x*+3/2, −*y*+1, *z*+1/2; (ii) −*x*+2, *y*+1/2, −*z*+1/2.